

of liquid ammonia was added 8.15 g (0.039 mole) of *p*-( $\beta$ -phenylethyl)benzotrile (IVa) in a little ether to give a bright red solution. After 15 min, 4.22 g (0.020 moles) of 1,4-dibromobutane in ether was added portionwise. About one-fourth of the dihalide solution was required to change the color to orange-brown. After 1 hr, the reaction mixture was worked up to give a mixture of a solid and an oil. The solid was removed by filtration to give 1.46 g of 1,8-diphenyl-2,7-di(*p*-cyanophenyl)octane (XV), mp 121.5–127.5°. After two recrystallizations from ethanol the white solid melted at 135–137.5°. The remaining oil was distilled up to 150° (0.07 mm) to remove starting nitrile IVa. Pot residue was recrystallized from ethanol (Norit), extracted into hot hexane, then recrystallized from acetic acid to give 0.33 g of white solid, mp 112–127°. Recrystallization from ethanol raised the melting point to 120–128°. The total crude yield was 20%. The very wide melting ranges are possibly indicative of a mixture of diastereomers. The nmr spectrum of compound XV exhibited peaks at  $\delta$  6.8–7.5 (multiplet, aromatic), at 2.8 (singlet, benzylic), and at 0.8–1.8 (multiplet, methylenic) with area ratios 17.3:5.8:8.9. The calculated area ratios are 18:6:8. Infrared absorption peaks were found at 2194 cm<sup>-1</sup> (CN), lit.<sup>6a</sup> 2240–2221 cm<sup>-1</sup>; 818 cm<sup>-1</sup> (*para*

substitution), lit.<sup>6b</sup> 860–800 cm<sup>-1</sup>; 750 and 699 cm<sup>-1</sup> (mono-substituted phenyl), lit.<sup>6b</sup> 760–740 and 710–690 cm<sup>-1</sup>.

*Anal.* Calcd for C<sub>24</sub>H<sub>22</sub>N<sub>2</sub>: C, 87.14; H, 6.88; N, 5.96; mol wt, 468.6. Found: C, 86.70; H, 6.91; N, 6.02; mol wt, 449.

**Conversion of *p*-Tolunitrile into Amidine IIa.**—To a suspension of 0.11 mole of sodium amide in 300 ml of liquid ammonia was added 11.72 g (0.1 mole) of *p*-tolunitrile in anhydrous tetrahydrofuran (THF). The liquid ammonia was replaced by THF and the resulting mixture was refluxed for 5–10 min. After cooling (ice bath), 11 g (*ca* 0.1 mole) of 12 *M* hydrochloric acid was added, and the mixture was filtered. The filtrate was acidified with about 15 g of 12 *M* hydrochloric acid to precipitate 6.94 g (41%) of crude *p*-toluamidine hydrochloride, which was reprecipitated twice from methanol with dry ether, mp 213.5–215.5°, lit.<sup>28,29</sup> mp 213° and 215–216°. The amidine hydrochloride was also converted into the picrate, mp 225–228°, lit.<sup>3</sup> mp 219°.

(28) G. Glock, *Ber.*, **21**, 2650 (1888).

(29) P. E. Fanta and E. A. Hedman, *J. Am. Chem. Soc.*, **78**, 1434 (1956).

## The Proton Magnetic Resonance Spectra of $\alpha$ -Chloroacetamidinium Chlorides and Their Corresponding Thiolsulfates (Bunte Salts)<sup>1</sup>

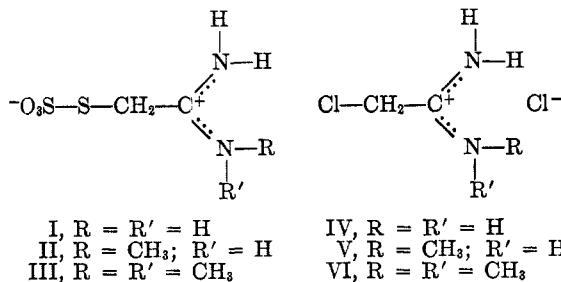
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The nmr parameters of the  $\alpha$ -chloroacetamidinium chlorides, ClCH<sub>2</sub>C(=NH<sub>2</sub><sup>+</sup>)NRR' Cl<sup>-</sup> (R = R' = H; R = H; R' = CH<sub>3</sub>; and R = R' = CH<sub>3</sub>), and the corresponding Bunte salts, <sup>-</sup>O<sub>3</sub>S<sub>2</sub>CH<sub>2</sub>C(=NH<sub>2</sub><sup>+</sup>)NRR', are recorded and the chemical shifts and coupling constants are interpreted in terms of the functional groups present in these molecules. Hindered rotation about the CN bond in these amidinium ions was observed in all these salts and the coalescence temperatures of the NH and NCH<sub>3</sub> protons were determined in a number of solvents. The collapse of these signals is discussed in terms of proton exchange and barriers to rotation. Long-range coupling of the NCH<sub>3</sub> to the methylene group in the N,N-dimethylacetamidinium salts was used to assign the NCH<sub>3</sub> group *cis* and *trans* to the CH<sub>2</sub> group.

This study was initiated at the time when a number of  $\alpha$ -chloroamidinium chlorides and  $\alpha$ -amidinium thiolsulfates (Bunte salts) were synthesized,<sup>3</sup> and it became evident from their nuclear magnetic resonance (nmr) spectra that there existed hindered rotation in the amidinium moiety of these salts. At that time, the then unknown  $\alpha$ -amidinium Bunte salts were presented as zwitterions (I), this assignment being



supported by their infrared spectra.<sup>4</sup> It was hoped that the nmr spectra would support the zwitterionic struc-

ture of these Bunte salts and in general reveal some additional information about hindered rotation in the amidinium cation. Toward this end the nmr spectra of the simplest unsubstituted monomethyl and N,N-dimethylacetamidinium Bunte salts (I–III) were examined in detail in a number of different solvents and at various temperatures and their chemical shifts and coupling constants are compiled in Table I. The nmr spectra of the corresponding  $\alpha$ -chloroamidinium chlorides, IV to VI, served as model compounds since their structure was well established and their nmr data are recorded in Table I also.

Although hindered rotation about a CN bond has not been observed in amidines,<sup>5</sup> this phenomenon is evident in amides, their salts and complexes,<sup>5–7</sup> thio-

*Can. J. Chem.*, **37**, 1260 (1959); R. Mecke and W. Kutzelnigg, *Spectrochim. Acta*, **16**, 1216 (1960); P. Bassignana, C. Cogrossi, G. Polla, and S. Franco, *Ann. Chim.*, (Rome), 1212 (1963)]. In addition, I showed two strong bands near 1030 and 1220 cm<sup>-1</sup> attributable to the thiolsulfate anion from a study of the spectra of sodium and potassium S-alkylthiolsulfates [A. Simon and D. Kunath, *Chem. Ber.*, **94**, 1980 (1961)] and in a number of S-( $\beta$ -aminoethyl)thiolsulfuric acids [T. P. Johnston and A. Gallagher, *J. Org. Chem.*, **27**, 2452 (1962)].

(5) R. C. Neuman, Jr., and L. B. Young, *J. Phys. Chem.*, **69**, 2570 (1965).

(6) For some recent leading references, see (a) T. H. Sidall, III, and W. E. Stewart, *Chem. Commun.*, 612 (1966); (b) A. J. Carty, *Can. J. Chem.*, **44**, 1881 (1966); (c) E. S. Gore, D. J. Blears, and S. S. Danyluk, *ibid.*, **43**, 2135 (1965); (d) S. J. Kuhn and J. S. McIntyre, *ibid.*, **43**, 375 (1965); (e) R. M. Moriarty, *J. Org. Chem.*, **28**, 1296 (1963); (f) L. A. LaPlanche and M. T. Rogers, *J. Am. Chem. Soc.*, **85**, 3728 (1963); (g) R. J. Gillespie and T. Birchall, *Can. J. Chem.*, **41**, 148 (1963).

(7) (a) R. C. Neuman, Jr., and L. B. Young, *J. Phys. Chem.*, **69**, 1777 (1965); (b) W. Walter, G. Maerten, and H. Rose, *Ann.*, **691**, 25 (1966).

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(2) Taken in part from the M.S. thesis of K. R. Sandberg, University of Illinois at the Medical Center, Chicago, Ill., June, 1964.

(3) (a) L. Bauer and T. L. Welsh, *J. Org. Chem.*, **27**, 4382 (1962); (b) L. Bauer and K. R. Sandberg, *J. Med. Chem.*, **7**, 766 (1964).

(4) The infrared spectra (Nujol) of all  $\alpha$ -amidinium thiolsulfates (I) exhibited a characteristic strong band around 1700 cm<sup>-1</sup> which has been assigned to the >C=N< stretching mode [see J. C. Grivas and A. Taurins,

TABLE I

NMR PARAMETERS<sup>a</sup>

Compd	Solvent <sup>b</sup>	Chemical shifts ( $\delta$ ), ppm			$T_{\text{NCH}_3}$ <sup>c</sup>	$T_{\text{NH}}$ <sup>c</sup>
		NCH <sub>3</sub> <sup>c</sup>	CH <sub>2</sub>	NH <sup>d</sup>		
I	DMF	...	4.12	8.95	...	60
				9.16		
	DMSO	...	3.92	8.62	...	~40
				8.85		
				8.49		
H <sub>2</sub> O	...	4.10	8.49	...	...	
TFAA	...	4.30	7.86	...	...	
II	DMF	3.09	4.11	8.96	...	52
				9.26		
				9.60		
	DMSO- <i>d</i> <sub>6</sub>	2.82	3.89	8.68	82	82
				9.00		
				9.40		
	H <sub>2</sub> O	3.07	4.03	8.70	72	<35
	TFAA	3.17	4.30	7.37	>80	...
			7.95			
			8.25			
H <sub>2</sub> SO <sub>4</sub>	2.87	4.00	6.90	120	65	
			7.51			
III	DMF	3.27	4.18	8.86	120	~35
				9.50		
	DMSO	3.06	4.00	8.55	...	...
				8.93		
				8.08		
	H <sub>2</sub> O	3.18	4.20	8.08	>98	<35
			3.32			
	TFAA	3.31	4.35	7.30	...	...
			3.41	7.80		
	H <sub>2</sub> SO <sub>4</sub>	3.01	4.07	...	>130	<35
		3.13				
IV	DMF	...	4.82	9.69	...	53
				9.98		
	DMSO	...	4.64	9.29	...	...
				9.75		
				8.41		
H <sub>2</sub> O	...	...	...	...	...	
D <sub>2</sub> O	...	4.53	...	...	...	
V	DMF	3.12	4.84	9.71	60	76
				10.18		
				10.95		
	DMSO- <i>d</i> <sub>6</sub>	2.95	4.60	9.41	62	~102
				9.93		
				10.60		
	H <sub>2</sub> O	3.03	4.52	8.83	50	<35
	H <sub>2</sub> SO <sub>4</sub>	3.06	4.38	7.00	160	60
			7.28			
			7.61			
VI	DMF	3.37	5.08	9.80	84	56
				10.75		
				9.50		
	DMSO	3.19	4.88	9.50	...	...
				10.28		
				8.40		
	H <sub>2</sub> O	3.20	4.58	8.40	>96	<35
			3.32			
	PA	3.35	4.77	8.56	139	68
				9.03		
			...			
H <sub>2</sub> SO <sub>4</sub>	3.18	4.41	...	175	<35	
			3.26			

<sup>a</sup> All spectra were determined at 60 Mc on a Varian A-60 spectrometer fitted with a variable-temperature probe using tetramethylsilane (TMS) as an internal standard for organic solvents and sodium 3-(trimethylsilyl)propanesulfonate (TPS) as an internal standard for H<sub>2</sub>O, D<sub>2</sub>O, and sulfuric acid solutions. All signals are recorded in parts per million ( $\delta$ ) downfield from the internal standard. It was observed that, on standing in or being heated in concentrated sulfuric acid, TPS gave rise to a new signal  $\delta$  0.33 downfield from TPS. This new signal was readily recognized either by noting the diminution of the TPS signal if its concentration was high enough or by the addition of more TPS when the height of the original peak increased. <sup>b</sup> The solvents were abbreviated as follows: N,N-dimethylformamide, DMF; dimethyl sulfoxide, DMSO; trifluoroacetic acid,

TABLE I (Continued)

TFAA; propionic acid, PA. <sup>c</sup> In compounds II and V, coupling of the methyl group protons to the NH proton was observed in all solvents and measured to be 5.0 cps. <sup>d</sup> All of these signals were very broad and the value reported is the center of the peak. <sup>e</sup> Coalescence temperature was taken as that temperature when the signals merged into a broad signal with no discernible valley between them.

amides,<sup>7</sup> urethans,<sup>8</sup> and amidinium salts.<sup>5,7,9</sup> The inherent difficulties and general unreliability in the measurement of rotational barriers by high-resolution nmr spectroscopy have been discussed by several authors,<sup>5,10,11</sup> and the initial plan for a systematic study of the rotational barriers for the amidinium Bunte salts (I) was abandoned in view of this and the as yet inadequate understanding of the effect of solvent-solute interaction. The importance of a solvent has been demonstrated with N,N-dimethylacetamide where the rotational barrier increases from approximately 12 kcal/mole in neat liquid<sup>12,13</sup> to 24.7 kcal/mole in formamide.<sup>5</sup> It was hoped that large discrepancies in rotational barriers among compounds I to VI could be demonstrated simply by a comparison of coalescence temperatures. However, as will be shown for our systems, solvents play such an extremely important part owing to specific solvent-solute interaction and the actual coalescence temperature observed may not be a measure of the difficulty of rotation about the CN bond.

The purpose of this study was to establish the presence or absence of restricted rotation about the CN bond in the  $\alpha$ -acetamidinium thiolates and to investigate the effect of solvent, acids, and bases on the potential equilibrium between the zwitterionic and charge-free forms of the Bunte salts. Relatively rapid rotation about the CN bond has been shown to occur in N,N-dimethylacetamide<sup>5</sup> since only a single methyl signal was observed even at  $-40^\circ$  in chloroform. The existence of the equilibrium of the salts (I to III) with the free amidine form, HO<sub>2</sub>SCH<sub>2</sub>C(=NH)NRR', and the possibility of cyclic hydrogen-bonded species stabilizing the rotational transition state in the zwitterionic form, both argued for a lower barrier to rotation in these compounds. For comparison, the corresponding  $\alpha$ -chloro compound was selected for study. The effect of an  $\alpha$  substituent and of the associated free anion was not known and information was anticipated from chemical-shift data for these two series of compounds.

## Results and Discussion

Restricted rotation about the CN bond was observed for all the Bunte salts as well as their  $\alpha$ -chloro

(8) T. M. Valega, *J. Org. Chem.*, **31**, 1150 (1966).

(9) (a) G. S. Hammond and R. C. Neuman, Jr., *J. Phys. Chem.*, **67**, 1655, 1659 (1963); (b) J. Ranft and S. Dähne, [*Helv. Chim. Acta*, **47**, 1160 (1964)] reported that tetramethylformamidinium perchlorate in CDCl<sub>3</sub> at 30° showed one sharp signal at  $\delta$  3.35, which became broad at 20°, and was split into two NCH<sub>3</sub> signals (to the base line) by  $-20^\circ$ ; (c) H. E. Ulery [*J. Org. Chem.*, **30**, 2464 (1965)] found that the nmr spectrum of tetramethylformamidinium benzenesulfonate in D<sub>2</sub>O displayed a single CH<sub>3</sub> resonance at  $\delta$  3.16; (d) C. Jutz and H. Amschler [*Chem. Ber.*, **96**, 2100 (1963)] reported only one NCH<sub>3</sub> resonance in N,N'-dimethyl-N,N'-diphenylacetamidinium cation in 2 N HCl at  $\delta$  3.32 (against external TMS).

(10) A. Allerhand, H. S. Gutowsky, J. Jonas, and R. A. Meinzer, *J. Am. Chem. Soc.*, **88**, 3185 (1966).

(11) A. Allerhand and H. S. Gutowsky, *J. Chem. Phys.*, **41**, 2115 (1964).

(12) H. S. Gutowsky and C. H. Holm, *ibid.*, **25**, 1228 (1956).

(13) M. T. Rogers and J. C. Woodbrey, *J. Phys. Chem.*, **66**, 540 (1962).

analogous in organic and acidic media as evidenced by separate NH and NCH<sub>3</sub> resonances.

**Analysis of Chemical-Shift Data.**—A comparison of the tabulated chemical shifts presented in Table I for the two series of compounds revealed several differences due to the effect of different  $\alpha$  substituents on the signal positions in the same solvent. For example, in all instances, the methylene signal for the  $\alpha$ -chloroacetamidinium cation was downfield from the methylene group signal of the corresponding thiosulfate, the difference being 0.34 to 0.90 ppm. This behavior is easily explained by the greater deshielding ability of the adjacent chlorine atom compared to the negatively charged thiosulfate group. The substituent shift of the methylene group protons was most pronounced in organic solvents (0.7 to 0.9 ppm) and decreased considerably in aqueous solution where rapid proton exchange is occurring or in strongly acidic media where protonation of the thiosulfate moiety would remove the negative charge on that group (to 0.34 to 0.49 ppm).

Somewhat surprisingly, the NH resonances showed greater differences between the two series of compounds. These protons are not in rapid exchange in organic or acidic solvents since the nonequivalent NH protons exhibited individual resonances. The internal shift between NH signals was greater for the chloro compounds and also appear significantly farther downfield (up to 1.35 ppm) than for the thiosulfate compound in the same solvent. The smaller separation of NH resonances for the thiosulfate salt can be rationalized by a consideration of the likely preferred molecular conformation that is dictated by the closest approach of positive and negative centers. Such a conformation requires the negative oxygens of the thiosulfate moiety to be centered above the positive and planar amidinium group. This presents a somewhat uniform field to the amidinium protons.

Comparing this with the likely preferred conformation of the  $\alpha$ -chloro compound in which the chloro group is two atoms closer to the amidinium portion of the molecule, it is seen that dipolar attraction would require the chlorine atom to be skewed or even coplanar with the amidinium group. This orientation causes the  $\alpha$ -chloro substituent to be closer to one of the amidinium nitrogen and the associated dipolar and anisotropic effects of the chlorine to be felt quite differently by the protons residing on the amidinium nitrogens, thus accounting for the greater separation of signals.

The large downfield substituent shift of the NH resonances in the  $\alpha$ -chloro compounds cannot be explained in the same way as the methylene proton signal positions since this would require the inductive effect to operate over four bonds and five bonds in the case of the N-methyl compounds in which the methyl signals for the chloro compounds in organic or acidic solvents showed small downfield substituent shifts also.

It seems more probable that the  $\alpha$  substituent exerted its influence on these resonances by the differences in spatial requirements discussed above. This presents to these nuclei grossly different group anisotropies and dipolar interactions.

The upfield position of the NH signals in the thiosulfate series of compounds appears to rule out the possibility of this zwitterionic species forming cyclic hydrogen-bonded structures since this would argue for

additional *deshielding* of the NH protons in this compound compared with its chloro counterpart where no such structures are possible.

No conclusions can be based on the data obtained for the NH signal in aqueous media since the NH protons are in rapid exchange and only a single, broad signal was obtained with its position dictated by the exchange process.

**Unsubstituted Amidinium Salts.**—In the unsubstituted compounds I and IV it was not possible to assign the changes in the spectra with temperature to rotational effects or to hydrogen exchange, since no large differences in behavior were seen. At room temperature two NH resonances occurred in both compounds, establishing the existence of a rotational barrier to the CN bond. These signals coalesced in the same temperature region (50–60°).

**Monomethylamidinium Salts.**—Since the NH signals were broad, the methyl signals in the N-methyl salts were used to monitor restricted rotation about the CN bond and exchange processes. The NCH<sub>3</sub> signal in the monomethylamidinium salts II and V consisted of a doublet owing to coupling with the proton on the same nitrogen ( $J \approx 5$  cps).<sup>14</sup> In D<sub>2</sub>O, these NCH<sub>3</sub> protons appeared as singlets in II and V which indicated only one type of NCH<sub>3</sub> group. If restricted rotation existed in II and V, and the presence of three different NH signals suggest this, one might conclude that the NCH<sub>3</sub> occupied one position preferentially. However, no such distinction could be made between what Hammond<sup>9a</sup> called the "inside" (II and V, R = CH<sub>3</sub>) and "outside" (II and V, R' = CH<sub>3</sub>) positions.

The presence of only the single NCH<sub>3</sub> signal but three NH signals is explained by the difference the rate of rotation about the CN bond has on protons having magnetically similar sites (for NCH<sub>3</sub> protons the chemical-shift difference being only 0.15 ppm) and significantly different sites (for the NH protons the chemical-shift differences were ca. 0.50 ppm).

Cooling the monomethylamidinium compounds (II and V) in DMSO and H<sub>2</sub>O (to 15 and 0°, respectively), failed to show separate methyl resonances. On heating II and V in various solvents, the NH protons coalesced before the NCH<sub>3</sub> doublet. In strongly acid medium, it would be expected that the exchange of the proton on the NCH<sub>3</sub> nitrogen of II and V would be slower and the collapse of the CH<sub>3</sub> doublet would be expected to occur at higher temperatures. When 0.5 ml of an aqueous solution of II or V was heated in an nmr tube to the point where the NCH<sub>3</sub> signal coalesced and then treated with 1 drop of very dilute mineral acid (e.g., 0.01 N HCl), the doublet was restored instantly and collapsed only at still higher temperatures. It was felt this effect would be observed at its limit in concentrated sulfuric acid. Thus, this NCH<sub>3</sub> doublet finally coalesced at 160° in V and at 120° in II. Care had to be exercised in studying these effects in concentrated sulfuric acid to avoid decomposition of the solutes. It was found that N-methyl- $\alpha$ -chloroacetamidinium chloride (V) was stable in hot, concentrated sulfuric acid to 160°, but the corresponding Bunte salt (II) decomposed on prolonged heating in sulfuric acid.

(14) For a discussion of the spin-spin interaction of the RNHCH<sub>3</sub> system, see I. D. Rae, *Australian J. Chem.*, **19**, 409 (1966); M. Freifelder, R. W. Mattoon, and R. W. Kriese, *J. Phys. Chem.*, **69**, 3645 (1965); *J. Org. Chem.*, **31**, 1196 (1966).

Thus, the high-temperature required for the collapse of the  $\text{CH}_3$  signal in sulfuric acid is interpreted to be a consequence of the slower rate of exchange of the NH proton on the  $\text{NCH}_3$  nitrogen. The coalescence temperatures reported in aqueous or organic media are therefore not a consequence of hindered rotation but of the rate of proton exchange.

**N,N-Dimethylamidinium Salts.**—In the two N,N-dimethylamidinium salts (III and VI) restricted rotation about the CN bond was clearly discernible since the spectra in  $\text{D}_2\text{O}$  and other solvents revealed two  $\text{NCH}_3$  signals. At elevated temperatures, the NH peaks coalesced at considerably lower temperatures than the  $\text{CH}_3$  signals, reflecting an increase in proton exchange rate. In concentrated sulfuric acid, the barrier to rotation about the CN band in VI was considerable since the two  $\text{CH}_3$  peaks did not merge until  $175^\circ$ . Unfortunately, the coalescence temperature of the  $\text{NCH}_3$  signals of the corresponding Bunte salt (III) could not be measured in sulfuric acid since this salt decomposed above  $130^\circ$  as witnessed by the appearance of an additional peak at  $\delta$  3.71 which remained on cooling, although the chemical shifts of the other signals remained unchanged.

The coalescence temperature of the two  $\text{CH}_3$  signals of N,N-dimethyl- $\alpha$ -chloroacetamidinium chloride (VI) in DMF at  $84^\circ$  seemed unusually low, particularly since in the corresponding Bunte salt (III) this event did not occur until  $120^\circ$ . It was suspected that DMF might compete with the amidine for the acid present. To test such a hypothesis a 0.5-ml solution of VI in DMF was treated with 5 drops of a saturated solution of HCl gas in DMF, and then the  $\text{NCH}_3$  signals did not coalesce until  $130^\circ$ .

This finding is significant in view of the discussions in the literature<sup>5,10,11</sup> concerning possible sources of errors in determining barriers of rotation. That such a large change can occur with traces of acidity, further emphasizes the difficulties in the high-resolution nmr method of determining rotational barriers. The pronounced effect observed here is undoubtedly a consequence of the specific involvement of the solvent in this system, as suggested by Neuman,<sup>5</sup> being destroyed by establishing a rapid equilibrium with the added acid.

The effect of acid on the coalescence temperature of the dimethyl compounds in aqueous solution could not be determined since in neutral water solution these temperatures already exceeded  $98^\circ$ .

It was also of interest to study the effect of aqueous bases on the spectra in  $\text{H}_2\text{O}$  of these N,N-dimethylamidinium salts (III and VI). The addition of catalytic quantities of base caused the collapse to a central singlet of the two  $\text{NCH}_3$  signals without affecting the chemical shift of the  $\text{CH}_2$  protons or the appearance of new signals. The quantity of base required for this spectral change, although small, was dependent on the strength of the base. For example, coalescence of the  $\text{NCH}_3$  peaks of VI in  $\text{D}_2\text{O}$  occurred with only 0.005 equiv of NaOH (0.01 *N*) but required 0.08 equiv of pyridine and 0.14 equiv of sodium acetate. Neutralization of the added base with hydrochloric acid caused the immediate regeneration of the original methyl signals.

The action of the base is to establish an equilibrium with the free amidine species in which the methyl groups are now equivalent since rotation about the CN bond in the free base is relatively unhindered.<sup>5</sup>

In addition to catalyzing a proton exchange reaction which resulted in the reported methyl signal behavior, the added base also caused the exchange of the methylene protons for deuterium if the experiment was carried out with  $\text{D}_2\text{O}$  as the solvent in place of  $\text{H}_2\text{O}$ . This indicates, as might be expected, that the protons on the carbon adjacent to the amidine function are "active" hydrogens. Again, the behavior of the two types of compounds was the same and the zwitterionic structure of one series seems to have had little behavioral consequence.

Although the addition of base to III caused the immediate collapse of the  $\text{NCH}_3$  signals, the quantity required was greater for the thiolsulfate salt (0.05 equiv of NaOH) than for the chloro salt. Furthermore pyridine would not bring about the merger of the signals for the thiolsulfate salt. After the collapse of the methyl signals with NaOH a chemical reaction occurs<sup>15</sup> which causes the slow reappearance of the two methyl group signals.

A number of previous reports in the literature<sup>7,16-18</sup> have dealt with the magnitudes of *cis* and *trans* coupling across carbon-nitrogen partial double bonds. Similar long-range coupling is found in III and VI based on the differences in widths at half-height for the two  $\text{NCH}_3$  resonances. The high-field  $\text{NCH}_3$  signal had a half-width of  $1.0 \pm 0.05$  cps while the low-field methyl had a half-width of  $0.60 \pm 0.05$  cps. If the methylene group protons in III and VI are exchanged for deuterium (see above), the half-widths suffer a reduction to 0.6 and 0.5 cps for the upfield and downfield signals, respectively. Since the *trans*-homoallylic type coupling has been reported larger than the *cis*, the upfield methyl signal is assigned to the methyl group *trans* to the methylene group in these compounds. This follows the same pattern reported for amides<sup>7,16-18</sup> and for N,N-dimethylacetamidinium chloride.<sup>7</sup>

(15) When an aqueous (colorless) solution of III was treated with 0.05 equiv of 0.01 *N* NaOH at  $35^\circ$ , an orange-red solution was obtained immediately. Further small additions of 0.01 *N* NaOH continued to deepen the color of the solution to purple and after about 0.5 equiv of NaOH had been added, small additional signals commenced to emerge, which indicated that definite chemical changes were taking place. In an experiment in which an aqueous solution of III was treated at once with 0.75 equiv of NaOH and permitted to stand 0.5 hr, acidification produced a deep orange-brown solution which showed the  $\text{CH}_2$  and  $\text{NCH}_3$  of III but significantly two additional  $\text{NCH}_3$  signals (about 5%) at  $\delta$  3.20 and 3.29. Furthermore, a solution of III containing 3 equiv of NaOH turned green and its nmr spectrum clearly indicated that reactions were taking place but attempts to isolate definite products from this or related reaction mixtures have proved to be futile thus far. These observations are quite similar to those previously reported for the basic hydrolysis of Bunte salts which is known to be quite complex [B. Milligan and J. M. Swan, *Rev. Pure Appl. Chem.*, **12**, 72 (1962)] as revealed by a detailed study on S-1-anthraquinonethiolsulfuric acid [H. Z. Lecher and E. M. Hardy, *J. Org. Chem.*, **20**, 475 (1955)]. The latter authors obtained deeply colored solutions and postulated that the immediate product from the basic hydrolysis of a Bunte salt is a sulfenic acid, although they could not isolate it or its salts.

(16) V. J. Kowalewski and D. G. de Kowalewski, *J. Chem. Phys.*, **32**, 1272 (1960); *Arkiv Kemi*, **16**, 373 (1960).

(17) The largest coupling constant of the  $\text{NCH}_2$  proton in N,N-dialkylformamides was also assigned to the *trans* (*cis* to  $\text{C}=\text{O}$ ) N-alkyl group, although the chemical shifts of the *cis*- and *trans*-alkyl groups to the  $\text{C}=\text{O}$  inverted [A. G. Whittaker, D. W. Moore, and S. Siegel, *J. Chem. Phys.*, **68**, 3431 (1964)].

(18) B. B. Wayland, R. S. Drago, and H. F. Henneke, *J. Am. Chem. Soc.*, **88**, 2455 (1966).