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Carbon-13 NMR Analyses of TATB and Related Compounds in Sulfuric Acid

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ACRONYMS

TATB	1,3,5-Triamino-2,4,6-trinitrobenzene
TMS	Tetramethylsilane
DMSO	N,N-Dimethylsulfoxide
HMPA	Hexamethylphosphoric triamide
TCB	1,3,5-Trichlorobenzene
TCTNB	1,3,5-Trichloro-2,4,6-trinitrobenzene
TADNB	1,3,5-Triamino-2,4-dinitrobenzene
TACDNB	1,3,5-Triamino-2-chloro-4,6-dinitrobenzene
T_4CDNB	1,2,3,5-Tetrachloro-4,6-dinitrobenzene
T_3CDNB	1,3,5-Trichloro-2,4-dinitrobenzene
DATNB	1,3-Diamino-2,4,6-trinitrobenzene
DACDNB	1,5-Diamino-3-chloro-4,6-dinitrobenzene
DCTNB	1,3-Dichloro-2,4,6-trinitrobenzene

CARBON-13 NMR ANALYSES OF TATB AND RELATED COMPOUNDS IN SULFURIC ACID

by

Betty W. Harris

ABSTRACT

The insensitive explosive 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), which is used in explosive systems, is insoluble in most solvents. Thus, a suitable assay has not been developed for it. Strong acids such as trifluoromethane sulfonic acid and sulfuric acid dissolve TATB, but very little was known about the chemical nature of these systems.

This study determined ^{13}CNMR data on substituted nitrobenzene and substituted nitroaniline derivatives that are starting materials for and intermediate products from the synthesis of TATB. These data were correlated with those from the TATB-strong acid system, clarifying the nuclear structure of TATB in these solvents. TATB became protonated at C_4 and exists as an equilibrium mixture of the amino and imino forms in sulfuric acid, with the imino form as the predominate one. These results can be used to develop an assay for TATB.

Special attention was given to the solvent effects, substituent effects, and protonation effects on the ^{13}CNMR spectra of the compounds studied. Nitrogen-15 labeled compounds were used where the carbon-13 absorption was questionable. Coupling constants for $^{13}C^{15}N$ and $^{13}C^{1}H$ were determined.

I. INTRODUCTION

Although TATB is an excellent, insensitive, thermally stable explosive, it is insoluble in most solvents. Thus, its chemical properties are difficult to study. To develop an assay for TATB, we needed information on its chemical nature. Strong acids and superacids dissolve TATB, but we did not know the structural form of the compound upon dissolution. Carbon-13 nuclear magnetic resonance (^{13}CNMR) was used to determine how protonation and solvation are responsible for the dissolution of TATB in acid medium. Model compounds, intermediates, and impurities were also analyzed by ^{13}CNMR.

II. THEORY

Protonation of basic sites in chemical compounds causes substantial changes in the charge densities of neighboring carbon nuclei and also in their ^{13}CNMR chemical shifts, δ.[1,2] Studies of the protonation of amino acids revealed that the α carbon becomes shielded (resonance shifted to a higher field) when protonation occurs.[3,4] Horsley et al. suggested that protonation causes transmission of negative charge from hydrogen through carbon to the $-NH_3^+$ group. Also, the charge density about the carbon atom remains unchanged or becomes slightly negative. While studying solvation of anilinium salts,

Fraenkel and Kim[5] found that in quaternary salts the inductive effect of $-N^{+}-$ on the carbon atoms around the benzene ring decreases progressing from the protonated amine group and that it does not alternate. They observed that primary anilinium salts in polar media have spectra that are independent of the anion, but that $-NH_3^{+}$ does influence the charge densities about the ring carbons. They suggested that the ammonium substituent is attached to a solvent shell and that some of the positive charge on the nitrogen is shared with the solvent through the N-H bond.

When the proton acts as an electrophile, arenes are known to become protonated at the ring. Olah et al. suggested that a cyclohexadienyl-type sigma complex is the species formed.[6] When they nitrated hexamethylbenzene with NO_2BF_4-FSO_3H-SO_2 at −78°C, the ^{13}CNMR spectrum showed a pronounced upfield shift, 33 ppm, compared to that of hexamethylbenzene, 132.3 ppm. Resonances of the carbons at the ortho and para positions were deshielded (resonance shifted to a lower field), which indicated a decrease in the electron density at these positions when the arene ion was formed. The meta positions were also slightly positive. These data suggested that hybridization of the ring carbons changes from sp^2 to sp^3 when the ion is formed. This type of change in hybridization was also observed in the formation of the mesitylenonium ion.[7]

III. RESULTS AND DISCUSSION

Previous studies have shown that ^{13}CNMR spectroscopy is a valuable method for obtaining information on the structural behavior of organic compounds in solvation. However, we needed model compounds to compare with unfamiliar or unpredictable systems such as TATB in H_2SO_4. The TATB was prepared by sequential nitration and amination of TCB (Fig. 1). Preparation of related compounds and synthesis of TATB intermediates are given in the Appendix. By ^{13}CNMR spectroscopy, we analyzed several compounds in DMSO, HMPA, and H_2SO_4. Changes in chemical shifts were used to assess the degree of protonation and solvation in each compound. Proton magnetic resonance spectroscopy was used to assign carbon resonances.

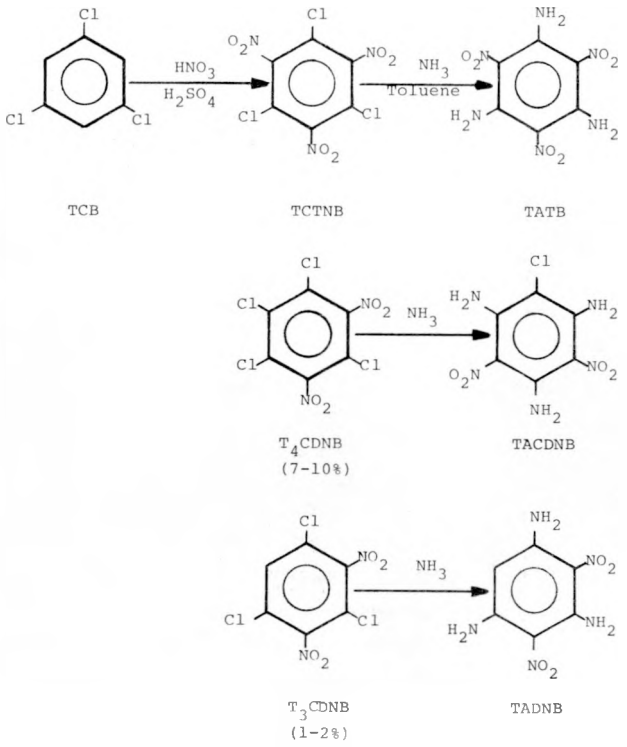


Fig. 1.
The most probable intermediates and impurities in the synthesis of TATB from TCB.

A. Model Compounds

We compared the chemical shifts we observed for chloronitrobenzene and chloronitroaniline derivatives with calculated chemical shifts[8] (Tables I and II). For chloronitrobenzene derivatives, there was no substantial change in chemical shifts in basic and acidic solvents. Therefore, we concluded that H_2SO_4 did not protonate these compounds. However, dichlorotrinitrobenzene was strongly solvated as indicated by an upfield shift of 10 ppm for C_5 in DMSO compared to the calculated value.

Studies of aromatic systems in superacids, for example HF-SbF_5, have shown that protonation can occur on substituent groups, such as $-NH_2$ and -NHR, and also on the benzene ring. Aniline derivatives showed a large change in chemical shifts of carbons bonded to amino groups in H_2SO_4. This proved that these aniline compounds were protonated at the amino group in this solvent (Table III). The differences in the relaxation times of

TABLE I

CARBON-13 CHEMICAL SHIFTS OF CHLORONITROBENZENE DERIVATIVES IN VARIOUS SOLVENTS AT 20-25°C

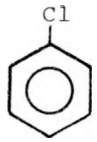
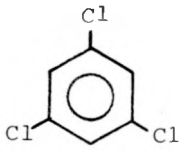
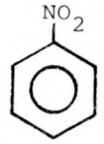
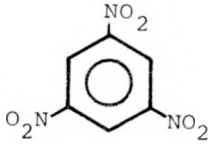
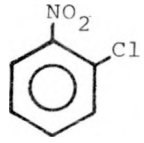
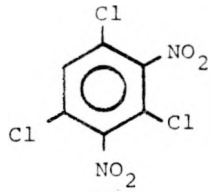
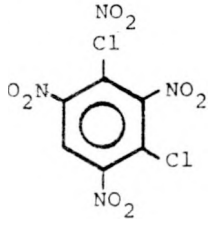
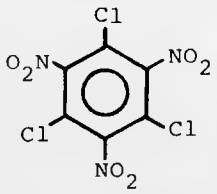
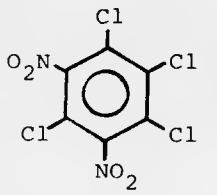
Compound	Solvent[a]		Chemical Shifts,[b] δ (ppm) C_1	C_2	C_3	C_4	C_5	C_6
		Calc	**135.1**	**128.9**	**129.7**	**126.7**	**129.7**	**128.9**
	DMSO		134.3	129.2	130.8	127.5	130.8	129.2
	HMPA		134.4	128.9	130.3	127.0	130.3	128.9
	H_2SO_4		134.3	129.2	130.8	127.5	130.8	129.2
		Calc	**137.1**	**129.1**	**137.1**	**129.1**	**137.1**	**129.1**
	DMSO		134.8	122.2	134.8	122.2	134.8	122.2
	HMPA		136.2	128.0	136.2	128.0	136.2	128.0
	H_2SO_4		Insoluble					
		Calc	**148.3**	**123.4**	**129.5**	**134.7**	**129.5**	**123.4**
	Neat		148.1	123.2	129.4	134.7	129.4	123.2
	DMSO		148.3	123.8	130.1	135.5	130.1	123.8
	HMPA		148.3	123.5	130.0	135.3	130.0	123.5
	H_2SO_4		147.1	124.1	130.1	136.9	130.1	124.1
		Calc	**149.9**	**124.1**	**149.9**	**124.1**	**149.9**	**124.1**
	DMS0		149.3	124.9	149.3	124.9	149.3	124.9
	HMPA		149.5	124.7	149.5	124.7	149.5	124.7
	H_2SO_4		149.3	126.3	149.3	126.3	149.3	126.3
		Calc	**148.5**	**129.8**	**127.9**	**135.7**	**127.5**	**124.4**
	Neat		148.6	129.3	127.9	135.7	127.2	133.6
	DMSO		147.2	129.8	128.8	134.4	126.1	132.2
	HMPA		148.4	126.3	128.7	134.1	126.0	132.2
	H_2SO_4		147.4	128.8	128.6	136.4	127.4	133.3
		Calc	**137.8**	**147.5**	**126.5**	**147.5**	**137.8**	**128.7**
	DMSO		129.8	149.0	120.8	149.0	129.8	133.0
	HMPA		134.3	147.0	120.4	147.8	134.3	129.4
	H_2SO_4		Insoluble					
		Calc	**131.5**	**150.3**	**131.5**	**147.3**	**126.1**	**147.3**
	DMSO		129.5	151.2	129.5	148.0	116.4	148.0
	HMPA		124.3	150.1	124.3	147.9	125.8	147.9
	H_2SO_4		Insoluble					

TABLE I (cont)

Compound	Solvent[a]		Chemical Shifts,[b] δ (ppm) C_1	C_2	C_3	C_4	C_5	C_6
		Calc	**124.5**	**148.3**	**124.5**	**148.3**	**124.5**	**148.3**
	DMSO		122.7	146.4	122.7	146.4	122.7	148.3
	HMPA		123.6	148.5	123.6	148.5	123.6	148.5
	H_2SO_4		Insoluble					
		Calc	**138.0**	**135.1**	**138.0**	**148.5**	**124.5**	**148.5**
	DMSO-d_6		129.4	131.7	129.4	148.0	118.6	148.0
	HMPA		135.8	129.6	135.8	148.2	118.5	148.2
	H_2SO_4		Insoluble					

[a]One-molar solutions were used. If the solubility was less than one molar, then saturated solutions were used.

[b]Relative to TMS.

TABLE II

CARBON-13 CHEMICAL SHIFTS OF ANILINE DERIVATIVES IN VARIOUS SOLVENTS AT 20-25°C

Compound	Solvent[a]		Chemical Shifts,[b] δ (ppm)					
			C_1	C_2	C_3	C_4	C_5	C_6
Aniline		Calc	**147.9**	**116.3**	**130.0**	**119.2**	**130.0**	**116.3**
	Neat		147.6	115.9	130.3	119.0	130.3	115.9
	DMSO		148.8	115.5	130.0	117.8	130.0	115.5
	HMPA		148.8	115.5	129.8	117.8	129.8	115.8
	H_2SO_4		131.4	123.7	131.4	129.1	131.4	123.7
Aniline hydrosulfate	DMSO		139.2	119.3	129.5	122.8	129.5	119.3
o-Chloroaniline		Calc	**148.1**	**112.7**	**130.2**	**120.7**	**127.7**	**117.3**
	DMSO		145.2	118.8	130.0	118.5	128.6	116.7
	HMPA		145.6	122.9	131.5	126.2	129.9	124.8
	H_2SO_4		132.8	129.7	131.6	125.6	128.5	129.7
p-Chloroaniline		Calc	**145.9**	**117.3**	**130.2**	**125.6**	**130.2**	**117.3**
	DMSO		148.0	116.5	129.5	120.8	129.5	116.5
	HMPA		149.2	115.8	128.9	119.5	128.9	115.8
	H_2SO_4		137.6	125.3	131.3	127.5	131.3	125.3
o-Nitroaniline		Calc	**142.6**	**135.9**	**124.7**	**120.0**	**136.0**	**117.1**
	DMSO (2 M)		146.3	130.5	125.5	119.3	135.7	115.5
	HMPA		148.0	131.3	126.0	120.4	136.3	116.0
	H_2SO_4		133.3	141.4	132.5	128.6	138.7	124.0
m-Nitroaniline		Calc	**148.7**	**111.0**	**149.6**	**113.9**	**130.8**	**122.3**
	DMSO		150.9	108.3	149.8	111.0	130.7	121.0
	HMPA		152.6	107.9	149.9	109.0	129.9	120.5
	H_2SO_4		133.3	120.3	148.7	127.0	131.8	130.2
p-Nitroaniline		Calc	**153.9**	**117.1**	**124.7**	**138.8**	**124.7**	**117.1**
	DMSO		155.8	112.6	126.5	135.9	126.5	112.6
	HMPA		157.9	112.9	126.7	136.1	126.7	112.9
	H_2SO_4		135.4	126.2	127.4	148.8	127.4	126.2

TABLE II (cont)

Compound	Solvent[a]		Chemical Shifts,[b] δ (ppm)					
			C_1	C_2	C_3	C_4	C_5	C_6
2,4-Dinitroaniline		Calc	**148.6**	**136.7**	**119.4**	**139.6**	**130.7**	**117.1**
	DMSO		150.9	129.6	124.2	136.1	130.1	120.8
	HMPA		141.0	135.1	114.9	135.0	135.1	114.9
	H_2SO_4		129.8	142.5	124.5	149.3	133.2	130.3
2,6-Dinitroaniline		Calc	**137.3**	**136.7**	**129.4**	**120.8**	**129.4**	**136.7**
	DMSO		141.9	135.8	135.1	114.8	135.1	135.8
	HMPA		141.8	135.9	134.8	115.1	124.8	135.9
	H_2SO_4		120.5	143.8	135.1	134.6	135.1	143.8
2,4,6-Trinitroaniline (Picramide)		Calc	**143.3**	**137.5**	**125.4**	**140.4**	**125.4**	**137.5**
	DMSO		144.7	135.2	129.1	133.7	129.1	135.2
	HMPA		144.8	135.3	128.5	133.3	128.5	135.3
	H_2SO_4		137.9	138.6	130.7	139.9	130.7	138.6
m-Phenylenediamine[c]		Calc	**149.2**	**103.9**	**149.2**	**106.8**	**131.3**	**106.8**
	DMSO		150.2	130.4	150.2	104.5	101.3	104.5
	HMPA		149.2	129.7	149.2	103.8	100.6	103.8
	H_2SO_4		126.6	134.0	126.6	130.5	119.4	130.5
4-Nitro-1,2-phenylenediamine		Calc	**155.2**	**104.7**	**143.9**	**126.4**	**126.0**	**107.6**
	DMSO		144.4	109.3	135.3	138.0	116.0	112.6
	HMPA		145.1	108.1	136.1	137.5	114.5	111.2
	H_2SO_4		129.8	129.8	130.1	149.3	129.7	125.2
4,5-Dinitro-1,2-phenylenediamine		Calc	**142.3**	**142.3**	**113.1**	**134.8**	**134.8**	**113.1**
	DMSO		140.3	140.3	109.5	135.1	135.1	109.5
	HMPA		141.4	141.4	113.0	134.9	134.9	113.0
	H_2SO_4		126.8	126.8	130.1	149.3	144.3	130.1
1,3,5-triaminobenzene		Calc	**150.5**	**94.4**	**150.5**	**94.4**	**150.5**	**94.4**
	$CH_3C(=O)OC_2H_5$		148.2	92.0	148.0	92.0	148.2	92.0
	H_2SO_4		132.6	74.5	132.6	74.5	132.5	74.5

TABLE II (cont)

Compound	Solvent[a]		Chemical Shifts,[b] δ (ppm) C_1	C_2	C_3	C_4	C_5	C_6
1,3-Diamino-2,4,6-trinitrobenzene (DATNB)		Calc	**144.6**	**125.1**	**144.6**	**126.0**	**126.7**	**126.0**
	DMSO		146.9	123.5	146.9	123.0	132.8	123.0
	HMPA		146.3	122.7	146.3	123.2	131.4	123.6
	H_2SO_4		145.7	124.5	145.7	127.0	134.9	127.0
1,3,5-Triamino-2,4-dinitrobenzene (TADNB)		Calc	**151.2**	**114.8**	**151.2**	**114.8**	**139.9**	**96.0**
	DMSO		152.2	114.0	152.2	114.0	151.5	86.3
	HMPA		152.5	114.6	152.5	114.6	151.4	87.7
	H_2SO_4		161.8	114.6	161.8	114.6	156.7	37.2
1,3,5-Triamino-2-chloro-4,6-dinitrobenzene (TACDNB)		Calc	**151.4**	**102.4**	**151.4**	**105.8**	**139.9**	**105.8**
	DMSO		149.3	91.1	149.3	114.0	148.1	114.0
	HMPA		150.0	91.3	150.0	114.8	149.0	114.8
	H_2SO_4 (concd)		138.3	121.1	138.3	124.9	131.9	124.9
	H_2SO_4 (90%)		140.9	111.8	140.9	119.2	148.2	119.2
1,3,5-Triamino-2,4,6-trinitrobenzene (TATB)		Calc	**147.9**	**119.6**	**147.9**	**119.6**	**147.9**	**119.6**
	$DMSO-d_6$					86.0		
	H_2SO_4 (concd)		155.7	114.5	152.7	84.8	152.7	114.5
	H_2SO_4 (90%)		155.5	114.3	152.5	84.7	152.5	114.5

[a]One-molar solutions were used. If the solubility was less than one molar, then saturated solutions were used.

[b]Relative to TMS.

[c]The C_2 and C_5 chemical shifts may be reversed; however they were assigned from the coupled spectrum.

TABLE III

HOW PROTONATION IN H_2SO_4 AFFECTS THE CHEMICAL SHIFTS OF CARBONS ATTACHED TO AMINO GROUPS IN SOME ANILINE DERIVATIVES AT 20-25°C

Compound	Solvent	Chemical Shifts,[a] δ (ppm)					
		C_1-NH_2	ΔC_1-NH_2[b]	C-NH_2	ΔC-NH_2[b]	C^c-NH_2	ΔC^c-NH_2[b]
Aniline	Neat	147.6	16.2				
	H_2SO_4	131.4					
o-Chloroaniline	DMSO	145.2	12.4				
	H_2SO_4	132.8					
p-Chloroaniline	DMSO	148.0	10.4				
	H_2SO_4	137.6					
o-Nitroaniline	DMSO	146.3	13.0				
	H_2SO_4	133.3					
m-Nitroaniline	DMSO	150.9	17.6				
	H_2SO_4	133.3					
p-Nitroaniline	DMSO	155.8	20.4				
	H_2SO_4	135.4					
2,4-Dinitroaniline	DMSO	150.9	21.1				
	H_2SO_4	129.8					
2,6-Dinitroaniline	DMSO	141.9	20.9				
	H_2SO_4	121.0					
2,4,6-Trinitroaniline	DMSO	144.7	6.6				
	H_2SO_4	137.9					
m-Phenylenediamine	DMSO	150.2	25.6				
	H_2SO_4	126.6					
4-Nitro-1,2-phenylenediamine	DMSO	144.3	14.2			135.0	12.1
	H_2SO_4	130.1				123.9	
1,3,5-Triaminobenzene	$CH_3\overset{O}{\overset{\|}{C}}-O-CH_2CH_3$	148.2	16.6				
	H_2SO_4	132.6					
1,3-Diamino-2,4,6-trinitrobenzene (DATNB)	DMSO			146.7	1.0		
	H_2SO_4			145.7			
1,3,5-Triamino-2,4-dinitrobenzene (TADNB)	DMSO			152.5	−9.3	141.2	−15.5
	H_2SO_4			161.8		152.7	
1,5-Diamino-3-chloro-4,6-dinitrobenzene (DACDNB)[d]	DMSO			151.8	7.6		
	H_2SO_4			144.2			
1,3,5-Triamino-2-chloro-4,6-dinitrobenzene (TACDNB)	DMSO			149.3	11.0	148.1	16.2
	H_2SO_4			138.3		131.9	
1,3,5-Triamino-2,4,6-trinitrobenzene (TATB)	H_2SO_4			155.7		152.7	
3,4-Diaminofurazan	DMSO			151.8	9.0		
	H_2SO_4			142.8			
Hexanitrosobenzene	DMSO			141.3	0.1	102.7	
	H_2SO_4			141.2			

[a]Relative to TMS.

[b]Positive values indicate shielding; negative values deshielding.

[c]Carbons, other than C_1 or its equivalent, that are bonded to amino groups.

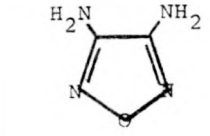
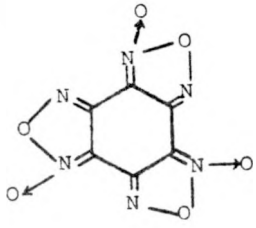
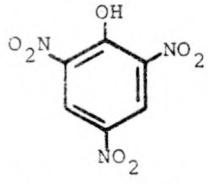
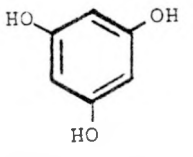
[d]Chemical shifts for DACDNB were assigned without the use of the labeled compound; some uncertainty in the assignment does exist.

-CNH_2, -CNO_2, and -CH groups were very small in acid medium. Therefore, we could not assign chemical shifts based on relative peak heights. For the mono-, di-, and tri-substituted nitroanilines, compounds labeled with nitrogen-15 at the amino group were used to assign chemical shifts. The coupling constants for $^{13}C^{15}N$ were important in identifying the carbon bonded to the amino group in picramide. The 6.8-ppm upfield shift in this carbon was evidence that picramide was protonated at this site. This would not have been easy to predict from the pKa values.

Data collected on compounds related to TATB are shown in Table IV. The furazan derivative was included to estimate the behavior of a heterocyclic amine in H_2SO_4. The carbon resonances for 3,4-diaminofurazan appeared at 151.8 ppm in DMSO and 142.8 ppm in H_2SO_4. This is the expected behavior for an aromatic amine system. During our preliminary discussions, it was suggested that TATB had a structure similar to hexanitrosobenzene. However, the ^{13}CNMR spectra of these compounds in H_2SO_4 did not show any similarities, disproving the suggestion at least for this solvent. Picric acid gave the expected aromatic carbon resonances in DMSO and HMPA. In H_2SO_4, all carbon resonances, except that for the carbon attached directly to a hydroxyl group, appeared in the aliphatic region of the spectrum. A cyclohexadienyl cation is probably the species in solution. Symmetrical trihydroxybenzene in acid medium is a mixture of the mono and di cations because it is protonated on both the ring and the oxygen atom.[9]

TABLE IV

CARBON-13 NMR OF SOME RELATED COMPOUNDS IN THE STUDY OF TATB IN H_2SO_4

Compound	Solvent		Chemical Shifts,[a] δ (ppm)					
			C_1	C_2	C_3	C_4	C_5	C_6
	DMSO		151.8	151.8				
	H_2SO_4		142.8	142.8				
	DMSO		141.3	102.7				
	H_2SO_4		141.2					
		Calc	**151.0**	**137.3**	**119.9**	**142.0**	**119.9**	**137.3**
	DMSO		159.5	142.5	126.2	127.2	126.2	142.5
	HMPA		161.1	143.2	125.5	124.4	125.5	143.2
	H_2SO_4		153.8	64.3	82.6	81.9	82.6	64.3
		Calc	**158.2**	**105.6**	**158.2**	**105.6**	**158.2**	**105.6**
	HMPA		161.2	95.5	161.2	95.5	161.2	95.5
	H_2SO_4[b]		(192.1	182.2	177.1	109.7	100.1)	

[a]Relative to TMS.

[b]1,3,5-Trihydroxybenzene exists as a mixture of the mono- and di-protonated species; therefore, precise assignment of chemical shifts were not made.

B. TATB and Related Compounds

Our ^{13}CNMR analyses of TATB and its impurities in H_2SO_4 showed a large upfield shift in the resonance of the carbon bonded directly to a hydrogen atom. This large shift can be explained by a loss of aromatic character when the cyclohexadienyl cation is formed.

Unlike DATNB, DACDNB, and TACDNB, the spectrum of TADNB was almost identical to the spectrum of TATB. Sulfuric acid did not seem to protonate DATNB. However, the downfield shift of 8 ppm from the calculated value for C_5 suggested a strong solvent effect. Protonation occurred at the amino group in TACDNB with the proton residing for some finite time on each amine group. Shielding effects of 11 and 16 ppm were observed (Table III). This compound was also strongly solvated as shown by the 20-ppm deshielding effect of the -CCl and $-CNO_2$ groups in acid medium. The behavior of TADNB and TATB in H_2SO_4 was just the reverse of that seen in similar compounds. The carbons bonded to the amino groups were deshielded in acidic solvents and the carbon bonded to the nitro group was shielded. When TATB was analyzed in trifluoromethane sulfonic acid, a much stronger acid than H_2SO_4, only minor changes in chemical shifts were observed. The carbon bonded to the hydrogen atom in TADNB was shifted from 86.3 ppm in DMSO to 37.2 ppm in H_2SO_4. This large shielding effect is caused by a change in hybridization of C_5 from sp^2 to sp^3.

Liquid chromatography has shown that DACDNB is also an impurity in TATB. We would assume that it is easily removed because it is extremely soluble in common organic solvents and TATB is not. However, ^{13}CNMR data suggest that unlike DMSO, HMPA and H_2SO_4 react with DACDNB forming a species that gives an unexplained spectral pattern. This species may behave differently in the TATB crystal lattice. The ^{15}N-labeled compound was not available; so chemical shifts were assigned from the coupled spectrum. The assignments at C_1 and $C_{4,6}$ might be reversed. However, the minimum upfield shift of 7.6 ppm is supporting evidence that DACDNB is protonated in H_2SO_4.

Some possible structures for TADNB are shown in Fig. 2. From the coupled spectrum of TADNB, we can see that protonation did not occur at the carbon bonded to a nitro group. From the shielding effect, structure B is most reasonable. The coupled spectrum confirmed the two hydrogens attached at C_4. More precise data will be obtained from freezing-point depression studies.

Compounds labeled with ^{15}N at the amino groups (DATNB, TADNB, and TATB) were analyzed by ^{13}CNMR spectroscopy. There was one $-^{13}C^{15}N$ functional group in DATNB, two different ones in TADNB, and possibly three different groups in TATB. The ^{15}NNMR coupled and decoupled spectra confirmed three different ^{15}N environments in the TATB-H_2SO_4 system. The coupled spectrum exhibited two sets of triplet ^{15}N resonances (intensity ratio 1:2:1) and one singlet ^{15}N resonance. The triplets were the results of $^{15}NH_2$ coupling, and the singlet probably was caused by a ^{15}N atom that was associated with a rapidly exchanging proton.

Table V shows coupling constants for TATB and some of its impurities. Govil[10] and others have concluded that coupling constants can be used to predict the amount of *s*- character in a carbon atom. Nuclear-spin coupling constants between ^{13}CH, bonded and nonbonded, were about the same as those observed by Govil. His value for ^{13}CH coupling in methane (sp^3 hybridized) was 125 Hz; ethylenic and aromatic ^{13}CH coupling constants were 154 to 160 Hz (sp^2 hybridized); and the acetylenic ^{13}CH coupling constant was 248 to 251 Hz (sp hybridized). Our coupling-constant data on TADNB and TATB confirmed that these compounds lost much of their aromatic character when dissolved in H_2SO_4

When we analyzed TADNB, TATB, and aniline using deuterated H_2SO_4 as a solvent, the carbons were more shielded than they were in the protonated solvent. A solvent effect in which almost all carbons

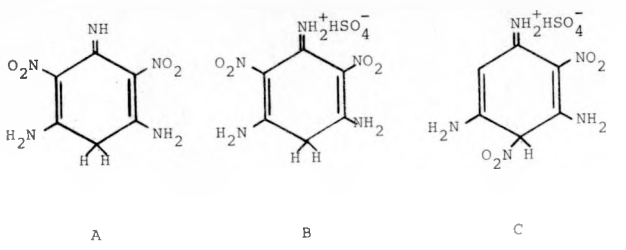


Fig. 2.
Possible structures of TADNB in H_2SO_4.

TABLE V

CARBON-13 COUPLING CONSTANTS FOR NITROANILINE DERIVATIVES IN CONCENTRATED H_2SO_4

Compound	Coupling Constants (Hz)				
	$J^{13}C_1{}^{15}N$	$J^{13}C_{3,5}{}^{15}N$	$J^{13}C_4H$	$J^{15}N_1H$	$J^{15}N_{3,5}H$
1,3-Diamino-5-imino-2,4,5-trinitrobenzenium bisulfate	18.8	20.2	176.8	96.5	94.2
	$J^{13}C_{1,3,5}{}^{15}N$				
1,3,5-Triamino-2,4,6-trinitrobenzene (TATB)	19.1				
	$J^{13}C_{1,5}{}^{15}N$	$J^{13}C_3{}^{15}N$	$J^{13}C_6H$		
1,3,5-Triamino-2,4-dinitrobenzene (TADNB)	19.9	19.2	135.0		
	$J^{13}C_{1,3}{}^{15}N$	$J^{13}C_{4,6}H_6{}^{15}N$	$J^{13}C_5H$		
1,3,5-Trinitro-2,4-diaminobenzene	16.9	5.5	177.3		
	$J^{13}C_5H$	$J^{13}C_{1,3}H_6$	$J^{13}C_{4,6}H$	$J^{13}C_{1,3}{}^{15}N$	
1,3-Diamino-2,4-6-trinitrobenzene (DATNB)	176.2	6.8	5.7	16.9	
	$J^{13}C_{1,3}{}^{15}N$	$J^{13}C_5{}^{15}N$			
1,3,5-Triamino-2-chloro-4,6-dinitrobenzene (TACDNB)	16.7	14.2			
	$J^{13}C_1{}^{15}N$	$J^{13}C_{3,5}{}^{15}N$	$J^{13}C_{3,5}H$		
2,4,6-Trinitroaniline (Picramide)	18.5	4.6	178.1		

were deshielded was observed in DMSO-d_6 (Table VI). The ibso carbon of *o*-nitroaniline is the exception, showing a slight shielding effect. A similar solvent effect was observed with TACDNB and the undeuterated solvent. The spectra pattern of TACDNB in DMSO was similar to those of TADNB and TATB.

Mixtures of TATB and its impurities (DATNB, TADNB, and TACDNB) were analyzed in H_2SO_4. Their peaks did not overlap at any point. However, after 36 h, the peaks caused by TACDNB absorption disappeared and an entirely new and much weaker spectrum was observed. After 21 and 90 days, similar results were observed with TADNB and TATB, respectively. The order of stability of these compounds in H_2SO_4 was TACDNB << TADNB < TATB.

TABLE VI

DEUTERIUM ISOTOPE EFFECT IN THE CARBON-13 CHEMICAL SHIFTS OF SOME ANILINE DERIVATIVES AT 20-25°C

Compound	Solvent		Chemical Shifts,[a] δ (ppm)					
			C_1	C_2	C_3	C_4	C_5	C_6
Aniline		Calc	**147.7**	**116.3**	**130.0**	**119.2**	**130.0**	**116.3**
	DMSO		148.8	115.5	130.0	117.8	130.0	115.5
	DMSO-d_6		152.0	119.0	133.4	121.1	133.4	119.0
	H_2SO_4		132.4	123.7	131.4	129.1	131.4	123.7
	D_2SO_4		125.5	117.7	125.5	122.6	125.5	117.7
o-Chloroaniline		Calc	**148.1**	**112.7**	**130.2**	**120.7**	**127.7**	**117.3**
	DMSO		145.2	118.8	130.0	118.5	128.6	116.7
	DMSO-d_6		147.8	122.9	133.5	122.8	132.0	120.3
o-Nitroaniline		Calc	**142.6**	**135.9**	**124.7**	**120.0**	**136.0**	**117.1**
	DMSO		146.3	130.5	125.5	119.3	135.7	115.5
	DMSO-d_6		145.5	130.9	135.8	119.7	136.0	116.0
1,3,5-Triamino-2,4-dinitrobenzene (TADNB)		Calc	**151.2**	**114.8**	**139.9**	**114.8**	**151.2**	**96.0**
	DMSO		152.2	114.0	151.5	114.0	152.2	86.3
	H_2SO_4		161.8	114.6	156.7	114.6	161.8	37.2
	D_2SO_4		155.9	108.5	150.9	108.5	153.9	31.3
1,3,5-Triamino-2,4,6-trinitrobenzene (TATB)		Calc	**147.9**	**119.6**	**147.9**	**119.6**	**147.9**	**119.6**
	H_2SO_4		155.7	114.5	152.7	84.8	152.7	114.5
	D_2SO_4		149.8	108.6	146.8	77.6	146.8	108.6

[a]Relative to TMS.

IV. CONCLUSIONS

Figure 3 gives three possible explanations for the behavior of TATB in sulfuric acid. (A) This compound becomes protonated at the amino group and is strongly solvated. (B) This compound is protonated at the ring and is strongly solvated. (C) This compound is not protonated but highly solvated in the imino form. Because of the nature of the solvent and the type of substituents on the ring, strong hydrogen bonding accounts for the solvation effect in both DMSO and H_2SO_4. The rapid exchange of protons from the amino group with deuterium from D_2SO_4 leads us to conclude that structure B is the most probable. Freezing-point depression studies are being performed to determine if the imino form is protonated. Preliminary studies do confirm that the molecule is strongly solvated.

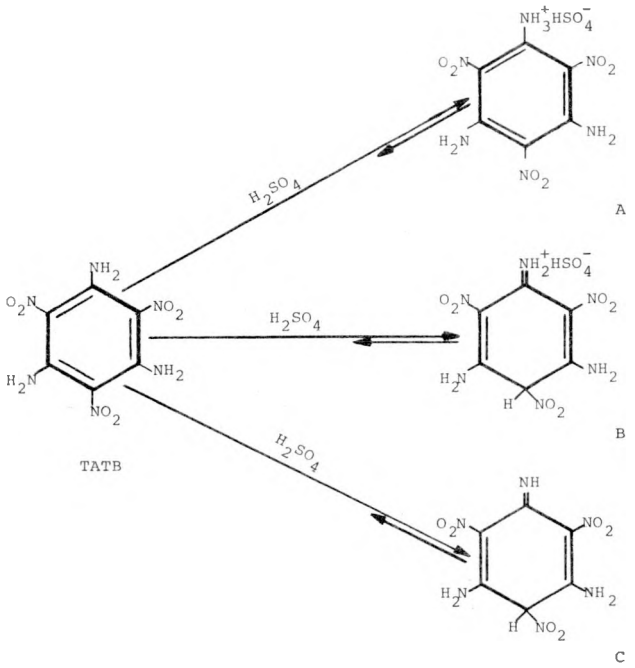


Fig. 3.
Possible structures of TATB in H_2SO_4.

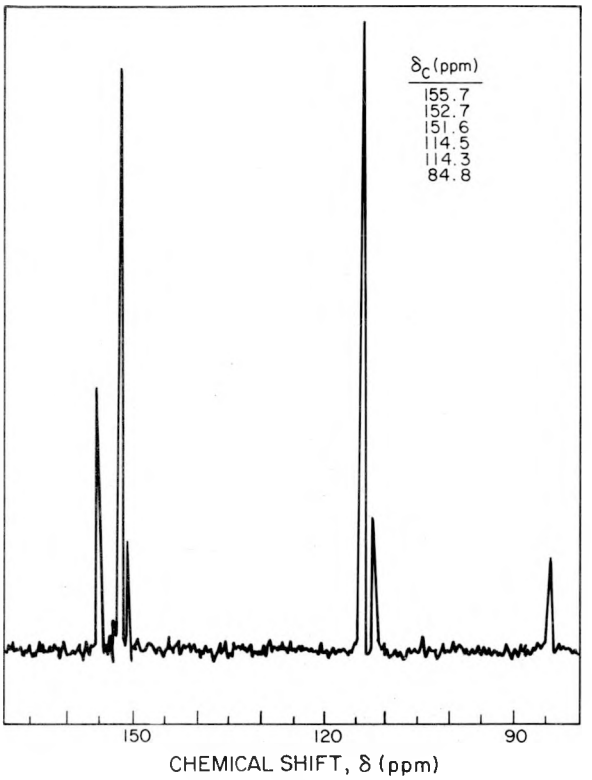


Fig. 4.
Carbon-13 NMR spectrum of TATB in H_2SO_4.

The imino carbon absorption is 155.7 ppm (Fig. 4). Carbons 3 and 5 are bonded to unprotonated amino groups with chemical shifts of 152.7 ppm. Carbons 2 and 6 absorb at 114.5 ppm, and carbon 4 at 84.8 ppm. The nitro group at C_4 causes this carbon atom to be more deshielded than C_4 of TADNB (Fig. 2). The ratio of the peaks in TATB is 1:2:2:1, the same as we would expect from structure B. The ^{13}C resonance at 84.8 ppm is split into a doublet in the coupled spectrum. The minor peaks at 151.6 and 114.3 ppm are caused by a small amount of unprotonated TATB in equilibrium with the imino form. The relative ratio of the major peaks to the minor ones can be altered by changing the concentration of the sample being analyzed. We determine the equilibrium constant by uv and $^{13}CNMR$ spectroscopy. Its value is positive but not reproducible with consistent results. However, these data do suggest that TATB exists predominately in the imino form in H_2SO_4. A more detailed thermodynamic study is in progress.

Solid-state NMR studies suggested that TATB is paramagnetic before and after it has been precipitated from H_2SO_4. The compound became pale green during precipation. In addition to peaks for aromatic protons, a small peak was observed to the right (downfield) of each aromatic proton in both samples. This peak was not characterized.

This $^{13}CNMR$ study has provided enough information on the behavior of TATB in H_2SO_4 to develop an assay for the compound. However, a more sensitive instrument is needed for the measurements.

APPENDIX

EXPERIMENTAL PROCEDURE

I. PREPARATION OF COMPOUNDS

Several compounds were obtained from commercial sources; the others were prepared by general procedures from the literature.[11,12] We obtained the best results with one-molar samples. However, when solubility was limited, we used saturated solutions. The solvents were DMSO, HMPA, and H_2SO_4. The temperature range was 20 to 25°C.

A. 1,3-Dichloro-2,4,6-trinitrobenzene (DCTNB)

A solution of 65% oleum (210 mℓ) and concentrated H_2SO_4 (170 mℓ) was cooled to 10°C, and 90% nitric acid (50 mℓ) was added. Small quantities of a 14.7-g (0.1-mol) sample of 1,3-dichlorobenzene were added carefully to the acid solution. The temperature was raised gradually to 130°C and maintained for 30 min. The reaction mixture was cooled to room temperature and quenched with crushed ice (1000 mℓ). The product was filtered and washed several times with ice water. A quantitative yield (93%) of DCTNB was obtained. The carbon, hydrogen, and nitrogen analyses agreed with calculated values.

B. 1,3,5-Trichloro-2,4-dinitrobenzene (T_3CDNB)

The same proportions of the oleum and nitric acid solution were used to dissolve 18.1 g (0.1 mol) of TCB. The temperature was raised to 100°C and maintained for 15 min. The heating mantle was removed, and the reaction mixture was cooled to room temperature. The reaction was quenched with crushed ice (1000 mℓ). The product, mp 126.7°C, was filtered and washed several times with cold water. If thin-layer chromatography analyses of the product revealed traces of TCTNB, mp 191 to 193°C, the product was recrystallized from CH_2Cl_2. A yield (89.2%) of the expected product was obtained. The carbon, hydrogen, and nitrogen analyses agreed with calculated values.

C. 1,3-Diamino-2,4,6-trinitrobenzene (DATNB)

A solution of 15.0 g (0.06 mol) of DCTNB in toluene (30 mℓ) was placed in a glass container and inserted into an oil bath. Anhydrous ammonia was added slowly in 344.7-kPa intervals until the pressure gauge stabilized. The product was filtered, washed with water, and recrystallized from CH_2Cl_2. A yield (97.0%) was obtained.

D. 1,3,5-Triamino-2,4-dinitrobenzene (TADNB)

The amination of 15.0 g (0.06 mol) of T_3CDNB was performed using the same procedure as above. However, the temperature was raised to 90°C, and the reaction time was increased to 24 h. The product was recrystallized from CH_2Cl_2. Approximately 67% of the product was obtained. About 3% of the product was TATB, which was insoluble in organic solvents.

E. 1,3,5-Triamino-2-chloro-4,6-dinitrobenzene (TACDNB)

The amination of T_4CDNB was more difficult than that of the compounds previously described. Here, 15 g (0.6 mol) of the starting material was dissolved in 30 mℓ of toluene heated at 90°C for 48 h. Ammonia was added as described above. When the ammonia reaction stopped, the cooled solution was filtered and washed with several portions of water. A yield (62%) of product, mp 325.2°C (uncorrected), was obtained.

II. MEASUREMENTS OF SPECTRA

Carbon-13 Fourier-transformed NMR spectra were obtained using a Varian Associates model CFT-20 spectrometer with an 8-mm probe. Complete suppression of the nuclear Overhauser effect was used to characterize the TATB spectrum.

Relaxation times also were used. Nitrogen-15 spectra of TATB in H_2SO_4 were obtained using a Varian Associates XL-100-15-FT spectrometer.

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