The George Washington University
Contract AT-(40-1)-3797
ORO-3797-38

ANNUAL PROGRESS REPORT ON CONTRACT AT-(40-1)-3797

Lanthanide Ions as Sensitive Probes in Intermolecular Energy Transfer and Organic Photochemistry

January 1974

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This annual progress report covers the one-year period between January 1973 and January 1974. During this interval, emphasis has been placed on (1) the spectroscopic properties and behavior of positively charged organic sensitizers, for lanthanide ion energy acceptors, (2) distant interaction between nonconjugated electronic π-systems in rigid model molecules, (3) generation of stable paramagnetic species from selected organic heterocyclic energy donors, (4) preliminary experiments of hydroxycarbonium ion - Europium energy transfer, and (5) photochemical reactions of donors of excitation energy competing effectively with transfer of energy to lanthanide acceptors.

1. Spectroscopic Properties of Aromatic Ketone Energy Donors in Acidic Media. The behavior of carbonyl compounds in their electronically excited states has been subject of extensive investigation by both spectroscopic and photochemical methods. In contrast, the excited-state properties of the hydroxycarbonium ions, the protonated derivatives of the carbonyl compounds, have received much less attention mainly because the strongly acidic inorganic media required for complete protonation to carbonium ions are much less familiar to most spectroscopists and photochemists than the usual organic or aqueous solvents. In view of the potential advantages and feasibility of using these positively charged ions as donors of electronic energy to rare-earth ion acceptors (see (4) below), we have examined

quantitatively the absorption and emission properties of several representative hydroxycarbonium ions. Details are given in the preprint manuscript attached to this progress report (ORO-3797-39). Some conclusions are given in brief below.

Aromatic ketones are readily soluble in acidic solvents such as sulfuric acid, are completely protonated, and yield very stable solutions of hydroxycarbonium ions. These ions exhibit quantitatively measurable fluorescence and phosphorescence. Being planar, they are very well suited for both theoretical and experimental studies in molecular spectroscopy, photochemistry, and energy transfer.

2. Intramolecular Electronic Interaction Between Nonconjugated Chromophores in Rigid Model Compounds. Several rigid model molecules have been synthesized in which two aromatic π systems have been incorporated in a nonconjugated fashion by attachment to an inflexible σ-bond frame. The electronic interaction between the two chromophores was studied by both spectroscopic and photochemical means, specifically by exciting one of the two aromatic systems and quantitative evaluation of either emission from or photochemical reaction of the other chromophore. Spectral differences between the model molecule and a mixture of its component chromophores were examined theoretically by an SCF-CI-CNDO-MO procedure. The agreement between theoretically predicted spectra and experimental observations was satisfactory. Details of this work are presented in the attached manuscript (ORO-3797-41) and reprint (ORO-3797-40).

3. Stable Paramagnetic Species from Organic Heterocyclic Ketones. During our examination of positively charged heteroaromatic ketones as potential energy donors to lanthanides, we found that under certain experimental conditions -e.g. in alkaline media - some of these compounds generated stable free radicals. These paramagnetic species were very interesting not only as long-lived radicals but also relevant to understanding the mechanism of photochemical transformation and energy transfer from these ketones. The identity and properites of the radicals were studied by chemical and spectroscopic means including no visible and electron-spin-resonance techniques. Results are given in the attached

manuscript-preprint (ORO-3797-43).

4. Preliminary experiments have been carried out in which some aromatic hydroxycarbonium ions were excited electronically in the presence of europium ion. Enhanced emission from the lanthanide ion acceptor established the presence of active energy transfer from th e carbonium ion to europium.

So far, the great majority of the sensitizers employed in intermolecular energy transfer to lanthanide ion acceptors have been carbonyl compounds. Recently, we have directed some effort toward the use of positively charged energy-donors, such as the protonated derivatives of aromatic ketones, the hydroxycarbonium ions. There are several distinct advantages in this approach. (a) Being positivel y charged, the carbonium ions would have a vanishing probability of forming complexes with the tripositive rare-earth acceptors; the the possibility of complex-formation, especially at high concentrations, introduced some uncertainty regarding the energy-transfer mechanism in the case of neutral donors; (b) Because of electrostatic repulsion, the frequency of random donor-acceptor collisions in liquid solutions is also diminished; (c) the statistical treatment of the system will provide a valuable check on the transfer mechanism; (d) the carbonium-ion-sensitizers are remarkably stable and planar; therefore, they are suitable for both accurate spectroscopic determinations and theoretical calculations. They have also proven to populate efficiently both the excited singlet and triplet manifolds, and to emit efficiently fluorescence and phosphorescence.

Preliminary experiments have clearly shown that energy transfer from excited positive hydroxycarbonium ions to tripositive lanthanide ions does take place. Quantitative measurements are now in progress.

The following reprints, preprints, and manuscripts are attached to the report with their respective ORO numbers and made an integral part of this report.

1. "Electronic Absorption and Emission of Aromatic Hydroxycarbonium Ions" by N. Filipescu , S. K. Chakrabarti, and P. G. Tarassoff, accepted for publication in the Journal of Physical Chemistry. (Preprint ORO-3797-39).

2. "Interaction between p-Dimethoxybenzene and Norbornylene in two Rigid Model Compounds" by N. Filipescu and D. S. C Chang, Journal of th e American Chemical Society, 94, 5990 (1972). (Reprint ORO-3797-40).

3. "On the Configuration of Dienestrol" b I. Maienthal, T. D. Doyle, W. R. Benson, E. B. Sheinin, and N. Filipescu. (Manuscript to be submitted for publication, ORO-3797-44).

4. "Through-space Interaction between Nonconjugated Naphthalene and Phenanthrene in a Rigid Molecule", by N. Filipescu, F. L. Minn, and A. V. Thomas, accepted for publication in Journal of the Chemical Society, Perkin Transactions, (Preprint ORO-3797-41).

5. "Rotational Vibrations of 1,3-Diazine from Temperature Dependent ^{14}N Nuclear Quadrupole Resonance and X-ray Tensors" By B. L. Barton, Journal of Chemical Physics, 57, 5610 (1972) (Reprint ORO-3797-42).

6. "Formation of Long-lived Free Radicals from Acylpyridinium Salts with Alkali" by M. Frangopol, P. T. Frangopol, C. L. Trichilo, F. E. Geiger, and N. Filipescu, accepted for publication by the Journal of Organic Chemistry. (Preprint ORO-3797-43).

7. "Photochemical Addition of Anthronylidene to Alkenes", by J. W. Pavlik, N. Filipescu, P. T. Frangopol and M. Frangopol, Rev. Roum. Chim. 18, 1793 (1973) (Reprint ORO-3797-45).

The George Washington University
Contract AT-(40-1)-3797
ORO-3797-39

Electronic Absorption and Emission of Aromatic Hydroxycarbonium Ions.[1]

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Abstract: The spectroscopic properties of representative aromatic hydroxycarbonium ions have been investigated and compared with those of the parent unprotonated carbonyl compounds. The energy levels, oscillator strengths, polarizations, and charge densities of the planar carbonium ions were calculated by a MO-SCF-CI procedure. Comparison of theoretical values with experimental quantities yielded satisfactory structural models for the cations. The aromatic ketones studied are readily soluble in sulfuric acid, are completely monoprotonated, and form very stable solutions. In contrast to the parent ketones, most hydroxycarbonium ions exhibited strong $\pi^* \rightarrow \pi$ fluorescence ($\phi_f > 0.5$) and less intense $\pi^* \rightarrow \pi$ phosphorescence.

Whereas the excited-state properties of carbonyl compounds have been extensively investigated both spectroscopically and photochemically,[2] those of their protonated derivatives, the hydroxycarbonium ions, have received much less attention mainly because the strongly acidic inorganic media required for the preparation of carbonium ions are less commonly employed by most spectroscopists and photochemists than the usual organic or aqueous solvents. Since many hydroxycarbonium ions are remarkably stable and since others are active photochemically,[3] they represent an important class of compounds of potentially high interest both in photochemistry and molecular electronic spectroscopy.

In this paper we report on the uv-visible absorption and emission spectra of selected aromatic carbonyl compounds dissolved in sulfuric acid or, at low temperatures, in sulfuric-acetic acid mixtures. The following representative ketones and

lactones are grouped together in the present work: coumarin (C), xanthone (X), flavone (FLA), fluorenone (FLU), perinaphthenone (PN), di-p-methoxybenzophenone (DMB), and 2-acetonaphthone (2AN). These aromatic compounds were selected because they present common features that may allow valuable generalizations, because they yield stable and planar protonated derivatives which lend themselves both to accurate quantitative spectral measurements and to useful theoretical analysis, and because their spectroscopy and photochemistry in non-acidic solvents has received previous attention.[4]

Results and Discussion

The ketones studied were readily soluble in sulfuric acid; 10^{-3}M standard solutions remained stable over extended periods (weeks). No significant spectral differences could be detected in samples in which atmospheric oxygen was partially or rigorously excluded. Since concentrated sulfuric acid is known to have oxidative properties and is a medium of choice in the preparation of a variety of aromatic free radicals, all our ketone solutions were examined in an esr spectrometer.[5] Absence of esr signal indicated that no paramagnetic species was present. Except for protonated coumarin, the other solutions did not exhibit significant photochemical changes when irradiated for several hours with a 500 W high-pressure Hg arc.

Absorption Spectra. The uv-visible absorption spectra of the seven hydroxycarbonium ions in sulfuric acid are compared to those of the respective parent ketones in 3-methylpentane (3MP) in Figure 1. In sulfuric acid solutions diluted with 1:1 ethanol:water to 0.1 N H_2SO_4, the electronic absorption spectra of the ketones were consistent with the coexistence of both ketone molecules and respective hydroxycarbonium ions. This undoubtedly corresponds to a state of partial protonation of the carbonyl groups with the two absorbing species in dynamic equilibrium.

In pure sulfuric acid solution, all ketones exhibited a pronounced bathochromic shift of the band of lowest energy. For coumarin and flavone this red shift was not sufficient to determine visible absorption and consequently their

H_2SO_4 solutions remained colorless. The others, however, became vividly colored from different shades of yellow and green for DMB, PN, X, and 2AN to purple FLU.

The differences between the absorption spectra of the ketones in 3MP and those in H_2SO_4 are sufficiently pronounced to suggest that in pure acid the ketones exist only as the respective hydroxycarbonium ions, or, that there are no significant amounts of unprotonated carbonyl molecules in solution.

Theoretical Analysis of Absorption Spectra. On inspection, there seems to be no obvious correlation between the near ultraviolet absorption bands of the ketones and those of their protonated derivatives. One should mention, however, that except for the usual $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ classification based on relative energies and extinction coefficients there has been no reported attempt to assign individual bands in the absorption spectra of the above ketones to specific electronic transitions. Therefore, we will not try in this paper to establish theoretical ketone-protonated ketone correlations; instead, we analyze the absorption spectra of the hydroxycarbonium ions independently. The results of this analysis will provide not only some reasonable agreement between calculated and experimental spectra but also additional significant information such as extent of π-delocalization, whether mono- or di-protonation takes place (where hypothetically possible), and charge densities in ground and excited states (related to chemical and photochemical reactivities).

Method of Calculation. Energy levels, oscillator strengths, polarizations, and charge densities were derived via a π-electron calculation employing a semi-empirical MO-SCF-CI procedure which included only singly-excited configurations. The structures of all cations were considered planar with C-C and C-O distances of 1.40 Å, C=O 1.25 Å, and C-OH 1.36 Å. Within hexagonal cycles or in sp^2 hybridized atoms, the bond angles were taker to be 120°; for ether oxygen the bond angle was 114°. Slight variations in bond-distances and angles did not alter significantly

the calculated data. The following optimized parameters were used: valence-state ionization potentials for C^+ 8.26 ev, for O^+ 17.70 ev, and for O^{2+} 28.50 ev; one-center repulsion integral for C 11.13 ev, for O^+ 15.23, and for O^{2+} 21.53 ev; both bond resonance integrals β_{CC} and β_{CO} were -2.37 ev. The two-center repulsion integrals were evaluated by the Mataga-Nishimoto approximation.[6] Self-consistency was reached after six or seven iterations. This method of calculation is known to give good results for evaluating spectral properties of heteroaromatic and non-alternant systems.[7] A modification to Bloor and Gilson's closed-shell SCF-CI program[8] was used on an IBM 360/50 computer.

Calculated values for singlet and triplet energy levels, oscillator strengths for transitions to and from the ground state and polarizations are compared with experimental quantities in Table 1. The values listed are those obtained for the configurations 1 - 7 shown in Figure 2.

The valence-bond structures have been purposely written as oxonium ions for 1, 2, and 3, and carbonium ions for the remaining four. In fact the results of our calculations indicate that there is little π-delocalization over the hydroxyl oxygen in the first three ions in contrast with the latter four. When the core of the exocyclic oxygen atom of 1 - 3 ions was included in the π-electron calculation the derived spectral values became unacceptable on comparison with experiment. For instance, if the OH oxygen in coumarinium ion is included in the delocalization with a total of 12 π-electrons, then the energies of the first excited singlet state come out to be about 2 ev lower than the observed value. In addition, the calculated lowest triplet comes also unacceptably low compared to experimental values. On the other hand, the hydroxyl oxygens of cations 4 - 7 must be included in the MO calculation to obtain reasonable agreement with experimental spectral quantities. That protonation does not take place in the aromatic rings of the ketones was clearly shown by their nmr spectra in D_2SO_4 which showed no additional H-splitting or H-exchange.

The agreement between theoretical and experimental values in Table 1 is as good as any previously reported on aromatic and heteroaromatic molecules.

Charge Densities. The calculated charge densities for the ground and first excited singlets and the lowest triplet of the hydroxycarbonium ions are given in Figure 3. These values may prove valuable in estimating the reactivity of the cationic species in both the ground and the S_1 and T_1 states. Several interesting generalizations can be obtained from examination of the numerical values in Figure 3. For the hydroxycarbonium ions derived from DMB, 2AN, PN, and FLU which have no ether or lactone oxygen and which have substantial π-delocalization over the hydroxyl oxygen, the electronic charge density increases slightly on going from the ground state to either the lowest singlet or lowest triplet excited states. On the other hand, the increase in density on the carbon atom adjacent to the OH increases substantially in the T_1 and S_1 states with somewhat higher values for the S_1 level. This behavior is common to all compounds in this study and is analogous to that of the unprotonated ketones in which the natural C → O polarity in the ground state has been shown to reverse to a considerable extent in the S_1 and T_1 states.[2] On those carbon atoms included in the aromatic ring system, there are changes in the electron density on going from ground to excited states; however, none of them comes close to those observed for the carbon atom attached to the hydroxyl group. For the ions containing an ether-linked oxygen, a consistent increase in electron density on that atom is observed in the S_1 and T_1 states when compared to the ground state.

Emission Spectra. The fluorescence, phosphorescence, and excitation spectra of four representative hydroxycarbonium ions are shown in Figure 4. Those of the remaining three have been omitted for the following reasons: FLU emits only a very weak, broad-band fluorescence in the red spectral region (~ 610 nm), which seems to be concentration-dependent,[9] 2AN shows only intense fluorescence in a broad-band between 500 and 600 nm, but no phosphorescence, and DMB emits fluorescence and phosphorescence similar to that of benzophenone.[10]

The emission quantum yields and phosphorescence lifetimes of the hydroxycarbonium ions which exhibited both fluorescence and phosphorescence are given in Table 2. The corresponding emission parameters of the parent carbonyl compounds determined under identical conditions in nonacidic solvent (3MP) are also included in Table 2 for comparison. While the ketones exhibit characteristic, short-lived $\pi^* \rightarrow n$ phosphorescence and virtually no fluorescence in 3MP, in acid, the respective cations, with the exception of coumarin, emit significant fluorescence and weaker phosphorescence of 2-3 sec lifetime characteristic of $\pi^* \rightarrow \pi$ spin-forbidden transitions. The change in emitting state from n,π^* to π,π^* is readily understood since protonation takes place at the nonbonding electrons of the carbonyl oxygen. The decrease in phosphorescence quantum yield associated with protonation reflects a corresponding decrease in intersystem crossing efficiency. This, again, can be explained satisfactorily by analyzing the respective changes in energy levels both observed experimentally and derived theoretically. Thus, the S_1-T_1 gap is substantially larger in the cation than in the ketone. This sizable difference should decrease the spin-orbit coupling matrix element accordingly.

In addition, the theoretically-derived T_2 state, which is known to be instrumental in intersystem crossing when properly located energetically with respect to S_1, seems to be distinctly higher than S_1 in the hydroxycarbonium ions which emit poorly or not at all from T_1 but lower in those exhibiting phosphorescence. Nevertheless, even in the latter, the T_2-mediated crossover does not seem to compensate for the larger effect of the increase in the $S_1 - T_1$ gap. Consequently, the cations remain poorer phosphorescence emitters than their respective unprotonated ketones.

The fact that there was no detectable $\pi^* \rightarrow n$ phosphorescence in acidic glass and that $T_1 \rightarrow S_0$ emission was distinctly singly-exponential seems to confirm the totally-protonated state of dissolved ketone suggested by the absorption spectra.

The fluorescence maxima at ambient temperature and at 77°K and the calculated fluorescence lifetimes are also included in Table 2. It is interesting that the

hypsochromic shift in λ_{max} of fluorescence on going from room to liquid nitrogen temperature is quite sizable (20-25 nm). This, however, is not unexpected since both the cationic solute and the solvent are highly polar and this is reflected in ground-excited state differences in solvation and equilibrium configurations.

Polarization. The calculated polarizations corresponding to different singlet-singlet electronic transitions are given in Table 1. The main feature of these derived values is that by comparison with experimental fluorescence-excitation polarization measurements shown in Figure 1, they confirm the validity of cationic configurations 1 - 7. Possible structures other than those shown for 1 - 7 and diprotonated species considered in calculations failed grossly to agree with the experimental values. On the other hand, the calculations for species 1 - 7 gave a satisfactory overall consistency between calculated and experimentally measured quantities. For example, configuration 2 for protonated xanthone predicts theoretically that the first electronic transition should be short-axis and the second and third be long-axis polarized. In agreement with these predictions, the measured polarized fluorescence excitation spectrum shown in Figure 1 shows the first electronic transitions to be positively polarized while the second and third absorption bands are negatively polarized.

Figure 1 also shows the phosphorescence polarization curves of the hydroxycarbonium ions which emit phosphorescence. In general, these measurements indicate an out-of-phase polarization for the $0 \rightarrow 0$ bands of the $T_1 \rightarrow S_0$ emissions. As expected, this is characteristically associated with phosphorescence.

Conclusion

Aromatic ketones are readily soluble in acidic solvents such as sulfuric acid, are completely protonated, and yield very stable solutions of hydroxycarbonium ions. These ions exhibit quantitatively-measurable fluorescence and phosphorescence. Being planar, they are very well suited for both theoretical and experimental studies in molecular spectroscopy and photochemistry.

Experimental Section

The selected ketones and lactones were purified by repeated recrystallization from appropriate solvents followed by vacuum sublimation. Fluorometric sulfuric and acetic acids were obtained from Matheson Coleman and Bell and 3-Methyl-pentane from Phillips Petroleum Co.

When ketone solutions in pure sulfuric acid were cooled to 77°K, they formed a poor quality glass. In contrast, the samples dissolved in a mixture of sulfuric acid and acetic acid (3:1 by volume) yielded a clear rigid glass at 77°K. Since no significant differences could be detected in either the absorption or emission spectra on going from pure sulfuric to sulfuric-acetic acid mixtures, all quantum yields, lifetimes, and polarization measurements of the hydroxycarbonium ions at 77°K were carried out in sulfuric-acetic acid mixtures.

All samples were deaerated by passing pure dry nitrogen gas for 20 mins. before measurements. The emission spectra (both fluorescence and phosphorescence) were measured with the Perkin-Elmer Model MPF-2A Fluorescence Spectrophotometer with a 150 Watt xenon light-source and the necessary phosphorescence accessories. The exciting and emission monochromators had 600 lines/mm gratings blazed at 3000Å. An R106 photomultiplier was used for the blue region and an R136 for the red region. Two film type polarizers were used for the polarization measurements. Quartz tubes of 2 mm i.d., contained in a quartz Dewar flask, were used for the low temperature emission spectra. A 3 mm slit width (22 mμ band pass) in the excitation monochromator and a 2 mm slit width (15 mμ band pass) in the emission monochromator were normally used. Higher slit widths had to be used for recording emission of low intensity in a few cases. The emission was observed at right angle to the exciting beam. The recorded luminescence spectra were not corrected for instrument response.

The polarization of emission and its excitation was obtained by photoselection. The degree of polarization (P) was calculated from the formula, $P = (I_{\parallel} - I_{\perp})/(I_{\parallel} + I_{\perp})$. All polarization graphs represent an average of at least four different

measurements. The results were reproducible within ± 6%.

Quantum yields of emission were measured relative to 9,10-diphenylanthracene whose fluorescence quantum yield was taken to be unity. Fluorescence quantum yields at room temperature were also checked with quinine bisulfate standard (ϕ_f = 0.55); the agreements were good. The results of several measurements agree within ± 10%.

The phosphorescence lifetime measurements were made on the Perkin-Elmer Fluorescence Spectrophotometer with phosphorescence attachements and the decay curve was displayed on a Hewlett-Packard Oscilloscope (Model 10175B).

All absorption spectra measurements were made using a Cary 15 recording spectrophotometer.

Acknowledgement. This work was supported in part by the Atomic Energy Commission on Contract AT-(40-1)-3797. The time made available by the University Computer Center and the partial support from the Research Committee of The George Washington University are also greatly acknowledged.

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Figure Captions

Figure 1. Absorption spectra of the selected aromatic ketones in 3MP and in sulfuric acid.

Figure 2. Hydroxycarbonium ions investigated.

Figure 3. Calculated charge densities.

Figure 4. Emission, excitation, and polarization spectra of coumarin, xanthone, flavone, and perinaphthenone in rigid glass at 77°K. Solvents were 3MP for ketones and H_2SO_4:AcOH for their cations. Fluorescence excitation of cation (——) and ketone (···). Emission spectra of cation (-⊙-⊙-) and ketone (---). Polarization spectra (-○-○-): 1 - excitation, 2 - fluorescence, and 3 - phosphorescence.

Table 1. Comparison of Experimental and Calculated Spectral Parameters of Hydroxycarbonium Ions

$\Delta E_{calc.}$ eV (nm)	$f_{calc.}$	Polarization[a]	$\Delta E_{obs.}$ eV (nm)	$f_{obs.}$	Main Configuration
		COUMARIN (1)			
3.81 (325)[b]	0.59	11°	3.88 (319)	0.30	0.97 (5→ 6)
4.16 (297)[b]	0.08	108°	4.13 (300)	0.05	0.92 (4→ 6) + 0.32 (5→ 7)
5.80 (213)[b]	0.52	72°	5.14 (241)	0.20	0.94 (5→ 7)
6.49 (191)[b]	0.60	21°			0.99 (4→ 7)
2.38 (519)[c]		11°	—	—	0.97 (5→ 6)
3.48 (355)[c]		21°	—	—	0.94 (4→ 7)
3.67 (338)[c]		108°	—	—	0.94 (4→ 6)
4.65 (267)[c]		72°	—	—	0.97 (5→ 7)
		XANTHONE (2)			
3.30 (375)[b]	0.29	90°	3.17 (390)	0.07	0.99 (7→ 8)
3.54 (350)[b]	0.65	0°	3.72 (333)	0.25	0.97 (6→ 8)
5.45 (227)[b]	1.07	180°	4.93 (251)	0.44	0.97 (7→ 9)
6.17 (200)[b]	1.52	90°	5.71 (217)	—	0.99 (6→ 9)
2.01 (620)[c]		90°	2.36 (525)		0.99 (7→ 8)
2.61 (474)[c]		0°			0.99 (6→ 8)

$\Delta E_{calc.}$ eV (nm)	$f_{calc.}$	Polarization	$\Delta E_{obs.}$ eV (nm)	$f_{obs.}$	Main Configuration
4.64 (267)[c]		180°			0.99 (7→ 9)
4.81 (257)[c]		90°			0.99 (6→ 9)
		FLAVONE (3)			
3.59 (345)[b]	0.92	8°	3.47 (357)	0.52	0.97 (8→ 9)
3.92 (316)[b]	0.21	54°	3.90 (318)	0.10	0.98 (7→ 9)
5.23 (237)[b]	1.2	68°	4.86 (255)	0.59	0.98 (8→10)
5.69 (217)[b]	0.85	168°			0.97 (7→10)
2.61 (475)[c]		6°	2.70 (447)		0.72 (7→ 9) - 0.33 (7→10)
2.74 (451)[c]		54°			0.79 (8→ 9) + 0.59 (7→10)
4.06 (305)[c]		68°			0.91 (8→10) + 0.40 (7→10)
5.08 (244)[c]		168°			0.85 (7→10) - 0.39 (8→10)
		PERINAPHTHENONE (5)			
3.30 (376)[b]	0.75	64°	2.74 (452)	0.30	0.99 (7→ 8)
3.87 (320)[b]	0.27	164°	3.44 (360)	0.19	0.92 (6→ 8)
5.21 (238)[b]	1.2	176°	4.93 (251)	--	0.91 (7→ 9)
6.10 (203)[b]	0.59	121°	5.73 (216)	--	0.99 (6→ 9)
1.70 (731)[c]		61°	--		0.99 (7→ 8)
2.70 (459)[c]		162°			0.99 (6→ 8)

$\Delta E_{calc.}$ eV (nm)	$f_{calc.}$	Polarization[a]	$\Delta E_{obs.}$ eV (nm)	$f_{obs.}$	Main Configuration
4.38 (283)[c]		164°			0.89 (7→ 9)
4.84 (256)[c]		95°			0.90 (6→ 9)
		9-FLUORENONE (4)			
3.01 (411)[b]	0.31	15°	3.06 (406)	0.16	0.99 (6→ 7)
4.48 (276)[b]	0.00	45°	4.21 (344)	0.12	0.70 (6→ 8) - 0.70 (5→ 7)
5.31 (233)[b]	1.19	45°	4.65 (267)	0.77	0.70 (5→ 7) + 0.70 (6→ 8)
6.63 (187)[b]	0.28	127°	--	--	0.99 (5→ 8)
1.24 (1000)[c]		15°	--	--	0.96 (6→ 7)
3.28 (378)[c]		43°			0.68 (5→ 7) + 0.68 (6→ 8)
		4,4'-DIMETHOXYBENZOPHENONE (6)			
3.88 (318)[b]	0.94	180°	3.60 (344)	0.29	0.99 (7→ 8)
4.11 (301)[b]	0.13	90°	4.24 (292)	0.09	0.98 (6→ 8)
6.31 (196)[b]	0.34	90°	--	--	0.98 (7→ 9)
6.38 (194)[b]	0.43	180°	--	--	0.99 (6→ 9)
2.97 (418)[c]		180°	2.75 (451)		0.99 (7→ 8)
3.36 (369)[c]		90°			0.99 (6→ 8)
5.24 (236)[c]		90°			0.99 (7→ 9)
5.39 (230)[c]		180°			0.99 (6→ 9)

$\Delta E_{calc.}$ eV (nm)	$f_{calc.}$	Polarization[a]	$\Delta E_{obs.}$ eV (nm)	$f_{obs.}$	Main Configuration
		2-ACETONAPHTHONE (7)			
3.43 (361)[b]	0.17	153°	2.96 (420)	0.08	0.95 (6→ 7)
4.25 (291)[b]	0.20	30°	3.66 (339)	0.30	0.81 (5→ 7) - 0.54 (6→ 8)
5.05 (245)[b]	1.56	44°	4.57 (271)	0.47	0.83 (6→ 8) + 0.55 (5→ 7)
5.57 (222)[b]	0.69	33°	—	—	0.97 (5→ 8)
2.30 (537)[c]		152°			0.89 (6→ 7) + 0.45 (6→ 8)
3.09 (401)[c]		44°			0.88 (6→ 8) - 0.44 (6→ 7)
3.53 (350)[c]		60°			0.98 (5→ 7)
4.44 (279)[c]		33°			0.98 (5→ 8)

[a]The angle made with respect to the direction of x-axis

[b]Singlet state ($S_0 \rightarrow S_1$)

[c]Triplet state ($S_0 \rightarrow T_1$)

Table 2. Emission Spectral Parameters of the Ketones, Lactones, and their Protonated Derivatives

Compound	λ_{fl}^{max} nm H_2SO_4/HOAc (3:1) 77°K	298°K	ϕ_F	ϕ_P	ϕ_F/ϕ_P	τ_p (sec)	τ_{fl}° (msec)
Coumarin	400	435	--[a]	--[a]	~ 0.20[c]	--	--
			0.12[b]	0.84[b]	0.143	2.4 ± 0.10	5.0
Xanthone	425	458	--	0.689[a]	--	--	
			0.72[b]	0.12[b]	6.00	2.2 ± 0.10	34.0
Flavone	375	402	0.09[a]	0.697[a]	0.129	--	
			0.47[b]	0.36[b]	1.30	2.1 ± 0.10	4.0
Perinaphthenone	490	503	--	0.58[a]	--	--	
			0.82[b]	--	--	--	33.7
4,4'-Dimethoxybenzophenone	435	445	--	0.70[a]	--	--	
			0.626[b]	0.235[b]	2.66	2.80 ± 0.15	4.2
2-Acetonaphthone	490	537	--	--	--	--	
			0.690	--	--	--	38.0

a = 3 MP b = H_2SO_4/HOAc (3:1) c = J. B. Gallivan, Mol. Photochem., 2, 191 (1970)

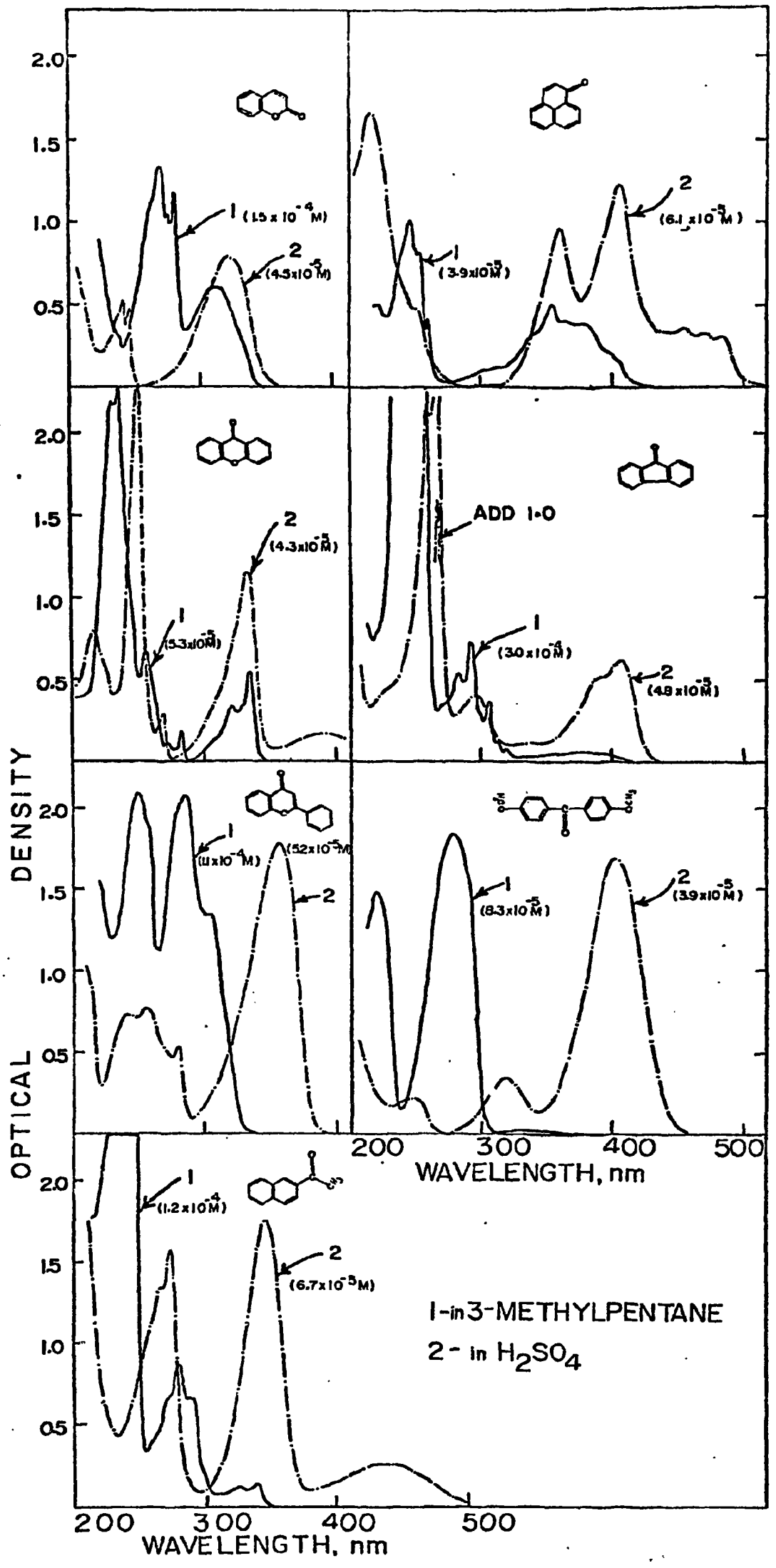
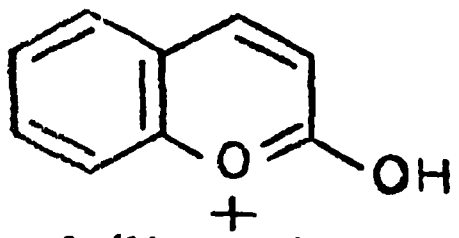
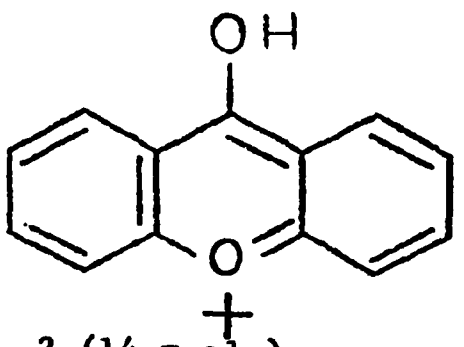

OPTICAL DENSITY
WAVELENGTH, nm
1 (1.5 x 10⁻⁴ M)
2 (4.5x10⁻⁵ M)
1 (3.9x10⁻⁵ M)
2 (6.1 x10⁻⁵ M)
1 (5.3x10⁻⁵ M)
2 (4.3x10⁻⁵ M)
ADD 1·0
1 (3.0x10⁻⁵ M)
2 (4.9x10⁻⁵ M)
1 (1.1x10⁻⁴ M)
2 (5.2x10⁻⁵ M)
1 (8.3x10⁻⁵ M)
2 (3.9x10⁻⁵ M)
1 (1.2x10⁻⁴ M)
2 (6.7x10⁻⁵ M)
1-in 3-METHYLPENTANE
2 - in H2SO4

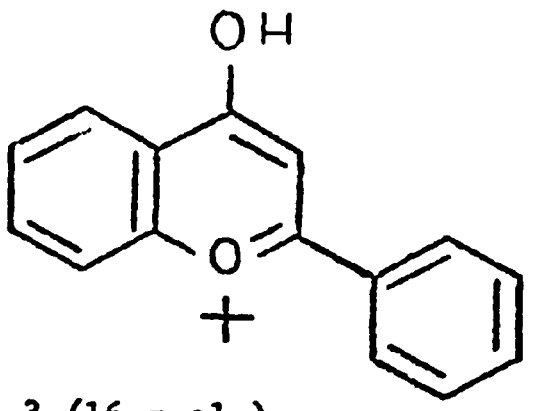
Figure 1



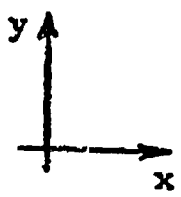
1 (10 π el.)

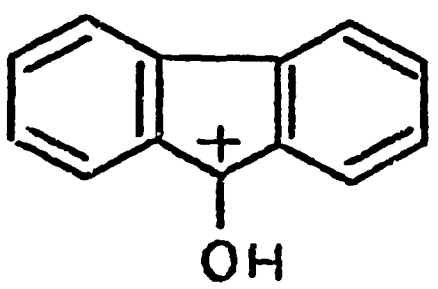


2 (14 π el.)

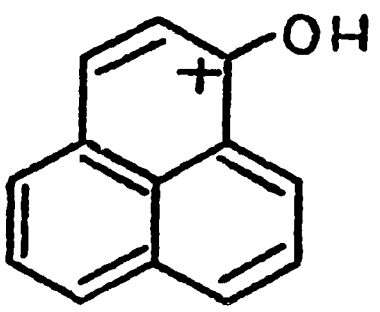


3 (16 π el.)

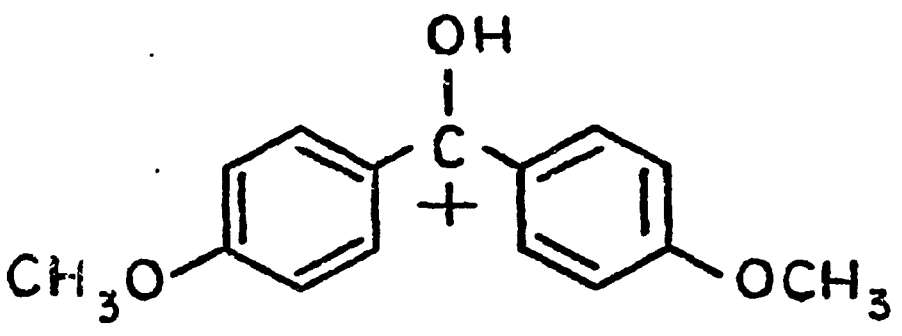




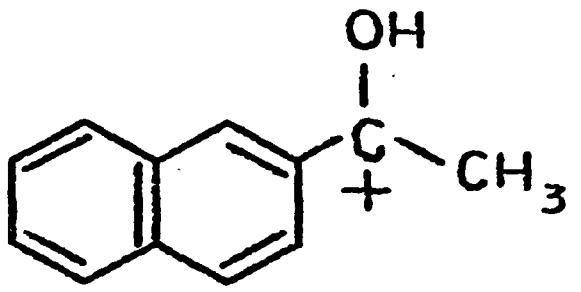
4 (14 π el.)



5 (14 π el.)



6 (14 π el.)



7 (12 π el.)

Figure 2

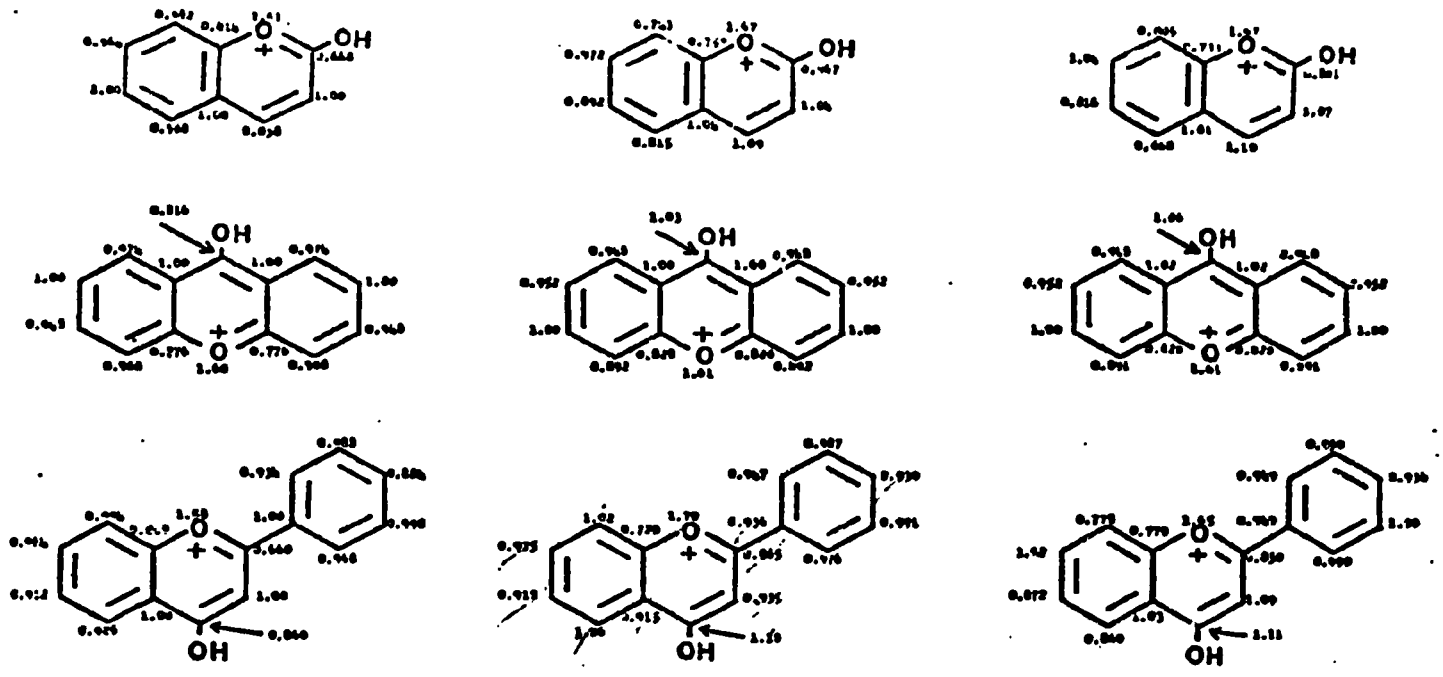


Figure 3. Calculated charge densities for the ground and first excited singlets and the lowest triplet of the hydroxycarbonium ions.

S_0 S_1 T_1

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ORO-3797-41

THROUGH-SPACE INTERACTION BETWEEN NONCONJUGATED NAPHTHALENE AND PHENANTHRENE IN A RIGID MOLECULE

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ABSTRACT

The transannular interaction between naphthalene and phenanthrene in 7,8-11',11'-spiro-4,5-methylenephenanthrenylene acenaphthene (1) and between naphthalene and fluorene in 7,8-9',9'-spiro-fluorenylene acenaphthene (2) was studied spectroscopically and photochemically. The difference between electronic absorption of these rigid model compounds and that of their component chromophores was examined by an SCF-CI-CNDO-MO procedure with partial through-space bonding of the nonconjugated π systems. Satisfactory agreement between theoretically predicted absorption spectra and those determined experimentally was found for both 1 and 2 and their continuously conjugated photoproducts.

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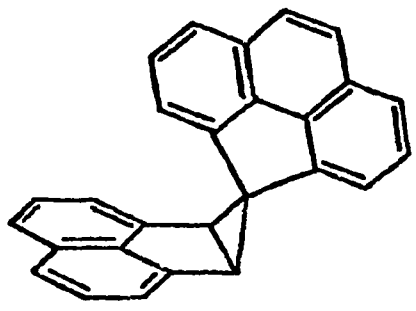
Interaction between closely spaced molecules or functional groups is of fundamental importance in virtually all problems in chemistry, photochemistry, and molecular spectroscopy. The detailed study of this interaction is carried out primarily by examination of deviations from additivity between the absorption of a mixture and that of its individual components,[2] by identification of products with the attendant limited ability to reconstitute the original interaction,[3] and by detection of energy transfer by either spectrophotofluorometric or photochemical means.[4] All consequences of the interaction between two species are critically dependent on their separation distance and mutual orientation. The relative spacial disposition of two molecules (or chromophores) is much better defined in rigid model compounds in which the two groups are connected to the same molecular frame[5] than in binary mixed solutions where one can use only "average" distances and random orientation.

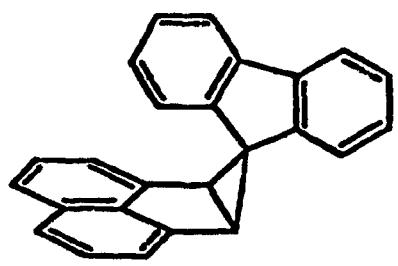
Here we report the spectroscopic and photochemical study of the interaction between the naphthalene and phenanthrene chromophores in model compound 1.



1

The fact that the two π-systems in 1 are mutually perpendicular preserves symmetry in the molecule and simplifies the interpretation of results. Furthermore, since the spectroscopic properties of chromophores naphthalene and phenanthrene have been previously studied in great detail both experimentally and theoretically, they are ideally suited for the present work. It was of interest to examine a model molecule such as 1, since the edge-to-edge interchromophoric separation of less than 3Å places the interaction in the strong-coupling case[2] despite the absence of direct bonding.

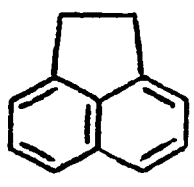
For comparison we also include the spectral analysis of an analogous model molecule 2 in which naphthalene is paired with fluorene (F) at virtually the same separation and perpendicular orientation as the chromophores in 1.



2

Results

Model molecules 1 and 2 were prepared by addition of either the carbene derived from 4,5-methylenephenanthrene[5] or fluoreneylidene[6] to acenaphthylene. Molecular weight, elemental analysis, and spectra (nmr and ir) were consistent with the symmetrical structures 1 and 2. The uv absorption spectrum of compound 1 is compared at two different concentrations with that of an equivalent equimolar mixture of acenaphthene (3, N) and 4,5-methylenephenanthrene (4, P) in Figure 1.



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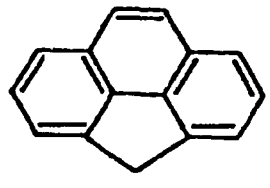

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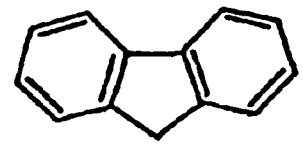


5

In Figure 2, the near-uv absorption of model compound 2 is shown with that of a mixture of its component chromophores, 3 and fluorene (5, F) at equivalent concentrations. Since the absorption spectra of 3, 4, and 5 are known, they will not be reproduced here. The differences in the uv absorptions of the two model compounds 1 and 2 and those of the mixtures are sufficiently large to suggest relatively strong mutual perturbations between the two constituent π-systems held in proximity by the rigid interconnecting σ-frame in the models. To estimate the effect of the spiro-cyclopropane link to P and F in 1 and 2, respectively, we have compared the absorption and emission spectra of unsubstituted 4,5-methylenephenanthrene and fluorene with those of 6 and 7. Although the norbornane frame to which P and F

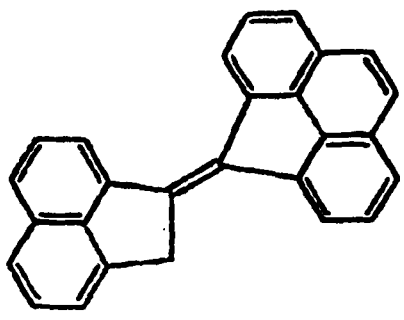
6 7

are connected by the spiro-cyclopropane in 6 and 7 is somewhat different from the 5-membered ring of acenaphthane in 1 and 2, no significant differences in the uv-absorption are expected.[5c] In fact, the differences in absorption between 6 and 7 and P and F are sufficiently small that in the present type of analysis the effect is marginal. In any case, the cyclopropane can be considered a part of P or F chromophore in 1, 2, 6, or 7. Despite the absence of large wavelength shifts in major absorption bands between the models and their "components", the changes in the band structure suggest electronic interactions stronger than those caused simply by coupling of new vibrational modes upon adding the other chromophore.

Neither 1 nor 2 exhibited any measureable emission either at room temperature or in rigid matrix at 77°K. This was not entirely unexpected, since the strained

cyclopropane structure provides an easily available pathway for radiationless deactivation by means of bond dissociation.[8] That this is the major quenching mechanism is confirmed by the photochemical reactions of the two model molecules in fluid solutions (see below).

The optical density of the uv-visible absorption of 1 upon successive short irradiations in dilute solution at 298°K decreased progressively with the extent of irradiation in the 287-331 nm range, while two new bands with clearly defined vibrational structure appeared in 272-287 and 331-475 nm ranges as the solution became yellow. Three distinct isosbestic points were identified in the successive spectra at 272, 287, and 331 nm. Preparative scale photochemical reactions of 1 were carried out at higher concentrations in benzene solutions. The yellow photoproduct was separated from the starting material using differences in solubility and was purified by chromatography on silica gel. Elemental analysis, molecular weight, ir, nmr, and uv-visible spectra were consistent with fulvene structure 8.

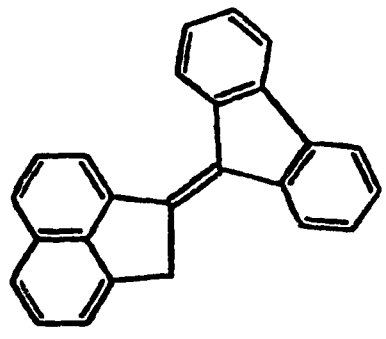


8

Figure 3 displays the uv-visible absorption spectrum of photoproduct. Fulvene 8 exhibits green fluorescence in a band centered at 485 nm. The excitation spectrum exhibits the quasi-mirror-image relationship with the fluorescence band and shows vibrational structure resembling that of the absorption spectrum. The extent of the 1 → 8 photoisomerization can be followed also by monitoring the increase in the emission with length of irradiation of the thawed solution. The 1 → 8 reaction takes place in rigid matrix, as well, but very inefficiently ($\Phi < 10^{-4}$) requiring

prolonged irradiation.

Compound 2 undergoes a similar photorearrangement to the analogous dibenzofulvene (9)



9

This reaction, however, is much less efficient than the similar rearrangement of 1. Photoproduct 9 was isolated from a preparative-scale experiment involving photolysis in benzene and column chromatography. Its uv-visible absorption spectrum is given in Figure 4. Like 8, compound 9 exhibited fluorescence, centered at 475 nm, but did not emit detectable phosphorescence.

Molecular Orbital Calculations

Molecular-orbital calculations were used to correlate the electronic absorption spectra of model compounds 1 and 2 with the through-space interaction of their two component π systems. In addition the same general method was applied to the two photoproducts 8 and 9, in which the same two chromophores as in 1 and 2 are coplanar and conjugated. The fact that all these molecules are inflexible makes the results more meaningful than for systems in which free rotation about single bonds connecting the two chromophores allows a variety of conformers. Electronic spectra were calculated with a semiempirical MO-SCF-CI procedure in which the π electrons of the two component chromophores were treated as parts of a single extended system delocalized over the entire molecule rather than as individual entities. The technique includes effects of local excitations and of electron transfer in a natural way.

Since the energetic states associated with the interconnecting sigma bonds are found at higher energies than those of the aromatic chromophores we neglected the electronic participation of the frame. Thus the only kind of interaction between N and P (or N and F) considered in the present treatment is a through-space mutual perpurbation. The p orbitals on the carbon cores part of aromatic nuclei were used as a basis set for a self-consistent-field (SCF) calculation assuming zero differential overlap. Interactions between the two π systems were introduced by the electrostatic repulsions between all pairs of contributing atomic orbitals and by partial bonding between the sites of the two chromophores nearest one another. Specifically, the electron-repulsion integrals γ were evaluated by the Mataga-Nishimoto formula[9] and the non-zero intra-ring bond-resonance integrals β by a distance-dependent equation whose form was suggested by Pariser and Parr[10]

$$\beta = 9.811 \exp(-1.032\ r) \qquad (1)$$

This equation was constructed to give literature values for benzene and ethylene at their experimental C-C distances.[10,11] Ionization potentials and one-center electrostatic repulsion integrals were taken from the literature[10] when known; the valence-state ionization potential for fluorene was taken to be the same as that for phenanthrene. Extensive examination of both β and γ has been done for planar systems; however, since our molecules are non-planar, an adjustment was made for the interaction of nonparallel p orbitals. Denoting the components of the unit vector between the two cores as x, y, and z, we have

$$\beta = x^2z^2\beta_{\sigma\sigma} + x^2z^2\beta_{\pi\pi}$$

$$\gamma = x^2y^2\gamma_{\sigma\sigma\sigma\sigma} + (x^2z^2 + z^4 + x^2y^2 + x^4)(x^2 + y^2)^{-1}\gamma_{\sigma\sigma\pi\pi}$$

$$+ y^2\gamma_{\pi\pi\pi\pi} + x^2z^2\gamma_{\pi\pi\pi'\pi'} + 4xyz(x^2 + y^2 + z^2)^{-3}/2\gamma_{\sigma\pi\sigma\pi}$$

for noncoplanar ring systems in which one ring is in the xy plane and the other in the yz plane. The subscripts serve to denote the components which are obtained from orbitals that point directly toward one another (σ) or are parallel to each other

and perpendicular to the line of centers (π). Since exact integration of the various σ and π combinations is known to give values which do not differ greatly, we took $\beta_{\sigma\sigma} = \beta_{\pi\pi}$ and $\gamma_{\sigma\sigma\sigma\sigma} = \gamma_{\sigma\sigma\pi\pi} = \ldots = \gamma_{\sigma\pi\sigma\pi}$.

The SCF ground-state wave functions were allowed to interact with the first four excited state wave functions in a configuration-interaction (CI) treatment. A modification to Bloor and Gilson's closed-shell SCF-CI program[12] was used on an IBM 360/50 computer.

Obviously the energy differences will depend on the dihedral angle made by the two chromophoric planes. Since an experimental value of the angle is not available, we must estimate it from scale-molecular models. These suggest 120°. Variations of this angle in the calculations allowed good correlations between experimental and theoretical spectra at 120°, as shown in Figures 3-6.

Discussion.

Most previous attempts to correlate electronic spectra with through-space interaction of two nonbonded chromophores were made on unsaturated polycyclic ketones[13] and on excimers.[14] Apparently the significant features in the uv absorption of rigid compounds containing C=C and C=O in transannular proximity are the appearance of an intense band between 220 and 250 nm and an increase in the intensity of the $n\rightarrow\pi^*$ band. The former was atrributed to an intramolecular charge transfer transition; whereas the latter was assumed to be caused by overlap of the nonbonding oxygen p orbital with the ground state of the olefinic chromophore. No detailed quantum-mechanical calculations have been carried out on these unsaturated carbonyl systems; most assignments were made from minor solvent effects and changes in intensity with respect to their saturated analogues. The interaction between carbonyl and olefin groups is not easily evaluated experimentally because of broad-band unstructured absorption.

In most recent theoretical work on the origin of excimer emission,[14] the

electronic states of the excited dimer were constructed by CI with neutral exciton and charge-transfer states. An alternative approach, applied to transannular interaction between identical chromophores in a sandwich configuration was used by Koutecky and Paldus[14c,d] in a "supermolecule" approximation which treated the π electrons in an MO-SCF calculation with limited CI. Since this method gives the best results for interpretation of electronic spectra of aromatic hydrocarbons, it was adopted in the present study. It should be pointed out that the two chromophores in compounds 1 and 2 are chemically different and are positioned at a distance smaller than van der Waals' radii in a mutually perpendicular orientation. Because of this proximity we have included partial bonding (nonzero resonance integrals) between the two chromophores in a fashion similar to that used by Longuet-Higgins and Murrell[15] for conjugated "composite" molecules such as biphenyl and styrene.

In our calculations on compounds 1 and 2 we varied the number of configurations, the dihedral angle between the naphthalene and cyclopropane planes, the distance-dependence of the intrachromophoric resonance integrals, and the size and number of interchromophoric β's. In addition, we examined the sensitivity of the predicted absorption bands to distortions within each of the two planar chromophores.

Extending the number of configurations beyond the lowest four did not affect significantly the outcome; this is consistent with the findings of Zahradnik et al.[16] for single planar chromophores. A change in the naphthalene-cyclopropane dihedral angle modifies the separation between the two chromophores without affecting their perpendicularity; such a distortion has substantial effect on the predicted absorption. An angle of 120°, expected from bonding considerations on a fused cyclopentadiene-cyclopropane system, gave the best spectral fit. An increase or decrease of 10° yielded theoretical spectra which could no longer be considered acceptable.

The arbitrary assumption that β is independent of separation distance leads to substantial disagreement with experiment. The distance-dependent formulation

(Equation 1) is known to lead to excessively low values of β for large distances. Accordingly, adoption of Equation 1 for intrachromophoric β's in connection with fixed interchromophoric β's, appropriately adjusted for orientation of p orbitals, gave satisfactory results. Like others,[17] we used the non-conjugated β corresponding to approximately 1/4 of a bond between positions 1 (or 8) of naphthalene and the nearest atom of P (or F) with the usual angular adjustment for the more distant atoms. It was apparent that bonding interaction only between the atoms on N and P closest to one another was insufficient; additional interaction with at least the next nearest atoms was necessary.

In our calculations we placed the carbon atoms of the aromatic rings at sites suggested by X-ray crystallographic studies[18] on the respective chromophores. However, distortions from these coordinates toward a perfect hexagonal model do not affect the overall results.

Although no vibronic analysis was attempted, the agreement between predicted and detected uv-absorption of compounds 1 and 2 is comparable to the best previously reported calculations on planar aromatic molecules.[16]

The principal advantage of the new photorearrangements of 1 and 2 in fluid solution is that it permitted us to apply the same method of calculation to the photoproducts, 8 and 9, containing continuously conjugated coplanar chromophores. As shown in Figures 5 and 6, the agreement between their predicted and experimental spectra is satisfactory. Presumably the rearrangements take place by either a homolytic or a heterolytic fission of the cyclopropane ring followed by hydrogen-atom or proton 1, 2 shift, respectively, and recombination of the diradical or zwitterion intermediate. These photoisomerizations resemble those reported other spiro-linked fluorene compounds.[7]

Experimental.

The uv-visible absorptions were determined with a Cary Model 15 Spectropho-

tometer, the emission spectra with an Aminco-Bowman Spectrophoto-fluorimeter, and the nmr spectra with a Hitachi-Perkin-Elmer R20 instrument. Elemental analysis was performed with an Aminco C-H Analyzer. Spectrograde solvents were used except for preparative-scale photolyses.

The preparation of model compound 2 from 9-diazofluorene and acenaphthylene was described previously.[19]

Model Compound 1. 4,5-Methyenephenanthrene was oxidized with chromic acid to the ketone, which in turn was converted to the hydrazone with N_2H_4 and then to the diazoalkane with mercuric oxide.[5c] 11-Diazo-4,5-methylenephenanthrene (200 mg, 0.93 mmol) and acenaphthylene (400 mg, 2.62 mmol) in 10 ml anhydrous ether were left in a stoppered flask for four weeks. The white cyrstals formed on standing were filtered and recrystallized from benzene. Mp 253-4° (red-brown melt). Anal. Calcd for $C_{17}H_{16}$: C, 95.2; H, 4.70. Found: C, 94.8; H, 4.52. M^+ 340. Ir (KBr): 720, 741, 765, 810, 830, 862, 895, 960, and 1400 cm^{-1}. Nmr ($CDCl_3$): δ 4.4 (singlet, 2H); δ 7.6-7.9 ppm (complex, 14 H).

Photoproducts 8 and 9. Model compound 1 (34 mg) in 20 ml benzene was flushed with N_2 for 15 min and irradiated for 3 hr with a 150-W Hg lamp. The bright yellow solution was evaporated and the residue extracted three times with 20-ml portions of heptane. The concentrated heptane extract was chromatographed on silica gel with cyclohexane eluant. A final recrystallization from ethanol gave yellow crystals. Mp 228-9°. Anal. Calcd for $C_{17}H_{16}$: C, 95.2; H, 4.70. Found: C, 94.7; H, 4.85. Nmr (CCl_4): δ 4.2 (singlet, 2H); δ 7.3-7.8 ppm (complex, 14H). Model compound 2 (31 mg) was irradiated in benzene for 24 hr and treated in a similar way. The yellow photoproduct melted at 233-4°.

Acknowledgement. We thank the University Computer Center for machine time and the Atomic Energy Commission for partial support on Contract AT-(40-1)-3797. Part of this work was carried out at Goddard Space Flight Center, Optical Systems Branch.

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FIGURE CAPTIONS

Figure 1. Uv-absorption spectra of model compound 1 (A, 0.25×10^{-4} M) and of an equimolar mixture of acenaphthene 3 and 4,5-methylenephenanthrene 4 (B, 0.25×10^{-4} M each) in dioxane.

Figure 2. Uv-absorption spectra of model compound 2 (A, 10^{-4} M) and of an equimolar mixture of 3 and 7 (B, 10^{-4} M each) in dioxane.

Figure 3. Uv-visible absorption of photoproduct 8 (4×10^{-5} M) in cyclohexane. Bars represent calculated transitions; their height corresponds to oscillator strength in arbitrary units.

Figure 4. Uv-visible absorption spectrum of photoproduct 9 (5×10^{-5} M) in cyclohexane. Bars have the same significance as in Figure 3.

Figure 5. Uv absorption of 1 (2.5×10^{-5} M) in dioxane. Bars have the same significance as in Figure 3.

Figure 6. Uv absorption of 2 (3.5×10^{-5} M) in dioxane. Bars have the same significance as in Figure 3.

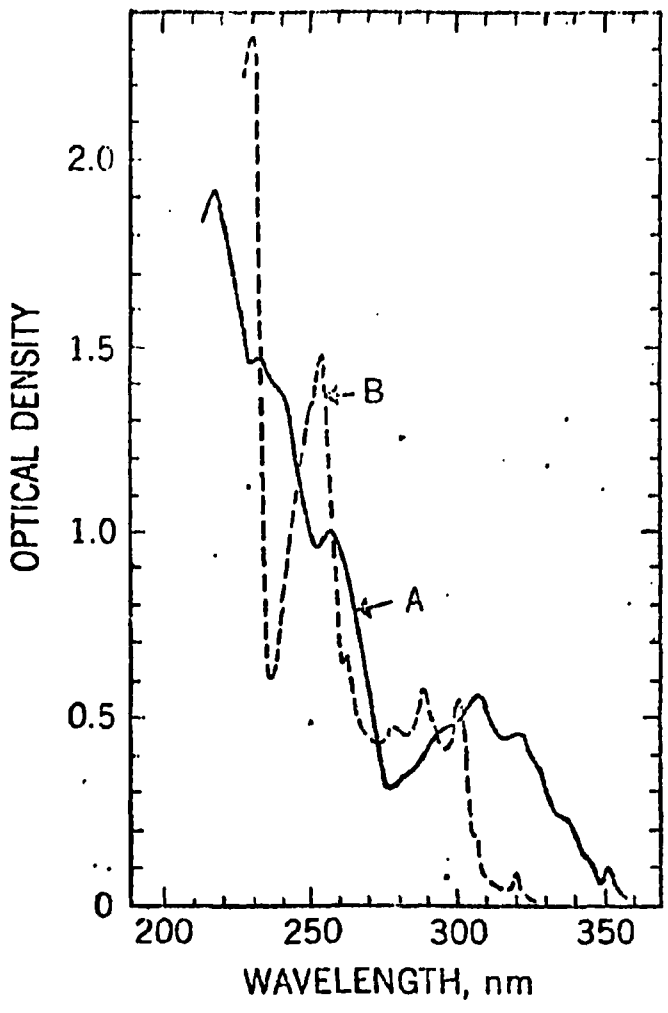

Figure 1

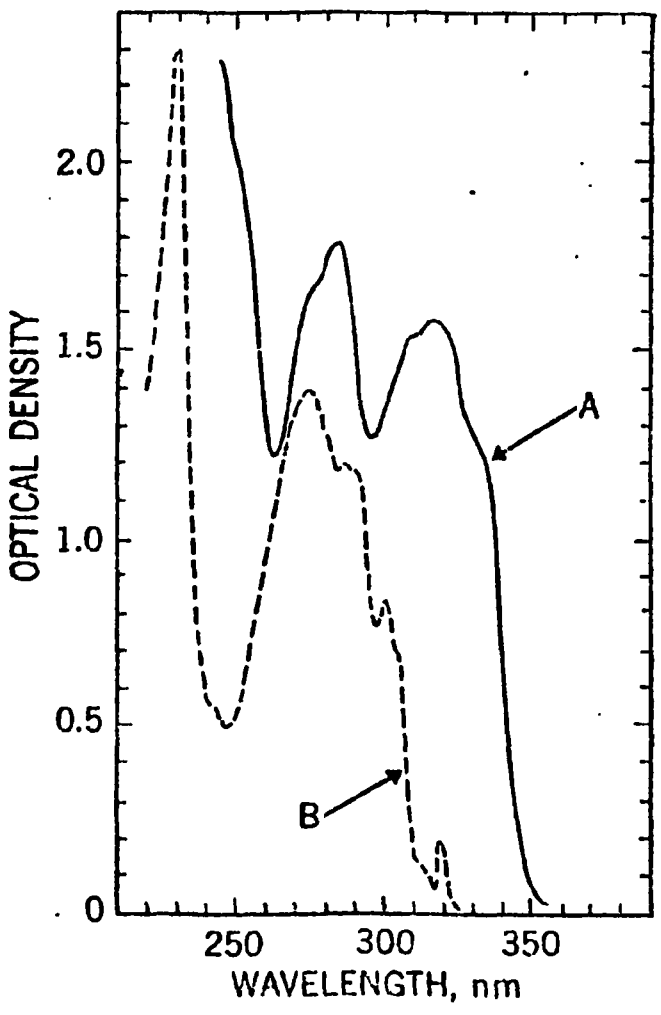

Figure 2

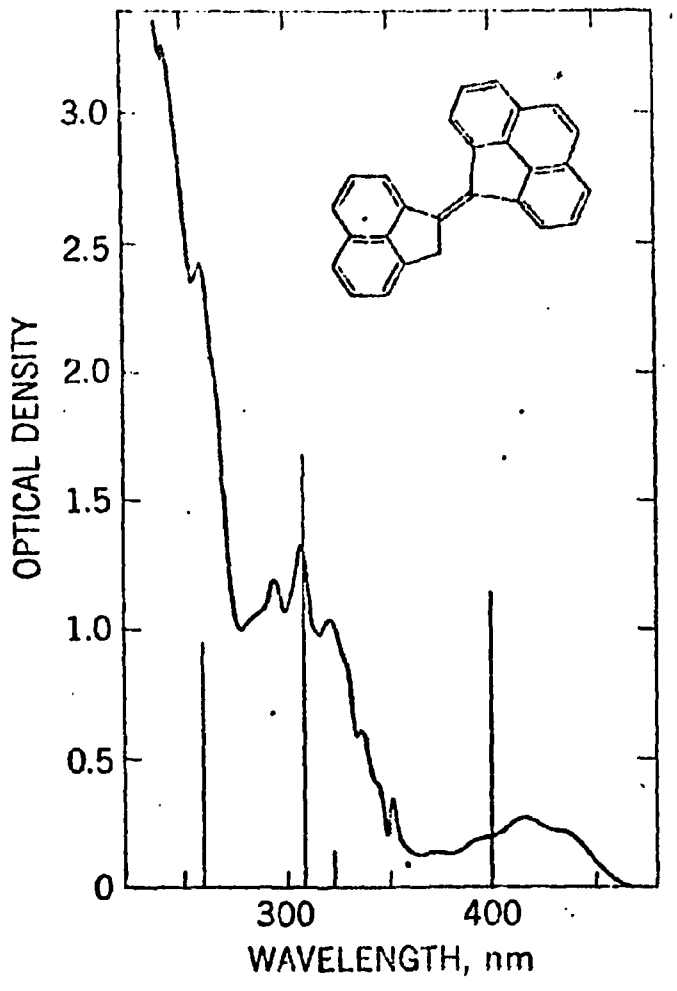

Figure 3

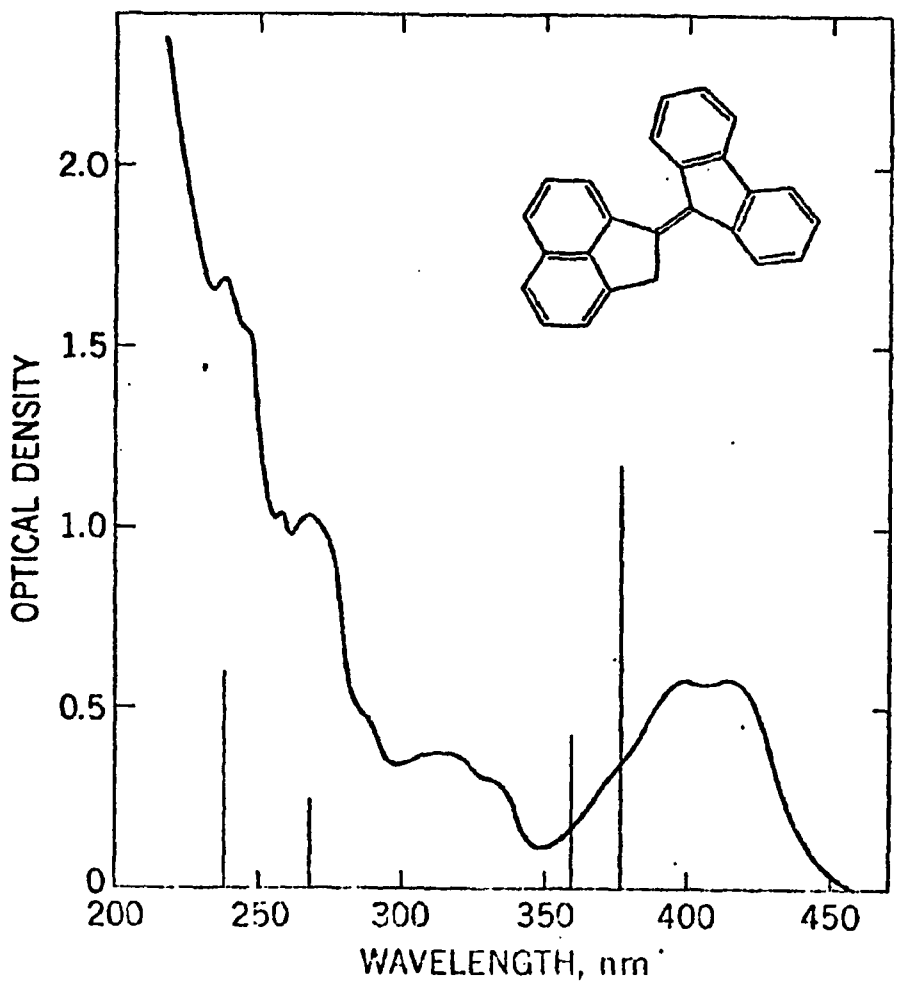

Figure 4

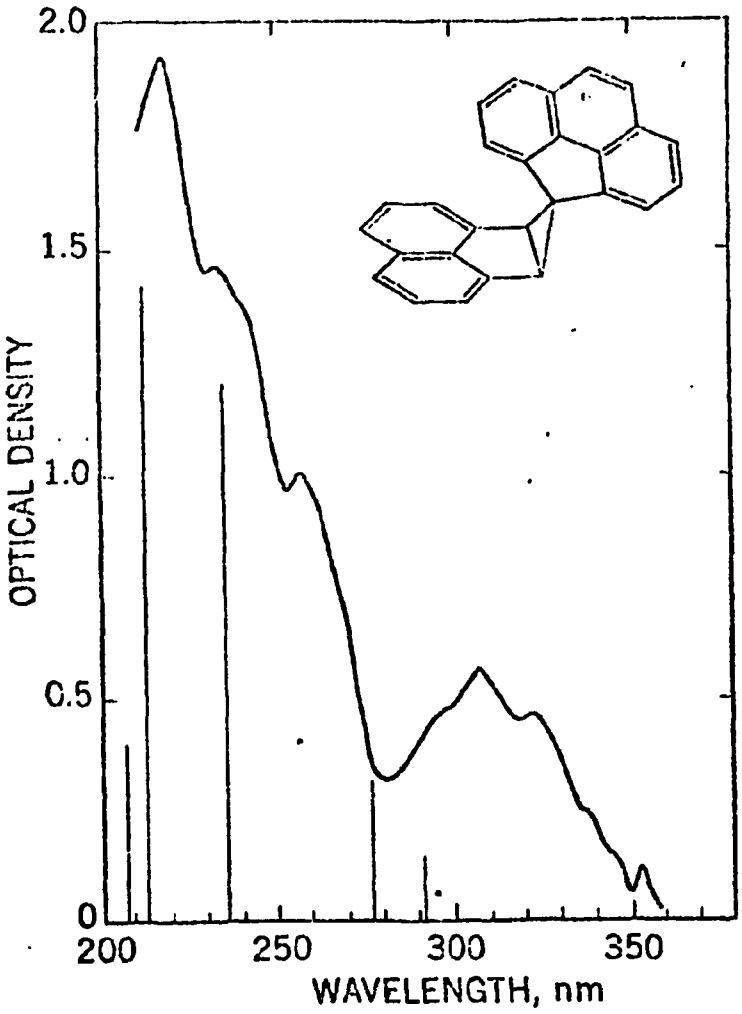

Figure 5

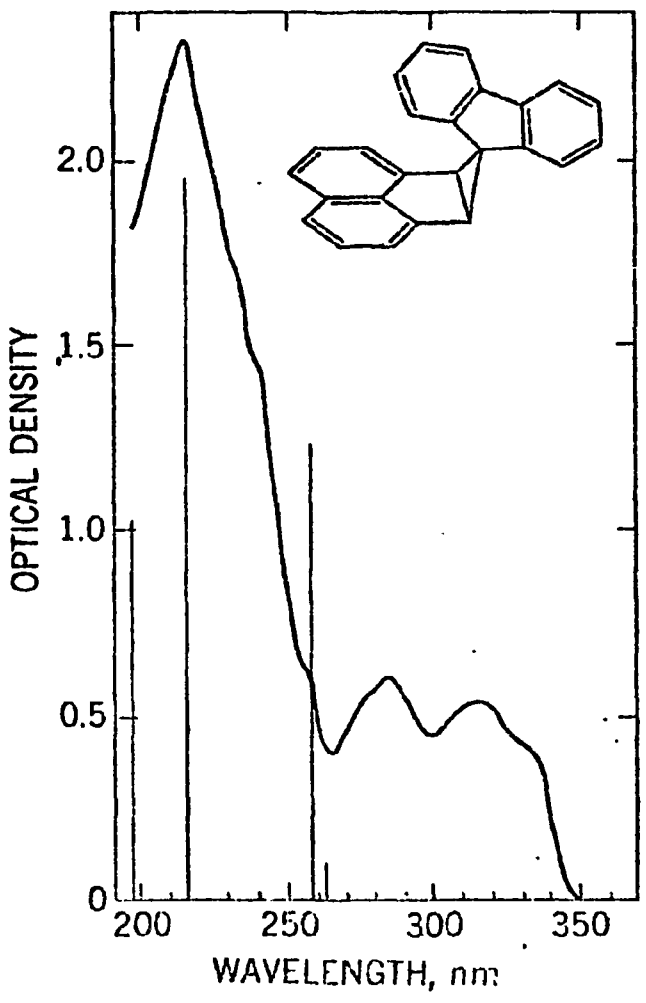

Figure 6

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ORO-3797-43

Formation of Long-lived Free Radicals from Acylpyridinium Salts with Alkali.

Maria Frangopol,[1] Petre T. Frangopol,[2] Charles L. Trichilo,

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Abstract: 4-Acetylpyridinium methiodide reacted with concentrated aqueous alkali to yield a non viologenic stable long-lived crystallizable free radical whose esr spectrum indicated molecular symmetry. Several stable nonparamagnetic derivatives of the radical have been prepared and characterized. In contrast to the acetyl and valeryl derivatives, the bulkier alkyl analog 4,4-dimethylvaleryl pyridinium salt reacted with hydroxide to yield dimethylviologen radical. On the other hand, di(4-pyridyl)methylcarbinol dimethiodide underwent a several step transformation when dissolved in concentrated aqueous hydroxide to yield the same symmetrical stable radical as that obtained from 4-acetylpyridinium iodide. The reaction of the latter with sodium ethoxide in alcohol yielded still another radical which is different from that formed in hydroxide. The identity and esr spectra of the radicals and their derivatives and the overall mechanism of reaction are discussed.

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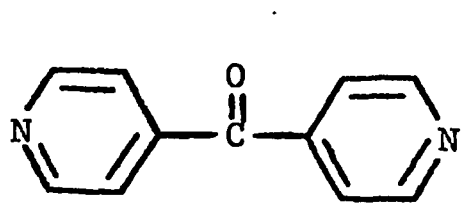
We have recently reported[4-6] on the formation of several different long-lived free radicals from methiodide derivatives of di(4-pyridyl) ketone (1). The dimethiodide of 1, in an unusual reaction, yielded rapidly the stable viologen cation-radical 2 on simple mixing with concentrated aqueous hydroxide.[5] Since the



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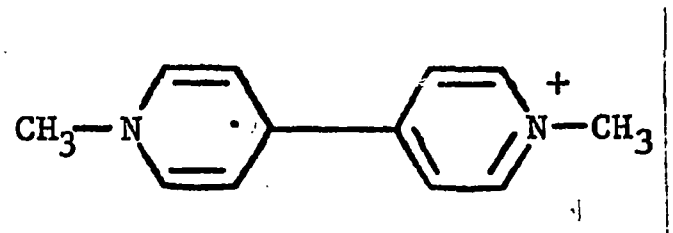

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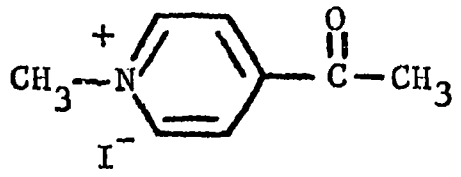
long-lived pyridinyl radicals remain of high research interest because of their relevancy to basic chemical and biological reactions[7-14] we have extended the study of N-heteroaromatic methiodides with bases to other acyl-pyridinium salts. In this paper, we report the formation of a non-viologen stable symmetrical radical from 4-acetylpyridinium methiodide 3 in aqueous alkali. Whereas the non-branched homolog of 3, 4-valerylpyridine methiodide 4, behaved analogous to 3, its bulkier 4,4-dimethyl derivative 5 yielded dimethylviologen 2 with aqueous hydroxide in a manner resembling that of the dimethiodide of 1. On the other hand, the same stable radical obtained from 3 was generated from an apparently unrelated compound, di(4-pyridyl)methylcarbinol dimethiodide 6 in the same reaction with aqueous hydroxide. Structurally different stable radicals were obtained from 3 with ethoxide in ethanol or with secondary amines in aprotic solvents.



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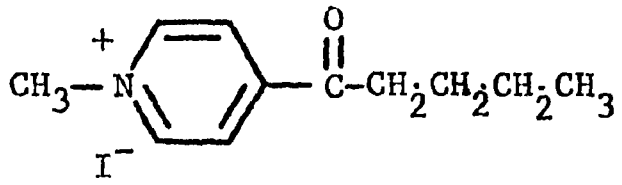

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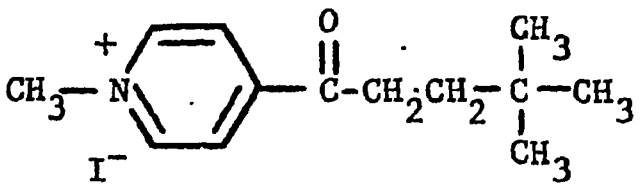

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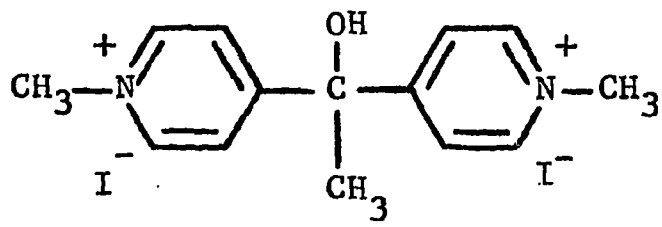

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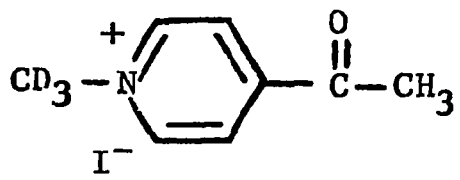
Results

When crystalline methiodide 3 was mixed with 1N sodium hydroxide in the absence of oxygen a deep blue color developed progressively.[15] The colored solutions were intensely paramagnetic. Changes in the uv-visible absorption spectrum of a degassed 1.5×10^{-3} M solution of 3 in 1N aqueous hydroxide are shown in Figure 1. It is apparent that the blue color is caused by the progressive formation of a visible absorbing species with a prominent band centered at 635 nm and several overlapping and less intense bands in the 300-500 nm regions. One can also see that after reaching a maximum, the concentration of the visible-absorbing species deminishes slowly in about one week following mixing. Although numerous curves have been recorded throughout this transformation, only a few are shown in Figure 1 for clarity. Sufficient spectra were recorded to determine accurately the kinetics of the radical disappearance and its half-limetime in the absence of oxygen. The esr spectrum of a blue solution prepared by dissolving crystalline 3 in aqueous hydroxide is shown at the top of Figure 2. The intensity of the esr signal paralleled the absorbance at 635 nm suggesting that the blue color is associated with the paramagnetic species. On admission of air both the 635 nm

absorption (curve 6, Figure 1) and esr signal disappeared. As expected, the N-methyl-d_3 analog of 3, compound 7, reacted with concentrated hydroxide to give



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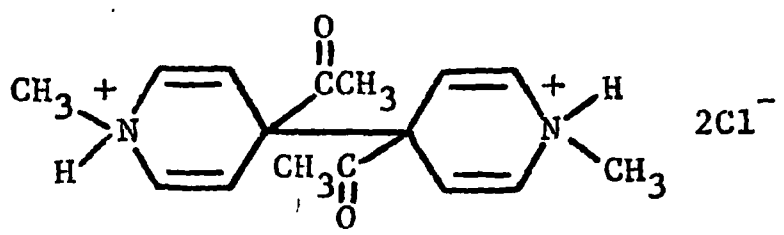
uv-visible absorption spectra indistinguishable from those of 3 shown in Figure 1. On the other hand, the esr spectrum, shown at the top of Figure 3, was distinctly different from that obtained with 3.

In order to uncover chemical evidence regarding the identity of the stable free radical, several large scale (gram-size) reactions of 3 with 1N sodium hydroxide have been carried out. When the concentrated blue solution prepared with 2N sodium hydroxide was allowed to stand overnight, green crystals with metallic luster and paramagnetic properties precipitated. Although these crystals can be filtered in an inert atmosphere, their inherent instability in the presence of air prevented accurate elemental analysis and other direct analytical tests. A 10^{-4} - 10^{-5} M solution of green crystals in degassed DMSO gave the visible absorption shown in Figure 4, curve 1 which changed progressively as indicated with decrease in the intensity of the band at 625 nm and concomitant increase in concentration of a component absorbing at λ_{max} = 445 nm. The presence of an isosbestic point at 505 nm suggests a clean one-to-one transformation.

When redissolved, the emerald green solid melting at 236-8°C reexhibited all the spectroscopic and chemical properties of its precursor blue free radical. This confirmed the fact that the paramagnetic green crystalline product is the blue radical in its crystalline form. Its ionic character is illustrated by its ready solubility in polar solvents such as H_2O, alcohols, CH_3CN, DMSO and insolubility in nonpolar solvents. In spite of its lability the green crystalline com-

pound could be preserved for several days under refrigeration in inert atmosphere. It reacted vigorously with concentrated H_2SO_4 forming a stable red solution which gave uv-visible absorption spectrum shown in Figure 5. The uv-visible spectrum remained unchanged for weeks and the solution was diamagnetic. The analogous red-crystalline hydrochloride prepared from the green solid radical and dry HCl was quite stable and therefore lended itself to thorough characterization. Elemental analysis, nmr (in D_2O), ir, and uv-visible spectra were all consistent with dihydrochloride structure 8. In addition the nmr spectrum of green solid radical in 100% D_2SO_4 agreed with trication structure 9. Thus, comparison of the nmr spectra of 8 in D_2SO_4 and D_2O with that of 3 in DMSO-d_6 and D_2SO_4 allowed good assignments of individual nmr signals shown in Figure 6.



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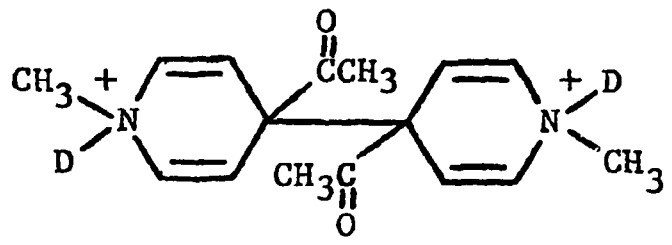

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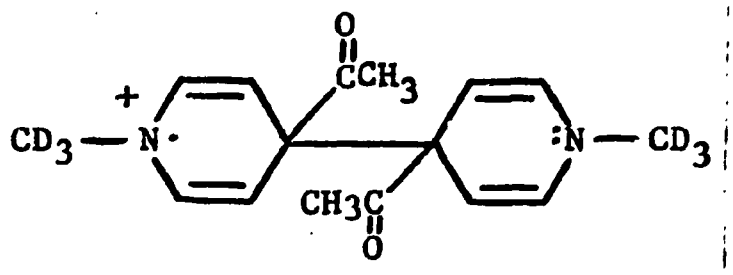
Catalytic hydrogenation of the emerald green crystals in the presence of platinum gave an oil which was difficult to characterize but which exhibited a pronounced uv absorption maximum at 280 nm in acetonitrile suggesting the hydrogenated product did not have a 4,4'-dipiperidyl saturated structure. Such a structure should be transparent in the near uv down to about 230 nm. This observation

in conjunction with the absence of the carbonyl stretching band in the ir suggested that the hydrogenation took place only at the acetyl groups and did not affect the heterocyclic rings. This suggestion was confirmed also by the reappearance of a deep blue color when the hydrogenation product was placed in 1 N sodium hydroxide. The formation of a stable visible-absorbing radical analogous to 10 is consistent with the above data and implies π-delocalization incompatible with a completely saturated structure.



10

It is interesting that 4-acetylpyridinium iodide 3 yielded structurally different stable radicals when reacted with ethoxide in alcoholic solution or with secondary amines in nonprotic solvents.

Both 4-acetylpyridine methiodide 3 and its CD_3 derivative 7 reacted with sodium ethoxide in ethanol to give the same brown-green free radical whose uv-visible absorption spectrum showed prominent bands at 326 and 435 nm and a weaker broad band around 735 nm. Its esr spectrum in approximately 1 N sodium ethoxide is displayed in Figure 7. Despite the fact that the line-width is remarkably narrow, about 100 mOe, the complexity of the spectrum, showing approximately 250 distinct lines, did not allow accurate determination of the splitting constants.

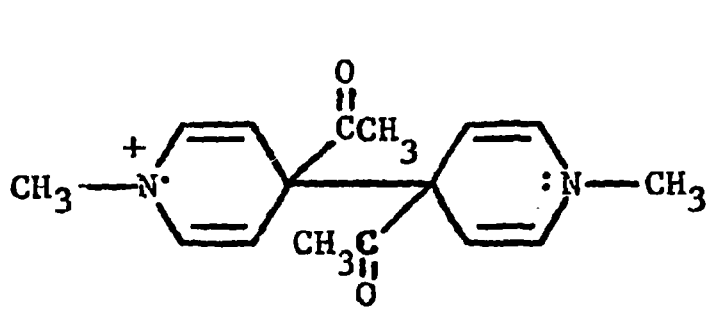
The fact that both compounds 3 and 7 gave the same paramagnetic species in EtOH-NaOEt may be explained in two ways: either the CH_3 or CD_3 groups no longer exist in the free radical, or fast exchange of methyl deuterons takes place in the presence of the powerful alkoxide base. The behavior of 7 in ethoxide is mentioned

here mainly to exhibit the contrast with its reaction in aqueous hydroxide.

The reaction of 4-acetylpyridinium iodide with pyrrolidine in deoxygenated dimethoxyethylene (DME) resembled more that with aqueous hydroxide since 3 and 7 yielded two different stable radicals whose esr spectra are shown in Figure 8. Neither the radicals formed in alcoholic ethoxide nor those in DME-pyrrolidine were identical to those prepared in aqueous hydroxide.

Discussion

The reaction of 4-acetylpyridinium iodide with concentrated aqueous hydroxide yielded a crystallizable stable new free radical for which we tentatively propose structure 11. This structure was derived from a variety of spectroscopic and other analytical tests on radical 11 itself and on some of its more stable derivatives such as dihydrochloride 8 and trication 9.

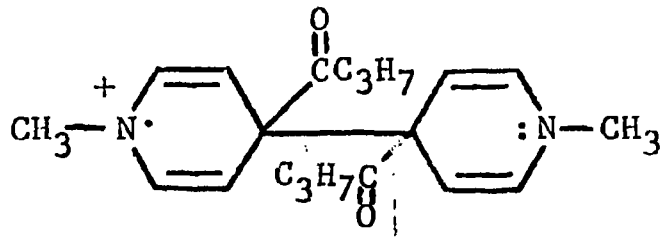


11

Free radical 11 exhibited visible absorption with λ_{max} in the 600-700 nm range which is characteristic of viologen-like radicals. Its ir spectrum retained the carbonyl stretching band at 1640 cm^{-1}. The nmr spectrum of diamagnetic trication 9 in D_2SO_4 was indistinguishable from that of the dihydrochloride 8 in D_2SO_4. Qualitatively, dihydrochloride 8 also showed evidence for preservation of the acetyl groups of 3 by forming 2,4-dinitrophenylhydrazone (m 184°C) and positive iodoform test. In addition, consistent with the apparently high instability of crystalline 11, the absence of iodide agreed with the N-hydroxide configuration. Probably, the most convincing evidence for structure 11 is the esr spectrum of the blue aqueous solution shown in Figure 2. The hyperfine splitting constants

indicated on the diagram were determined very accurately by computer analysis, since the fit between simulated and experimental curves is extremely sensitive to even very slight changes in the values of the his constants. Very useful information was obtained from the comparison of esr spectra of 11 ($N-CH_3$) with that of the free radical derived from the $N-CD_3$ analog of 3 structure 10.

The spectrum of the free radical 10 containing $N-CD_3$ groups should differ from that containing $N-CH_3$ groups only in the splitting constants of the deuterons. Indeed, the hyperfine splitting constants a^N = 5.39 Oe, a^H_1 (α to N) = 1.54 Oe, and a_2 (β to N) = 1.80 Oe are identical for the two free radicals derived from 3 and 7, whereas $a^H_{CH_3}$ (from $N-CH_3$) = 5.10 Oe in 11 and $a^D_{CD_3}$ = 0.79 Oe in 10. Since $a^H_{CH_3}/a^D_{CD_3}$ should be equal to the gyromagnetic ratio of H to D, namely 6.51, one can easily verify that there must be six deuterium atoms in the free radical derived from compound 2, or two equivalent CD_3 groups. That implies that there are two 4-substituted N-methyl pyridine groups in the paramagnetic species and no other atoms with nuclear magnetic moment within the delocalized domain of the unpaired spin. The esr spectra also indicate that the presence of the two acetyl groups in radical 11 does not interfere sufficiently with the π through-space delocalization to prevent the equal time-distribution of the unpaired spin on each of the two pyridine rings. On the other hand, it seems quite reasonable that there should be no additional splitting in the esr spectrum caused by the CH_3 groups of the acetyls, since any hyperconjugative structures suggestive of unpaired-spin proximity to the H's of those CH_3 groups would represent highly improbable configurations. In addition we found that the esr spectrum of the radical derived from N-methyl-4-valeryl iodide 4 in hydroxide, presumably 12, was virtually identical to that of 11. In contrast, the bulky derivative 4,4-dimethylvaleryl pyridyl ketone methiodide 5 yielded a totally different stable radical in deoxygenated 1 N aqueous sodium hydroxide. The intensely blue solution exhibited characteristic dimethyl viologen

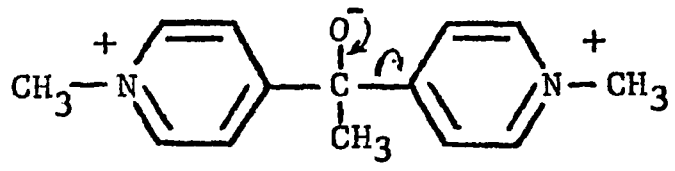


12

radical uv-visible absorption[4] and esr spectrum indistinguishable from that of viologen 2 prepared from different reagents.[5,6] The only tentative explanation for the difference in behavior of 5 compared to 3 is that the bulkyness of the dimethylvaleryl group sterically inhibits the formation of a radical retaining the two acyl groups analogous to 11. To support this argument the unsubstituted valeryl analog 4 yielded uv-visible and esr spectra consistent with 12, a radical similar to 11.

We find it worth mentioning that di(4-pyridyl)methyl carbinol 6, prepared by treatment of di(4-pyridyl)ketone with methyl magnesium iodide and then with excess methyl iodide, also generated radical 11 when reacted with hydroxide. Immediately after mixing crystals of 6 with aqueous concentrated hydroxide an intense red color developed which persisted for several minutes only to change abruptly into a more stable deep blue color. Both uv-visible and esr spectra of this blue solution were identical to those derived from 4-acetyl pyridine methiodide 3 with base under the same conditions. Whereas the uv-visible absorption is only moderately indicative of minor changes in alkyl substituent, the hyperfine splitting in the esr spectrum is extremely sensitive to even minor changes in the molecule. Therefore, the superposable identity of the paramagnetic signals of the blue radicals derived from both 3 and 6 in hydroxide testifies to the formation of the same stable radical 11 and the necessary cleavage adjacent to the carbinol carbon of 6. It is

quite possible that the observed red intermediate is ion 13 which subsequently cleaves to form 3, which, in turn, reacts with hydroxide to generate radical 11.



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EXPERIMENTAL SECTION

Spectrograde solvents were used throughout. Alkoxide solutions were freshly prepared by dissolving metallic sodium in alcohol. Degassed solutions were prepared by repeated freeze-thaw cycles under high vacuum in either silica absorption cells or esr tubes provided with side reservoirs and constrictions for flame sealing. Degassing was carried out with the solvent in the side bulb and the crystals of solute in the sample compartment. Because of dielectric loss in the solvent, aqueous esr samples were placed in 1 mm ID quartz tubes and those in alcohol in 1, 2 or 3 mm ID tubes.

Uv-visible absorption spectra were recorded on the Cary Spectrophotometer Model 15 in double beam mode. Esr spectra were recorded on a modified Varian V-4502 Spectrometer with 10 kHz modulation. The microwave bridge of the spectrometer consisted of circulator in the sample arm and precision attenuator and phase shifter in the bucking arm. Computer simulations were carried out on an IBM 360/91 Computer and drawn by the Cal-Comp Associates Plotter; other calculations were performed on an IBM 360/50 Computer.

Nmr spectra were recorded on a Hitachi Perkin-Elmer nmr spectrometer, Model R-20, with internal and in some cases external TMS standard. Infrared spectra were taken on a Perkin-Elmer 221 Infrared Spectrometer. Mas spectra were run on a Perkin-Elmer 270 GC Mass Spectrograph.

The preparation of di(4-pyridyl) ketone 1 and di(4-pyridyl) methyl carbinol dimethiodide 6 was described previously.[4]

4-Acetylpyridinium Methiodide 3. Treatment of 10 g, 82.6 mmole of 4-acetylpyridine (Aldrich) with excess CH_3I gave 19 g of orange crystalline methiodide. Yield: 87%, mp 172-173°; ir ν (KBr) 1690 cm^{-1} (C=O); nmr (DMSO-d_6), δ 9.26 (2H, doublet), 2,6-pyridinium H's), δ 8.47 (2H, doublet, 3,5-pyridinium H's), δ 4.50 (3H, singlet, N-CH_3), δ 2.79 (3H, singlet, acetyl H's).

Anal. Calcd. for $C_8H_{10}NOI$: C, 36.5; H, 3.80. Found: C, 36.3; H, 3.90.

4-4'-dimethylvaleryl)pyridine. To a stirred solution of dry 4-cyanopyridine (41.0 g, 0.39 moles) dissolved in 300 ml of anhydrous ether under N_2 atmosphere was added dropwise 1 M t-butyllithium in n-pentane (200 ml, 0.39 moles). The dark red-brown solution was stirred for 8 hr, then hydrolyzed with dilute HCl. The organic layer was extracted with five 60 ml portions of dilute HCl; the combined aqueous extracts were made basic with concentrated NaOH and extracted with eight 50 ml portions of chloroform, which were then dried over $MgSO_4$. The $CHCl_3$ was evaporated off leaving a red oil which was distilled at reduced pressure. The fraction bp 96-98°/0.5 mm showed only one peak upon VPC analysis and was identified as 4-(4',4'-dimethylvaleryl)-pyridine. Yield: 5 g, 9.3%; ir ν (neat) 1685 cm^{-1} (C=O); nmr (neat), δ 8.35 (2H, doublet, 2,6-pyridyl H's), 7.32 (2H, doublet, 3,5-pyridyl H's), 2.60 (2H, triplet, methylene adjacent to C=O), 1.22 (2H, triplet, methylene adjacent to t-butyl), 0.55 ppm (9H, singlet, t-butyl group); mass spectrum m/e (rel intensity) 191 (19, M^+), 176 (23), 135 (41), 134 (14), 122 (31), 107 (26), 106 (100), 79 (28), 78 (42), 57 (61), 51 (23), 41 (28).

4-Valerylpyridine was obtained by treatment of dry 4-cyanopyridine (10.4 g, 0.1 moles) with 2.67 M n-butyllithium in n-hexane (60 ml) followed by hydrolysis with dilute HCl and similar work-up as with 4-(4',4'-dimethylvaleryl) pyridine. Yield: 5 g (30%), bp 94-96°/0.5 mm; ir ν (neat) 1694 cm^{-1} (C=O); nmr (neat) δ 8.20 (2H, complex doublet, 2,6-pyridyl H's), 7.14 (2H, complex doublet, 3,5-pyridyl H's), 2.51 (2H, triplet, methylene adjacent to C=O), 1.07 and 0.50 ppm (7H, multiplet, n-propyl group).

4-valerylpyridinium methiodide 4. Treatment of 4-valerylpyridine (2.2 g; 13.5 mmoles) with CH_3I (5 ml) in benzene gave the orange-red methyl iodide. Yield: 3.7 g (89%); mp 87-89°; ir ν (KBr) 1680 cm^{-1} (C=O); nmr (Me SO-d_6) δ 9.10 (2H, doublet, 2,6-pyridinium H's), 8.35 (2H, doublet, 3,5-pyridinium H's), 4.49 (3H, singlet, N-CH_3), 3.15 (2H, triplet, methylene H's adjacent to carbonyl group), 1.41 and 0.90 ppm (7H, multiplet, n-propyl group).

Anal. Calcd for $C_{11}H_{16}NOI$: C, 43.29; H, 5.28. Found: C, 42.77; H, 5.38.

4',4'-dimethylvalerylpyridine methiodide 5. Treatment of 4- (4',4'-dimethylvaleryl pyridine (1.0 g, 5.24 mmoles) with CH_3I (3 ml) in methylethylketone formed orange methyliodide: Yield 1.4 g (81%); mp 177.5-178.5°; ir ν (KBr) 1695 cm^{-1} (C=O); nmr (Me_2SO-d_6) δ 9.16 (2H, doublet, 2,6-pyridinium H's), 8.42 (2H, doublet, 3,5-pyridinium H's), 4.38 (3H, singlet, N-CH_3), 3.12 (2H, triplet, methylene H's adjacent to carbonyl), 1.47 (2H, triplet, methylene H's adjacent to t-butyl group); 0.89 ppm (9H, singlet, t-butyl H's).

Anal. Calcd for $C_{13}H_{20}NOI$: C, 46.85; H, 6.05. Found: C, 46.23; H, 6.22.

N-Methyl-d_3-4-acetyl-pyridinium iodide 7 was prepared with CD_3I (ICN Corp., 99.5%) by a procedure[16-18] similar to that described for 3. Orange crystals: Yield 68%, mp 172.5-173.5°; ir ν (KBr) 1690 cm^{-1} (C=O); nmr (Me_2SO-d_6) δ 9.22 (2H, doublet, 2,6-pyridinium H's), 8.49 (2H, doublet, 3,5-pyridinium H'), 2.79 ppm (3H, singlet, acetyl H's).

1,1'-Dimethyl-4,4'-diacetyl-1,1',4,4'-tetrahydro-4,4'-dipyridinium dihydrochloride 8. Radical cation 11 (1.1 g, 3.8 mmoles) was suspended at room temperature in 30 ml of 0.5 M HCl. The green crystals turned red immediately. Within 25 minutes the crystals were completely dissolved. After filtering the yellow solution, 5 ml of 1 N NaOH was added dropwise to pH ∿ 9. The solution turned purple, violet, and then blue. The red crystals were reprecipitated with 37% HCl to pH_{fa} = 2. The crystals were suction filtered and washed with ethyl ether. Yield: 125 g. (96.15%); mp 296-7°; uv (H_2SO_4) λ_{max}, nm (ε), 390 (16,900), 372 (14,600), 355sh (8,300), 316 (3,000), 305 (2,900), 295sh (2,600), 285sh (2,500), 262sh (3,400), 250 (5,900), 244 (5,800); ir (KBr) 1640 cm^{-1} (C=O); the nmr spectrum is shown in Figure .

Anal. Calcd for $C_{16}H_{22}N_2O_2Cl_2$: C, 55.62; H, 6.42; N, 8.11; O, 9.26; Cl, 20.53. Found: C, 55.92; H, 5.59; N, 8.29; O, 9.04; Cl, 20.96.

Preparation of Radical Cation 11. -- All work described below was carried out in oxygen-free atmosphere. N-Methyl-4-acetyl-pyridinium iodide 3 (5 g, 0.019 moles) was introduced into a 250 ml three necked-flask equipped with pressure-equalizing addition funnel and magnetic stirrer. Freshly prepared aqueous 2 N NaOH (30 ml) previously deaerated for 20 minutes by N_2-bubbling was added dropwise at room temperature. A green solution developed and within 10-15 minutes a green precipitate appeared. After 2 hr the apparatus was transferred to a nitrogen glovebox, the precipitate filtered off by suction and washed with ethyl ether. Yield: 1.5 g (54.74%); uv, ir, nmr, esr spectra are given in text.

Acknowledgement. This work was supported by the Atomic Energy Commission on Contract AT-40-1-3797. Some contribution from The Research Committee of The George Washington University is also acknowledged.

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(3) To whom correspondence should be addressed at G.W.U.

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FIGURE CAPTIONS

Figure 1. Changes in the uv-visible absorption spectrum of a degassed 1.5×10^{-3} M solution of 4-acetylpyridine methiodide in ~ 1 N NaOH: (1) after mixing, (2) 3 hr, (3) 24 hr, (4) 212 hr, (5) 598 hr, (6) open to air.

Figure 2. Top: esr spectrum of 4-acetylpyridine methiodide in 1 N aqueous NaOH. Bottom: computer simulated spectrum with hfs constants $a^N = 5.39$, $a_1^H = 1.54$, $a_{CH_3}^H = 5.10$ and $a_2^H = 1.80$.

Figure 3. Top: esr spectrum of N-Methyl-d_3-4-acetylpyridinium methiodide 7 in 1 N aqueous NaOH. Bottom: simulated spectrum with hfs constants $a^N = 5.39$, $a_1^H = 1.54$, $a_{CD_3}^D = 0.79$ and $a_2^H = 1.80$.

Figure 4. Visible absorption of crystalline radical 11 in degassed dimethyl sulfoxide at different times: (1) after solubilization, (2) - (4) 135, 195, and 540 min later, respectively.

Figure 5. Uv absorption spectrum of free radical 11 in deoxygenated H_2SO_4 .

Figure 6. Nmr spectrum of crystalline free radical 11 in D_2SO_4 .

Figure 7. Esr spectrum of 4-acetylpyridine methiodide in sodium ethoxide-ethanol solution.

Figure 8. Esr spectra of stable radicals generated from 4-acetylpyridine methiodide 3 (top) and its d_3 derivative 7 (bottom) in pyrolidine - dimethoxyethylene solution.

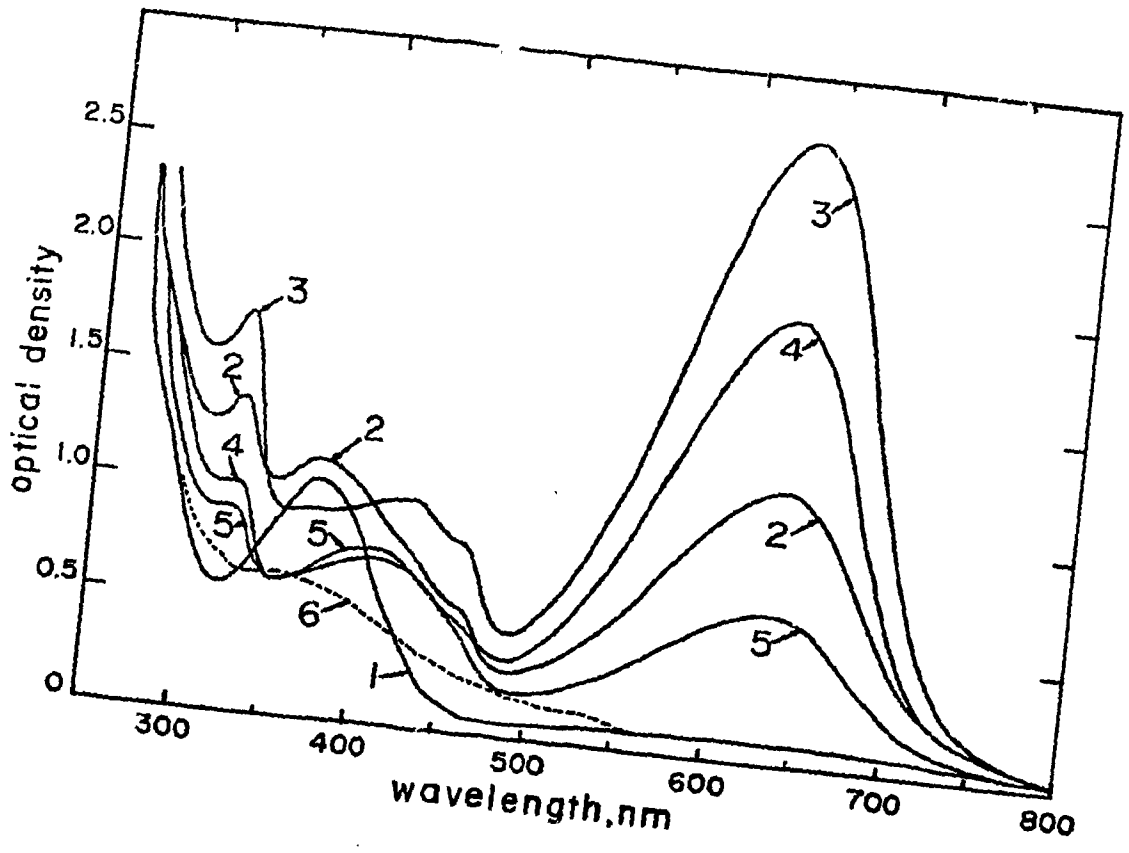


Figure 1

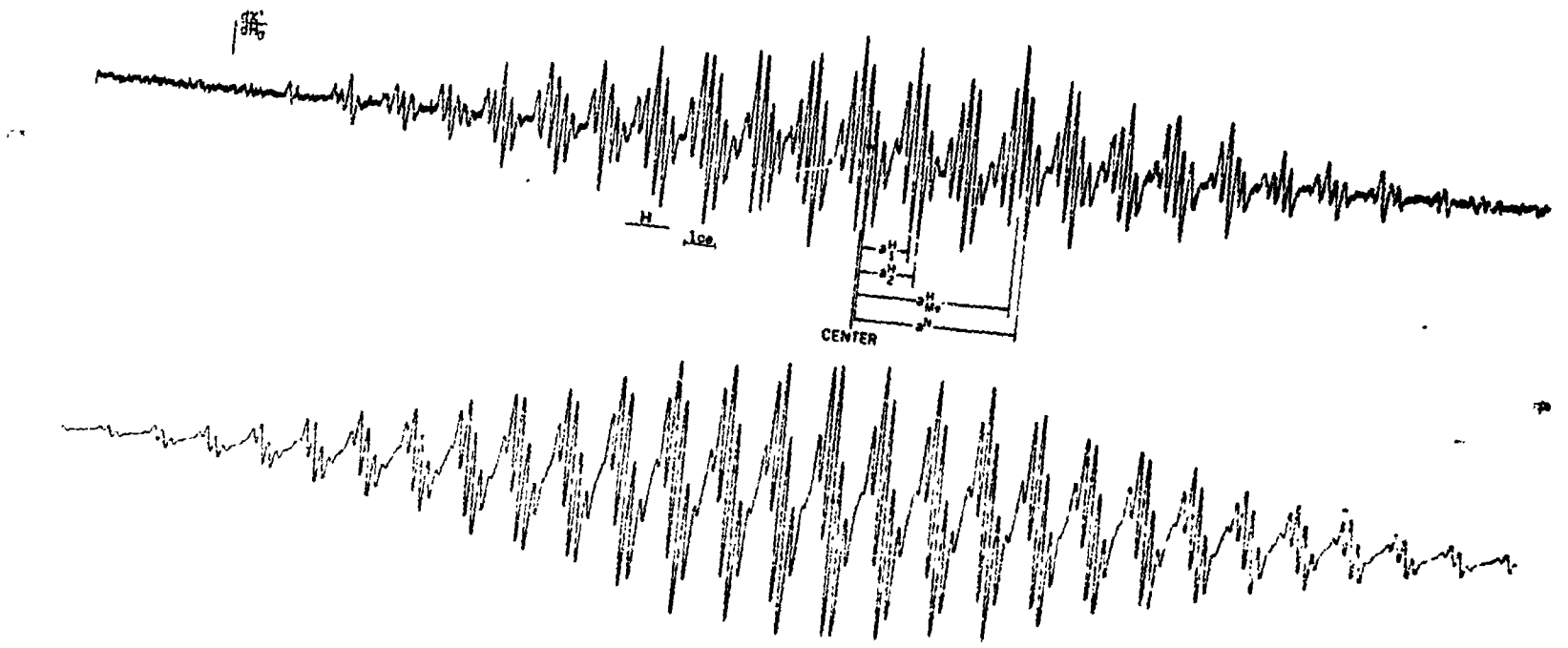


Figure 2

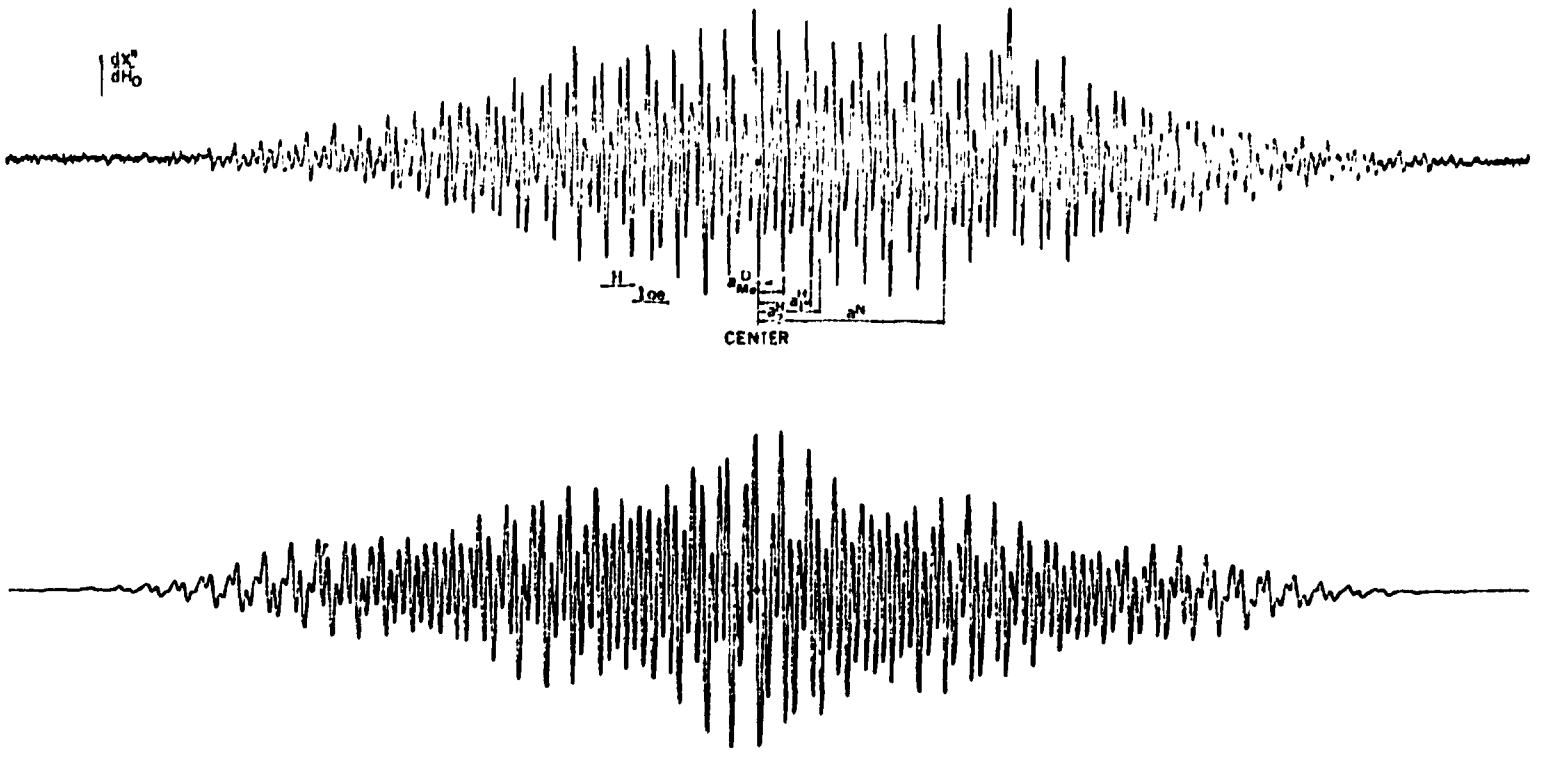


Figure 3

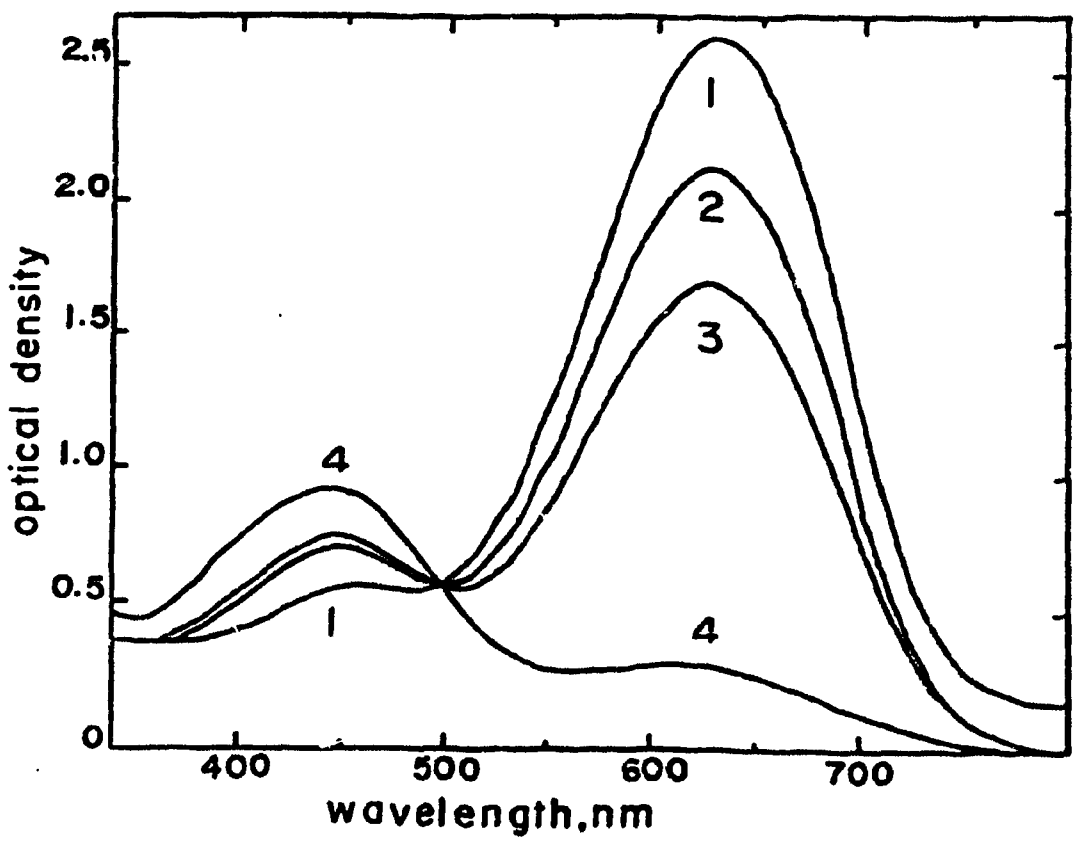
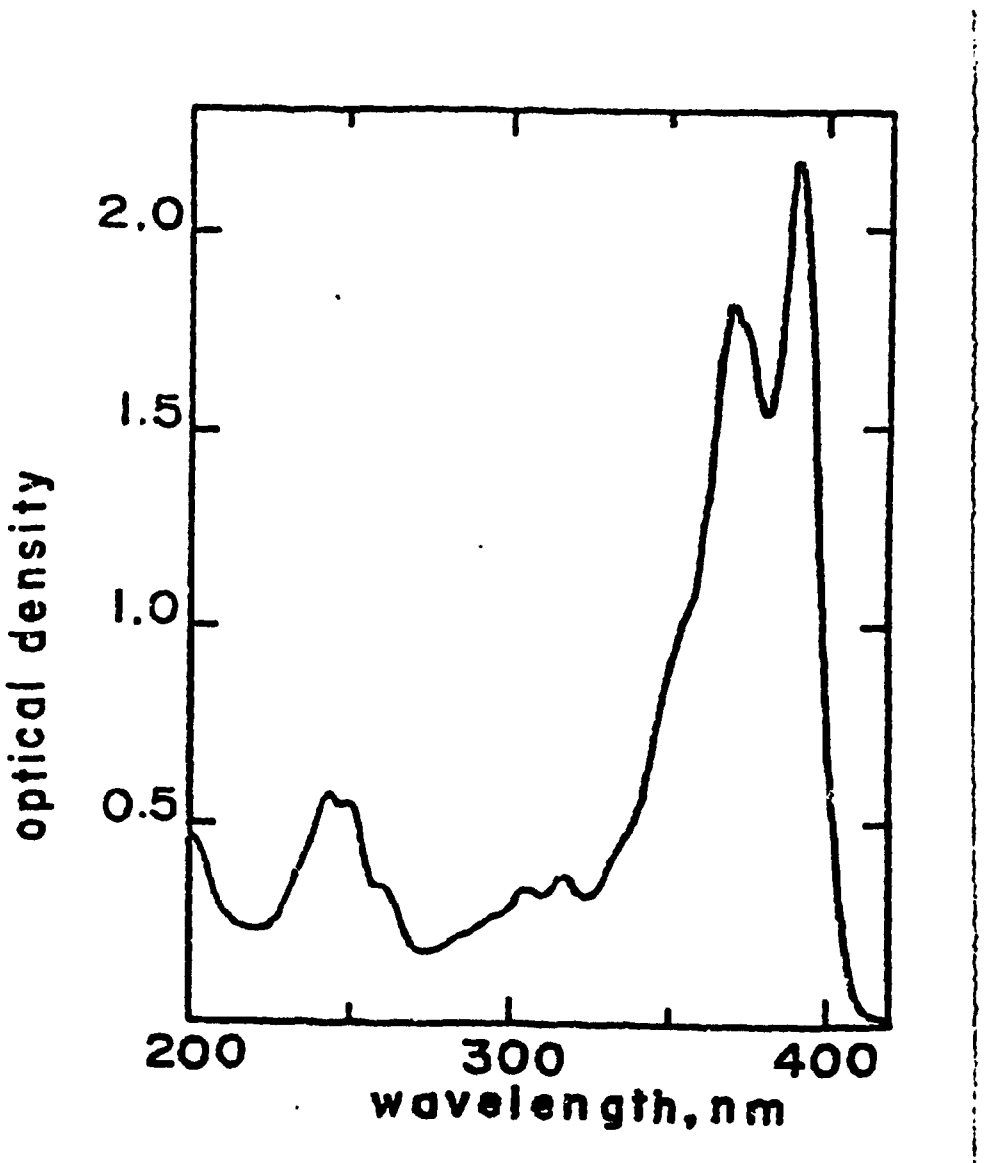


Figure 4



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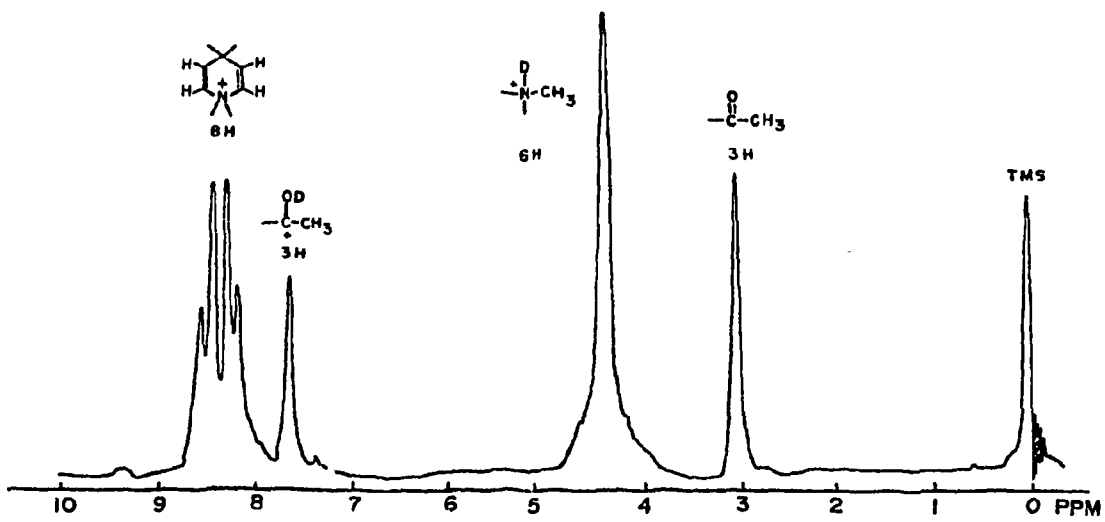


Figure 6

Figure 7

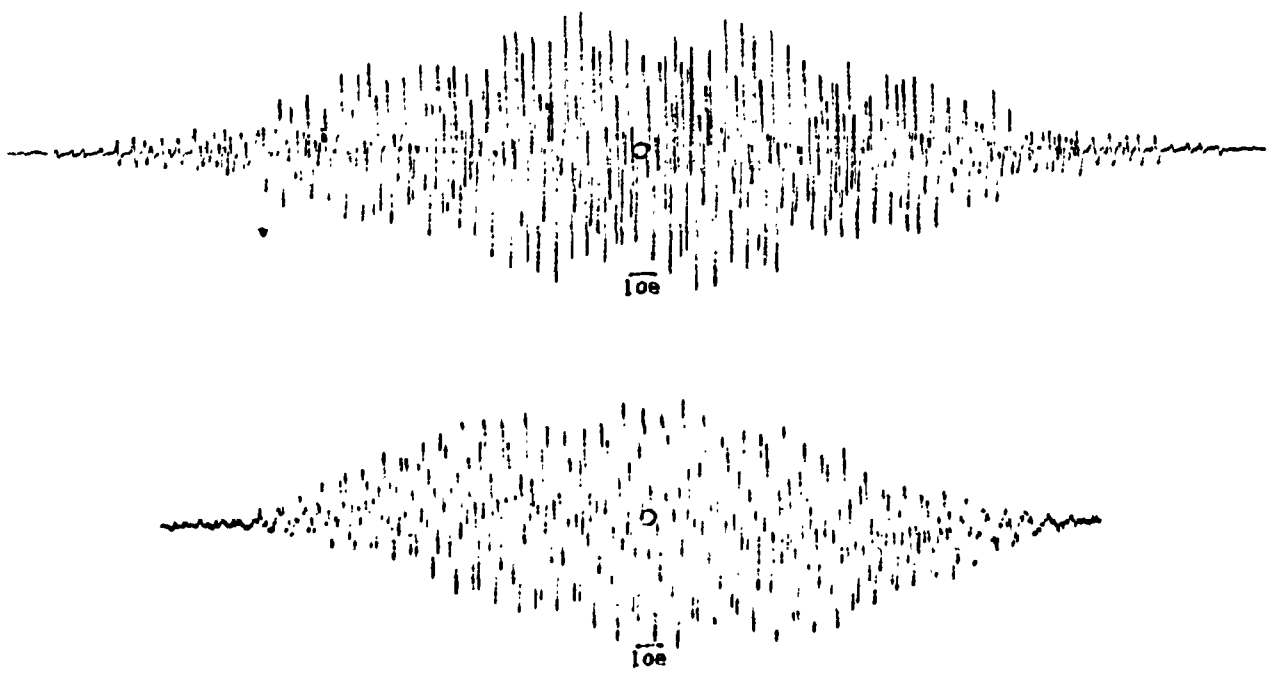
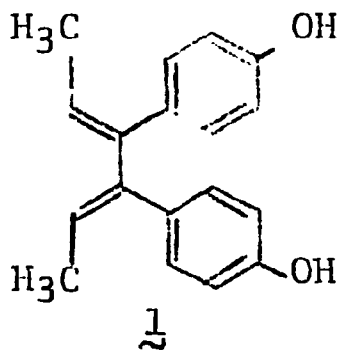


Figure 8

The George Washington University
Contract AT-(40-1)-3797
ORO-3797-44

On the Configuration of Dienestrol

The synthetic estrogen 3,4-bis(p-hydroxyphenyl)-2,4-hexadiene, dienestrol, has been originally prepared in 1939 by Dodds and Robinson[1]. Its exact structure, however, has not been proven satisfactorily and has remained a controversial subject[2-5]. Theoretically, there are three possible stereoisomers, 1-3. Koch and coworkers suggested configuration 1 for the



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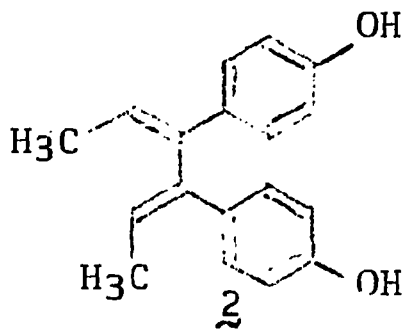

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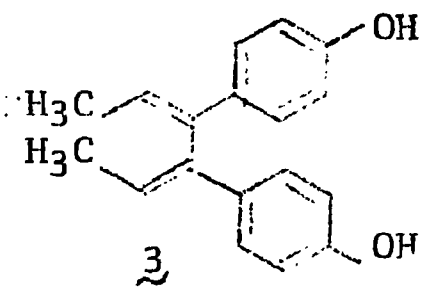

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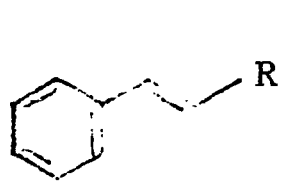
only isomer available to them[2,3]. Later, presumed authentic samples of each stereoisomer were synthesized[4,5]: Their corresponding diacetates were prepared by dehydration of mixtures of meso and racemic 3,4-bis(p-acetoxyphenyl)-3,4-hexanediols. On the basis of the infrared absorbtion of the diacetates, Lane and Spialter[5] concluded that the drug dienestrol has steric configuration 3.

In view of our interest in stereochemistry and photoreactivity of synthetic estrogens[6], we have reexamined the structure of dienestrol. The nmr spectrum of the pharmacologic product, prepared by the method of Dodds and Robinson or purchased from K & K Laboratories, recorded in acetone-d_6 (A-60 Varian Spectrometer, TMS internal standard) showed that the two methyl groups have equivalent molecular environment and

identical chemical shifts: δ = 1.50 ppm (doublet, =CH-$\underline{CH_3}$, 6H) and that the two vinyl protons are equivalent: δ = 5.37 ppm (quartet, =$\underline{CH}$-CH_3, 2H) The only other signals in the nmr spectrum were caused by the aromatic protons at δ = 6.65 to 7.30 ppm (multiplet, 8H), and the hydroxylic protons at δ = 8.45 ppm (singlet, 2H). These findings eliminate the low-symmetry structure 2 as possible dienestrol configuration. Differentiation between the remaining two alternatives, 1 and 3, was made by analyzing the ultraviolet absorbtion spectra of dienestrol and the diacetoxy derivatives of stereoisomers 1, 2, and 3. The three diacetates were obtained from White Laboratories[7]. Dienestrol diacetate was separately prepared from dienestrol by treatment with acetic anhydride in pyridine and recrystallization from ethanol-water, m.113-4°. The near-uv absorption of dienestrol and its diacetate are compared to those of the other two isomeric diacetates in Figure 1. The pharmaceutical form displays an absorption maximum at 227 nm, its diacetylated derivative at 221 nm, and the other diacetates at 247 and 250 nm. Evaluation of these absorption curves in terms of steric interference of substituents with normal styrene chromophore absorption allows unambiguous assignment of configuration 1 for the drug dienestrol.

Unsubstituted styrene, simple trans-β-alkylstyrenes (4), and simple α-alkylstyrenes (5) exhibit absorption maxima in the 243-255 nm



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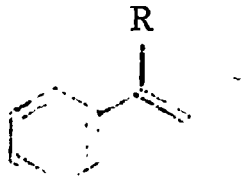

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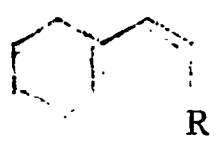

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spectral region[8]. On the other hand, cis-β-alkylstyrenes (6) lack the characteristic styrene-chromophore absorption because of out-of-plane distortions

of the vinyl group with respect to the aryl π-system brought about by the steric hinderance between the alkyl substituent and the ortho hydrogen[9]. Consequently, the λ_{max} at 221 nm displayed by dienestrol diacetate in Figure 1 is compatible only with the cis-β-alkylstyrenic structure 1. The fact that the other two stereoisomeric diacetates exhibit near-uv absorption consistent with the preservation of the styrene chromophore confirms their concordance with structures 2 and 3. Consistency with the above interpretation was also obtained from examination of scale-molecular models of the geometric isomers. The models also indicate that the two olefinic bonds in stereoisomer 1 readily attain coplanarity with each other without strain outside the planes of the aryl nuclei, whereas prohibitive tension would be required to reach double-bond conjugation in structures 2 and 3. The conjugation of the two vinyl groups in 1 offers compensatory stabilization energy for the lost styrene π-delocalization and retains a cis-butadiene chromophore which is characterized by an absorption maximum at 217 nm. This may be interpreted as additional evidence for the assigned configuration 1 to dienestrol since, of the four compounds in Figure 1, only the drug and its diacetate have absorption maxima compatible with the presence of a non-conjugated substituted butadiene chromophore.

Acknowledgement. This work has been supported in part by the Atomic Energy Commission on Contract AT-(40-1)-3797.

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Washington D.C.

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