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ORGANIC MATERIALS FOR SECOND HARMONIC GENERATION

Robert J. Twieg

International Business Machines Corporation
Research K91/282
5600 Cottle Road
San Jose, CA 95125

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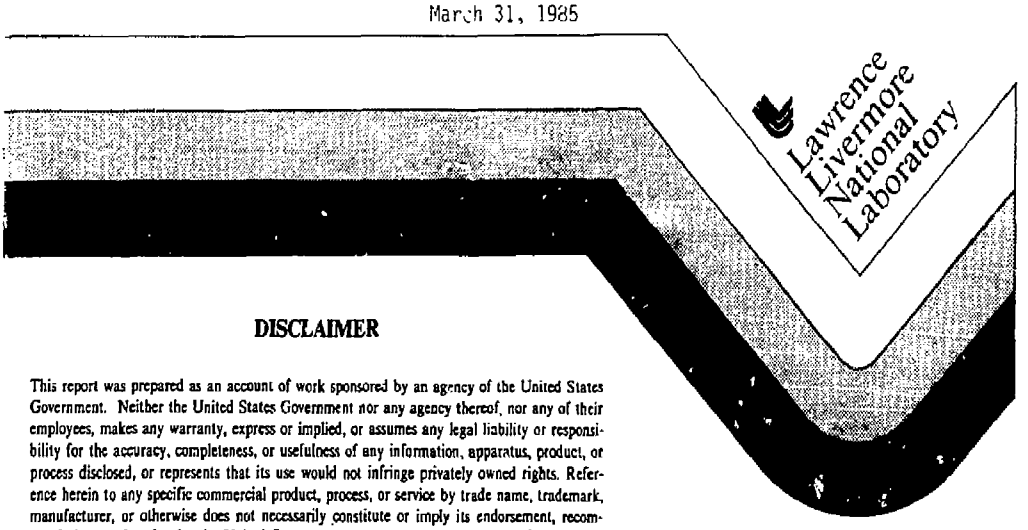

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ORGANIC MATERIALS FOR SECOND HARMONIC GENERATION

FINAL REPORT (LLNL-2689405)

March 31, 1985

compiled by:

Robert J. Twieg
IBM Research K91/282
5600 Cottle Rd
San Jose, CA 95125

FINAL REPORT CONTENTS

I. Organizational Matters

A number of individuals have been involved in the project over the last year; they are (in no particular order) and their roles:

Dr. Robert Twieg: synthesis, administration

Dr. Carl Dirk: post-doc; synthesis, Cambridge File study, calculations

Dr. George Wagniere: visiting summer faculty from the University of Zurich; hyperpolarizability calculations

Dr. Diane Dobrowolski: supplemental; synthesis, laser measurements

Dr. Juergen Rabe: IBM World Trade post-doc; Langmuir-Blodgett deposition

Dr. Steve Mumby: IBM World Trade post-doc; Langmuir-Blodgett deposition, dipole moment measurements

Dr. Jerry Swalen: Langmuir-Blodgett effort

Dr. Yves Levy: visiting scientist from the Optics Institute in Orsay; Langmuir-Blodgett thin film analysis

Dr. Ernesto Marinero: laser powder stability and phase-matching

Benjamin Yoo: summer student; laser powder measurements

Also thanks to E. Nazzal for samples and Dr. Al Sporer for vapor deposition

Dr. John Crowley passed away early in the program. His overall candor his insights into the crystallographic and other aspects of the work were missed. May he rest in peace.

II. Introduction

The purpose of this study was to identify organic materials suitable for use for optical second harmonic generation (SHG). In general, there are two configurations in which organic materials might be employed for SHG. The first is the use of large crystals of organic compounds in a fashion reminiscent of now common applications of a variety of inorganic crystals such as KDP, lithium niobate, etc. The second configuration involves thin films of organic materials such as are obtained by Langmuir-Blodgett deposition.

The organic compounds which were tested were selected on a variety of criteria. Past experience has taught which molecular functionality is useful to obtain the dipole moments required and experience is slowly being accumulated on how molecular shape and functionality can influence crystal packing. A first approach, in which molecular issues supercede crystal issues, has been quite productive in the past but is admittedly highly stochastic in nature. It is somewhat dangerous to rely on past experience alone since prejudices develop and other opportunities might be overlooked. Hence, we decided to simultaneously adopt a second (and just opposite) approach as well. This opposite approach entails examining all the single crystal data (the Cambridge File) and sorting out those organic compounds which have been demonstrated to crystallize in a space group appropriate for SHG. Here the crystallographic issues supercede the molecular issues and this approach potentialy opens up many new opportunities for discovering functionality useful for production of the molecular dipole moment and control of molecular crystal packing.

Materials potentially useful for harmonic generation in the crystal form have been obtained from commercial sources and by total synthesis. Commercial

sources and total synthesis were valuable in obtaining materials selected from the Cambridge file and after evaluation of these candidates further synthetic structural modification was undertaken whenever possible.

In terms of both materials and optical techniques harmonic generation in thin films is a largely unexplored area. There were no commercially available materials we were aware of which might function as thin films thus all materials examined were obtained by total synthesis.

One might inquire why, in general, is it of any value to examine organic materials in the first place since a large number of nonlinear inorganic substances have already been well developed. There are a variety of answers to this inquiry. First, organic compounds far outnumber the inorganics and it would be absurd to ignore this largest single class of substances. Second, organics have a significantly wider range of hyperpolarizabilities than inorganic salts (excluding the metallic substances such as tellurium). Third, there is some indication (still not adequately substantiated) that in many cases organic materials have very good optical damage properties. Fourth, organics offer new possibilities for fabrication such as Langmuir-Blodgett monolayers. Fifth, last and highly relevant is the fact that inorganics tend to crystallize in the relatively inefficient high symmetry point groups and those groups useful for NLO (nonlinear optical) applications are poorly populated. This situation is essentially favorably reversed for organics which tend to crystallize in point groups of lower symmetry which have more intrinsic efficiency and ease of phase matching.

III. Calculations

The PPP-SCF-CI hyperpolarizability calculation has been used as a screening technique as well as a guide for further synthetic efforts. This program was prepared by Professor George Wagniere in the summer of 1984 while a visiting scientist at IBM, San Jose. The hyperpolarizability subroutine is an exact calculation based upon a perturbation theory derivation by Flytzanis[5]. The PPP calculation provides the necessary transition moments and eigenvalues of the ground and excited states. The PPP method represents the absolute minimum required in terms of sophistication of molecular orbital calculation. More refined and exact methods are available, up to and including ab initio, and for some systems, these will be necessary. The PPP calculation has the advantage that even for large molecules, computational time is relatively low. Thus, crystal fragments containing several or many molecules can be calculated. The PPP technique solely uses p-π orbitals to treat valence π and nonbonding electrons in an SCF manner, with all other electrons frozen on their respective atomic cores. Because the σ frameworks are poorly polarizable, neglecting those electrons is acceptable in the prescence of significant π networks. Comparison of calculation with experiment bares this out (vide infra). This result comes about in straightforward manner from the Flytzanis expression:

$$\beta_{ijk} = \frac{1}{2} \sum_{\rho} \sum_{ee'} \frac{\langle 0|\mu_i|e\rangle\langle e|\mu_j|e'\rangle\langle e'|\mu_k|0\rangle}{\left[(E_e - E_0) - 2\hbar\omega\right]\left[(E_{e'} - E_0) - \hbar\omega\right]}$$

where E_0, E_e represent the ground and higher eigenstates respectively; and $\langle 0|\mu_i|e\rangle$ are transition moments between eigenstates. Individual terms for the

hyperpolarizability are seen to be inversely proportional to the difference between ground and excited eigenvalues. Excitation of the σ framework involves large eigenvalues, consequently resulting in smaller hyperpolarizability contributions. Some systems, particularily those transparent below 240nm, will require CNDO (or higher refinement) calculations to take the σ framework into consideration. For instance, phosphineborane and amineborane adducts,

$R_3B \leftarrow PR_3$ $\qquad$ $R_3B \leftarrow NR_3$

are essentially only σ frameworks, yet they possess large (4.0-5.2 D)[6] dipole moments. These materials are probably transparent below 240nm if not down to 200nm for some.

Because of the nature of the molecular orbital calculation, calculations are restricted to first row elements, B, C, N, O, F. Other types of MO programs are being considered to extend the calculation to at least the second periodic row. However, this represents a refinement at least a year away. Upon Professor Wagniere's return to Switzerland, the program was completely flexible only for C, N, and O. The Charged Sphere approximation[7] within the Gamma matrix subroutine, "GAMIX", was limited to interactions between these three atoms. This subroutine has since been modified to include fluorine, and will be modified to include boron when a need demonstrates itself. In addition, Professor Wagniere's parameter set was limited to C, N, and O, and only for a restricted set of bonding interactions. For instance, while an sp^2sp^2 C-O bond (a carbonyl) could be treated, an sp^2sp^3 C-O bond (phenol) could not be treated. The necessary parameters have been determined along with some

concomitant program modifications.

Two other modifications have been implemented since Professor Wagniere's departure. To simplify data preparation, he had idealized some structures somewhat rather than use actual crystallographic data. For instance, the three nitroanilines had the same symmetric benzene ring (R_{CC}=1.395A for all distances) and the same C-N and N-O bond lengths. In addition, resonance integrals were invariant with internuclear distances. Currently, all calculated structures are based on actual crystallographic data, and resonance integrals are scaled using the Linderberg relationship[8] ($\beta_{ij}=C_L(1/r)dS_{ij}/dr$), where S_{ij} are general expressions for the overlap integrals by Mulliken.[35] The constants C_L have been introduced to bring the absolute values of β_{ij} (resonance integrals) more into line with those used by Professor Wagniere. Table III-I illustrates the difference between the two calculations.

As can be seen from table III-I the use of crystallographic data and scaled resonance integrals seems to result in better agreement between experiment and calculation. There is a poorer fit for p-nitroaniline, but the relative deviation is now no worse than for any of the other predictions. The improvement in o-nitroaniline is noteworthy. Table III-II represents the results from the most recent calculations.

TABLE III-I

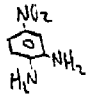
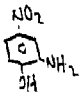
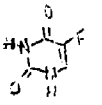
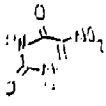
	β_{avg} (10^{-30} esu)			μ (D)			λ_{max} (nm)		
	I	II	exp.	I	II	exp.	I	II	exp.
urea	1.44	-7.0	2.3[9]	5.33	4.98	4.56[9]	207	203	210[10]
PNA	26.8	35.3	34.5[9]	7.24	8.25	6.3[11]	315	325	323[12]
MNA	8.1	12.9	6[13]	6.24	6.51	4.9[14]	390	383	346[15]
ONA	9.9			4.64			345		
		26.4	10.2[13]		4.96	4.22[14]		404	375[12]
	8.6			5.41			360		

I-calculation using crystal structure data and scaled resonance integrals. Two calculated values for ONA because of two unique molecules in unit cell.

II-caiculation by G. Wagniere using idealized structures;fixed resonance integrals

PNA=p-nitroaniline,MNA=m-nitroaniline,ONA=o-nitroaniline

TABLE III-II

	β(10^{-30} esu)		μ (D)		λ_{max} (nm)	
	calc.	exp.	calc.	exp.	calc.	exp.
	41.6		7.31		378	408[17]
	37.7		7.07	5.92[16]	349	370[17]
	51.9		7.88		406	394[17]
	17.4		6.71	4.95[18]	327	345[19]
	5.45		7.11	4.83-5.09[20]	292	285[21]
	0.03		0.91	2.10-2.17[20c,22]	308	285[23]
	-1.29	-0.17[24]	1.55	1.32-1.86[25]	267	271[26]
	0.94	0.53[28]	1.38	1.32-1.54[27]	256	261[26]
	-2.55 -1.90 -0.59 -3.90		3.52 3.73 3.83 4.04	4.11[28]	301 303 313 294	266[29] 280[30]
	5.6		6.31	5.47[28]	335	340[31]

The compound 5-fluorouracil (5FU) crystallizes centrosymmetrically. However, since we can't calculate 5-iodouracil (5IU) using the PPP program, it was decided to calculate this halogen analog instead. The results are still very instructive. There are four unique and somewhat different 5FU molecules in the unit cell[32]. Each of these have been calculated separately, illustrating the difference between hyperpolarizabilities across a range of structures. The uracils contain the urea moiety in conjugation with an -ene and acyl group. The total hyperpolarizability of 5FU is not much different than urea itself, and the measured powder SHG of 5IU is of the same magnitude. Even in the case of 5-nitrouracil (a known SHG compound) ,the resulting calculated value is only ~ 2x urea. Substitution at the 5- position seems to have little effect. Calculations of 5FU are probably a good approximation to calculations of 5IU. In addition, improvements in the uracil hyperpolarizability probably require modifications at other atoms, particularily at the nitrogens.

Comparison of p-nitroaniline (PNA) to p-nitrophenol (PNH) would be instructive to compare the effect of an oxygen donor versus a nitrogen donor. PNH has not been measured in solution, and consequently it was calculated using the PPP-hyperpolarizability routine. The calculational result suggests that PNH has a significantly poorer hyperpolarizability than PNA. An experimental determination needs to be done to verify this result and the parameters used. The oxygen parameters used for the phenolic portion of the molecule were determined by fitting the experimental results of phenol itself. The parameter fit to phenol, while intuitively acceptable, is probably not unique. Experimental hyperpolarizability determinations on some SHG active phenols would help to firmly anchor the parameter set.

Given the parameters we have, calculations of a number of nitrophenols and nitroaminophenols have been done. Calculation of 4-nitrocatechol (4NC) results

in a hyperpolarizability 3x that of PNH and only 1/2 that of PNA. In the solid state this compound has been verified to be ~5x urea. This result, while not of a solution, engenders somewhat more confidence in the parameter set. Replacement of either OH with an amine raises the hyperpolarizability by 2-3x. Of these two aminonitrophenols, the 2-amino-4-nitrophenol (2A5NH) would probably be the least colored, but still as active as PNA. It is curious that while replacement of one hydroxy with with an amine results in such large increases, replacement of both results in no further increase.

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IV. Cambridge File

All the 588 compounds we have selected from the Cambridge File for further study are found in Table IV-I. A copy of the complete sorted list of all noncentrosymmetric space groups has previously been provided to Dr. Eimerl. Thus far, 132 compounds from the Cambridge File have been tested. This includes 71 centric compounds which were inadvertantly tested and later found in the Cambridge File. Even so, 7 of these compounds displayed obvious SHG activity suggesting different space groups than previously determined. Of the 61 acentric compounds (five of which appear both in centric and acentric space groups) tested, 36 displayed some obvious activity. Test results on all compounds from the Cambridge File are included in Table VIII-II just before the master list VIII-III of all compounds tested. Most compounds measured have been from biaxial crystal classes, with a predominance in point groups 2 and 222. The large number of 222 systems is unfortunate considering that noncritical phase matching is impossible. A very small number of uniaxial crystals have been measured. The best of these, and quite promising because of available crystal sizes, is triethylphosphine sulfide (#665). The crystal structure (Acta Cryst. 12,1053-1054(1959)) of this compound shows the PS moiety to be located at special sites with axial alignment along the six fold axis. These compounds are nearly perfectly one dimesional since polarization occurs only along the PS axis; only the d_{33} component will be nonzreo. Unfortunately, even though 100% of the microscopic hyperpolarizability will be seen in this macroscopic component, this component will not be noncritically phase matchable. A second noncentrosymmetric phosphine sulfide is readily available: tricyclohexylphospine sulfide (Canad. J. Chem. 55,3081-3085(1977)). This structure was refined in a centric space group because of some difficulties in

refining in the preferred acentric group. However the authors demonstrated the structure to be acentric by SHG of a Nd YAG laser. Because the structure was refined in the wrong space group, the Zyss analysis (Phys. Rev. A 26, 2028-2048 (1982)) (involving determination of how the microscopic hyperpolarizability tensor β projects on the macroscopic tensor **d**) may not be strictly valid. If however, the orientation of indivual molecules is correct with respect to the unit cell axes regardless of the space group, then the analysis can be done. For point group mm2, the analysis requires knowledge of two angles. Angle θ is made between the polarization axis and the diad axis (**c**). The angle ϕ comes from that angle made from the intersection of the molecular plane and (001) plane, and the **a** axis. In the case of phosphine sulfides a 'molecular plane' does not exist. We shall therefore instead use the Euler angle ψ as defined by Zyss. From the crystal structure these two angles can be easily determined: θ=82.10°, ψ=7.908°. The following components (in the crystallographic coordinate system) will be nonzero and will achieve the stated fraction of their maximum value:

b_{zzz} 0.26%

b_{zyy} 0.66%

b_{zxx} 34.4%

The value of the zzz component is quite small though this component is not noncritically phase matchable. Most of the efficiency is confined to components which are noncritically phase matchable. This compound has been purchased and tested. Unfortunately, the material presently in our possession shows no activity!? Attempts at recrytallization have indicated that two crystal forms exist, one of which is unstable towards conversion to the inactive form. The other (active?) crystal form has not yet been isolated. The phosphine sulfides

and compounds with similar structures are perhaps the only compounds which are strictly one dimensional in their polarization. It should be possible to very accurately predict macroscopic tensor components given a knowledge of the lone microscopic component and the crystal structure. Further study is warranted.

Table IV-II supplies the frequency of occurrence of organic compounds in all noncentrosymmetric space groups. Of the total of all (29052; ca. 1981) compounds in the Cambridge File, 8004 were found to be noncentrosymmetric. Of these 7259 are in biaxial classes, 693 in uniaxial classes, and only 52 in anaxial classes. Clearly the study of nonlinear optics in organics will be restricted primarily to biaxial crystals. Investigations on uniaxial or anaxial systems will almost certainly require first selecting a known compound from the Cambridge File rather than synthesizing many new materials with the hope one may crystallize uniaxilly or anaxilly. With regards to the biaxial systems, 3430 (47%) crystallize under 222 point symmetry and thus offer no possibility for noncritical phase matching. In uniaxial systems six classes (6mm, 6, 3m, 3, 4bar2m, 4) permit the possibility of noncritical phase matching. This includes 392 compounds. These statistics emphasize the difficulties in finding useful organic materials for second harmonic generation. Of the 29052 entries in the Cambridge File, only 4221 (15%) compounds will permit noncritically phase matched second harmonic generation. For the synthetic chemist this means that only one out of every seven crystalline compounds made are capable of noncritrically phase matched second harmonic generation. When the vagaries of molecular orientation are considered, only a small percentage of new compounds may ever be of practical use. The case for inorganics, however, is even more bleak as demonstrated in Table IV-III. The population of noncentrosymmetric and efficient space groups for the inorganics is significantly less than the

organics.

Recently, Zyss's methods which relate microscopic and macroscopic hyperpolarizabilities have begun to be applied to the Cambridge File. For instance, it is possible to sort out all 81 p-nitroanilines from the Cambridge File. Of these, 34 can be considered one dimensional in their polarization. Eleven of these compounds are noncentrosymmetric. The hyperpolaizability of p-nitroaniline (PNA) is known and predominant along the axis of the two nitrogens. It should be possible using Zyss's methods to determine how this microscopic hyperpolarizability projects onto the macroscopic tensor. Of the eleven compounds, four are in point group 2 or m. These are the easiest to applv the one dimensional model to, and the results for these are given below:

p-dimethylaminonitrobenzene $P2_1$ DIMNAN

b_{yyy} 7×10^{-7}%
b_{yzz} 0.5%

4,5-dimethylcarbonyl-3-(2,3-O-isopropylidene-β-D-erythrofuranosyl)-1-p-nitrophenylpryazole

$P2_1$ IEFNPZ

b_{yyy} 11%
b_{yzz} 96%

1-p-nitrobenzene-azo-2-napthol Pc NBZANO

b_{zzz} 45.8%
b_{zyy} 81.3%

p-nitrodiazoaminobenzene $P2_1$ NDZABZ

b_{yyy} 38%
b_{yzz} 89.5%

The percentages are those out of the 100% maximum obtainable in any one macroscopic component. Examination of these predictions is instructive. Para-dimethylaminonitrobenzene is known to be only weakly active for SHG, and in fact this is because of unfavorable alignment with respect to the macroscopic axes. The other three compounds are expected to be quite active, and in fact the noncritically phase matchable components should be relatively large. The other seven compounds are in space groups which require somewhat more analysis and results for these will be included in a future report. The utility of the Zyss analysis is apparent. It should be relatively easy to rank compounds in terms of SHG without the need to make or measure them. Many poor candidates can be eliminated at an early stage.

For non-one-dimensional compounds (e.g. 2,4-dinitroanilines) which can be calculated using the PPP-SCF-CI hyperpolarizability routine, it should be possible using Zyss's two dimensional analysis to determine the macroscopic components. This way, all calculable two dimensional compounds of certain classes can be compared to eliminate poor candidates. In addition, these predictions can be compared to experimental d_{ijk} both as a test of the model, and a diagnostic of the effects of intermolecular induced polarizations.

TABLE IV-I

REFCODES Contained in Specific Noncentrosymmetric Space Groups
(cross index for 588 compounds selected for further study)

Under each space group heading refcodes are in alphabetical order from left to right.

#1 P1 1

ACHIST20 BPEPOT FURSEM01 HPHGER KHNESA KINTIN01 LCDMPP01 LCDMPP10 LDOXAL LHOXAL LHOXAL01 NDTBUO NPNYCC NAKCYB01 NALCYS PTHAZ010 SULASC THYNDN TRIMES10

#4 $P2_1$ 2

AARBOX ACGLUA10 ACGLUA11 ACKYNU ACNPEC ACPABR ADPOSD ADPOSM AMBZAM10 AMCHXC AMCPCX AMTART AMTART11 ATCPEN01 ATOTZC10 BANBZY BANMNA BHBYMN BIOTND BIOTNE BISLEU BNFNCH BOAYPI BORMAL BOZETY BPTHNB BRANTO BTFZEP01 BTFZEP10 BUCPCD BZMPIZ BZOSTB BZOXZT BZTRAZ CAASCO CAASCO01 CAASCO02 CBPTHX CHOENO CLANTO CLPCPN CPHTCI10 CXMCYT CXPROL CYHEXO CYHEXO01 CYSURC10 CYTIDN DACYCM DAMCOU DCLPOL DEXBEN DGLACM10 DIMNAN DLCAMX DMPHOL DMPHOL11 EBPVPO ECYSCU EDCDMP EDCDMP10 FBCMT2 FNETAM FPMPHI10 FUMRAM FUMRAM01 GLFUIZ GLULAD GLYCIN GLYTAU HCSBTZ HDRZDO HMNAPQ10 HXOCTN HXSUCB INDAZL INMTZ0 INOSIN10 IONTRQ KETHYS LASCAC01 LASCAC02 LASCAC10 LCARVX LCYSTN LDOPAC LDOPAC01 MABNST MBIBOX MBZAUR10 MBZCLB MBZCLF MBZIND MBZTBS MBZYAN01 MCMOX2 MEPHSA MFRMYC MIEBSC MNPOXC MNPPHN MOBZAC MPATHA MPPAZD MPROSA MRIBPH MTBCEY MXPOXC NAPANT NATZCX NIBZAL NIBZALC1 NOPCYS NPASPG NPMALA OAPASA PATAZL10 PBORNZ PCLPYR01 PEHCMP10 PHENAN PHENAN01 PHENAN04 PHENAN12 PHENAN13 PHENOL02 PHENOL10 PIPPTC01 PIPPTC11 PNBZNT SRTART SUCROS SUCROS03 SUCROS04 SUCROS05 SUCROS11 TARTAC TARTAC01 TARTAC02 TARTAC04 TARTAC05 TARTAC06 TARTAC07 TARTAC23 TBZPHO TCANIL TCNPNB TETROL01 THAQFO TMOCPN10 TRBZAM TUPRBN URAMBR

#5 B2 or C2 2

ACYTID CAMALO01 CAMPQU HXBIUR10 MNIURC NCUREA

#7 Pb or Pc m

AMFORM CANAPQ CAPURP CHNAPQ DGLYCN01 DNTDPH NMBYAN22 PRPHOS10

#8 Bm or Cm m

BRBNIT DACROC

#9 Bb or Cc m

BRACPH20 ETCYPY HYZMAC KNTMET LISUUR MAEPTZ MENPDL

#17 $P222_1$ 222

PHENOL01

#18 $P2_12_12$ 222

AGFINT AMOXAL AMOXAL01 AMOXAL02 AMOXAL03 LIATRH LIATRH01 OBNZQU PROAPH

#19 $P2_12_12_1$ 222

ABIMAZ ABNCAM ABSFCN ABSFCN11 ABZSLM ACCMTS ACMTZT ACNAQU ACPIXZ ADEHXL10 ADESON10 ADHELA10 ADMTZB ADPOSM01 AMACAM AMACAM01 AMCHPA AMCHPA01 AMCOCA AMHMAM AMPYRZ ANTHAL AOXOVA AOXOVA01 ARSACP ARSACP01 ATAZCX ATBOXM ATMHYD ATYRAN BAFORM BAFORM01 BBPHOL BBPHOL01 BCSTIL BDNFAN BDSOXI BPHENO01 BPHENO10 BRONCP BSALAN BZHYDX BZIMTZ BZOXZO BZTRZO CAMALH CATART CBALOA10 CBTHAZ10 CBZTNB CBZYAN CDNPOL CDPACN CETOAP CHLSAN CHONDR CINMER10 CLACPH CLACRF CLBENQ CLBZAM11 CLOFUL10 CMATZP CMXBBE CMXLCS CNANTH CPIMCM CHHTAR10 CTTSTB CXMCYS DAPSUO01 DAPSUO10 DBEZPO DCBUDO DCLPHL DETBAR10 DETSBR01 DETSBR10 DIMPHE10 DIMPHE11 DIMPHE12 DMANAP10 DMCHAL DMDPPN10 DMFUSC DMHXCA DMOXBA DNBOIM DNITPY DNLTYR10 DNOPHL DNOPHL01 DNTNAP01 DNTNAP02 DNTNAP10 DPHTPT10 DPPHOL EDMDXO EMSDXO EPSVIN FORAMO FTCYME GALLAD GFIMZT GLUCUR20 GLULAC10 GLYCNI GULONO10 HACTPH10 HBIURT10 HBZPHO HEXHEL HIPPAC HIPPAC01 HIPPAC02 HMALAC01 HMALAC10 HNIDPA HOMSAN HOXCUM HPCBDP HPHLOX HSBOPH HXQUIO INICAC INICAC01 INOSIN11 IPRMAL ITOLEN KANHXD KDNACN KDNACN01 KETBAR KGLUCO KNPCYM10 LAANNA LCYSTN12 LCYSTN21 LYFURA LYXOSE01 LYXOSE10 MBZOPI10 MCASIM MDAPOS MDXPHO MENFXN MEOXPI MEPHSB METOLS10 MEUREA MGMALA MHCEPO MINSAN MIURCL MIURCL01 MLEICA MNPHOL01 MNPYDO MORTBA01 MORTBA10 MPIACP MSCYPS10 MTMCBA MUMBEL NAETBA NAETBA11 NAPRLA NAPRLA01 NAPRLA02 NIPHAZ NMALAM NPBDXY NPBUDO NTMCPO PGFINT PHENAC10 PHGLOL PHTHDA PNBPIP POSLAN PPATDZ PRCYPH10 PROLIN PSALAN10 PSMFOX PYRIDO RBDNAC01 RBDNAC10 SALPTS SANAPY SMDTHZ10 SMECYO SRFORA SRFORA01 SRFORM01 SRFORM10 SSESOX01 SSESOX10 SUCPYR10 SULAMH10 TBRMBZ TBZPSO10 TCHLBZ TCHLBZ01 TCYCPR TCYCPR01 TMETHS TMEYPH URARAF01 URARAF10 USNICA01 USNICA10 XDHURC YFORMD

#20	$C222_1$	222

AMETZN ASBTRT10 CLMPCL CLMPCL01 DKSBTR DKSBTR01 TGUANS10 TPHYDZ TPHYDZ01

#21	C222	222

IMACZN

#25	Pmm2	mm2

SULOAK

#26	$Pmc2_1$	mm2

KNOACE THIOUR02 THIOUR03

#29	$Pca2_1$	mm2

BZCBUO BZYACO COUMAR01 COUMAR02 COUMAR10 CSALAN CSALAN01 IMDIAC02 KHPHAL MALMND MALMND01 MAMPOL MBZHIC MEHBPH MENPPO MNIANL10 MNQUON10 NAMALN10 NASUAM NIPALA NMBZAX PHHPRD PICRAC PICRAC01 PICRAC11 PINDON PIPPTC RAFXND RBHPHT SIPDTZ SLFSMD SULTAM01 TEAMBO TEAMBO01 TEAMBO02 TEAMBO03 TEAMBO04 TNPHNT TOXANO

#31	$Pmn2_1$	mm2

DTHDSX HOTAUR10

#32	Pba2	mm2

CMNFLU10 MCYTSH

#33 $Pna2_1$ mm2

ACTOLD02 AMBAC001 AMMALA AMPHOL ANPHAC BBDMAN10 BENZNP10 BRACTN BRN1BZ BUAMPI BUTSUL10 BZOFOX CAFUMT CHEXPS CLACTN CLNIBZ CLONAN CLTROP10 CMNBEN CPGXMR20 DEPO4M01 DMFUSC02 DNBENZ01 DNBENZ10 DNPHOL DPUREA DUTRES DUTRES01 DUTRES02 EOBABB FAMTZT10 FUCOUN HTHPYO IDBZCN IFORAM INTHYD LHPHTL01 LHPHTL20 LIFORM LIFORM01 LIFORM02 LIFORM03 MBRPHE10 MBYINO01 NCBURL10 NEHBPH NPRACM10 NSORAM10 NEYACM NIPCIM NIPCOT NOMESL NPBRBY NPCBNZ NPCPAZ NPMBPY PHPYRO PHYDAN PXTMPN RESORA RESORA02 RESORA13 SMORTS TCHXPS TCXCPD TMPSUL10 TOLSAM01 TRIRED

#34 Pnn2 mm2

ACXMAC NOEURA

#35 Cmm2 mm2

LIACET LIACET01

#36 $Cmc2_1$ mm2

AMACDA BMAIAL BMALAL01 DMCYHX HPHTSR VIOLND VIOLND01

#37 Ccc2 mm2

PBRPHE

#39 Abm2 mm2

BBCPEO IBCPEO

#40 Ama2 mm2

AMACDA01 THIETS

#41	Aba2	mm2

CATOLS

#43	Fdd2	mm2

ACANAC10 BTSITZ DMSDIN DMSDIN01 ETHSUL HCYSAC NTRGUA OVANIL PURURE URFORD

#45	Iba2	mm2

PHBORA

#76	$P4_1$	4

DHANQU IPRPOL LCYSTI11 MEOXAL

#78	$P4_3$	4

ALEUIP

#81	P4bar	4bar

MNPOXZ

#82	I4bar	abar

ABACOX10 ANPRAL NDFORM PERYTO PERYT001 PERYT002 PERYT003 PERYT004 TPRANB

#92	$P4_12_12$	422

ALOXAN CAFORM05 CAFORM06 DMNPYO DTFNPS ENHTAR ETDAMS LIHMAM PCLPYR PYMDON

#94 $P4_{2}2_{1}2$ 422

ACTYRA

#96 $P4_{3}2_{1}2$ 422

PHETAC

#97 I422 422

PBTURF

#104 P4nc 4mm

BAEDTA OMCAZP

#109 $I4_{1}md$ 4mm

TEAMSB

#110 $I4_{1}cd$ 4mm

TIKIND

#113 $P4bar2_{1}m$ 4bar2m

ACUODO CYBTOL METAMM TMOSPC UREAXX UREAXX01 UREAXX03 UREAXX04 UREAXX14 UREAXX22

#114 $P4bar2_{1}c$ 4bar2m

ADAMAN01 ADAMAN02 OPYCTP10 PERYTN02 PERYTN10 PHPPNT PHPPNT01 PIPACQ TEPHME TEPHME02 TEPHME03 TEPHME11 TMOSCA TPENGE TPENGE01 TPENGE02 TPENSI TPENSI01 TPENSI02 TPHEPB TPHESN TPHESN01

#118 P4barn2 4barm2

DTHOLC

#121 I4bar2m 4bar2m

AMPHEB AMPHEB01 KTPHEB01 RBPBOR

#122 I4bar2d 4bar2m

AMHTCA GUANZS KHTCAC RBHOXY RBHOXY01

#143 P3 3

HQUACN

#144 $P3_1$ 3

DAZSND DCPHOL OCRSOL SEUREA SEUREA

#145 $P3_2$ 3

GLYCIN01 GLYCIN15 GLYCIN16

#146 R3 3

PCLNBZ

#147 P3bar 3bar

PROBOR

#152 $P3_121$ 321

BENZIL

#156 P3m1 3m1

BIFORM

#157 P31m 31m

GUALSU10

#159 P31c 31m

ENCDSS ENDACD ENZNTS

#160 R3m 3m

HMCSIO HMCSI001 HMTAMB HMTRAO10

#161 R3c 3m

ACEMID01 ACEMID02 ACEMID03 ETSULM MESMET TCYMET TCYMPH

#173 $P6_3$ 6

CATSIA TANPHN TPYRZP

#178 $P6_122$ 622

LCYSTI10

#179	$P6_522$	622

DLACAN10

#186	$P6_3mc$	6mm

EPHOSS ETACIN ETAMCL HNTAAB TETASS TNARSB TMASBR

#190	P6bar2c	6bar2m

NACNMA

#198	$P2_13$	23

NAHNLA NAUACE

#213	$P4_132$	432

GUANSL

#215	P4bar3m	4bar3m

CSTMSI KTMSIO RBTMSI

#219	F4bar3c	4bar3m

BUPHE

TABLE IV-II

Frequency of Occurrence in Noncentrosymmetric Space Groups
(organic compounds)

column A = space group sequential number; column B = international symbol; column C = frequency

A	B	C	A	B	C	A	B	C
1	P1	304	82	$I\bar{4}$	44	156	P3m1	1
3	P2	6	89	P422	0	157	P31m	2
4	$P2_1$	1866	90	$P42_12$	3	158	P3c1	3
5	B2	258	91	$P4_122$	1	159	P31c	5
6	Pm	1	92	$P4_12_12$	97	160	R3m	14
7	Pb	102	93	$P4_222$	0	161	R3c	34
8	Bm	24	94	$P4_22_12$	8	168	P6	0
9	Bb	256	95	$P4_322$	1	169	$P6_1$	16
16	P222	1	96	$P4_32_12$	40	170	$P6_5$	15
17	$P222_1$	3	97	I422	2	171	$P6_2$	3
18	$P2_12_12$	163	98	$I4_122$	1	172	$P6_4$	0
19	$P2_12_12_1$	3174	99	P4mm	0	173	$P6_3$	32
20	$C222_1$	78	100	P4bm	0	174	$P\bar{6}$	1
21	C222	3	101	$P4_2cm$	0	177	P622	0
22	F222	0	102	$P4_2nm$	3	178	$P6_122$	4
23	I222	6	103	P4cc	0	179	$P6_522$	2
24	$I2_12_12_1$	2	104	P4nc	3	180	$P6_222$	3
25	Pmm2	1	105	$P4_2mc$	0	181	$P6_422$	1
26	$Pmc2_1$	11	106	$P4_2bc$	1	182	$P6_322$	1
27	Pcc2	0	107	I4mm	2	183	P6mm	0
28	Pma2	0	108	I4cm	1	184	P6cc	0
29	$Pca2_1$	224	109	$I4_1md$	6	185	$P6_3cm$	1
30	$Pnc2_1$	3	110	$I4_1cd$	9	186	$P6_3mc$	14
31	$Pmn2_1$	31	111	$P\bar{4}2m$	1	187	$P\bar{6}m2$	0
32	$Pba2_1$	8	112	$P\bar{4}2c$	0	188	$P\bar{6}c2$	0
33	$Pna2_1$	467	113	$P\bar{4}2_1m$	12	189	$P\bar{6}2m$	0
34	$Pnn2_1$	11	114	$P\bar{4}2_1c$	55	190	$P\bar{6}2c$	8
35	Cmm2	1	115	$P\bar{4}m2$	1	195	P23	0
36	$Cmc2_1$	52	116	$P\bar{4}c2$	0	196	F23	0
37	$Ccc2_1$	5	117	$P\bar{4}b2$	2	197	I23	4
38	Amm2	0	118	$P\bar{4}n2$	4	198	$P2_13$	16
39	Abm2	5	119	$I\bar{4}m2$	1	199	$I2_13$	0
40	Ama2	10	120	$I\bar{4}c2$	1	207	P432	0
41	Aba2	34	121	$I\bar{4}2m$	11	208	$P4_232$	0
42	Fmm2	7	122	$I\bar{4}2d$	15	209	F432	1
43	Fdd2	106	143	P3	8	210	$F4_132$	1
44	Imm2	2	144	$P3_1$	16	211	I432	0
45	Iba2	30	145	$P3_2$	8	212	$P4_332$	2
46	Ima2	4	146	R3	39	213	$P4_132$	1
75	P4	1	149	P312	0	214	$I4_132$	0
76	$P4_1$	47	150	P321	5	215	$P\bar{4}3m$	4
77	$P4_2$	2	151	$P3_112$	0	216	$F\bar{4}3m$	0
78	$P4_3$	7	152	$P3_121$	27	217	$I\bar{4}3m$	12
79	I4	13	153	$P3_212$	1	218	$P\bar{4}3n$	4
80	$I4_1$	8	154	$P3_221$	8	219	$F\bar{4}3c$	3
81	$P\bar{4}$	8	155	$R32$	12	220	$I\bar{4}3d$	4

Table IV-III

Distribution of Inorganic and Organic Crystals
by Space Group Population

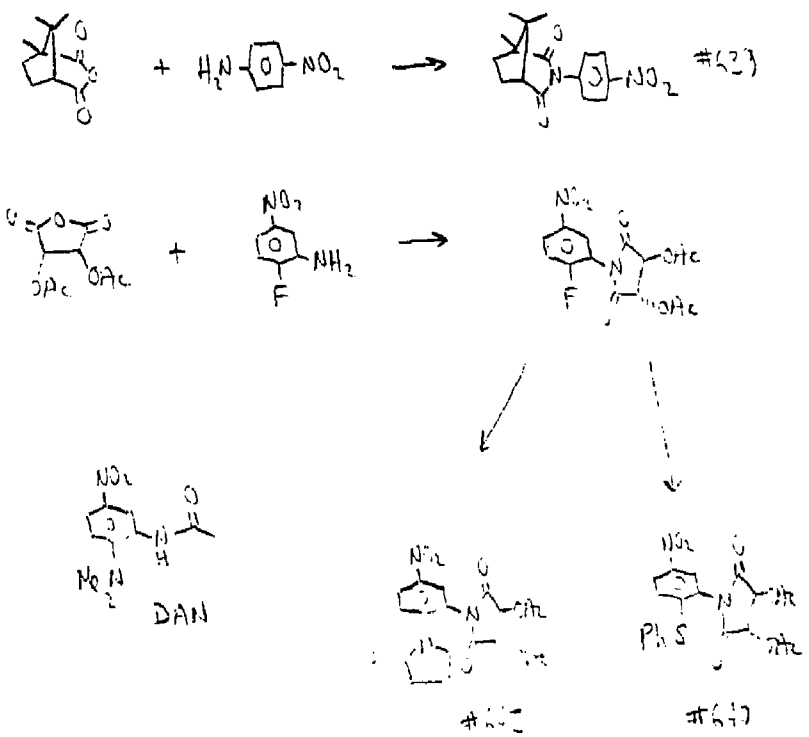
INORGANIC			ORGANIC		
#	%	PM%	#	%	PM%
225	8.5	-	14	35.9	-
62	6.8	-	2	13.7	-
227	5.5	-	19	11.6	19
194	5.3	-	4	6.7	38
14	4.9	-	15	6.6	-
221	4.8	-	61	4.3	-
166	3.7	-	62	1.9	-
12	2 5	-	33	1.8	38
15	2.5	-	60	1.2	-
63	2.2	-	1	1.0	38
148	1.9	-	9	0.9	38
164	1.9	-	5	0.9	38
191	1.8	-	29	0.8	38
139	1.8	-	11	0.8	
2	1.7	-	12	0.6	-
129	1.3	-	18	0.6	19
141	1.3	-	13	0.5	-
216	1.2	19	148	0.4	-
205	1.2	-	43	0.4	38
88	1.1	-	7	0.3	38
230	1.1	-	56	0.3	-
11	1.0	-	92	0.3	x
80	1.0	-	88	0.3	-
136	0.9	-	64	0.3	-
167	0.9	-	20	0.3	-
186	0.9	19	176	0.3	-
176	0.7	-	114	0.2	19
140	0.7	-	57	0.2	-
61	0.7	-	82	0.2	x
193	0.7	-	63	0 2	-
19	0.6	19	36	0.2	38
220	0.6	19	86	0.2	-
-	71.7			95%	

Inorganic Data: A. D. Mighell, J. R. Rogers, Acta. Cryst., A36, 321 (1980) obtained from Fig. 4.
Organic Data: A. D. Mighell, V. L. Himes, J. R. Rodgers, Acta. Cryst., A39, 737 (1983).

V . Synthesis

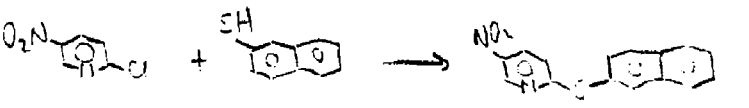
In this section aspects of the synthetic work of the program will be described as a function of class of material. This tabulation is not comprehensive but is intended only to reflect the general area in which synthetic activity occurred. All the synthetic materials prepared and measured in the course of this study are found in the Compound Master List VIII-III.

A number of new groups of nitroaromatics have been prepared during the program. The first group includes compounds which employ tartaric acid and its derivatives as chiral auxilliary. Reaction of the optically active diacetylated tartaric acid anhydride or camphoric anhydride can potentially produce an optically active imide from an aniline, particularly nitroanilines in the case at hand. This procedure is illustrated for the camphoric acid imide derivative of 4-nitroaniline (#639). This procedure has also been applied to compounds formally derived from 3-amino-4-fluoronitrobenzene such as 3-diacetyltartarimido -4-pyrrolidino nitrobenzene (#645) and the thiophenol adduct (#640). and others. All these compounds had some SHG activity but no single compound had any really exceptional properties at least relative to some of the 3-acetamido compounds (such as DAN) examined earlier which possess remarkable (75-150 x urea) efficiency.

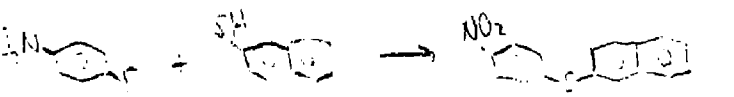


The second group of compounds involve sulfur derivatives as a donor on nitroaromatics. Nitrobenzenes and nitropyridines have been examined and the sulfur moieties have been derived from benzenethiol and β -napthalenethiol. These materials have been prepared in analogy to the class of nitrodiaryl ethers which have been prepared in the past; a few of these compounds have novel SHG activity and in addition have cutoffs which are blue-shifted from the usual amine-substituted nitroaromatics. Among this class of materials is the bisthiophenol derivative (#672) which is also in the cambridge file and the 2-napthylthiodinitropyridine (#617) and the 2-napthylthio-4-nitrobenzene (#618) which are both noncentrosymmetric. The use of sulfur donors should be more thoroughly pursued but is made intrinsically more difficult for two reasons: first, the number of sulfur donors is smaller than the corresponding amines and second, very few of the sulfur donors available are optically active unlike the amines for which many are optically active (and their derivatives therefore appear in noncentrosymmetric space groups).

#672

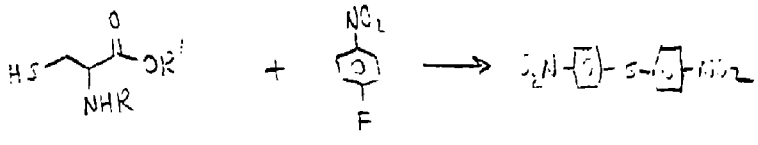


#617

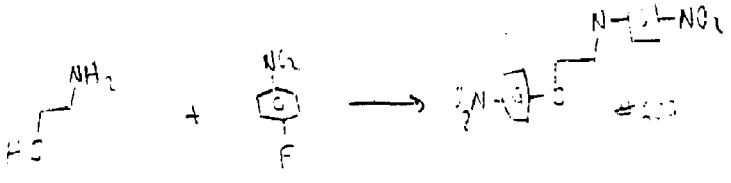


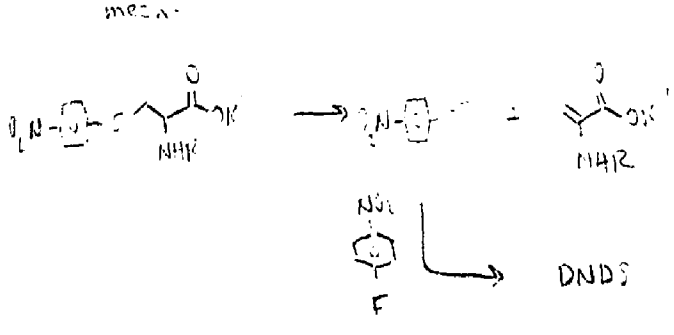
#618

When cysteine methyl ester was employed in an attempt to produce an optically active sulfur donor product some unusual and unanticipated chemistry was obtained. For example, in the specific case of reaction between cysteine methyl ester with p-fluoronitrobenzene the expected N,S-diadduct was not obtained. Instead 4,4'-dinitrodiphenylsulfide (#624) was obtained in greater than 50% yield. Subsequently, under optimized conditions we have now been able to isolate 4,4'-dinitrodiphenylsulfide (DNDS) in 70-80% yield from the reaction of cysteine methyl (or ethyl) ester with 4-fluoronitrobenzene. DNDS has also been obtained from cysteine itself, N-acetylcysteine and even cystine methyl ester. The diaryl sulfides are apparently also isolated from the reaction of other substrates such as 2-chloro-5-nitropyridine and Sanger's reagent. In contrast to these results cysteinamine (which does not contain the acid or ester group) gives the expected diadduct (#649) and none of the diarylsulfides. Our current thinking involves the participation of β-elimination (retro-Michael) reaction to produce the nitroarylmercaptide as a reactive intermediate. This reaction has been utilized to prepare a variety of diaryl sulfides intended for testing for nonlinear optical applications.

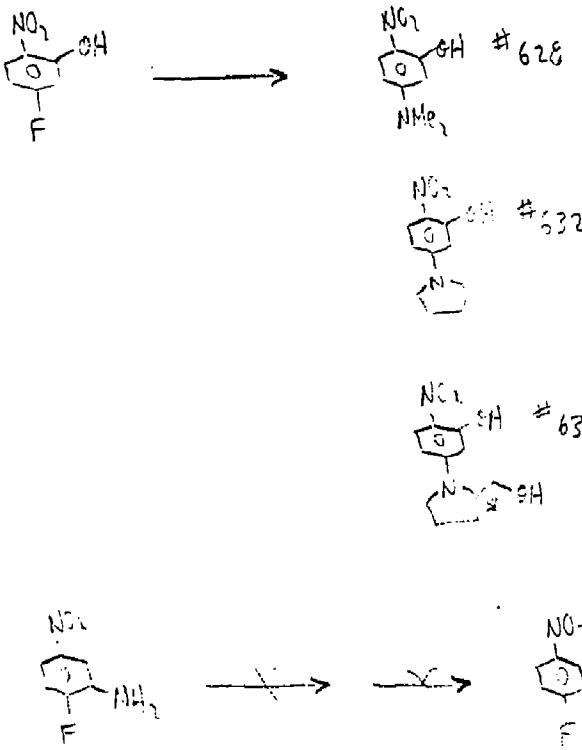


DNDS
#624



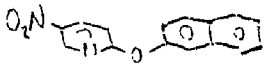


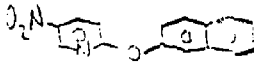
Another class of materials comprises the 5-substituted-2-nitrophenols which are prepared by aromatic nucleophilic substitution of amines on 2-nitro-5-fluorophenol. A number of related nitrobenzenes are well-known SHG materials and it is of interest to assay the effect of the phenol group on the nonlinear optical properties of these substances. To date the few materials (#628, 632, 633, 634, 636, etc.) prepared in this class are unexceptional. Attempts were made to prepare 3-hydroxy-4-fluoronitrobenzene as an intermediate for preparation of phenol analogs of the well sudied 3-amino system. Unfortunately these efforts failed and the requisite precursor was never successfully prepared and as a result a potentially very interesting class of materials could not be examined.

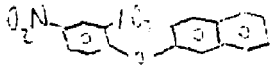


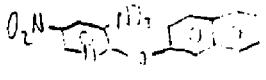
The nonlinear optical properties of 2-(2'-napthyloxy)-5-nitropyridine (#657) have been reexamined following the synthesis of a new quantity of this material. Our earlier studies had indicated that this substance had a powder efficiency ~8 x urea and so we were very surprised to find that the new batch of this substance had an efficiency of zero! This dichotomy is due to the existance of two crystal forms. The lower melting yellow form, which can be obtained as beautiful yellow blades from evaporation of an ethyl acetate-hexane solution, is the SHG active isomorph while the higher melting form must have an SHG inactive centrosymmetric crystal form. For comparison the related nitrobenzene (#654), dinitrobenzene (#651) and dinitropyridine (#655) analogs were prepared. All showed only weak to moderate SHG activity; no evidence for multiple crystal forms in these compounds has been found.

This behavior has not been encountered very often but it is important to recognize that any compound, organic or inorganic, can exist in a variety of crystal forms with signifiicantly differing optical properties. This behavior, of course, greatly complicates the screening process for new nonlinear optical materials. There are undoubtedly a few instances in the screening work we have done in which a change of solvent composition, cooling rate or some other subtle factor would have produced a useful crystal modification. In only very few cases has a single compound intentionally been recrystallized from a variety of solvents to test for the existance of new isomorphs.

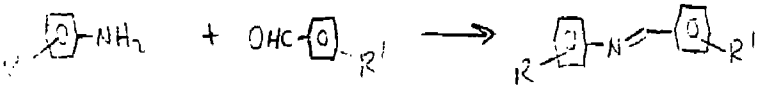


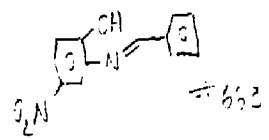


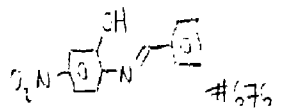


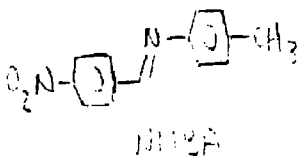


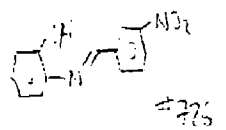
Our examination of the Cambridge File indicated the presence of what seemed to be the presence of an inordinate number of compounds in the benzylidene aniline class in noncentrosymmetric space groups. Many of the compounds which were noncentrosymmetric were ortho substituted in either of the aromatic rings although this substitution pattern is by no means mandatory. Since these compounds are generally straightforward to make we have examined this class in some detail (#663, 676, 726, 793, 799). Although some of the compounds were active no exceptional activity was found. In addition as a group these materials appeared to be somewhat unstable to 1.06 μ laser radiation. However, more effort is probably warrented in this general class of compounds. The material NMBA (Filipenko, et. al., Sov. Phys. Crystallogr., 22(3), 305 (1977)) is reported to be highly efficient given its transparancy (cutoff about 400 nm). It is also instructive to note that in regard to the complexities of multiple crystal structures just discussed that NMBA has three different crystal structures and is just another case in point.

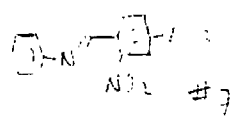




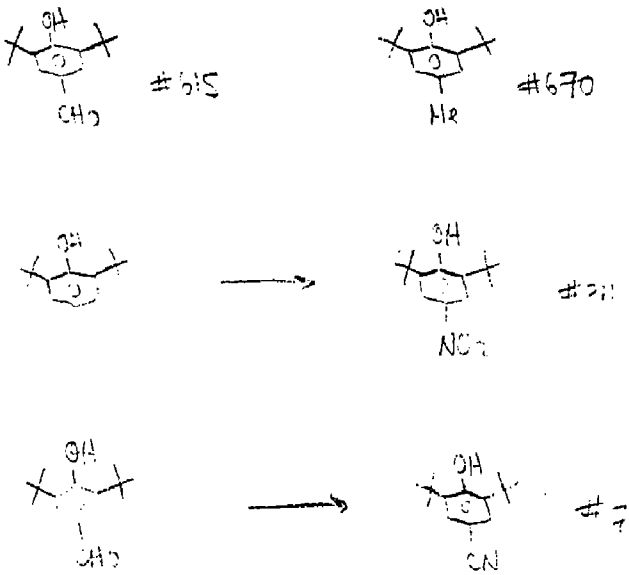




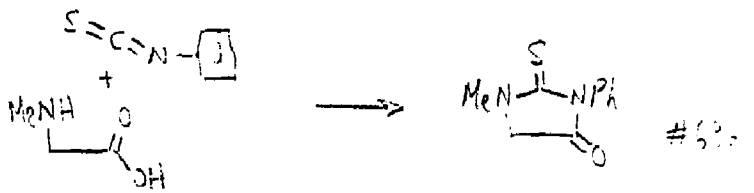


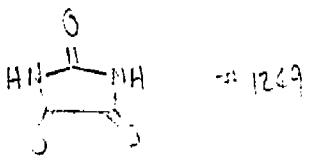


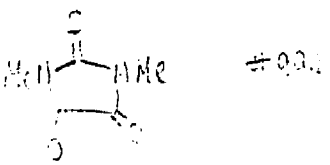
Our examination of the Cambridge File also indicated that a number of derivatives of 2,6-di-t-butylphenol appeared in the Cambridge file and that many of them were in noncentrosymmetric space groups. We have purchased a variety of these compounds (#615, 670) and synthesized a number of others. The syntheses fall within two general groups; first, electrophilic reactions on 2,6-di-t-butylphenol (#811) and second derivatives of the 4-carboxaldehyde (#723, 796, 826). Of these compounds the '-carboxaldehyde and the 4-nitro derivative are of interest for further study. The 4-nitro compound is quite efficient (about 10 x urea) but is easily damaged in spite of multiple recrystallizations. On the other hand the 4-aldehyde is relatively stable; the reasons for this dichotomy in behavior should be studied in much more detail. Further effort, particularly the derivatization of the phenol (by acylation or alylation) is warrented.



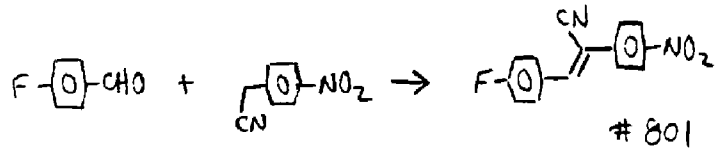
From an earlier project a variety of thiohydantoins and hydantoins (#682-696) were available and since they are formally derivatives of thiourea and urea respectively it was felt that examination of their optical properties was warranted. Of these compounds only one compound (#686) showed any, even feeble, activity. Of special interest are those hydantoin and thiohydantoin derivatives derived from optically active amino acids assuming that the adducts can be prepared with out significant racemization. Also of interest are the thioparabanic and parabanic acids in which the methylene group is replaced by a -CO- group. For example parabanic acid itself (#1249) has been found to be inactive but the dimethyl thioparabanic acid (#994) has moderate efficiency and high damage stability. This latter compound also appears to have a propensity for the growth of large crystals and may be of value in this regard.



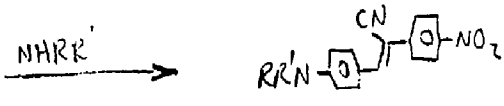


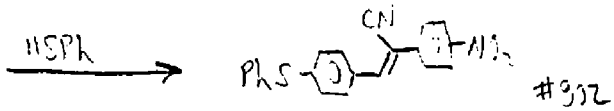


We have prepared 4-fluoro-4'-nitro-β-cyanostilbene (#801) by the condensation of 4-fluoronitrobenzaldehyde with 4-nitrophenylacetonitrile. This material has, in turn, been reacted with a variety of nucleophiles in order to learn about the utility of the molecule as a substrate for aromatic nucleophilic substitution. Secondary amines and aryl thiols (e.g. #802) appear to displace the fluorine in a reasonably straightforward fashion but primary amines are much more troublesome. It appears that with primary amines the original condensation is reversed (retro-Knoevenagel condensation) and the substrate is destroyed. The nitro stilbene adducts are of great interest because it is well known that some of them (such as 4-dimethylamino-4'-nitrostilbene) have very large solution β values; unfortunately none of these compounds have the appropriate crystal symmetry so that the large β value is available in the solid state. A drawback of the polar stilbenes which have both amine donors and nitro acceptors is that they are strongly absorbing in the visible. A related cyanostilbene (#1405) from the Cambridge file was also prepared and shows reasonable SHG activity.

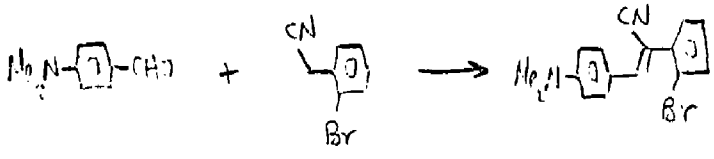


#801



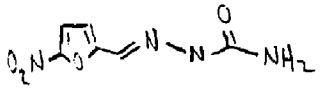


#802

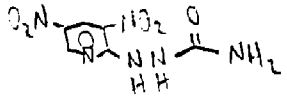


#1405

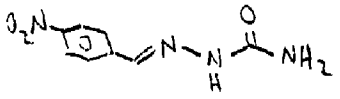
During the screening of commercially available materials we found that nitrofurazone (#1087) is a very efficient second harmonic generator. In fact, unknown to us the compound had been described earlier by some Russian workers (Davydov, et. al., Opt. & Spectr., 30, 274 (1971)) who report the material to be about as effective as lithium niobate. Our measurements indicate this estimate is probably low and that further more quantitative measurement is warrented. In addition the material seems to have good laser stability. This compound is very similar in structure to the material DNP-SC which we described a couple of years ago. It appears that the semicarbazide group may be of great value to influence noncentrosymmetric crystallization and since it is essentially a urea derivative this is not altogether surprising. A number of new nitrofurazone and DNP-SC analogs have been prepared. These include the dinitropyridine analog of DNP-SC (#1336, 6x urea), the nitrofurazone analogs with benzene (#1416, 0 x urea) and thiophene (#1418, 0 x urea) rings. Note the simple change from the oxygen in the nitrofurazone furan to the sulfur in the analogous thiophene is sufficient to render the thiophene analog completely inactive. The preparation of some more UV transparent analogs of nitrofurazone such as those obtained from simple carbonyl compounds and aldehydes (#1398-1401) has also been done. A study of substituted semicarbazides as simple urea derivatives is probably also warrented but remains to be examined.



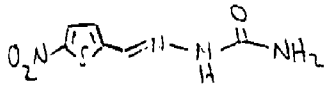
#1087



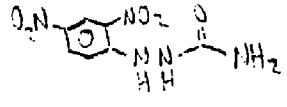
#1336



#1416

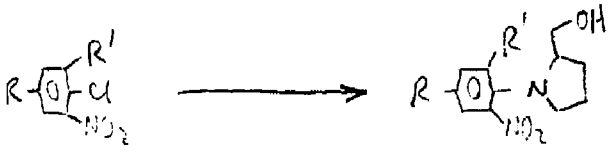


#1418



DNP-SC

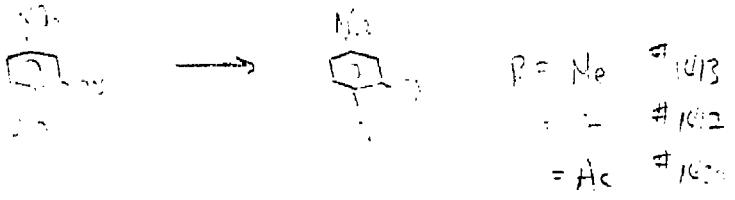
Studies have been initiated to attempt to blue-shift the chromophores of the typical nitro-amine aromatic compounds by the introduction of ortho-substituents into the ring. The reactions of a variety of amines with certain commercially available precursors such as the chlorodinitrobenzonitrile (to give #1392, 1395) and the chlorodinitrobenzotrifluoride (to give #1397) have been run. Optimization of the reaction conditions was required to obtain clean reaction from these highly reactive aromatic halides. Initial results indicate that the chromophores are shifted in the desired fashion but not to a sufficient extent. Even with a variety of donors, some of them optically active, little SHG activity was obtained from any of the compunds in this class.



R, R' = NO_2, CF_3
R', R = NO_2, CF_3, etc

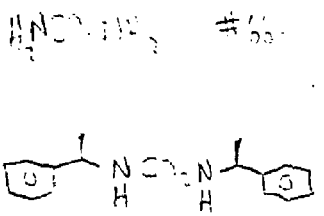
#1392

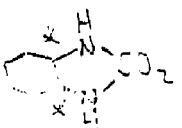
The 4-nitrocatechol (#614) is a particularly interesting substance since it has a hydroxy donor (two hydroxy donors in fact) and has retained good efficiency (5-6 x urea). We have done some simple synthetic modifications of this compound such as ether (#1413, 1417) and acetate (#1420) derivatization to assay the effect on crystal habit and chromophore. A few attempts to use nitrocatechol as a diol for ketal formation (potentially with optically active ketones) failed. The monofunctionalization of this diol has not proved to be straightforward and a variety of monohydroxy-monoethers were not obtained in a pure fashion. Selective reaction conditions or blocking groups must be developed to accomplish this.

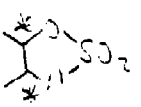


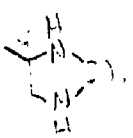
R = Me #1413
= Et #1412
= Ac #1420

The most important general continuity in new chemical structure which has appeared in the course of this study involves the sulfone and sulfonamide functionality. Sulfamide (#664) has an efficiency about a third that of urea with similar exceptional UV transparancy. Damage tests on this compound also indicate that it is exceptionally stable The more accurate quantification and study of this substance appears warrented. The replacement of hydrogen by aliphatic residues will change the chromophore only a small amount but may have a profound effect on crystal behavior. The preparation of a series of these materials in parallel with their urea analogs would be a very worthwhile undertaking. The common chemistry involved in the preparation of the ureas and sulfamides with optically active amines may be particularly useful. By coincidence, the optically active sulfamides such as (#1467) (which has just become commercially available) are of current interest as ligands for asymmetric reduction with aluminum hydrides in organic synthesis (J. Org. Chem., 49, 3862 (1984). This particular compound has only weak SHG activity. Cyclic analogs of optically active diamines and the mixed sulfonic ester-amides which are derived from amino-alcohols are also of potential interest. Fortunately, the optically active diamines required to prepare and are commercially available. This class of compounds merits significant attention in future efforts.

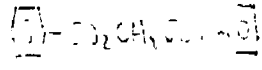




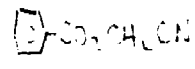




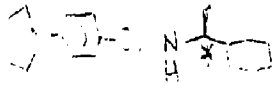
A variety of active aromatic sulfonamides and aryl sulfones have also been found from commercial sources. These include hydrochlorothiazide (#1237), hydroflumethazide (#1240) (both veterinary diuretics), sulfisomidine (#666) (a veterinary antibacterial agent) and the synthetic intermediates bis(phenylsulfonyl)methane (#701), phenylsulfonylacetonitrile (#705) and dihydroxydiphenylsulfone (#858). Little is presently known about the potential nonlinear activity of these substances and a more focused effort on such materials is required. Work has been done on some arylsulfonamide derivatives using some of the same iterative procedures which have proved successful in the past during the optimization of the nitro-amine substituted systems. Fortunately, the synthetic precursor 4-fluorobenzenesulfonylchloride is available which conceptually allows a versatile route to a host of these materials. Reaction with an amine gives the fluoroaromatic sulfonamides which can be reacted again with an amine (or other nucleophile) in the aromatic nucleophilic displacement mode to install the donor amine in the polar adducts. The compounds depicted below (#1393, 1423, 1424, 1426) have been prepared in this fashion. The SHG properties of these compounds is disappointing, however. A good deal of flexibility exists since optical activity can be introduced into the sulfonamide or arylamine portion of the molecule at will. No single material has been found with any exceptional stability but it is felt that more effort is required in this new class of materials.



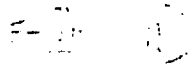
#701



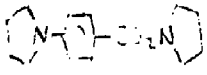
#705



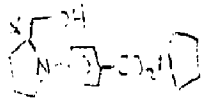
#1393



#1423



#1424



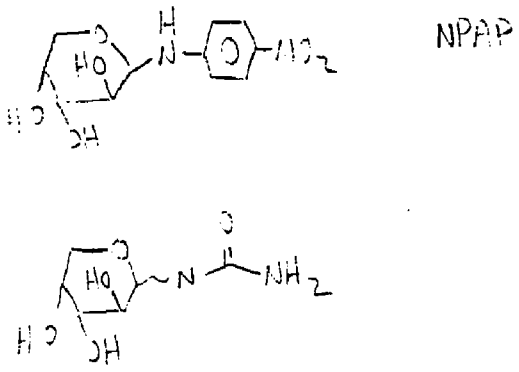
#1426

Other compounds which include novel sulfur-containing functionality are the thiocarbamate salts (e.g., #1008). The thiocarbamates are easily prepared from an amine and carbon disulfide. A number of these have been prepared from a variety of amines (some of them optically active) but the only material with any exceptional activity is the pyrrolidine derivative. The piperidine derivative (#1058) although known to be noncentrosymmetric from the Cambridge search, shows only weak activity. Since this compound has at least three different crystal structures it is uncertain we are working with the potentially most useful form. Further work is warrented on this class of materials especially since the pyrrolidinium salt appears to have excellent optical stability.

#1008

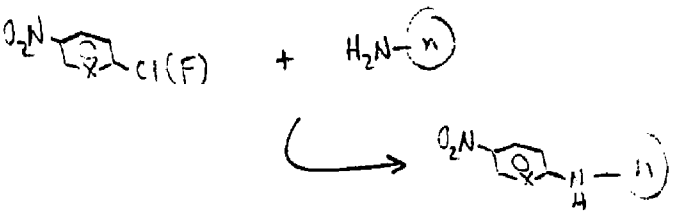
#1053

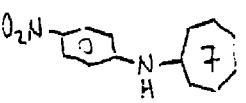
During the second quarter a sample of a carbohydrate derivative of p-nitroaniline, N-(4-nitrophenyl)arabinosylpyranosylamine (NPAP), was submitted to Livermore for more detailed testing. This compound is one of a group of materials we have prepared in which a carbohydrate functions as the chiral ancillary to nitro aniline. Other carbohydrates such as xylose, glucose, lyxose, ribose, deoxyribose, etc. been found to function in this way although arabinose is the best ancillary to nitroaniline found to date. There are two general concepts which are the basis for the study of materials of this type. First, the carbohydrate itself is optically active and will therefor render the adduct optically active and hence noncentrosymmetric and active for SHG. Second, the carbohydrates have been studied in their own right, such as in the case of sucrose (J. M. Halbout, C. L. Tang, IEEE J. Quantum Electron., QE-15, 176 (1979)) and an assortment of others (M. J. Rosker, C. L. Tang, IEEE J. Quantum Electron., QE-20, 334 (1984)). The carbohydrates may be generally characterized by a combination of a high degree of crystallinity but very low SHG efficiency.



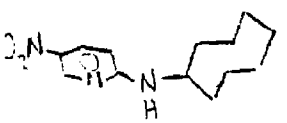
The new compounds we have developed hopefully will deliver both a high degree of crystallinity and simultaneously the high efficiency of the conjugated and polar portion such as nitroaniline in NPAP. There exist a bewildering array of possible useful modifications which could be pursued in this area. Of all of these two stand out as particularly useful. Both modifications would render the derivative more transparent by substituting a less absorbing group than nitroaniline. The first modification would be to use nitrile or sulfonamide groups or the like instead of the nitro group. The second modification would be to use urea instead of the aromatic amines. Urea adducts of the carbohydrates have been known for many years (N. Scoorl, Rec. trav. chim., 22, 31 (1903)) and are a conspicuously interesting set of materials to pursue.

A new and very interesting class of nitrogen donors, the cycloaliphatic amines, for the donor-acceptor substituted aromatics has been examined at the end of the contract period.Here the commercially available cycloaliphatic amines (ring sizes 3, 4, 5, 6, 7, 8, 12) are reacted with the appropriate nucleophilic aromatic substitution substrate. The most interesting materials found to date are 4-N-cycloheptylamino nitrobenzene (CHANB) (#1326) and 2-N-cyclooctylamino-5- nitropyridine (COANP) (#1323). CHANB has moderate activity (about 5 x urea) and is very highly crystalline. COANP is an exceedingly interesting material. It has a transparancy comparable to MBANP but its powder efficiency is on the order oif half-again as large (perhaps up to 40 times urea). COANP appears to have good laser damage stability and an X-ray crystal structure determination, crystal growth and NLO studies are strongly warrented. None of the other derivative from the other amines show any exceptional activity but further work on using methylated aromatic rings is underway. The role of the amine ring size vs. crystal structure is a facet of this study which warrents study in order to apply this knowledge elsewhere.





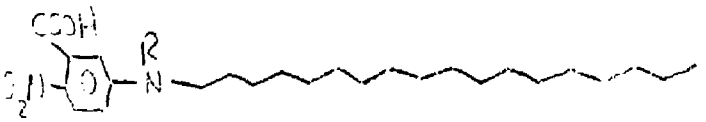
CHANB



COANP

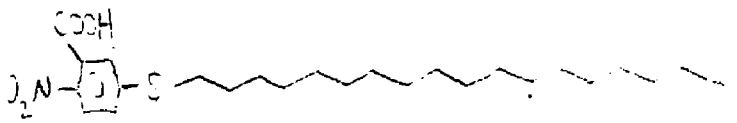
Langmuir-Blodgett Synthesis

Two related but different molecules have been synthesized. The methyl ester of 2-nitro-5-chlorobenzoic acid was reacted with either octadecylamine or N-methyloctadecylamine and finally the ester group was hydrolyzed to the free carboxylic acid. The synthesis using N-methyloctadecylamine proceded in a much more straightforward fashion in terms of overall yield and purity of the final product; this is fortunate since the secondary amine product has significantly superior monolayer forming properties.

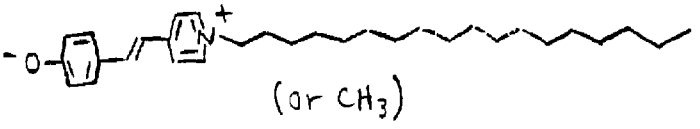


R = H, Me

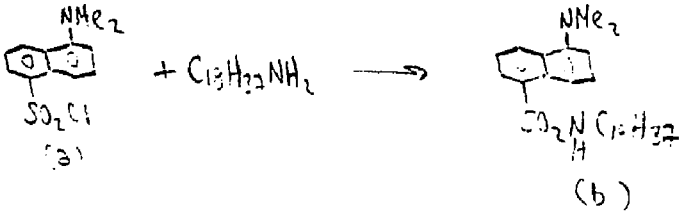
In view of the attempts to blue-shift the absorption of the crystalline materials a new colorless monolayer precursor has been prepared and is undergoing purification prior to deposition experiments. In analogy to the TYS molecule a new monolayer forming candidate in which sulfur replaces the amine donor of TYS has been prepared. The synthesis entails condensation of 2-nitro-5-chlorobenzoic acid methyl ester with octadecylmercaptan with subsequent hydrolysis of the ester to the free carboxylic acid.



Merocyanine (R = CH3) has the largest β value of any known organic compound as determined by EFISH (electric field induced second harmonic generation) experiments; it is roughly 1000 times as nonlinear as urea. Because our thin film experimentswith TYS have produced no observable second harmonic it is appropriate to attempt to observe a second harmonic from a LB film prepared from a molecule which contains a much more nonlinear conjugated and polarized functionality than the nitrobenzene in TYS. Towards this end the synthesis of a potentially monolayer forming dye containing the merocyanine functionality. This dye is synthesized in the same way as merocyanine itself except that octadecyliodide is substituted for methyl iodide.



Dansyl chloride (a), a commercially available compound which is often used for tagging in biological applications, was reacted with octadecylamine to give the desired monolayer precursor ("ODD", OctaDecylDansyl (b)). This compound is an aromatic sulfonamide related to some of the materials discussed earlier; the only difference being that a napthalene is involved instead of the benzene ring. This compound is also somewhat unique when compared to typical monolayer forming materials in that the most hydrophilic portion of the molecule resides in the sulfonamide which is at an internal position rather than at the end of the molecule as in arachidic acid or TYS.



VI. Stability Tests

In second harmonic generation studies of nonlinear materials a key issue is the radiation induced-damage of the medium. The exact failure mechanism could be of thermal or photochemical origin, in any case, it determines the stability of the material and its overall use from the device point of view.

In this quarter we have measured the stability of 17 organic powders by irradiating them for periods up to 1 hour with the fundamental of a YAG laser operated at 10 Hz. The pulse energy utilized was 100 mJ/pulse and this was continuously monitored during the lifetime test by means of a box-car photodiode combination. The samples were chosen based on their measured SHG efficiency relative to urea and in some cases because of their interesting group functionalities.

Our results are summarized as follows:

(1) Urea: a sample of urea was irradiated for 1.5 hours in order to establish a source of comparison as far as stability is concerned, during this period, no measurable degradation of this material was observed.

(2) 614 : this compound has been determined to be at least 4 times more efficient than urea. An 11% decrement in the SHG efficiency was measured over a period of 30 minutes and this followed a linear decay mode.

(3) 670 : chosen because of its interesting functionality, it was found to be 21 times less efficient than urea. The second harmonic generated by this compound disappeared within less than a minute and strong near ir fluorescence was detected. At the end of the 22 minute exposure period, a black deposit was evident.

(4) 665: showed an efficiency at least twice that of urea. This was observed to degrade only 8% during the 35 minute irradiation period.

(5) 615 : approximately 4 times more efficient than urea. Over a period of 23

minutes this efficiency dropped by 70% in a linear form. Burnt particles were clearly seen at the end of test.

(6) 1323: an extremely efficient SHG generator, approximately 50 times stronger than urea. A 15% decrement in the SHG efficiency was measured after 28 minutes.

(7) 1057: this complex was measured to be approximately twice as efficient as urea. A 10% decrement within 18 minutes of testing was observed.

(8) 994: With an efficiency, approximately 5 times that of urea this complex showed no degradation over 25 minutes of testing.

(9) 666: Over 30 minutes the efficiency of this complex degraded 23% from an initial value of 3 times the efficiency of urea.

(10) 672: The initial SHG signal (5 times that of urea) reduced to zero over a 4 minute period in an exponential form.

(11) 664 : this complex showed no degradation over the test period however its efficiency is only 0.4 that of urea.

(12) 843: initial SHG (2x urea) reduced by 95 % over a 9 minute period in a linear fashion.

(13) 1406: over 30 minutes its efficiency (4x urea) decreased 38%.

(14) 768: an inefficient complex (.3x urea) underwent a 85% reduction of SHG output in 4 minutes exhibiting burnt deposit formation. An induction time in the decay mode was observed after which the SHG decreased nonlinearly.

(15) 1047: a very weak SHG generator (.12x urea) decreased to zero in the first 2 minutes.

(16) 791: no measurable change was observed within 35 minutes of test of this compound, its efficiency however is only 1/7 that of urea.

(17) 1405: a decrement of 98% in SHG efficiency was observed within 15 minutes of testing from its initial value of 3 times that of urea.

(18) 1087: a very strong SHG generator (43 times urea) showed virtually no

degradation over the 30 minute test period.

One cannot draw a simple conclusion from this data regarding the cause or causes for degradation. It is intriguing to note however that two trends are evident in one case the decay is linear whilst an exponential deterioration was observed for some compounds. More work needs to be done to understand the mechanisms involved, experiments must be conducted that can identify thermal from photochemical pathways.

PHASE MATCHING MEASUREMENTS

The following compounds 1087, 791,666, 994 and 665 have been selected for phase-matching experiments. An examination of their second harmonic efficiency as a function of wavelength in the 850 to 532 range will be determined. A variety of near infrared and rhodamine dyes will be utilized to derive the fundamental pump wavelengths.

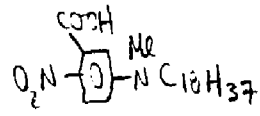
VII. Langmuir-Blodgett

In our search for thin film SHG materials, we have made a number of L-B films from various compounds just described in Section V. Now a number of investigators have found weak SHG from a few monolayers of organic materials, sometimes the organic overlayer even reduces the SHG from a metal film, instead of increasing it.

Our first experiments were done by looking the SHG from a bulk powder sample, unfortunately none was seen. Next a resonance optical cavity was designed. It was the hope and intent that this optical cavity would have an enhanced optical field. The cavity consisted of a high index material, TiO2, on a low index material, SiO2, on a prism and was made in our Central Scientific Services Thin Film Shop. Light was coupled in through the prism and becomes trapped in the high index layer. Unfortunately we saw no SHG with the nitro amino benzoic acid compound, TYS, on the surface of TiO2, where high optical fields are present.

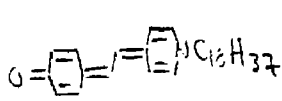
To further increase the effect an L-B film of the same nitro amino benzoic acid compound, TYS, was prepared with 151 layers on each side of microscope slide. Experiments were then conducted at Livermore to measure the second harmonic generation. A comparison with urea showed little or no SHG. Since the experiments were done at normal incidence or at best a few degrees from normal incidence, we concluded that either the in-plane component cancels and we could not excite the out-of-plane component with the current apparatus or the material is not second harmonic active. This later possibility, if it occurs, could be caused by a head to head packing which could be approximately centro-symmetric.

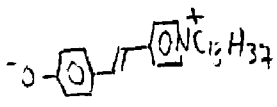
We are currently re-designing and building a rotatory dipping arrangement for the L-B tank to have alternate layers of an inert compound and, therefore, prevent any possible symmetric deposition. (In recent discussions with Gareth Roberts, University of Durham, he stated that they were able to obtain good films by this technique.)



TYS

Spectral measurements were done on three new dyes to determine their absorption characteristics including the merocyanine dye:





This dye in solution exhibited strong solvent shifts and strong spectral shifts with pH.

SOLVENT	ABSORPTION	COLOR
ethanol	405 & 535 nm	orange
chloroform	395 nm	yellow
tetrahydrofuran	390, 570 & 612 nm	blue

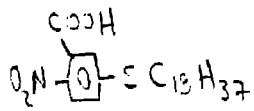
The influence from pH can be stated as

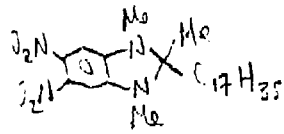
low pH --> yellow

high pH --> blue-violet.

L-B films produced at pH 4.0 - 4.6 hexane/ethanol solvent started with head to tail deposition arrangement but soon leveled off to head to head and tail to tail (Y deposition). Films exhibited an absorption maximum at 380 nm, but gave no SHG. Deposition at high pH gave similar spectroscopic results.

The sulfur analog of the nitro-long chain substituted amino benzoic acid showed an absorption maximum at 350 nm. Since the nitrogen analog has not produced any SHG, no L-B films were made up to this time. The dinitro compound exhibited absorption maxima at 365 and 465 nm in hexane/ethanol. At 530 nm, the second harmonic wavelength, this compound had a small but sufficient absorption to cast some doubt as to the acceptability of this compound for SHG. No L-B films have been made at this time.





VIII. Master List Section

Table VIII-I gives a breakdown, by structural class, of a few of the general types of molecules dealt with in this study. This section is not intended to be comprehensive but rather representative of the most important groups of materials which have been studied. In certain cases a given compound will appear in more than one class; in other cases certain materials in the master list do not appear in the sort list at all.

TABLE VIII-II COMPOUNDS SORTED BY CLASS

aromatic nitriles

638, 712, 714, 727, 732, 769, 817, 826, 843, 929, 1014, 1017, 1047, 1070. 1331, 1395, 1396, 1408, 1478, 1481.

uracils

656, 876, 1118, 1119, 1125, 1126, 1129, 1133, 1157, 1165, 1170, 1186, 1195, 1197, 1218, 1220, 1239, 1247, 1259, 1260, 1263, 1265, 1268, 1270, 1289, 1290, 1372, 1379, 1461, 1525, 1529, 1537

thiourea and urea

659, 1152, 1283, 1284, 1336, 1398, 1399, 1400, 1401, 1418, 1524, 1529, 1406, 1407, 1410, 1445, 1453, 1533

sulfone, sulfonamide, -SO2- derivatives

603, 606, 608, 609, 610, 611, 612, 613, 664, 666, 667, 669, 697, 698, 699, 700, 701, 702, 703, 704, 705, 718, 832, 854, 858, 1067, 1071, 1102, 1128, 1158, 1185,

1223, 1240, 1241, 1246, 1262, 1265, 1266, 1267, 1269, 1271, 1272, 1273, 1274, 1275, 1282, 1285, 1295, 1302, 1304, 1367, 1376, 1378, 1383,1384, 1391, 1393, 1394, 1403, 1409, 1411, 1412, 1415, 1419, 1423, 1424, 1425, 1427, 1441, 1444, 1448, 1449, 1467, 1472, 1485, 1520, 1521, 1523, 1530, 1486, 1534

P=X (X=O, S, Se)

665, 809, 812, 896, 1086, 1169, 1251, 1255, 1256, 1504, 1505

nitrobenzene

601, 602, 603, 604, 606, 608, 609, 610, 611, 612, 613, 614, 618, 620, 623, 624, 628, 630, 631, 632, 633, 634, 636, 637, 639, 640, 641, 642, 643, 644, 645, 647, 648, 649, 651, 658, 659, 660, 661, 662, 663, 671, 672, 673, 674, 676, 677, 717, 726, 733, 737, 764, 768, 777, 781, 782, 793, 794, 795, 797, 798, 799, 800, 801, 802, 806, 811, 813, 833, 836, 843, 844, 845, 875, 878, 879, 881, 882, 883, 889, 895, 897, 898, 899, 900, 923, 925, 939, 947, 963, 967, 993, 996, 998, 999, 1004, 1022, 1041, 1047, 1050, 1052, 1053, 1056, 1094, 1097, 1103, 1104, 1110, 1124, 1135, 1137, 1138, 1140, 1141, 1155, 1171, 1185, 1191, 1208, 1210, 1216, 1227, 1232, 1238, 1248, 1269, 1276, 1279, 1280, 1282, 1291, 1301, 1307, 1310, 1311, 1312, 1313, 1314, 1316, 1317, 1318, 1324, 1325, 1326, 1327, 1331, 1332, 1333, 1337, 1343, 1346, 1347, 1348, 1349, 1355, 1360, 1361, 1362, 1364,1366 1369, 1370, 1374, 1377, 1378, 1382, 1383, 1387, 1389, 1390, 1392, 1395, 1396, 1397, 1402, 1404, 1406, 1407, 1408, 1409, 1410, 1412, 1413, 1414, 1416, 1417, 1419, 1420, 1421, 1422, 1430, 1445, 1450, 1474, 1475, 1479, 1481, 1483, 1496,1511, 1526, 1528.

nitropyridine

616, 617, 619, 621, 622, 650 654, 655, 657, 816, 898, 899, 1046, 1051, 1320, 1321, 1322, 1323, 1334, 1335, 1336, 1344, 1442, 1446.

nitroheterocycle (anything besides nitrobenzene)

605, 679, 680, 849. 876, 877, 965, 987, 1042, 1087, 1088, 1100, 1104, 1110, 1113, 1114, 1134, 1139,1153, 1172, 1199, 1286, 1305, 1306, 1308, 1309, 1418, 1428, 1494, 1509, 1511, 1513, 1517, 1519, 1526, 1528.

aromatic aldehyde

607, 615, 716, 760, 761, 762, 763, 764, 765, 766, 767, 768, 769, 770, 771, 772, 773, 774, 775, 776, 777, 778, 779, 780, 781, 782, 828, 842, 846, 972, 1151, 1155, 1026, 1279, 1375.,

phenol

614, 615, 628, 632, 633, 634, 636, 642, 643, 644, 648, 652, 653, 670, 676, 706, 716, 725, 726, 763, 764, 772, 773, 776, 723, 735, 738, 744, 748, 755, 767, 776, 778, 781, 787, 795, 796, 811, 819, 824, 826, 829, 830, 831, 832, 834, 835, 839, 840, 850, 855, 857, 858, 859, 860, 862, 863, 866, 873, 875, 878, 881, 889, 892, 901, 1094, 1111, 1191, 1228, 1301, 1375, 1388, 1430, 1518, 1527.

benzylidene aniline

663, 676, 793, 799

thiohydantoin

682-696, 1480

amino acid (and derivatives)

783, 791, 803, 804, 805, 807, 810, 838, 897, 913, 1035, 1036, 1038, 1038, 1063, 1096, 1102, 1105, 1121, 1128, 1130, 1132, 1141, 1149, 1159, 1164, 1168, 1171, 1194, 1196, 1200, 1203, 1210, 1211, 1213, 1216, 1221, 1227, 1230, 1253, 1287, 1347, 1350, 1360, 1361, 1363, 1367, 1459, 1515, 1534.

aromatic carbonyl (carboxylic acids)

669, 671, 717, 739, 741, 743, 753, 755, 756, 758, 776, 820, 821, 825, 836, 845, 856, 859, 862, 863, 866, 871, 886, 917, 1019, 1043, 1175, 1238, 1242, 1301, 1387, 1440.

aromatic carbonyl (ketones, esters, quinones, anhydrides, etc.)

635, 660, 712, 713, 720, 730, 731, 783, 790, 823, 827, 834, 835, 837, 839, 841, 857, 860, 868, 869, 872, 874, 879, 884, 885, 887, 888, 893, 894, 906, 912, 930, 939, 945, 953, 954, 956, 959, 961, 967, 989, 993, 996, 1004, 1010, 1021, 1022, 1027, 1028, 1030, 1037, 1040, 1064, 1069, 1070, 1082, 1101, 1111, 1124 1098, 1108, 1153, 1225, 1226, 1228, 1277, 1341, 1352, 1443, 1474, 1484, 1489.

aromatic carbonyl (amide) 625, 674, 675, 706, 797, 798, 800, 822, 902, 903, 973, 1034, 1048, 1049, 1078, 1103, 1117, 1278, 1340, 1342, 1368, 1457, 1528.

C=S compounds

907, 908, 919, 922, 935, 991, 994, 1004, 1016, 1264, 1296, 1319, 1328, 1329, 1330, 1482.

carbohydrates and derivatives

638, 646, 707, 910, 931, 932, 933, 1045, 1107, 1112, 1115, 1116, 1145, 1248,

1310, 1311, 1313, 1314, 1315, 1316, 1317, 1318.

ionic compounds

921, 975, 976, 978, 979, 980, 1003, 1005, 1006, 1008, 1038, 1058, 1060, 1062, 1072, 1073. 1075, 1088, 1090, 1185, 1221, 1257, 1076, 1285, 1296, 1319, 1328, 1329, 1330, 1364, 1378, 1381, 1432, 1434, 1437, 1438, 1454, 1463, 1475,1477 1488, 1493, 1497, 1498, 1499, 1500, 1501, 1503, 1506, 1508, 1520

non-oxidized sulfur containing

616, 617, 618, 619, 620, 621, 622, 623, 624, 629, 631, 637, 640, 647, 649, 660, 671, 672, 802, 813, 898, 899, 900, 1042, 1046, 1050, 1051, 1056, 1205, 1208, 1331, 1344, 1415, 1422.

KEY TO MASTER LISTTABLE VIII-II

Each compound has been assigned a number (600 - end). Whenever a source was available it was provided. The source may have been commercial (Aldrich, Fluka, Sigma, etc.) and the catalog number provided or synthesized in these laboratories (Dirk (cd), Twieg (rjt), Dobrowolski, Nazzal, etc) and the corresponding notebook number provided if available.

All samples were compared to powdered urea which was assigned an arbitrary intensity of one. Powdered samples were initially ranked on the following rather subjective basis:

v. weak - SHG observable (barely)
weak - SHG less than 1/4 urea
weak to moderate - SHG between 1/4 to 3/4 urea
moderate - SHG about equal to urea
good - SHG greater than but less than about ten times urea
excellent - SHG much larger than urea

In most cases the powder measurements were quantified for samples which were equal to or greater than urea. For those materials which were particularly transparent (cutoff less than about 300 nm) a quantitative measurement of SHG efficiency was often run even if the efficiency is less than urea (which is essentially always the case).

The powder SHG measurement is subject to many pitfalls but remains a very valuable tool for screening materials if these shortcomings are recognized. One

should not expect any more than an accuracy of +/- 100% for these determinations since the powders were ungraded, the microcrystals sometimes subject to spontaneous alignment in the sample, and other associated factors.

In most cases the compounds were used directly as obtained and no special attempts were made to recrystallize them from various solvents in order to obtain different crystal morphologies or co-crystallites.

A number of the compounds in the masterlist have appeared previously in the literature and we have made an effort to cross-reference these. These appear in the masterlist with a <reference> where relevent. The reference list at the end of this section is a comprehensive list of all powder SHG measurements we are aware of in the literature.

Modifications in the masterlist have been made since the original installments of the previous three quarterly reports. This final list supercedes the previous partial lists.

TABLE VIII-II (Materials Tested from Cambridge File)

0607	9-anthracenecarboxaldehyde ald 12,323-4 rjt/jc CFS-ANTHAL #19	moderate
0625	4-aminobenzamide sigma A-1658 CFS-AMBZAM10 #4	3-4× urea (dec)
0626	indazole ald I-240-1 CFS-INDZAL #4	0.1× urea
0627	5-iodouridine sig I-7500 CFS-IURIDN10 #4	zero
0646	(-)-inosine Aldrich I-640-7 CFS-INOSND10 #4 INOSIN10,11 #19	weak
0647	4-nitrophenyl-phenylsulfide ald S46100-8 CFS-PNDPHS #14	weak
0652	2,6-di-t-butyl-4-β,β-dicyanovinylphenol Twieg 106-9-4249 CFS-BABYMN #4	weak
0656	5-iodouracil Aldrich 85,785-8 CFS-IURACL10 #4	~urea
0664	sulfamide Sigma S4382 Spacegroup #43 (non CFS)	0.3× urea

0665	triethylphosphine sulfide Alfa 10561 CFS-EPHOSS #186	~urea
0666	sulfisomidine Sigma S-7505 CFS-SLFSMD #29	2x urea
0667	sulfanilamide *Sigma S-9251* CFS-SULAMD,05 #61 SULAMD01,02,03,04 #14	v weak
0668	tetraphenylhydrazine Alfa 16217 CFS-TPHYDZ,01 #20	zero
0669	furosemide Sigma F-4381 CFS-FURSEM #2 FURSEM01 #i	zero
0670	2,6-di-t-butyl-4-methylphenol Aldrich 24,002-8 CFS-MBPHOL10 #19	v weak
0672	2,4-(phenylthio)nitrobenzene 65-91672 cd CFS-BPTHNB #4	strong
0674	1-nitrobenzpiperidinamide rt CFS-PNBPIP #19	moderate
0677	4-dimethylaminonitroaniline rf CFS-DMNAN #4	weak
0678	hexamethylcyclotrisiloxane Petrarch H7260 CFS-HMCSIO,01 #160	zero

0702	phenylmethylsulfone Parish 1114 CFS-MPSUFO #14	zero
0707	α-thymidine Aldrich 85,500-6 CFS-THYDIN #19 THYMDN #1	weak
0708	pentachloropyridine Aldrich 13,800-2 CFS-PCLPYR #92 PCLPYR01 #4	≤urea (d)
0713	2,6-di-t-butylbenzoquinone Aldrich 15,393-1 CFS-TBUBZQ #14	zero
0719	hexaphenyldigermane Alfa 34132 CFS-HPHGER #1	vv weak
0722	acetone oxime Aldrich A1050-7 CFS-ACEOXM #176	zero
0724	hexaphenylditin Alfa 71143 CFS-HPHDSN #14	vv weak
0725	salicylideneaniline 77-9-1672 cd CFS-SALCAN #43	<urea
0727	4-chlorobenzonitrile Aldrich 11,562-2 CFS-CLBZNT #14	~urea (d)
0732	4-bromobenzonitrile Aldrich B5840-7	~urea (d)

CFS-BRBNIT #8

0739	4-bromoacetophenone Aldrich B5,640-4 CFS-BRACPH20 #9	~urea
0740	1,3,5-trichlorobenzene Aldrich T5,460-7 CFS-TCHLBZ (#19), 01 (#19)	zero (rap d)
0741	4-bromobenzoic acid Aldrich 10,851-0 CFS-BRBZAP #14	weak
0743	3-chlorobenzoic acid Aldrich C2,460-4 CFS-MCBZAC #14	weak
0757	4-bromochlorobenzene Aldrich 23,989-5 CFS-BCBENZ #14	weak
0764	5-nitrosalicylaldehyde Eastman 6241 CFS-NTSALA #14	zero
0767	4-hydroxybenzaldehyde mcb 6361 CFS-PHBALD10 #14	zero
0782	2-nitrobenzaldehyde Aldrich N1,080-2 CFS-NIBZAL (#4), 01 (#4)	~urea
0785	adamantanone Aldrich 14,604-8 CFS-ADMNTB #225	zero

0787	4-acetamidophenol Aldrich A730-2 CFS-HXACAN (#61), 01 (#14)	zero
0788	1,4-cyclohexanedione Aldrich 12,542-3 CFS-CYHEXO,01 #4	zero
0790	1-chloroanthraquinone Aldrich C2,320-9 CFS-CLANTO #4	weak
0791	N-acetylcysteine Aldrich 13,806-1 CFS-NALCYS #1	~urea
0792	kinetin Aldrich 85,264-3 CFS-KINTIN #1	weak
0808	phenylarsonic acid Alfa 12130 CFS-ARSACP,01 #19	zero
0809	trimethylphosphine sulfide Alfa 10376 CFS-METPHS #11	zero
0812	triphenylphosphinesulfide Alfa 10177 CFS-TPPOSS #14	zero
0814	4,4'-dibromodiphenylether P&B CFS-PBRPHE #37	zero
0815	2-benzoxazolinone Aldrich 15,795-8 CFS-BZOXZO #19	zero

0817	9-anthracenecarbonitrile Aldrich 15,276-5 CFS-CNANTH #19	zero
0819	2,6-dichlorophenol Aldrich D7020-1 CFS-DCLPHL #19	weak
0820	3,4-pyridinedicarboxylic acid Aldrich P6,400-6 CFS-CINMER10 #19	zero
0822	2-chlorobenzamide Aldrich 21,606-2 CFS-CLBZAM02,03 #N.A. CLBZAM10 #14 CLBZAM11 #19	zero
0824	2,6-diphenylphenol Aldrich 23,359-5 CFS-DPPHOL #19	zero
0825	2,6-dimethoxybenzoic acid Aldrich D13,160-1 CFS-DMOXBA #19	zero
0834	2,4-dihydroxybenzophenone Eastman 6904 CFS-DHXPZP10 #14	zero
0836	2-nitrobenzoic acid Aldrich 12,769-8 CFS-NBZOAO,01,02 #2	zero
0838	N-acetylglycine Aldrich A1,630-0 CFS-ACYGLY,02,11 #14	zero
0843	4-cyanonitrobenzene Aldrich N1,200-7 CFS-PNBZNT #4	2× urea

0848	triphenylphosphine Mallinckrodt 2751 CFS-PTRPHE #14	zero
0851	hippuric acid Aldrich 11,200-3 CFS-HIPPAC,01,02 #19	~urea
0852	3-methyl-2-pyrazolin-5-one Eastman 2671 CFS-MPYAZO10 #14	zero
0854	diphenylsulfone Aldrich P3,535-9 CFS-DPSULO #14	zero
0867	dimethylglyoxime Eastman P98 CFS-DMEGLY,01 #2	zero
0868	mellitic acid trianhydride Aldrich M272-I	zero
0869	1,3,5-triacetylbenzene Aldrich T4,420-2 CFS-TACBEN,01 #14	zero
0871	benzene-1,3,5-tricarboxylic acid Aldrich B440-6 CFS-BTCOAC #15 CFS-TRIMES #1	zero
0873	resorcinol Aldrich R40-6 CFS-RESORA,01,02,13 #33	v weak
0875	3-nitrophenol Aldrich 16,303-1 CFS-MNPHOL01 (#19); 02, 10 (#14)	weak

0876	5-nitrouracil Eastman 3484 CFS-NURAMH #14 Also space group 19	>urea 8x
0878	4-nitrophenol Aldrich 13,023-0 CFS-NITPOL #14	zero
0879	4-nitroacetophenone Aldrich N960-8 CFS-NACPON10 #14	zero
0881	2-nitrophenol CFS-ONITPH #14	zero
0883	4-nitrobiphenyl CFS-NBPHEN #61	weak
0889	2,4-dinitrophenol CFS-DNOPHL,01 #19	≈urea
0896	triphenylphosphine selenide Alfa 10565 CFS-TPPHSE #14	zero
0911	1,4-dimethoxybenzene MCB 2317 CFS-MOXBEN #61	zero
0913	β-alanine Eastman 4638 CFS-BALNIN #61	zero
0914	carbazole Aldrich 15,083-5 CFS-CRBZOL01,10 #62	zero

0919	ethylenetrithiocarbonate FLUKA 03950 CFS-DTOLTO #14	zero
0926	phenazine Aldrich P1,320-7 CFS-PHENAZ01,02,10 #14	zero
0928	thymine MCB 5873, Sigma T-0376 CFS-THYMIN, THYMMH #14	zero
0929	1,4-dicyanobenzene Aldrich D7672-2 CFS-TEPNIT #2	zero
0931	adenosine-3'-monophosphate Schwarz Bioresearch CFS-ADPOSD #4	<urea
0932	adenosine-5'-monophosphate Schwarz Bioresearch CFS-ADPOSM #4	zero
0944	E-1,2-dicyanostilbene E. Nazzal CFS-DCNSTI #15	zero
0953	chloranil E. Nazzal CFS-TCBENQ,01,02 #14	zero
1008	pyrrolidinium pyrrolidine dithiocarbamate E. Nazzal CFS-PYRCDT #4	~urea
1020	biphenylene E. Nazzal CFS-BIPHNE10 #14	zero

1030	1,3-indandione Aldrich I-200-2 CFS-INDDON #88	zero
1036	DL-homocysteic acid Aldrich 21,974-6 CFS-HCYSAC #43	zero
1078	1,4-diaminobenzene bis benzamide ELM 87-89483 CFS-BZOPDA10 #61	zero
1088	furaltadone Sigma F-9255 CFS-FURALA #14	zero
1091	tetramethyldiphosphine disulfide Alfa 10237 CFS-TMDPDS,01 #12	zero
1099	monophenylbutazone Sigma M-0882 CFS-BPYZDO20 #14	zero
1115	L-glutamine Sigma G-3126 CFS-GLUTAM,01 #19	v weak
1122	glycolic acid Sigma G-1884 CFS-GLICAC01,10 #14	zero
1134	2,4-dihydroxy-6-methyl 5-nitropyrimidine Sigma D-8378 CFS-NIMURC10 #14	zero
1158	dimethylsulfone Sigma D-3129 CFS-DMSULO #63	zero

1159	L-cysteic acid Sigma C-7630 CFS-CYSTEA #19	zero
1160	cimetidine Sigma C-4522 CFS-CIMETD #14	zero
1170	cytosine Sigma C-3506 CFS-CYTSIN,01 #19	zero
1180	ellagic acid Sigma E-2250 CFS-ELLAGC #14	zero
1195	dihydro-6-methyluracil Sigma D-6753 CFS-MDHURC10 #5	zero
1197	dihydrouracil Sigma D-7628 CFS-DHURAC10 #14	zero
1215	esculetin Sigma E-2631 CFS-ESCULT #14	zero
1222	endo-3-bromo-d-camphor Sigma B-6884 CFS-BRCMPH01,10 #4	zero
1223	isocytosine Sigma I-2127 CFS-ICYTIN #14	zero
1229	β-ketoglutaric acid Sigma K-1376 CFS-BKGLUT #62	zero

1236	2,4-dithiopyrimidine Sigma D-8630 CFS-DTURAC #14	zero
1248	thymidine Sigma T-5018 CFS-THYDIN #19	zero
1249	parabanic acid Sigma P-3635 CFS-PARBAC,02,11 #14	zero
1251	tricyclohexylphosphine sulfide Alfa 10558 CFS-TCHXPS #33	zero
1257	sodium oxalate Alfa 307844 CFS-NAOXAM #18, NAOXMP #14	zero
1259	2-thiouracil Sigma T-7750 CFS-TURCIL #2	zero
1262	salicylamide Sigma S-0750 CFS-SALMID #15	zero
1266	sulfathiazole Sigma S-9876 CFS-SUTHAZ,01,02 #14	zero
1267	sulfameter Sigma S-0383 CFS-SAMPYM #14, 01 #15	zero
1268	2-thiocytosine Sigma T-6000 CFS-THCYTO10 #5	weak

1270	thymine Sigma T-0376 CFS-THYMIN #14	zero
1271	sulfadimethoxine Sigma S-7007 CFS-SFDMOX #2	zero
1297	oxalic acid Sigma O-0376 CFS-OXALAL,02,03 #61; 01,04 #14	zero
1298	oxamide Aldrich O-932-8 CFS-OXAMID01 #2	zero
1317	p-nitrophenyl-β-D-xylo-pyranoside Sigma N-2132 CFS-NPBDXY #19	weak+ moderate
1341	khellin Sigma K-2750 CFS-KHELIN,01 #14	zero
1356	dipicolinic acid Sigma D-0759 CFS-DIPICA10 #19	zero
1365	sulfadiazine Sigma S-8626 CFS-SULDAZ #14	zero
1368	pyrazinamide Sigma P-7136 CFS-PYRZIN,01 #14; 02 #2	zero
1371	thioacetamide Sigma T-5250 CFS-THACEM #14	zero

1374	thymidine Sigma T-5018 CFS-THYDIN #19	zero
1388	2,6-di-t-butyl-4-bromophenol dcd R-0084-69 CFS-BBPHOL, BBPHOL01 #19	zero
1403	4,4'-diaminodiphenylsulfone rjt CFS-DAPSYO01,10 #19	0.3× urea
1405	2-bromo-4'-dimethylamino-α-cyanostilbene rjt R-0095-47 CFS-BCSTIL #18	6× urea
1537	5-fluorouracil Sigma F-6627 CFS-FURACL #2	zero

Table VIII-III Powder Test Master List

0601	2-methyl-4-nitroaniline-diacetyltartarimide 7-9-1672 cd	moderate
0602	4-nitroaniline-diacetyltartarimide 4-9-1672 cd	zero
0603	3-amino-4-piperidinonitrobenzene -N-toluenesulfonamide 88-9-4249 rjt	v weak
0604	4-(bis(hydroxyethyl)amino)nitrobenzene rjt	v weak
0605	1,2-dimethyl-6-nitrobenzimidazole 9-4249-71 rjt	zero
0606	3-amino-4-dimethylaminonitrobenzene-N-methyl- N-toluenesulfonamide 9-4249-79	weak
0607	9-anthracenecarboxaldehyde ald 12,323-4 rjt/jc CFS-ANTHAL #19	moderate
0608	3-amino-4-(dimethylamino)nitrobenzene -N-toluenesulfonamide 9-4249-73 rjt	weak
0609	3-amino-4-pyrrolidinonitrobenzene -N-toluenesulfonamide 9-4249-77 rjt	v weak
0610	3-amino-4-morpholinonitrobenzene -N-toluenesulfonamide 9-4249-89 rjt	zero

0611	3-amino-4-pyrrolidinonitrobenzene-N-methyl -N-toluenesulfonamide 9-4249-80 rjt	zero
0612	3,4-diaminonitrobenzene-3-N-methyl- -3-N-toluenesulfonamide 78-9-4249 rjt	weak
0613	3-amino-4-piperidinonitrobenzene -N-methyl-N-toluenesulfonamide 9-4249-83 rjt	v weak
0614	4-nitrocatechol ald N1,555-3 rjt	5.5× urea
0615	3,5-di-t-butyl-4-hydroxybenzaldehyde ald 14,040-6<32>	8× urea
0616	2-(2'-napthyl)thio-5-nitropyridine 18-9-1672 cd	~urea
0617	2-(2'-napthyl)thio-3,5-dinitropyridine 20-9-1672 cd	~urea
0618	1-(2'-napthyl)thio-4-nitrobenzene 17-9-1672 cd	1.5× urea burns
0619	2-(2'-napthyl)thio-3-methyl-5-nitropyridine 27-9-1672 cd	vv weak
0620	1-(2'-napthyl)thio-2-methyl-4-nitrobenzene 25-9-1672 cd	zero

0621	2-(thiophenyl)-5-nitropyridine 19-9-1672 cd	zero
0622	2-(thiophenyl)-3-methyl-5-nitropyridine 23-9-1672 cd	zero
0623	1-(thiophenyl)-2-methyl-4-nitrobenzene 22-9-1672 cd	zero
0624	4,4'-dinitrodiphenylsulfide 24-9-1672 cd	zero
0625	4-aminobenzamide sigma A-1658 CFS-AMBZAM10 #4	3-4× urea (dec)
0626	indazole ald I-240-1 CFS-INDZAL #4	0.1× urea
0627	5-iodouridine sig I-7500 CFS-IURIDN10 #4	zero
0628	2-hydroxy-4-(dimethylamino)nitrobenzene 9-4249-91 rjt	zero
0629	bis(2-napthyl)disulfide 32-9-1672 cd	zero
0630	3-nitroaniline camphoric acid imide 5-9-1672 cd	zero

0631	3-[illegible]ino-4-thiophenylnitrobenzene 28-9-1672 cd	zero
0632	2-hydroxy-4-pyrrolidinonitrobenzene 9-4249-95 rjt	vv weak
0633	2-hydroxy-4-piperidinonitrobenzene	zero
0634	2-hydroxy-4-morpholinonitrobenzene	zero
0635	2-benzoylphenothiazine 90-9-4249 rjt	zero
0636	2-hydroxy-4-(2'-hydroxymethylpyrrolidino) nitrobenzene 94-9-4249 rjt	~urea
0637	3-amino-4-(2'-thionapthyl)nitrobenzene 32-9-1672 cd	zero
0638	N-(4-cyanophenyl)arabinisoyl amine 9-4249-51 rjt	~urea
0639	4-nitroaniline camphoric acid imide 9-9-1672 cd	weak
0640	3-(diacetyltartarimido)-4-phenylthionitrobenzene 31-9-1672 cd	strong

0641	3-chloro-4-pyrollidinonitrobenzene 98-9-4249 rjt	weak
0642	methyl-(3-hydroxy-4-nitrophenyl)aminopropanoate 43-9-1672 cd	weak
0643	2-hydroxy-4-α-napthylethylaminonitrobenzene 42-9-1672 cd	weak
0644	2-hydroxy-4-(methyl-2-hydroxyethyl)amino- nitrobenzene 41-9-1672 cd	weak
0645	3-(diacetyltartarimido)-4-(N-pyrrolidino) nitrobenzene 37-9-1672 cd	strong
0646	(-)-inosine Aldrich I-640-7 CFS-INOSND10 #4 INOSIN10,11 #19	weak
0647	4-nitrophenyl-phenylsulfide ald S46100-8 CFS-PNDPHS #14	weak
0648	2-hydroxy-4-methylaminonitrobenzene 47-9-1672 cd	weak
0649	1-(4-nitrophenylamino)-2-(4-nitrophenylthio) ethane 108-9-4247 rjt	moderate
0650	2-(6-bromo-2-napthyloxy)-5-nitropyridine 102-9-4249 rjt	moderate

0651	2,4-dinitro-(2-napthyloxy)benzene 9-4249-105 rjt	moderate
0652	2,6-di-t-butyl-4-β,β-dicyanovinylphenol Twieg 106-9-4249 CFS-BABYMN #4	weak
0653	2,6-dibromo-4-β,β-dicyanovinylphenol 9-4249-107 rjt	v weak
0654	2-(2-napthyloxy)-5-nitrobenzene 9-4249-103 rjt	v weak
0655	2-(2-napthyloxy)-3,5-dinitropyridine 104-9-4249 rjt	v weak
0656	5-iodouracil Aldrich 85,785-8 CFS-IURACL10 #4	~urea
0657	2-(2'-napthyloxy)-5-nitropyridine form I (yellow) 9-4249-117A rjt form II (colorless) 9-4249-118B rjt (same as #174)	8× urea zero
0658	4-tartarimidonitrobenzene 113-9-4249 rjt	moderate
0659	N-(4-nitrophenyl)-N'-(phenyl)thiourea Twieg R-0095-65	zero
0660	2-carbomethoxy-4-(1-octadecylthio)nitrobenzene 58-9-1672 cd	zero

0661	3-diacetoxytartarimido-4-N-piperidino nitrobenzene 54-9-1672 cd	~urea
0662	3-(diacetoxytartarimido)-4-N-morpholino nitrobenzene	
	form I 48-9-1672 cd (yellow)	v weak
	form II 48-9-1672 cd (yellow)	~urea
0663	2-hydroxy-5-nitrobenzylideneaniline 71-9-1672 cd	zero
0664	sulfamide Sigma S4382 Spacegroup #43 (non CFS)	0.3× urea
0665	triethylphosphine sulfide Alfa 10561 CFS-EPHOSS #186	~urea
0666	sulfisomidine Sigma S-7505 CFS-SLFSMD #29	2× urea
0667	sulfanilamide Sigma S-9251 CFS-SULAMD,05 #61 SULAMD01,02,03,04 #14	v weak
0668	tetraphenylhydrazine Alfa 16217 CFS-TPHYDZ,01 #20	zero
0669	furosemide Sigma F-4381 CFS-FURSEM #2 FURSEM01 #1	zero
0670	2,6-di-t-butyl-4-methylphenol Aldrich 24,002-8 CFS-MBPHOL10 #19	v weak

0671	2-nitro-5-(octadecylthio)benzoic acid 60-9-1672 cd	zero
0672	2,4-(phenylthio)nitrobenzene 65-91672 cd CFS-BPTHNB #4	strong
0673	3-(diacetoxytartarimido)-4-N-homopiperidino-nitrobenzene 57-9-1672cd	strong
0674	4-nitrobenzpiperidinamide rt CFS-PNBPIP #19	moderate
0675	4-trifluorobenzamidobenzamide 118-9-4249 rjt	zero
0676	2-hydroxy-4'-nitrobenzylidene aniline 70-9-1672 cd	zero
0677	4-dimethylaminonitroaniline rt <18> CFS-DIMNAN #4	weak
0678	hexamethylcyclotrisiloxane Petrarch H7260 CFS-HMCSIO,01 #160	zero
0679	trinitroxanthone jc sample	vv weak
0680	tetranitroxanthone jc sample	v weak

0681	2-phenylmalonic acid diamide jc sample	zero
0682	thiohydantoin rjt	zero
0683	1,5-dibenzyl-3-phenylthiohydantoin rjt	zero
0684	1-phenyl-3-butylhydantoin rt	zero
0685	1,3-diphenylthiohydantoin rjt	zero
0686	1-phenyl-3-methylthiohydantoin rjt	weak
0687	1-phenylthiohydantoin rjt	zero
0688	3-phenylthiohydantoin rjt	zero
0689	1-acetylthiohydantoin rjt	zero
0690	1-(β-cyanoethyl)-3-methylthiohydantoin rjt	zero

0691	1,3-dimethylthiohydantoin rjt	zero
0692	1-(4-hydroxyphenyl)-3-phenylthiohydantoin rjt	zero
0693	3-methylthiohydantoin rjt	zero
0694	1-(β-cyanoethyl)-3-methylthiohydantoin rjt	zero
0695	1-(4-hydroxyphenyl)-3-methylthiohydantoin rjt	zero
0696	1-phenyl-3-ethylthiohydantoin rjt	zero
0697	trifluoromethylsulfinic acid potassium salt Parish 325[6]	zero
0698	methylsulfonylacetone Parish 2411	zero
0699	α-methylsulfonylacetamide Parish 1132	zero
0700	1-phenylsulfonyl-3,3-dimethyl-2-butanone Parish 1097	zero

0701	bis(phenylsulfonyl)methane Parish 1263	vv weak
0702	phenylmethylsulfone Parish 1114 CFS-MPSUFO #14	zero
0703	methanesulfonylhydrazine Parish 1035	zero
0704	α-(methylsulfonyl)acetic acid methyl ester 8-75433-39 E. Gipstein	zero
0705	phenylsulfonylacetonitrile Parish 1023	≤urea (d)
0706	4-hydroxybenzamide p&b HO9665	zero
0707	α-thymidine Aldrich 85,500-6 CFS-THYDIN #19 THYMDN #1	weak
0708	pentachloropyridine Aldrich 13,800-2 CFS-PCLPYR #92 PCLPYR01 #4	≤urea (d)
0709	2,6-napthaleneacetonitrile jc sample	zero
0710	1,1,2,2-tetraphenyl-1,2-dimethyldisilane Petrarch D3780	vv weak

0711	1,1,1-trimethyl-2,2,2-triphenyldisilane Petrarch T3810	zero
0712	ethyl 4-cyanobenzoate Aldrich E1,860-3	zero
0713	2,6-di-t-butylbenzoquinone Aldrich 15,393-1 CFS-TBUBZQ #14	zero
0714	4-methoxybenzonitrile Aldrich 13,247-0	zero
0715	tryptophol Aldrich T9,030-1	vv weak
0716	4-methoxysalicylaldehyde Aldrich 16,009-5	zero
0717	4,4'-dinitrobenzil jc sample	zero
0718	3-ethyl-2,5-dihydrothiophene-1,1-dioxide Aldrich 18,776-3	zero
0719	hexaphenyldigermane Alfa 34132 CFS-HPHGER #1	vv weak
0720	α-napthoflavone Aldrich N180-1	zero

0721	hexaphenyldisilane Petrarch H7325	zero
0722	acetone oxime Aldrich A1050-7 CFS-ACEOXM #176	zero
0723	2,6-di-t-butyl-4-(β-cyano-β-carboethoxy)vinyl-phenol R0034-5 rjt	v weak
0724	hexaphenylditin Alfa 71143 CFS-HPHDSN #14	vv weak
0725	salicylideneaniline 77-9-1672 cd CFS-SALCAN #43	<urea
0726	salicylidene-3-nitroaniline 76-91672 cd	<urea
0727	4-chlorobenzonitrile Aldrich 11,562-2 CFS-CLBZNT #14	~urea (d)
0728	2,5-dibromopyridine Aldrich D4,310-7	zero (d)
0729	4-bromobiphenyl Fluka 16479	weak
0730	2-acetylbromobenzene Aldrich 18,369-5	zero

0731	4-bromopropiophenone Aldrich B7,970-6	zero
0732	4-bromobenzonitrile Aldrich B5840-7 CFS-BRBNIT #8	~urea (d)
0733	4-bromonitrobenzene Aldrich 16,715-0	zero
0734	9-bromofluorene Aldrich B6,660-4	zero
0735	4-bromophenol Aldrich B7,580-8	zero
0736	4-iodoaniline Aldrich 12,936-4	zero
0737	4-iodonitrobenzene Aldrich I-950-5	zero
0738	3-iodophenol Eastman 8750	zero
0739	4-bromoacetophenone Aldrich B5,640-4 CFS-BRACPH20 #9	~urea
0740	1,3,5-trichlorobenzene Aldrich T5,460-7 CFS-TCHLBZ (#19), 01 (#19)	zero (rap d)

0741	4-bromobenzoic acid Aldrich 10,851-0 CFS-BRBZAP #14	weak
0742	4-bromo-N,N-dimethylaniline Fluka 16920	weak
0743	3-chlorobenzoic acid Aldrich C2,460-4 CFS-MCBZAC #14	weak
0744	2,6-dimethyl-4-bromophenol Aldrich 19,637-1	zero
0745	2,6-dimethyl-4-bromoaniline Aldrich 19,237-6	zero
0746	1,3-diiodobenzene Eastman 4852	~urea (rd)
0747	4-bromoiodobenzene Eastman 3165	zero (d)
0748	4-iodophenol Eastman 7782	zero
0749	4-bromophenylacetic acid Aldrich 13,867-3	zero
0750	2,7-dibromofluorene	weak (d)

0751	3,5-dichloroiodobenzene Aldrich 19,254-6	weak (rd)
0752	1,3,5-tribromobenzene Aldrich 14,006-6	weak (d)
0753	2-iodobenzoic acid Aldrich I-767-5	zero
0754	9-bromoanthracene Aldrich B5,660-9	weak (d)
0755	2,4,6-triiodo-4-hydroxybenzoic acid Aldrich (disc)	zero
0756	4-iodobenzoic acid Eastman 829	zero
0757	4-bromochlorobenzene Aldrich 23,989-5 CFS-BCBENZ #14	weak
0758	3,4,5-triiodobenzoic acid Aldrich T-6700	zero
0759	2-iodoaniline Aldrich I-700-4	weak
0760	piperonal Aldrich P4,910-4	zero

0761	2-chloro-4-dimethylaminobenzaldehyde Aldrich 12,502-4	zero
0762	2-nitro-3-methoxybenzaldehyde Aldrich 16,382-1	zero
0763	3,4-dihydroxybenzaldehyde Aldrich D10,840-5	zero
0764	5-nitrosalicylaldehyde Eastman 6241 CFS-NTSALA #14	zero
0765	4-dimethylaminobenzaldehyde Aldrich 10,976-2	zero
0766	3,5-dimethoxybenzaldehyde Aldrich 12,629-2	zero
0767	4-hydroxybenzaldehyde mcb 6361 CFS-PHBALD10 #14	zero
0768	4-nitrobenzaldehyde Eastman 2408 <18,21>	~urea
0769	4-cyanobenzaldehyde Aldrich C8,960-9	zero
0770	4-diethylaminobenzaldehyde Aldrich D8625-6	zero

0771	4-benzyloxybenzaldehyde Aldrich 12,371-4	zero
0772	3-ethoxy-4-hydroxybenzaldehyde Eastman 2664	zero
0773	3,5-dimethoxy-4-hydroxybenzaldehyde Aldrich 5760-2	zero
0774	4-acetamidobenzaldehyde Aldrich A180-0	zero
0775	3,4,5-trimethoxybenzaldehyde Aldrich T6,840-3	zero
0776	2-hydroxy-5-formylbenzoic acid Aldrich F1,760-1	zero
0777	2-nitro-5-chlorobenzaldehyde Aldrich C5,880-0	≥urea
0778	2,4-dihydroxybenzaldehyde Aldrich 16,863-7	zero
0779	3-indolecarboxaldehyde Aldrich 12,944-5	~urea
0780	2-napthaldehyde ICN 9432	zero

0781	3-hydroxy-4-nitrobenzaldehyde Aldrich 15,616-7	zero
0782	2-nitrobenzaldehyde Aldrich N1,080-2 CFS-NIBZAL (#4), 01 (#4)	~urea
0783	benzoic anhydride MCB BX380	zero
0784	cyanoethylglycine Aldrich 12,555-5	zero
0785	adamantanone Aldrich 14,604-8 CFS-ADMNTB #225	zero
0786	4-aminophenylacetic acid Aldrich A7,135-2	zero
0787	4-acetamidophenol Aldrich A730-2 CFS-HXACAN (#61), 01 (#14)	zero
0788	1,4-cyclohexanedione Aldrich 12,542-3 CFS-CYHEXO,01 #4	zero
0789	2-adamantanol Aldrich 15,382-6	zero
0790	1-chloroanthraquinone Aldrich C2,320-9 CFS-CLANTO #4	weak

0791	N-acetylcysteine Aldrich 13,806-1 CFS-NALCYS #1	0.2xurea
0792	kinetin Aldrich 85,264-3 CFS-KINTIN #1	weak
0793	2,4-dinitro-4'-methoxybenzylideneaniline R0034-32 rjt	zero
0794	3,4,5-trimethoxy-β-cyano-4-nitrostilbene R0034-28 rjt	zero
0795	3,5-di-t-butyl-4-hydroxy-β-cyano-4'-nitrostilbene R0034-24 rjt	zero
0796	3,5-di-t-butyl-4-hydroxybenzylidene barbituric acid R0034-7 rjt	≤urea
0797	4-nitrobenz(α-methylbenzyl)amide ROO34-17 rjt	zero
0798	4-nitro-N-methylbenzamide R0034-16 rjt	zero
0799	2,4-dinitrobenzylidene aniline R0034-31 rjt	zero
0800	4-nitro-N-(β-hydroxyethyl)benzamide R0034-15 rjt	zero

0801	4-fluoro-β-cyano-4'-nitrostilbene R0034-29 rjt	weak
0802	4-phenylthio-β-cyano-4'-nitrostilbene 103-9-1672 cd	≥urea
0803	poly-L-alanine PILOT	zero
0804	poly-γ-methyl-L-glutamate Sigma P-7631	zero
0805	poly-β-benzyl-L-aspartate PILOT	zero
0806	4-nitrophenylacetonitrile Aldrich15,157-2	zero
0807	poly-L-phenylalanine	zero
0808	phenylarsonic acid Alfa 12130 CFS-ARSACP,01 #19	zero
0809	trimethylphosphine sulfide Alfa 10376 CFS-METPHS #11	zero
0810	poly-L-leucine Gallard Schlesinger B1163	zero

0811	2,6-di-t-butyl-4-nitrophenol K0034-3 rjt	~10x urea rap dec
0812	triphenylphosphinesulfide Alfa 10177 CFS-TPPOSS #14	zero
0813	2,4-bis(4-methoxythiophenyl)nitrobenzene 108-9-1672 cd	zero
0814	4,4'-dibromodiphenylether P&B CFS-PBRPHE #37	zero
0815	2-benzoxazolinone Aldrich 15,705-8 CFS-BZOXZO #19	zero
0816	2-(N-(2'-methylpyrollidino)-5-nitropyridine Twieg R-0095-71	fluorescence
0817	9-anthracenecarbonitrile Aldrich 15,276-5 CFS-CNANTH #19	zero
0818	methylhydroxypyrone Aldrich	zero
0819	2,6-dichlorophenol Aldrich D7020-1 CFS-DCLPHL #19	weak
0820	3,4-pyridinedicarboxylic acid Aldrich P6,400-6 CFS-CINMER10 #19	zero

0821	6-hydroxynicotinic acid Aldrich 12,875-9	zero
0822	2-chlorobenzamide Aldrich 21,606-2 CFS-CLBZAM02,03 #N.A. CLBZAM10 #14 CLBZAM11 #19	zero
0823	2-iodoanthraquinone rjt	weak
0824	2,6-diphenylphenol Aldrich 23,359-5 CFS-DPPHOL #19	zero
0825	2,6-dimethoxybenzoic acid Aldrich D13,160-1 CFS-DMOXBA #19	zero
0826	2,6-di-t-butyl-4-cyanophenol rjt R0034-4	weak
0827	methyl nicotinoate Aldrich M5,920-3	weak
0828	2-hydroxy-1-napthaldehyde Aldrich H4535-3	zero
0829	2,4,6-trimethylphenol Aldrich T7,900-6	zero
0830	2,3,6-trimethylphenol T7,870-3	zero

0831	2,3,5-trimethylphenol T7,860-3	zero
0832	methyl(4-hydroxyphenyl)sulfone Parish 1827	zero
0833	2,5-bis(hydroxymethyl)nitrobenzene Aldrich 18,419-5	zero
0834	2,4-dihydroxybenzophenone Eastman 6904 CFS-DHXPZP10 #14	zero
0835	2,4-dihydroxyacetophenone Eastman 4425	zero
0836	2-nitrobenzoic acid Aldrich 12,769-8 CFS-NBZOAO,01,02 #2	zero
0837	2-hydroxynapthoquinone Aldrich H4,680-5	zero
0838	N-acetylglycine Aldrich A1,630-0 CFS-ACYGLY,02,11 #14	zero
0839	n-butyl(4-hydroxyphenyl)ketone Columbia H-3070	zero
0840	2,6-dichlororesorcinol K&K	zero

0841	2,6-diacetylpyridine Aldrich D880-1	zero
0842	terphthaldehyde Aldrich T220-Z	zero
0843	4-cyanonitrobenzene Aldrich N1,200-7 CFS-PNBZNT #4<32>	2x urea
0844	4-nitrobenzaldoxime Aldrich 29,989-4	weak
0845	3-nitro-4-aminobenzoic acid Eastman 5453	zero
0846	4-acetamidobenzaldehyde Aldrich A180-0	zero
0847	2,5-diketopiperazine Eastman 2460	zero
0848	triphenylphosphine Mallinckrodt 2751 CFS-PTRPHE #14 <36>	zero
0849	2-nitrothiophene Aldrich N2700-4	weak
0850	N-(4-hydroxyphenyl)imidazole Aldrich 18,372-5	zero

0851	hippuric acid Aldrich 11,200-3 CFS-HIPPAC,01,02 #19<4>	~urea
0852	3-methyl-2-pyrazolin-5-one Eastman 2671 CFS-MPYAZO10 #14	zero
0853	1-(4-phenylsulfonic acid)-3-methyl-2-pyrazolin-5-one Eastman 4380	zero
0854	diphenylsulfone Aldrich P3,535-9 CFS-DPSULO #14	zero
0855	pentachlorophenol Aldrich P260-4 CFS-PCPHOL #15	zero
0856	napthalene-1,4-dicarboxylic acid P&B N00280	zero
0857	methyl p-hydroxybenzoate Kodak 2844	≤urea
0858	4,4'-sulfonyldiphenol Crown Zellerbach<32>	≤urea
0859	3-methoxy-4-hydroxy benzoic acid Aldrich H3600-I	zero
0860	4,4'-dihydroxybenzophenone Aldrich 11,050-7	≤urea

0861	diphenylcarbonate Aldrich D20,653-9	zero
0862	3,5-dichloro-4-hydroxybenzoic acid Aldrich D6400-7	zero
0863	3-hydroxybenzoic acid Aldrich H2,000-8	zero
0864	dimethyl 2,6-napthoate Aldrich D17,130-1	zero
0865	phenyl p-hydroxybenzoate P&B P12660	≤urea
0866	4-hydroxybenzoic acid Aldrich H2,005-9	zero
0867	dimethylglyoxime Eastman P98 CFS-DMEGLY,01 #2	zero
0868	mellitic acid trianhydride Aldrich M272-I	zero
0869	1,3,5-triacetylbenzene Aldrich T4,420-2 CFS-TACBEN,01 #14	zero
0870	ketomalonic acid monohydrate Aldrich 16,343-0	zero

0871	benzene-1,3,5-tricarboxylic acid Aldrich B440-6 CFS-BTCOAC #15 CFS-TRIMES #1	zero
0872	1,4-diacetylbenzene Aldrich D820-8	zero
0873	resorcinol Aldrich R40-6 CFS-RESORA,01,02,13 #33 <36,37>	v weak
0874	4,4'-diacetylphenylether Trans World Chemicals B1887	zero
0875	3-nitrophenol Aldrich 16,303-1 CFS MNPHOL01 (#19); 02, 10 (#14)	weak
0876	5-nitrouracil Eastman 3484 CFS-NURAMH #14 Also space group 19 <11, 15>	>urea &×
0877	5-nitroindoline Aldrich 13,021-4	zero
0878	4-nitrophenol Aldrich 13,023-0 CFS-NITPOL #14	zero
0879	4-nitroacetophenone Aldrich N960-8 CFS-NACPON10 #14	zero
0880	β-nitrostyrene Aldrich N2,680-6	zero

0881	2-nitrophenol CFS-ONITPH #14	zero
0882	4-nitrophenyl acetic acid Aldrich N2,020-4	zero
0883	4-nitrobiphenyl CFS-NBPHEN #61	weak
0884	dibenzoylmethane Aldrich D3,345-4	zero
0885	1,2-dibenzoylbenzene Aldrich D3,260-1	zero
0886	4-aminocinnamic acid Aldrich D14,040-6	zero
0887	furil Aldrich 13,802-9	zero
0888	dimethylaminobenzoin Aldrich D13,947-5	weak
0889	2,4-dinitrophenol CFS-DNOPHL,01 #19 <187>	≈urea
0890	diphenylacetone Aldrich D20,460-9	zero

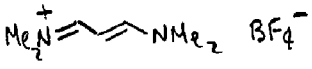
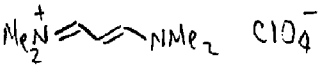
0891	TCNQ Aldrich 15,763-5	zero
0892	4-hydroxyphenylacetonitrile Aldrich H2,110-1	zero
0893	deoxybenzoin (desoxybenzoin) MCB 6238	zero
0894	4,4'-dimethoxybenzil Adrich 15,961-1	zero
0895	4-nitrobenzylchloride Aldrich 14,011-2	~urea
0896	triphenylphosphine selenide Alfa 10565 CFS-TPPHSE #14	zero
0897	3,5-dinitro-L-tyrosine Sigma D3130	zero
0898	4-nitrophenyl-4'-nitro-(2-pyridyl)sulfide Twieg R0034-57	zero
0899	4-nitrophenyl-3'-methyl-4'-nitro-(2'-pyridyl)sulfide Twieg R0034-60	zero
0900	ethyl-β-(4-nitrophenylmercapto)propionic acid Twieg R0034-38	zero

0901	(3'-5'-di-t-butyl-4'-hydroxy)-4-benzylidene-3-phenyl-4-isoxazolone Twieg R0034-38	zero
0902	6-piperidinonicotinamide Twieg R0034-51	zero
0903	6-pyrrolidinonicotinamide Twieg R0034-50	zero
0904	9-vinylanthracene Aldrich V170-8	zero
0905	formamidoxime Aldrich 14,019-8	zero
0906	p-methoxybenzal acetophenone	2.4 x urea
0907	1,3,4,5-tetraphenyl-1,3-diazolene-2-thione p16 Bk. 5705	zero
0908	4,5-diphenyl-1,3-diazolene-2-thione p8 Bk. 5705	zero
0909	(9-fluorenyl-4-isopropylphenyl)fluorilidene Clecak	zero
0910	D-glucuroninic acid lactone Sigma G-8875	weak

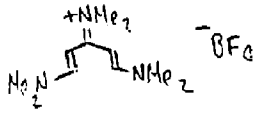
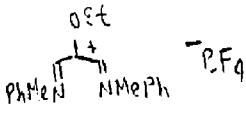
0911	1,4-dimethoxybenzene MCB 2317 CFS-MOXBEN #61	zero
0912	xanthen-9-one Eastman 940	zero
0913	β-alanine Eastman 4638 CFS-BALNIN #61	zero
0914	carbazole Aldrich 15,083-5 CFS-CRBZOL01,10 #62	zero
0915	4-aminoquinaldine Aldrich A7,900-0	0.4 x urea
0916	3-methylglutaric acid Aldrich M4,760-4	zero
0917	anthranilic acid Eastman 29	weak
0918	2-amino-5,6-dimethyl benzothiazole Aldrich A5,140-8	zero
0919	ethylenetrithiocarbonate FLUKA 03950 CFS-DTOLTO #14	zero
0920	fumaronitrile Aldrich 13,101-6	zero

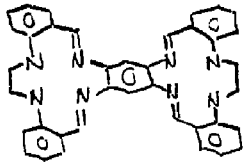
0921	dimethyldithiocarbamic acid, sodium salt dihydrate Aldrich D15,660-4	zero
0922	4,5-dimethyl-1,3-dithiolene-2-thione IBM V. Lee	zero
0923	4-cyclododecylaminonitrobenzene Twieg R-0095-71	weak
0924	2-ethyl-2-(hydroxymethyl)1,3-propanediol Aldrich 14,808-3	zero
0925	3,5-dinitroaniline Aldrich D19,340-2	v weak
0926	phenazine Aldrich P1,320-7 CFS-PHENAZ01,02,10 #14	zero
0927	N,N,N^1,N^1-tetra methylbenzidine Aldrich T1,980-1	zero
0928	thymine MCB 5873, Sigma T-0376 CFS-THYMIN, THYMMH #14	zero
0929	1,4-dicyanobenzene Aldrich D7672-2 CFS-TEPNIT #2	zero
0930	phenylglyoxal monohydrate Aldrich 14,243-3	zero

0931	adenosine-3'-monophosphate Schwarz Bioresearch CFS-ADPOSD #4	<urea
0932	adenosine-5'-monophosphate Schwarz Bioresearch CFS-ADPOSM #4	zero
0933	riboflavin Aldrich R170-6	v weak
0934	*ℓ*-malic acid Aldrich 11,257-7	v weak
0935	3,4-bis(dimethylamino)cyclobut-3-ene-1,2-dithione E. Nazzal	zero
0936	3,4-bis(dimethylamino)cyclobut-3-ene-1,2-diketone E. Nazzal	zero
0937	1,2,3,4-tetramethylcyclobutene-3,4-dicarboxylic acid E. Nazzal	zero
0938	N-acetyl-dibenzazopine E. Nazzal	zero
0939	4-nitrobenzil E. Nazzal	zero
0940	2-pyridal oxime E. Nazzal	zero

0941	N,N-dimethylpiperazine-2,3-dione E. Nazzal	zero
0942	E. Nazzal 	zero
0943	3,4-diacetyl-2,5-hexanedione E. Nazzal	zero
0944	E-1,2-dicyanostilbene E. Nazzal CFS-DCNSTI #15	zero
0945	dicyanovinylidene indane-1,3-dione E. Nazzal	zero
0946	E. Nazzal 	0.6 x urea
0947	p-dimethylamino-N-pyridinium-2,4-dinitrobenzene chloride E. Nazzal	zero
0948	fluorylidene-10-tosylate E. Nazzal	zero
0949	4,4'-dimethylaminobenzil monohydroxylamine E. Nazzal	zero
0950	1,3-propanedial bis-orthonitro anil E. Nazzal	zero

0951	Ethane-1,1,2,2-tetracarboxylic acid diimide E. Nazzal	zero
0952	ethylenediamine bis-pentanedione enamine E. Nazzal	zero
0953	chloranil E. Nazzal CFS-TCBENQ,01.02 #14	zero
0954	2-amino-1,3-carboethoxy azulene E. Nazzal	v weak
0955	E-dibromostilbene E. Nazzal	zero
0956	4-4'-dimethylaminobenzoin E. Nazzal	zero
0957	2,2'-biimidazole E. Nazzal	zero
0958	N,N'(phenyl-2-carboxaldehyde)ethylene diamine E. Nazzal	zero
0959	4,4'-dimethylaminobenzil E. Nazzal	zero
0960	N,N'-dimethyloxamide E. Nazzal	zero

0961	1,8-diacetylpyrene E. Nazzal	0.5×urea
0962	4,4'-bis dimethylaminobenzil bishydrazide E. Nazzal	zero
0963	3,3'-dinitrobiphenyl E. Nazzal <32>	0.6×urea
0964	N-chloroacetyldiphenylamine E. Nazzal	zero
0965	1,3-diphenyl-2-nitroindene E. Nazzal	zero
0966	phenanthrequinone bis hydroxylamine E. Nazzal	zero
0967	4'-nitrodeoxybenzoin E. Nazzal	zero
0968	E. Nazzal 	zero
0969	E. Nazzal B5 	zero SHG strong fluorescence
0970	4,4'-bis pyridylethylene E. Nazzal	v weak

0971  zero
E. Nazzal

0972 3,4-furandicarboxaldehyde zero
E. Nazzal

0973 3,4-furandicarboxamide v weak
E. Nazzal

0974 4,4'-azopyridine vv weak
E. Nazzal

0975 4-methylmercapto-N-methyl pyridinium iodide zero
E. Nazzal

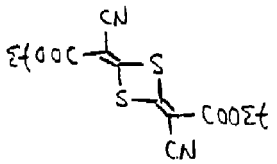
0976 N,N diethyl-bis-4,4'pyridinium ethylene diiodide zero
E. Nazzal

0977 E-4,4'-acetamidostilbene zero
E. Nazzal

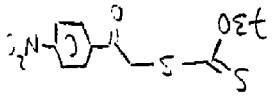
0978 N,N-dimethyl-4,4'-azopyridinium bis tetrafluoroborate vv weak
E. Nazzal

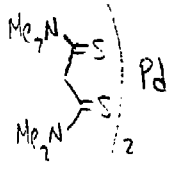
0979 N-ethyl-N-methyl-4,4'-azopyridinium diiodide zero
E. Nazzal

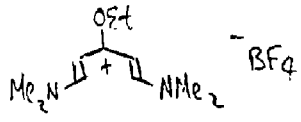
0980 N,N-dimethyl-4,4'-azopyridinium diiodide zero
E. Nazzal

0981	tetrathiomethoxyethylene E. Nazzal	zero
0982	bis(pyrrylthiocarbamoyl)disulfide E. Nazzal	v weak
0983	 E. Nazzal	<urea
0984	bis(dimethylaminothiocarbamoyl)disulfide E. Nazzal	zero
0985	2-oxo-3-mesityl-4-hydroxy-but-3-ene E. Nazzal	zero
0986	1,2,4,5-tetra(ethylsulfido)benzene E. Nazzal	zero
0987	5,6-dinitro dihydroacenapthene E. Nazzal	zero
0988	1,2-acenapthene dithiolone E. Nazzal	zero
0989	diketobiacenapthene E. Nazzal	zero
0990	Z-1,2-thiobenzylethylene E. Nazzal	zero

0991	tetramethyldithiooxamide E. Nazzal	zero
0992	benzaldehyde-1,3-propanethiol acetal E. Nazzal	zero
0993	4-nitrobenzoin acetate E. Nazzal	vv weak
0994	N,N-dimethylthioparabanic acid E. Nazzal	strong
0995	N,N-dimethyl-1,3-diazacyclopentane-4,5-dione E. Nazzal	zero
0996	dinitroacenapthaquinone E. Nazzal	zero
0997	4,5-diphenyl-1,3-dithiolene-2-oxone E. Nazzal	zero
0998	6-nitro-1,2-indene dithiolone E. Nazzal	zero
0999	4-(4'-nitrophenyl)-1,3-thiolene-2-oxone E. Nazzal	0.3× urea w/decomp.
1000	2,3-bis(benzylsulfide)napthalene E. Nazzal	zero

1001	tetramethylbicyclo[3.3.0]octane 2,4,6,8 tetracarboxylate E. Nazzal	zero
1002	1,2-indene dithiolone E. Nazzal	zero
1003	1,2,3,3-tetramethylindolium tetrafluoroborate E. Nazzal	weak
1004	E. Nazzal 	zero
1005	N,N-dimethyl-4,4'-pyridinium disulfide bis tetrafluoroborate E. Nazzal	zero
1006	hexamethylguanidinium tetrafluoroborate E. Nazzal	zero
1007	cyclohexane-1,4-dione monoethyleneglycol ketal E. Nazzal	zero
1008	pyrrolidinium pyrrolidine dithiocarbamate E. Nazzal CFS-PYRCDT #4	~urea
1009	t-butylaminofulvalene carboxaldehyde anilide E. Nazzal	weak/ fluorescence
1010	α-hydroxy-α-phenyl-2-acenapthone E. Nazzal	0.4 x urea w/decomp.

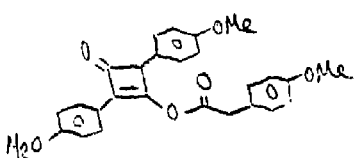
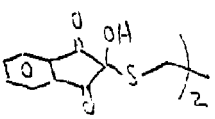
1011	1,1,2,2-tetracarboxyethane N-methylimide E. Nazzal	weak
1012	3,4-dicarbamoylfuran E. Nazzal	zero
1013	1,1'-bis thiomethoxy-2,2'-dicyanoethylene E. Nazzal	zero
1014	bis benzonitrile platinum dichloride E. Nazzal	zero
1015	2,5-diaza-2,5-dimethyl bicyclo[4.2-0]-7,8-dione-$\Delta^{1,6}$octene E. Nazzal	weak
1016	 E. Nazzal	zero
1017	bis benzonitrile palladium dichloride E. Nazzal	zero
1018	5,7-diaza-6-dimethylaminoazulene E. Nazzal	zero
1019	1-biphenylene carboxylic acid E. Nazzal	zero
1020	biphenylene E. Nazzal CF3-BIPHNE10 #14	zero

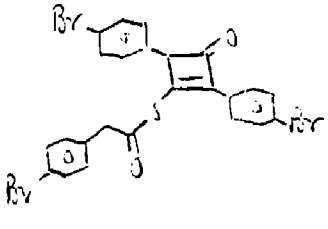
1021	1-acetylpyrene E. Nazzal	weak/ fluorescence
1022	nitroacenapthone RWL I80	zero
1023	RWL I80 	zero
1024	2-acetamido-2-deoxy-1,3,4,6-tetra-O-acetyl β-D-gluco pyranose Aldrich 85,999-0	weak
1025	3-acetyl-2,4-dimethylpyrrole Aldrich A1,480-4	zero
1026	5-acetoxymethyl-2-furaldehyde Aldrich 14,542-4	moderate
1027	dimethyl 4-nitrophthlate Eastman 3554	zero
1028	3-acetyl-2,6-bis(tert-butyl-amino)-4-methylpyridine Aldrich 21,411-6	zero
1029	acetazolamide Aldrich 27,195-0	zero
1030	1,3-indandione Aldrich I-200-2 CFS-INDDON #88	zero

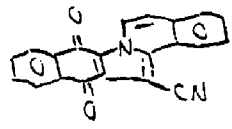
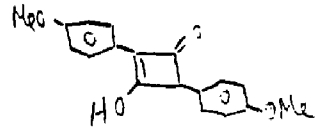
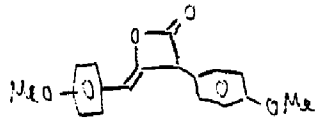
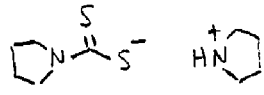
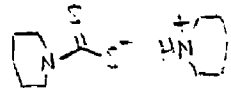
1031	4-acetamidoantipyrine Aldrich A160-6	zero
1032	1,2-dihydroxycyclobutane dione K&K 24592	zero
1033	D(−)-pantolactone Aldrich 23,781-7	zero
1034	benzanilide	zero
1035	poly-L-glutamic acid New England Nuclear PAA-006	zero
1036	DL-homocysteic acid Aldrich 21,974-6 CFS-HCYSAC #43	zero
1037	dimethyl-2,2'-biphenyl dicarboxylate	zero
1038	poly-L-glutamic acid sodium salt Sigma P-0129	zero
1039	hydroquinone bis cyanate SAM 93170-54	zero
1040	4,4'-diethylaminobenzoin	zero

1041	β-(4-nitrophenylamino)propionic acid cd Dirk R23-R0050	zero
1042	5-nitropyrimidine-4,6-bis mercaptopropionic acid rjt	zero
1043	4-trifluoromethylbenzoic acid Balanson	zero
1044	1-phenyl-1,3,8,triazaspiro[4,5]-decane-4-one Aldrich 16,049-0	zero
1045	D-galactonic acid γ-lactone Sigma	zero
1046	2,2'-bis(5-nitropyridyl)sulfide Twieg R0034-77	zero
1047	3-cyanonitrobenzene Eastman 3323 <32>	moderate+ very good
1048	6-morpholino nicotinamide Twieg R0034-79	moderate
1049	6-dimethylamino nicotinamide Twieg R0034-58	zero
1050	β-[2,4-dinitrophenyl]mercapto propionic acid Twieg R0034-68	zero

1051	β-[5-nitropyridyl]-2-mercapto propionic acid Twieg R0034-75	zero
1052	(2-keto-2-phenylethyl)-β-(4'-nitrophenyl)propionoate Twieg R0034-72	zero
1053	(2-keto-2-phenylethyl)-β-(2',4' dinitrophenyl)propionoate	zero
1054	diphenylvinylenecarbonate	zero
1055	tetramethyloxamide	zero
1056	2,4 bis(β-mercaptopropionyl)nitrobenzene Twieg	zero
1057	pentafluorophenylhydrazine Fluka 76752	zero
1058	piperidinium piperidine dithiocarbamate Dobrowolski R0084-17 CFS PIPPTC,01,11 (2,4)	zero
1059	2-thioethylnapthoquinone IBM 89483-120	zero
1060	tetranitroblue tetrazolium chloride heptahydrate Aldrich 13,316-7	zero

1061	N-acetylphenoxazine IBM 89483-99-2	zero
1062	blue tetrazolium Aldrich B5,480-0	zero
1063	S-benzyl-L-cysteine Aldrich B1,980-0	weak
1064	anthraquinone Chemical Service 926 (Media, Pennsylvania) CFS-ANTQUO01-06 #14	zero
1065	2,7-dimethoxyfluorene	zero
1066	N,N-dimethyl-2,2'-bipyridinium diiodide IBM 89483-59	zero
1067	IBM 89483-84 	zero
1068		zero
1069	IBM 75609-107 	zero
1070	cyanophenylnapthofuranquinone ELM	zero

1071	p-phenylenediamine bis p-toluene sulfonamide 89483-83	zero
1072	2,3,5-triphenyl-2H-tetrazolium chloride Eastman 6533	zero
1073	2-(p-iodophenyl)-3-(p-nitrophenyl) -5-phenyl-2H-tetrazolium chloride Eastman 9110	zero
1074	2-phenylbenzothiazole	zero
1075	tetrazolium violet Aldrich 15,059-8	zero
1076	nitro blue tetrazolium chloride Aldrich N1,540-5	moderate
1077	benzaldehyde phenylhydrazide	zero
1078	1,4-diaminobenzene bis benzamide ELM 87-89483 CFS-BZOPDA10 #61	zero
1079	indanetrione-1,3-bis propane dithiol ketal 75609-106	zero
1080		zero

1081	2-(4-methoxyphenyl)benzthiazole	zero
1082	ELM 	zero
1083	89463-23 	zero
1084	89483-14-5 	zero
1085	2-anisoylmethyl-3,5-dianisoyl-6-hydroxy-α-pyrone	zero
1086	trianisoylphosphine oxide Alfa 10580	zero
1087	5-nitro-2-furaldehyde semicarbazone Sigma N-9009<13>	30 x urea
1088	furaltadone Sigma F-9255 CFS-FURALA #14	zero
1089	Dobrowolski R0084-15 	moderate
1090	Dobrowolski R0084-17 	v weak

1091	tetramethyldiphosphine disulfide Alfa 10237 CFS-TMDPDS,01 #12	zero
1092	hydantoic acid Sigma H-3379	zero
1093	hydantoin-5-acetic acid Sigma H-2625	v weak
1094	2-nitro-4-(2',4'-dinitro-phenylazo)phenol Sigma N-0381	zero
1095	trans-1,4-diphalimido 2-methyl-2-butene Sigma D-8524	zero
1096	nicotinuric acid Sigma N-4751	zero
1097	nifedipine Sigma N-7634	zero
1098	2-benzoylpyridine Sigma B-5625	zero
1099	monophenylbutazone Sigma M-0882 CFS-BPYZDO20 #14	zero
1100	5-nitro-orotic acid methyl ester Sigma N-8251	zero

1101	flavone Sigma F-2003	zero
1102	L-methionine-S-methyl sulfonium bromide Sigma M-2006	zero
1103	niclosamide Sigma N3510	zero
1104	nifuroxime Sigma N-2633	moderate
1105	N-ω-nitro-L-arginine Sigma N-5501	zero
1106	α-ketopimelic acid dilactone Sigma K-4001	zero
1107	naringenin Sigma N-1251	zero
1108	6-methoxy-1-tetralone Sigma M-8130	zero
1109	ferulic acid Sigma F-3500	zero
1110	5-nitro-orotic acid Sigma N-8126	zero

1111	2,2'-dihydroxy-4-methoxy-benzophenone Sigma D-8265	moderate
1112	D(+) glucosamine • HCl Sigma G-4875	zero
1113	4-nitroimidazole Sigma N-9508	zero
1114	5-nitro-8-hydroxy-quinoline Sigma N-3879	zero
1115	L-glutamine Sigma G-3126 CFS-GLUTAM,01 #19	v weak
1116	D-galaturonic acid Sigma G-2125	zero
1117	N-methylnicotinamide Sigma M-4502	zero
1118	3-methyluracil Sigma M-6631	zero
1119	6-methyluracil Sigma M-9127	zero
1120	glutathione Sigma G-4251	zero

1121	S-ethyl-L-cysteine Sigma E-1878	zero
1122	glycolic acid Sigma G-1884 CFS-GLICAC01,10 #14	zero
1123	glycolaldehyde Sigma G-9376	zero
1124	2-nitro-4-carboxyphenyl-N,N-diphenylcarbamate Sigma N-7001	moderate
1125	5-carbethoxy-2-thiouracil Sigma C-6875	zero
1126	5-methyl-2-thiouracil Sigma M-2516	zero
1127	t-butyl-N-succinimido carbonate Sigma B-0633	zero
1128	L-methionine sulfone Sigma M-0876	zero
1129	6-chloro-1,3-dimethyl uracil Sigma C-2893	zero
1130	S-carbamyl-L-cysteine Sigma C-2767	zero

1131	3,4-dimethoxycinnamic acid Sigma D-0508	zero
1132	L-methioninesulfoxide Sigma M-1126	zero
1133	5-carbethoxyuracil Sigma C-7000	zero
1134	2,4-dihydroxy-6-methyl 5-nitropyrimidine Sigma D-8378 CFS-NIMURC10 #14	zero
1135	m-nitrophenylacetic acid Sigma N-4257	zero
1136	p-methoxybenzyl S-(4,6-di-methylprimidin-2-yl)-thiocarbonate Sigma M-5387	zero
1137	p-nitrophenylacetate Sigma N-8130	v weak
1138	o-nitrophenylacetate Sigma N-9001	weak
1139	5-nitro-1,10-phenanthroline Sigma N-8501	zero
1140	o-nitrophenylacetic acid Sigma N-0031	weak-red shifted

1141	p-nitro-L-phenylalanine Sigma N-0884	moderate
1142	2,5-dimethoxycinnamic acid Sigma D-3146	zero
1143	dihydroxyfumaric acid Sigma D-8128	zero
1144	4,6-dihydroxypyrimidine Sigma D-9878	zero
1145	D(+)-galactosamine Sigma G-0500	zero
1146	6-(diethylaminomethyl)-kojic acid•HCl Sigma D-4381	zero
1147	5,5-dimethyl-1,3-cyclo hexanedione Sigma D-3504	zero
1148	N^1-(4,5-dimethyl-2-oxazolyl)sulfarilamide Sigma D-9265	zero
1149	N-acetyl-3,5-dinitro-L-tyrosine Sigma A-7625	zero
1150	(–)-2,3-dibenzoyl-L-tartaric acid Sigma D-9126	v weak

1151	1-acetylindole-3-carboxaldehyde Sigma A-0126	zero
1152	dimethylolurea Sigma D-4879	zero
1153	1-acetyl-5-nitroindoline Sigma A-3126	zero
1154	p-dimethylaminocinnamic acid Sigma D-7387	moderate
1155	4-chloro-2-nitrobenzaldehyde Sigma C-4753	zero
1156	chlorthalidone Sigma C-2775	zero
1157	4-chlorouracil Sigma C-9525	zero
1158	dimethylsulfone Sigma D-3129 CFS-DMSULO #63	zero
1159	L-cysteic acid Sigma C-7630 CFS-CYSTEA #19	zero
1160	cimetidine Sigma C-4522 CFS-CIMETD #14	zero

1161	citrazinic acid Sigma C-7004	zero
1162	(+)-6-methoxy-α-methyl-2-napthalene acetic acid Sigma M-4015	zero
1163	DL-glyceraldehyde Sigma G-5001	zero
1164	5-carboxymethyl-L-cysteine Sigma C-7757	weak
1165	5-carboxy-2-thiouracil Sigma C-9375	zero
1166	dichlorophenamide Sigma D-3268	zero
1167	1,4-dicarbethoxycyclo-pentane 2,3-dione Sigma D-7259	zero
1168	N-acetyl-L-3-nitrotyrosine ethyl ester Sigma A-2635	weak-mo' rate
1169	diethyl-p-aminobenzylphosphonate Sigma D-2765	zero
1170	cytosine Sigma C-3506 CFS-CYTSIN,01 #19	zero

1171	N-acetyl-3,5-dini[illegible]o-L-tyrosine ethyl ester Sigma A-7750	v weak
1172	1-acetyl-6-nitroindoline Sigma A-3251	zero
1173	L(+) lactic acid Sigma L-1750	zero
1174	kynurenic acid Sigma K-3375	zero
1175	4-guanidinobenzoic acid Sigma G-4131	zero
1176	iso-orotic acidf Sigma I-3627	zero
1177	lumichrome Sigma L-7507	zero
1178	α-ketobutyric acid Sigma K-0875	zero
1179	L-djenkolic acid Sigma D-9255	moderate
1180	ellagic acid Sigma E-2250 CFS-ELLAGC #14	zero

1181	isopyrin Sigma I-3506	zero
1182	(–)-2,3-di-p-toluoyl-L-tartaric acid Sigma D-4891	zero
1183	L-mannonic acid α-lactone Sigma M-2261	zero
1184	ketomalonic acid, sodium salt Sigma K-4625	zero
1185	p-nitrobenzenesulfonic acid, methyl ester Sigma N-2384	zero
1186	5-hydroxymethyl uracil Sigma H-2627	zero
1187	2-bromo-2-nitro-1,3-propanediol Sigma B-0257	zero
1188	ketoprofen Sigma K-1751	zero
1189	1-butaneboronic acid Sigma B-7634	zero
1190	ketomalonic acid, free acid Sigma K-4500	zero

1191	4-hydroxy-3-nitro-phenylacetic acid Sigma H-0257	zero
1192	2,6-dimethyl-γ-pyrone Fluka 41567	zero
1193	diethylcarbamazine Sigma D-8765	zero
1194	N-formyl-DL-methionine Sigma F-3252	zero
1195	dihydro-6-methyluracil Sigma D-6753 CFS-MDHURC10 #5	zero
1196	N-formyl-DL-phenylalanine Sigma F-9501	zero
1197	dihydrouracil Sigma D-7628 CFS-DHURAC10 #14	zero
1198	trans-Δ^3-dihydromuconic acid Sigma D-2635	zero
1199	1-acetyl-5,7-dinitroindoline Sigma A-7500	zero
1200	N-formyl-L-leucine Sigma F-9251	zero

1201	DL-dithiothreitol Sigma D-0632	zero
1202	acetophenolisatin Sigma A-2625	zero
1203	N-formyl-L-aspartic acid Sigma F-9126	zero
1204	(-)-1,4-dithio-L-threitol Sigma D-9760	zero
1205	6,6'-dithiodinicotinic acid Sigma D-9759	zero
1206	acetarsone Sigma A-0259	zero
1207	kojic acid Sigma K-3125	zero
1208	5,5'-dithiobis-(2-nitrobenzoic acid) Sigma D-8130	zero
1209	formamidoxine Sigma F-7130	zero
1210	3,5-dinitro-L-tyrosine Sigma D-3130	zero

1211	formimino-glycine Sigma F-9001	zero
1212	lumazine Sigma L-0380	v weak
1213	N-formylglycine Sigma F-3127	zero
1214	dipyrone Sigma D-8890	zero
1215	esculetin Sigma E-2631 CFS-ESCULT #14	zero
1216	L-leucine-p-nitroaniline Sigma L-9125	moderate
1217	acetazolamide Sigma A-6011	zero
1218	dihydro-L-orotic acid Sigma D-7128	zero
1219	fraxin Sigma F-8133	zero
1220	dihydro-DL-orotic acid Sigma D-7003	zero

1221	ω-nitro-L-arginine methyl ester HCl Sigma N-5751	moderate
1222	endo-3-bromo-d-camphor Sigma B-6884 CFS-BRCMPH01,10 #4	zero
1223	isocytosine Sigma I-2127 CFS-ICYTIN #14	zero
1224	α-ketoisocaproic acid Sigma K-5625	v weak
1225	10-benzylidene-9-anthrone Sigma B-8500	zero
1226	4-benzoylpyridine Sigma B-5750	moderate
1227	N-p-nitrobenzoyl-L-glutamic acid Sigma N-4253	zero
1228	2,5-dihydroxyacetophenone Sigma D-3638	moderate
1229	β-ketoglutaric acid Sigma K-1376 CFS-BKGLUT #62	zero
1230	N-formyl-L-tyrosine Sigma F-9751	zero

1231	α-ketopimelic acid Sigma K-3876	zero
1232	p-nitrobenzyl alcohol Sigma N-6251	zero
1233	5-isatinsulfonic acid Sigma I-6631	zero
1234	glyoxylic acid Sigma G-4502	zero
1235	dulcin Sigma D-6631	zero
1236	2,4-dithiopyrimidine Sigma D-8630 CFS-DTURAC #14	zero
1237	hydrochlorothiazide Sigma H-4759	moderate
1238	3,6-dinitrophthalic acid Sigma D-2880	zero
1239	5-hydroxymethyl-6-methyluracil Sigma H-6384	zero
1240	hydroflumethiazide Sigma H-8760	moderate

1241	formamidine sulfinic acid Sigma F-5877	zero
1242	isonicotinic acid N-oxide Sigma I-6506	zero
1243	DL-lactamide Sigma L-0500	zero
1244	guanidoacetic acid Sigma G-6002	zero
1245	7-methoxy-4-methyl-coumarin Sigma M-7513	moderate
1246	sulfaquinoxaline Sigma S-7382	zero
1247	5-propyl-2-thiouracil Sigma P-0643	v weak
1248	3-methyl-4-N-(cyclopentylamino)nitrobenzene dobrowolski R-0084-85 CFS-THYDIN #19	zero
1249	parabanic acid Sigma P-3635 CFS-PARBAC,02,11 #14	zero
1250	(±)-sulfinpyrazone Sigma S-9509	zero

1251	tricyclohexylphosphine sulfide Alfa 10558 CFS-TCHXPS #33	zero
1252	phosphonoformic acid Sigma P-2895	zero
1253	L-phenylalanine amide Sigma P-1883	zero
1254	O-phosphorylethanolamine Sigma P-0503	zero
1255	diphenylphosphine sulfide Alfa 10489	zero
1256	tri(4-methylphenoxy)phosphine sulfide Alfa 18550	zero
1257	sodium oxalate Alfa 307844 CFS-NAOXAM #18, NAOXMP #14	zero
1258	phenylboronic acid Sigma P-5751	zero
1259	2-thiouracil Sigma T-7750 CFS-TURCIL #2	zero
1260	4-phenyl-2-thiouracil Sigma P-3252	zero

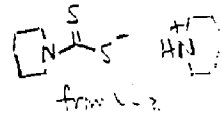
1261	sulfaguanidine Sigma S-8751	zero
1262	salicylamide Sigma S-0750 CFS-SALMID #15	zero
1263	5-trifluormethyl-uracil Sigma T-8008	zero
1264	thionicotinamide Sigma T-7250	zero
1265	sulfaminouracil Sigma S-9126	zero
1266	sulfathiazole Sigma S-9876 CFS-SUTHAZ,01,02 #14	zero
1267	sulfameter Sigma S-0383 CFS-SAMPYM #14, 01 #15	zero
1268	2-thiocytosine Sigma T-6000 CFS-THCYTO10 #5	weak
1269	sulfanitran Sigma S-0633	zero
1270	thymine Sigma T-0376 CFS-THYMIN #14	zero

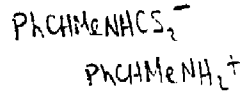
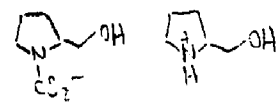
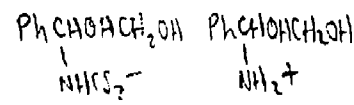
1271	sulfadimethoxine Sigma S-7007 CFS-SFDMOX #2	zero
1272	sulfamethoxypyridazine Sigma S-7257	zero
1273	sulfamerazine Sigma S-8876	zero
1274	sulfamethazine Sigma S-6256	zero
1275	sulfapyridine Sigma S-6252	zero
1276	2-chloro-3,5-dinitrobenzotrifluoride Aldrich 24,799-5	zero
1277	4,4'-difluorobenzophenone Aldrich 11,549-5	v weak
1278	6-chloronicotinamide Aldrich C5,800-2	zero
1279	2,6-dinitrobenzaldehyde Aldrich 11,750-1	moderate
1280	4-chloro-3,5-dinitrobenzotrifluoride Aldrich 19,701-7	zero

1281	2-mercaptobenzoxazole Aldrich M350-7	weak+moderate
1282	4-fluoro-3-nitrophenyl sulfone Pfaltz and Bauer, D25600	zero
1283	Acetylthiourea Fluka	zero
1284	4-phenylthiosemicarbazide Fluka	zero
1285	tetrabutylammonium toluene-4-sulfonate Fluka	zero
1286	5-nitro-2-furanacrolein Aldrich 22,656-4	zero
1287	N-formyl-L-methionine Sigma F-3377	zero
1288	α-oxo-2-furanacetamide Fluka 75850	good
1289	orotic acid, anhydrous Sigma O-2750	zero
1290	3-oxauracil Sigma O-6251	zero

1291	3,4-dichloronitrobenzene ICN 6098	zero
1292	orotic acid methyl ester Sigma O-3627	zero
1293	oxolinic acid Sigma O-0877	zero
1294	orotic acid Sigma O-2625	zero
1295	p-aminomethylbenzene-sulfonamide Sigma A-2134	zero
1296	ammonium dithiocarbamate Pfaltz & Bauer A30040	zero
1297	oxalic acid Sigma O-0376 CFS-OXALAL,02,03 #61; 01,04 #14	zero
1298	oxamide Aldrich O-932-8 CFS-OXAMID01 #2	zero
1299	oxamic hydrazide Aldrich O-930-1	zero
1300	oxalyl dihydrazide Aldrich 13,129-6	zero

1301	3-nitro-4-hydroxybenzoic acid Sigma N-5381	zero
1302	4-(aminomethyl)benzenesulfonamide HCl salt provided by Sigma	zero
1303	oxanic acid Aldrich O-920-4	zero
1304	sulfisoxazole Sigma S-6377	zero
1305	5-nitro-2-thiophenemethanediol diacetate Aldrich 18,474-8	~urea
1306	nitrofurantoin Aldrich 86,044-1	zero
1307	6-nitropiperonyl alcohol Aldrich 19,629-0	zero
1308	5-nitro-2-furaldehyde diacetate Aldrich 14,927-6	1.25× urea
1309	5-nitro-2-furoic acid Aldrich 15,571-3	weak
1310	p-nitrophenyl-α-L-fucopyranoside Sigma N-3628	~urea

1311	p-nitrophenyl-α-D-mannopyranoside Sigma N-2127	zero
1312	o-nitrophenyl dimethyl carbamate Sigma N-0753	zero
1313	p-nitrophenyl-β-D-galacto-pyranoside Sigma N-1252	weak+ moderate
1314	p-nitrophenyl-β-D-fucopyranoside Sigma N-3378	weak
1315	p-nitrophenyl-α-D-glucopyranoside Sigma N-1377	weak+ moderate
1316	p-nitrophenyl-α-D-galactopyranoside Sigma N-4633	weak+ moderate
1317	p-nitrophenyl-β-D-xylo-pyranoside Sigma N-2132 CFS-NPBDXY #19	weak+ moderate
1318	p-nitrophenyl-β-D-glucopyranoside Sigma N-7006	zero
1319	(1991) Dobrowolski R-0084-17 	zero
1320	2-cyclopentylamino-5-nitropyridine Dobrowolski R-0084-25	weak

1321	2-cyclohexylamino-5-nitropyridine Dobrowolski R-0084-27	v weak
1322	2-cycloheptylamino-5-nitropyridine Dobrowolski R-0084-29	zero
1323	2-cyclooctylamino-5-nitropyridine Dobrowolski R-0084-31	54× urea
1324	4-cyclopentylaminonitrobenzene Dobrowolski R-0084-33	zero
1325	4-cyclohexylaminonitrobenzene Dobrowolski R-0084-35	zero
1326	4-cycloheptylaminonitrobenzene Dobrowolski R-0084-37	8× urea
1327	4-cyclooctylaminonitrobenzene Dobrowolski R-0084-39	moderate+ good
1328	Dobrowolski R-0084-45 	moderate
1329	Dobrowolski R-0084-47 	weak+ moderate
1330	Dobrowolski R-0084-41 	weak

1331	4-cyano-4'-nitrodiphenylsulfide rjt R0034-	zero
1332	3-methyl-4-cyclopropylaminonitrobenzene rjt R0034-130	zero
1333	4-cyclopropylaminonitrobenzene rjt R0034-128	0.5× urea
1334	2-cyclopropylamino-3-methyl-5-nitropyridine rjt R0034-129	zero
1335	2-cyclopropylamino-5-nitropyridine rjt R0034-127	zero
1336	3,5-dinitro-2-pyridine semicarbazide rjt R0095-15	6× urea
1337	4-fluoro-3-nitroaniline Fluka 47130	zero
1338	4-ethoxymethylene-2-phenyloxazol-5-one Sigma E-0753	zero
1339	α-ketoglutaric acid (monosodium salt) Sigma K-1875	zero
1340	isonicotinamide Sigma I-3127	zero

1341	khellin Sigma K-2750 CFS-KHELIN,01 #14	zero
1342	isobarbituric acid Sigma I-0627	zero
1343	p-nitrobenzaldoxime Sigma N-3009	zero
1344	2,2'-dithiobis-(5-nitropyridine) Sigma D-9634	zero
1345	α-ketoglutaric acid (free acid) Sigma K-1750	zero
1346	2,4-dinitro-5-fluoroacetanilide Sigma D-6629	zero
1347	N-(3,5-dinitrobenzoyl)-L-leucine Sigma D-9770	1.3× urea
1348	o-nitrobenzaldehyde tosylhydrazone Sigma N-3509	zero
1349	o-nitrobenzaldoxine Sigma N-3634	zero
1350	S-methyl-L-cysteine Sigma M-6626	zero

1351	ethyl ethoxymethylene-cyanoacetate Sigma E-4628	zero
1352	α-isonitrosopropiophenone Sigma I-3502	zero
1353	ethyl acetamidocyanoacetate Sigma E-1251	zero weak fluorescence
1354	p-aminooxanilic acid Sigma A-7265	zero
1355	o-dinitrobenzene Sigma D-2638	zero
1356	dipicolinic acid Sigma D-0759 CFS-DIPICA10 #19	zero
1357	dipyridamole Sigma D-9766	zero
1358	α-ketoglutaric acid Sigma K-2000	zero
1359	p-dimethylamino-cinnamaldehyde Sigma D-4506	moderate fluorescence
1360	glycine-p-nitroanilide Sigma G-4254	zero

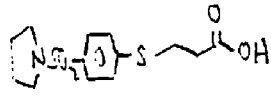
1361	N-(3,5-dinitrobenzoyl)-(R)-(-)-α-phenylglycine Sigma D-9270	0.3x urea
1362	1,2-epoxy-3-(p-nitrophenoxy)-propane Sigma E-7004	v weak
1363	N,N-bis(phosphonomethyl)-glycine Sigma P-4269	v weak
1364	dimethyl-(2-hydroxy-5-nitrobenzyl) sulfonium bromide Sigma D-6388	zero
1365	sulfadiazine Sigma S-8626 CFS-SULDAZ #14	zero
1366	2-methyl-4-N-(cyclohexylamino)nitrobenzene rjt	zero
1367	L-methioninesulfoximine Sigma M-5379	v weak
1368	pyrazinamide Sigma P-7136 CFS-PYRZIN,01 #14; 02 #2	zero
1369	2,4-dinitro-5-fluoroaniline Sigma D-6754	zero
1370	p-nitrophenyl anthranilate Sigma N-3506	zero

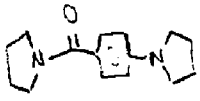
1371	thioacetamide Sigma T-5250 CFS-THACEM #14	zero
1372	5-diazouracil Sigma D-8752	zero
1373	picrolonic acid Sigma P-5628	zero
1374	3-methyl-4-N-(cycloheptylamino)nitrobenzene rjt CFS-THYDIN #19	zero
1375	2,3-dihydroxybenzaldehyde Sigma D-7136	zero
1376	1-dimethylaminonaphthalene-5-sulfonic acid Sigma D-7882	zero
1377	4-(p-nitrobenzyl)-pyridine Sigma N-3131	zero
1378	dimethyl-(2-methoxy-5-nitrobenzyl)-sulfonium bromide Sigma D-7511	zero
1379	5-(trifluoromethyl)uracil Sigma T-8008	v weak
1380	morin Sigma M-4008	zero

1381	ethambutol hydrochloride Sigma E-4630	zero
1382	2-methoxy-5-nitrobenzylbromide Fluka 65135	zero
1383	bis(4-fluoro-3-nitrophenyl)sulfone Sigma F-3626	zero
1384	sulfamethizole Sigma S-5632	zero
1385	santonin Sigma S-1250	zero
1386	acetophenetidine Sigma A-2375	zero
1387	3,5-dinitrosalicylic acid Sigma D-1510	0.3x urea
1388	2,6-di-t-butyl-4-bromophenol dcd R-0084-69 CFS-BBPHOL, BBPHOL01 #19	zero
1389	2-N-(cyclopropylamino)-4-nitrotoluene dcd R-0084-79	zero
1390	4-N-(cyclobutylamino)nitrobenzene	zero

1391	N-(2-hydroxymethylpyrrolidino)(4-N-piperidino)phenylsulfone dcd R-0084-59	0.3× urea
1392	2-N-(2'hydroxymethylpyrrolidino)-3,5-dinitrobenzotrifluoride dcd R-0084-73	zero
1393	N-(α-methylbenzyl)-4-(N-pyrrolidino)phenylsulfonamide dcd R-0084-77	zero
1394	N-(2-hydroxymethylpyrrolidino)(4-N-morpholino)phenylsulfone dcd R-0084-61	zero
1395	3,5-dinitro-4-N-(α-methylbenzylamino)benzonitrile dcd R-0084-67	0.3× urea
1396	3,5-dinitro-4-N-(t-butylamino)benzonitrile dcd R-0084-75	0.3× urea
1397	2-N-(t-butylamino)-3,5-dinitrobenzotrifluoride dcd R=0084-63	zero
1398	carvone semicarbazide rjt R-0095-63C	zero
1399	3-pentanone semicarbazide rjt R-0095-63B	v weak
1400	camphor semicarbazide rjt R-0095-63D	v weak

1401	acetone semicarbazide rjt R-0095-63A	v weak
1402	3,5-dinitro-4-N-pyrrolidino benzotrifluoride rjt R-0095-62	zero
1403	4,4'-diaminodiphenylsulfone rjt CFS-DAPSYO01,10 #19<32>	0.3× urea
1404	1,3,5-trichloro-2,4-dinitrobenzene Nazzal	zero
1405	2-bromo-4'-dimethylamino-α-cyanostilbene rjt R-0095-47 CFS-BCSTIL #18	6× urea
1406	N-(4-nitrophenyl)-N'-(methylbenzyl)urea rjt R-0095-49	12× urea
1407	N-(4-nitrophenyl)-N'-(2-hydroxymethyltetramethylene)urea rjt R-0095-54	0.6×urea
1408	3,5-dinitro-4-N-(2'-hydroxymethylpyrrolidino)benzonitrile rjt R-0095-22	weak-moderate
1409	di-(3-nitro-4-N(α-methylbenzylamino))phenylsulfone rjt R-0095-23	1.25× urea
1410	N-(4-nitrophenyl)-N'-(phenyl)urea rjt R-0095-50	weak-moderate

1411	N-(pyrrolidino)[4-N(2-hydroxymethylpyrrolidino)]phenylsulfone rjt R-0095-19	v weak
1412	3,3'-dinitro-4,4'-(N-pyrrolidino)diphenylsulfone rjt R-0095-13	weak-moderate
1413	3,4-diethoxynitrobenzene rjt R-0095-34	zero
1414	4-ethoxynitrobenzene rjt R-0034-133	zero
1415	rjt R-0095-39 	zero
1416	p-nitrobenzaldehyde semicarbazide rjt R-0095-26	zero
1417	3,4-dimethoxynitrobenzene rjt R-0095-29	zero
1418	5-nitro-2-thiofuraldehyde semicarbazide rjt R-0095-27	zero
1419	N,N-(tetramethylene)(4-N-α-methylbenzylamino)phenylsulfone rjt R-0095-21	1× urea
1420	3,4-diacetoxynitrobenzene rjt R-0095-33	zero

1421	3-bromo-4-methylaminonitrobenzene rjt R-0095-35	6× urea
1422	β-(2,4-dinitro-5-trifluoromethylphenylthio)propionic acid rjt R-0095-45	zero
1423	N,N-tetramethylene-4-fluorobenzene sulfonamide rjt R-0095-17	weak-moderate
1424	N,N-(tetramethylene)-4-N'-pyrrolidinobenzene sulfonamide rjt R-0095-18	zero
1425	rjt R-0095-24 	zero
1425	[N-(2-hydroxymethylpyrrolidino)]-4-(N-pyrrolidino) phenylsulfone rjt R-0095-28	zero
1427	N-(α-methylbenzyl)-4-fluorophenylsulfonamide ded R-0084-71	weak
1428	1-amino-4-nitronaphthalene Fluka	zero
1429	pinacryptol yellow Fluka	zero
1430	2-amino-4-nitrophenol Fluka	zero

1431	N-acetyl-homocystein-ethiolactone Fluka	weak-moderate
1432	ammonium sulfamate Fluka	zero
1433	L(+)-α-phenylglycinol Fluka	weak-moderate
1434	tetrabutylammonium hydrogensulfate Fluka	zero
1435	R(-)-1-phenyl-1,2-ethanediol Fluka	zero
1436	acetohydroxamic acid Fluka	zero
1437	4,5-diamino-2,6-dihydroxypyrimidine sulfate Fluka	zero
1438	tetrabutylamino trifluoromethane sulfonate Fluka	zero
1439	dehydro-L(+)-ascorbic acid Fluka	zero
.440	6-aminonicotinic acid Aldrich 21,687-9	good

1441	4-pyrrolidinobenzene sulfonamide Twieg R-0095-67	zero
1442	2-N-cyclobutylamino-5-nitropyridine Twieg	weak
1443	4,4'-bis-N-pyrrolidino benzophenone Twieg R-0095-36	zero
1444	4-fluorobenzene sulfonamide Twieg R-0095-66	zero
1445	N-4-nitrophenyl-N'-(α-phenethyl)thiourea Twieg R-0095-50	weak
1446	2-N-cyclooctylamino-3-methyl-5-nitropyridine Twieg R--95-69	weak
1447	β-octylthiopropionic acid Twieg	zero
1448	4-(2-hydroxymethylpyrrolidino)benzene sulfonamide Twieg R-0095-68	zero
1449	methyl-phenyl sulfoxide Fluka	zero
1450	1,2,3-trichloro-4-nitrobenzene Fluka	zero

1451	4-chloropyridine-N-oxide Fluka	zero
1452	maleinimide Fluka	zero
1453	1-methyl-2-thiourea Fluka	zero
1454	sparteine sulfate cryst. ph. helv. v Fluka	zero
1455	t-butyl carbamate Fluka	zero
1456	methyl-3-aminocrotonate Fluka	zero
1457	isonictinsaureamid Fluka	zero
1458	pyridoxal-5'-phosphate Fluka	zero
1459	S-methyl-L-cysteine Fluka	zero
1460	coumalic acid Fluka	zero

1461	4-(6)-propyl-2-thiouracil Fluka	zero
1462	(+)-biotin ph. helv. (vitamin H) Fluka	weak
1463	tetraethylammonium tetrafluoroborate Fluka	v weak
1464	DL-glyceraldehyde cryst. Fluka	zero
1465	4-methylmorpholine-4-oxide monohydrate Fluka	zero
1466	D(-)-tartaric acid dehydrazide Fluka	weak-moderate
1467	(R,R-(+)-N,N'-bis-(α-methylbenzyl)sulfamide Aldrich 27,608-1	weak
1468	methyl coumalate Fluka	zero
1469	(1S,2R,5S)-(+)-menthyl-(R)-p-toluenesulfinate Aldrich 27,874-2	weak-moderate
1470	(R)-(-)-camphorquinone Aldrich 27,628-6	weak

1471	(-)-camphanic acid Fluka	zero
1472	3-methoxycarbonyl-2,5-dihydroxthiophene-1,1-dioxide Fluka	weak-moderate
1474	ketone moschus Fluka	zero
1475	7-amino-4-methylcoumarin Fluka	vv weak
1475	tris(4-nitrophenyl)phosphate Fluka	vv weak
1476	(-)-usnic acid ex cladonia alpestris Fluka	weak-moderate
1477	tetrabutylammonium tetraphenylborate Fluka	zero
1478	phthalonitrile Eastman 7402<28,32>	good burns
1479	2-chloro-4-nitrotrifluoroacetanilide Twieg	zero
1480	1-acetyl-2-thiohydantoin Eastman 3882	zero

1481	4-chloro-3,5-dinitrobenzonitrile Aldrich C3,895-8	good
1482	1-(β-hydroxyethyl)-2-imidazolinethione Aldrich S37210-2	zero
1483	4-nitrophenyl isocyanate Aldrich 26,942-5	zero
1484	2,5-di-t-butyl-3,6-dichlorobenzoquinone	zero
1485	2,3-dihydro-1,2-benzisothiazol-3-on-1,1-dioxide fluka 12475	zero
1486	4,4'-difluorodiphenylsulfone Pfaltz and Bauer D25620	zero
1487	hexamethylenetetramine Fluka 52709	v weak
1488	sodium cyanate Fluka 71420	fluorescence
1489	piperin Fluka 80810	zero
1490	acetoacetamide Flka 00405	zero

1491	cyanoacetamide Fluka	weak-moderate
1492	actidione Fluka	zero
1493	tetraphenylphosphonium chloride Fluka	zero
1494	4-(4-methoxybenzylamino)-7-nitro-benzofurazan Fluka	large amount-fluorescence
1495	ajmalicine Fluka	v weak
1496	2-chloro-4-nitroaniline Fluka<16>	excellent
1497	1-pyrrolidinecarbodithionic acid ammonium salt Fluka	zero
1498	tetrabutylammonium perchlorate Fluka	zero
1499	tetrabutylammonium nitrate Fluka	zero
1500	tetrabutylammonium nitrite Fluka	zero

1501	tetrabutylammonium tetrafluoroborate Fluka	zero
1502	diphenylmaleic anhydride Fluka	weak-moderate
1503	tetrabutylammonium hexafluorophosphate Fluka	zero
1504	R-(-)-1-aminoethylphosphonic acid Fluka	zero
1505	trimethylphosphine oxide Alfa 10563	zero
1506	tetraphenylphosphonium bromide Fluka	zero
1507	trifluoroacetamide Fluka	zero
1508	potassium cyanate cryst. Fluka	ıorescence
1509	2-amino-5-nitrothiazole Sigma A-2634	zero
1510	esculin hydrate Sigma E-8250	zero

1511	m-dinitrobenzene Sigma D-6379	good
1512	(-)-epinephrine(+)bitartrate Sigma E-4375	zero
1513	metronidazole Sigma M-3761	zero
1514	3(α-acetonylbenzyl)-4-hydroxycoumarin Sigma A-2250	moderate
1515	cephalexin Sigma C-4895	zero
1516	acetohydroxamic acid Sigma A-4886	weak
1517	furazolidone Sigma F-9505	zero
1518	α-cyano-4-hydroxy-cinnamic acid Sigma C-2020	zero
1519	2,5-dimethoxy-4'-nitrostilbene Sigma D-0132	v weak
1520	picrylsulfonic acid Na salt Sigma P-3402	zero

1521	sulfamethoxazole Sigma S-7507	zero
1522	D-(-)-penicillamine Sigma P-4875	v weak
1523	2,3-dihydro-5,6-diphenyl-1,4-oxathin Sigma D-2015	weak-moderate
1524	thiocarbohydrazide Sigma T-2137	zero
1525	4-hydroxy-6-methyl-2-thiopyrimidine Sigma H-2502	zero
1526	2-hydroxy-5-nitrobenzyl-bromide Sigma H-3877	zero
1527	tioxolone Sigma T-5389	zero
1528	3,5-dinitrobenzamide Sigma D-9140	zero
1529	3-diazouracil Sigma D-3135	vv weak
1530	furosemide Sigma F-4381	zero

1531	ethionamide Sigma E-6005	moderate
1532	5,5-dimethyl-2,4-oxazolidinedione Sigma D-7631	zero
1533	hydroxyurea Sigma H-8627	zero
1534	DL-ethionine sulfone Sigma E-8251	zero
1535	N-methylmaleimide Sigma M-3627	zero
1536	N-ethylmaleimide Sigma E-3876	zero
1537	5-fluorouracil Sigma F-6627	zero

IX. Summary

During the first contract year the collaborative program was of broad scope in order to survey a variety of approaches to identify and utilize organic nonlinear materials for optical second harmonic generation (SHG). Our efforts included screening the Cambridge Crystallographic Index for new noncentrosymmetric crystalline compounds, the selection of commercially available substances, the total synthesis of unique new substances as well as many compounds from the Cambridge Crystallographic Index, the powder measurement of all samples, the synthesis of Langmuir-Blodgett film forming molecules, the deposition and optical measurement of these films and the development of a computer program to calculate the (hyper)polarizabilities of organic molecules which serves as a guide to select materials from the Cambridge Index and as a guide to assay which materials warrent ultimate synthetic effort. The materials which have been examined may be divided into three very general classes as a function of their absorption characteristics. The first class is comprised of the "conventional" nonlinear organics which are based on aromatic rings bearing both a strong donor and and strong acceptor group and a resultant absorption cutoff of 400-500 nm. The second class includes aromatics with weaker donor and acceptor groups with absorption cutoffs typically between 300-400 nm. The third class is comprised of the very highly UV transparent organic molecules with cutoffs between 200-300 nm. The "transparancy-efficiency" tradeoff dictates that the longer wavelength the absorption edge the larger the hyperpolarizability value for the molecule is likely to be. However, even the highly transparent compounds in the third class very often have efficiencies comparable or better than most typical inorganic crystals. New molecules with very promising properties have been found in each

of these three classes during the last year.

From the some 29,000 compounds in the Cambridge Crystallographic Index we have selected almost 600 unique compounds which we feel merit attention for further studies. Of these we have obtained documentation for at least 250 and we have purchased or prepared 50 of these compounds and run powder measurements. A variety of interesting new chemical functionalities and structural correlations have resulted from this exercise and more valuable compounds and structural insights will result from continued study of this group of materials. In addition to the 50 compounds we have dealt with to date from the Cambridge Index we have examined over 900 more. The majority of these samples were commercially available and were chosen on a basis of known functional group/SHG activity relationships. Many of the materials were custom-synthesized during the past year or were obtained from the sample collections of colleagues in our laboratory. This approach has resulted in the refinement of structural types for which activity had already been known and the discovery of new chemical functionality which has been found to produce SHG for the first time. Typical new polar functionality which has been demonstrated to produce SHG includes phosphine sulfides, and various forms or oxidized sulfur including sulfones, sulfamides and sulfonamides.

For the Langmuir-Blodgett thin film studies highly specialized molecules which contain known polarizable functionality have been prepared. For two of these molecules which contain a nitroaniline and a merocyanine functionality L-B film deposition has been optimized but no SHG has been observed from these films. The reasons why no SHG has been obtained is presently uncertain but may involve symmetry problems of the dipoles within a layer or interlayer symmetry problems. The structrure of these films is being analyzed and the L-B trough is being modified to allow deposition of alternating "buffer" layers to inhibit

crystal growth. We have also found a variety of other molecules with more modest efficiencies which have cutoffs in this range. In the third class of materials with cutoffs between 200-300 nm we have also found some molecules of great interest. Foremost is sulfamide which has absorption properties similar to urea, good damage stability and and an SHG efficiency some one-third that of urea. Also of great interest are triethylphosphine sulfide and N-acetylcysteine which have cutoffs near 250 nm and efficiencies comparable to and about one-fifth that of urea respectively. These substances are of interest not only in their own right but even more so due to the fact that analogs should prepared and examinedin a rational fashion. Samples of all these materials have been provided to Dr. Eimerl and we have suggested that Prof. Arend undertake a crystal growth study of sulfamide.

After Prof. Wagniere's work with us here this past summer he has returned to his position at the University of Zurich where he has continued work on the hyperpolarizability calculations. Prof. Wagniere has instigated a collaboration and invited Prof. Dr. Hanns Arend and Dr. Peter Gunter of the Solid State Physics Laboratory of the ETH to study the crystal growth and subsequent single crystal nonlinear optical properties of attractive organic materials. Prof. Arend is widely known as one of the most capable crystal growth experts in the world and his collaboration involving Dr. Gunter will prove to be extremely valuable. ****

centrosymmetric deposition.

Since September of last year we have had operating a program which calculates the hyperpolarizabilities of organic molecules. The program was written by Prof. George Wagniere of the University of Zurich and has since then been continuously refined by Dr. Carl Dirk. The program has be used to calculate the hyperpolarizabilities for a variety of organic molecules and has been calibrated by comparison with molecular hyperpolarizabilities which have been experimentally obtained via EFISH measurements. The program has found the greatest utility to predict the hyperpolarizabilities and the absorption spectra of organic molecules which contain novel functionality composed of first-row elements. This ability provides the synthetic chemist with a more judicious choice of what new types of molecules warrent preparation.

A few of the interesting new molecules, chemical functionalities and structural trends which have been discovered during the past year should be described in more detail. In the first class of materials with absorption between 400-500 nm we have discovered an important new material COANP (cyclooctylaminonitropyridine) which appears to be more nonlinear than MBANP (methylbenzylaminonitropyridine) which we had described earlier. Thus, COANP may have the highest nonlinearity for any known substance with comparable transparancy. A sample of COANP has been provided to Dr. Eimerl for further study. In the second class of materials with absorption cutoffs between 300-400 nm we have also found the very interesting and novel nonlinear classof 2,6-di-t-butylphenol derivatives. These include the parent substance itself, the 4-aldehyde (see also B. Davydov, et.al., Sov. J. Quant. Electron, 7(1), 129 (1977)) (DTBHB), the 4-nitro derivative and the 4-methyl compound. Further analogs should be examined in which the phenol is derivatized. A sample of DTBHB has been provided to Dr. Eimerl for study and to Prof. Arend at the ETH for

crystal growth. We have also found a variety of other molecules with more modest efficiencies which have cutoffs in this range. In the third class of materials with cutoffs between 200-300 nm we have also found some molecules of great interest. Foremost is sulfamide which has absorption properties similar to urea, good damage stability and and an SHG efficiency some one-third tnat of urea. Also of great interest are triethylphosphine sulfide and N-acetylcysteine which have cutoffs near 250 nm and efficiencies comparable to and about one-fifth that of urea respectively. These substances are of interest not only in their own right but even more so due to the fact that analogs should prepared and examinedin a rational fashion. Samples of all these materials have been provided to Dr. Eimerl and we have suggested that Prof. Arend undertake a crystal growth study of sulfamide.

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