be due either to a comparatively slower rate of elimination in this protic solvent or to a different mode of hydride addition, perhaps analogous to that occurring in the reduction of unsaturated ketones by sodium borohydride in ethanol and pyridine wherein 1,4 addition is favored in the latter solvent.[9,10]

Experimental Section

Melting points are uncorrected. Aromatic amines used as starting materials were commercially available. Infrared spectra were obtained using a Perkin-Elmer Model 21 infrared spectrophotometer. Mass spectra were recorded on an Hitachi Perkin-Elmer RMU-5E mass spectrometer. An Hitachi A-60D spectrometer was used to obtain nmr spectra.

Arylaminomethylsuccinimides (I).—These compounds were prepared by the method of Winstead, *et al.*[4] A solution of 0.1 mol of aromatic amine, 11.9 g of succinimide, and 9.1 ml of 37% aqueous formaldehyde in 100–150 ml of ethanol was refluxed for 2–5 hr (except in those instances where the product precipitated during reflux for which shorter periods of time were used). Cooling usually resulted in precipitation of the desired imide. If this did not occur, evaporation of the ethanol and trituration of the residue with water produced crystalline material.

***N*-Methyl Aromatic Amines (II).**—A warm solution of I in DMSO (2–3 ml of DMSO/g of I) was treated, during 5–10 min, with an equimolar amount of sodium borohydride. An exothermic reaction resulted but was easily controlled, the temperature not rising above *ca.* 100°. After heating on the steam bath for 10–15 min after completion of the borohydride addition, the reaction mixture was poured into cold water. The resulting mixture was extracted three times with ether. The combined ether extracts were dried; the ether was evaporated and the residual oil distilled. (Solid material was recrystallized.) In the case of water-soluble amines, the reaction mixture was poured into 10 *N* KOH instead of water.

***N*-(4-Carbethoxyanilinomethyl)-4-hydroxybutyramide (III).**—A solution of 2.7 g. (0.01 mol) of I (Ar = *p*-carbethoxyphenyl) and 0.42 g (0.011 mol) of sodium borohydride in 40 ml of ethanol was refluxed for 2.5 hr. The ethanol was evaporated under reduced pressure, and the residue was slurried in 50 ml of 3 *N* NH_4OH. The resulting solid was filtered free, dried, and recrystallized from toluene: mp 112–114°; mass spectrum *m/e* 280 (M^+); ir (KBr) 5.9 (ester carbonyl) and 6.05 μ (amide carbonyl).

Anal. Calcd for $C_{14}H_{20}N_2O_4$: C, 59.98; H, 7.19; N, 9.99. Found: C, 60.01; H, 7.12; N, 9.92.

***N*-(*N*-Methyl-*p*-toluidinomethyl)-5-hydroxypyrrolidin-2-one (VI).**—A warm solution of 11.6 g (0.05 mol) of V[4] in 20 ml of DMSO was treated, during 10 min, with 1.9 g (0.05 mol) of sodium borohydride. Internal temperature rose to 85°; stirring was continued for 0.5 hr after addition of the borohydride was complete. The reaction mixture was poured into cold water which was then extracted three times with methylene chloride. The combined methylene chloride extracts were dried. The methylene chloride was evaporated and the residue (8.0 g) recrystallized from benzene to yield VI: mp 121–122°; mass spectrum *m/e* 234 (M^+); ir (KBr), 6.0 μ (carbonyl); nmr (DMSO-d_6) δ 2.28 (s, 3, aromatic CH_3), 1.65–2.4 [m, 4, $-C(=O)CH_2CH_2$], 3.0 (s, 3, NCH_3), 4.68 (d, 1), and 5.12 (d, 1) (J_{gem} = 13 Hz, NCH_2N), 5.15 (m, 1, methine H), 6.05 (d, 1, *J* = 6 Hz, OH), 6.8–7.2 (m, 4, phenyl). Addition of D_2O caused the disappearance of the doublet at δ 6.05.

Anal. Calcd for $C_{13}H_{18}N_2O_2$: C, 66.44; H, 7.74; N, 11.96. Found: C, 66.33; H, 7.58; N, 11.64.

Registry No.—I-1, 13314-99-3; I-2, 38359-09-0; I-3, 38359-10-3; I-4, 38359-11-4; I-5, 38359-12-5; I-6, 17647-08-4; I-7, 38359-14-7; I-8, 38359-15-8; I-9, 38359-16-9; I-10, 18932-40-6; I-11, 38359-18-1; I-12, 38359-19-2; I-13, 38359-20-5; II-1, 100-61-8; II-2, 932-96-7; II-3, 3154-18-5; II-4, 6832-87-7; II-5, 13021-13-1; II-6, 10541-82-9; II-7, 4714-62-9; II-8, 104-96-1; II-9, 38359-26-1; II-10 (mono HCl), 27433-30-3; II-11 (*x*-oxalate), 38359-27-2; II-12, 38359-28-3; II-13, 2018-90-8; III, 38359-29-4; V, 38359-30-7; VI, 38359-31-8.

Acknowledgment.—The author thanks Mr. Charles Lamphere for expert technical assistance and Professor D. S. Kemp for helpful discussions.

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(9) W. R. Jackson and A. Zurqiyah, *J. Chem. Soc.*, 5280 (1965).

(10) S. B. Kadin, *J. Org. Chem.*, **31**, 620 (1966).

An ESCA Study of the Sulfur–Nitrogen Bond in Sulfimides

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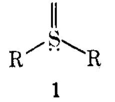
Received October 24, 1972

The O(1s), N(1s), and S(2p) binding energies have been measured from the X-ray photoelectron spectra of the sulfoxide, sulfone, *N*-tosylsulfimide, and *N*-tosylsulfoximide derivatives of benzyl methyl sulfide. The sulfur(IV) binding energy in the *N*-tosylsulfimide is found to be 0.4 eV larger than that in the sulfoxide. The sulfur atom in the sulfimide therefore carries a larger positive charge, and the S(IV)–NTs bond has a larger contribution from the semipolar form than in the sulfoxide. The data also indicate that the parent sulfimide bond, S(IV)–NH, is electronically very similar to the S–O bond in the sulfoxide.

The nature of the sulfur–nitrogen bond in sulfimides, like that of the sulfur–oxygen bond in sulfoxides, has perplexed chemists for several decades.[2,3] Two models have been proposed to explain the properties of these functionalities, a covalent form (1) and a semipolar form (2). The semipolar structure 2 conforms to the octet rule, whereas the covalent formulation does not. The double bond in 1 arises from donation of a 2p electron pair on oxygen or nitrogen to an empty 3d orbital on sulfur. The actual nature of the sulfoxide and sulfimide bonds lies between the canonical extremes, but no general agreement has been reached as to which form should be considered dominant. Recently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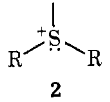
2

X = O, NH, NTs

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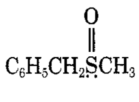
[1] (a) National Science Foundation Trainee, 1968–1969. (b) This work was supported by the National Science Foundation (Grant No. GP-22942 and GP-34259X) and by the Advanced Research Projects Agency of the Department of Defense through the Northwestern University Materials Research Center. The authors wish to thank Dr. J. E. Lester for useful discussions during the course of this work.

[2] For leading references to the sulfimide question, see (a) Á. Kucsman, F. Ruff, and I. Kapovits, *Tetrahedron*, **22**, 1575 (1966); (b) K. Tsujihara, N. Furukawa, and S. Oae, *Bull. Chem. Soc. Jap.*, **43**, 2153 (1970); (c) N. Furukawa, K. Harada, and S. Oae, *Tetrahedron Lett.*, 1377 (1972).

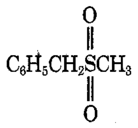
[3] For a review of the sulfoxide problem, see C. C. Price, *Chem. Eng. News*, 58 (Nov 30, 1964).

Lindberg, *et al.*,[4] approached the sulfoxide problem through the measurement of inner-shell electron binding energies by X-ray photoelectron spectroscopy. Atomic charges calculated for the two extreme structures (**1** and 2) were compared with the value determined from the measured binding energy, and the ionic character of the bond was found to correspond approximately to a 60% contribution from the covalent form **1**. These authors concluded that the best representation of the bond is a resonance hybrid of the two forms, but, as a single representation, the double-bond form (**1**) is to be preferred.

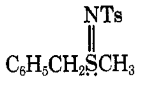
We have recently been engaged in studies of the conformational properties of cyclic sulfimides[5] and became interested in studying the nature of the sulfur–nitrogen bond in these compounds. Ir, uv, nmr, and crystallographic data have previously been brought to bear on this question.[2] Because of the success of the photoelectron study on the sulfoxide functionality,[4] we have taken a similar approach in the present work. The derivatives of benzyl methyl sulfide were chosen for this investigation by reason of their stable and crystalline nature: the sulfoxide (**3**), the sulfone (**4**), the *N*-tosylsulfimide (**5**), the sulfoximide (**6**), and the *N*-tosylsulfoximide (**7**). The unsubstituted sulfimide (**8**) was also prepared, but it decomposed on X-irradiation. As a result of these studies, we report that the sulfimide bond with the tosyl group on nitrogen is more polar than the sulfoxide bond and that the best single representation may be the semipolar form (2). Furthermore, the parent sulfimide bond (S–NH) is found to be very similar in polarity to the sulfoxide bond.


$\mathrm{C_6H_5CH_2}\overset{\overset{\displaystyle O}{\|}}{S}\mathrm{CH_3}$

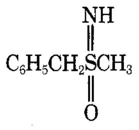
3


$\mathrm{C_6H_5CH_2}\underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle O}{\|}}{S}}\mathrm{CH_3}$

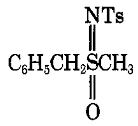
4


$\mathrm{C_6H_5CH_2}\underset{\cdot\cdot}{\overset{\overset{\displaystyle NTs}{\|}}{S}}\mathrm{CH_3}$

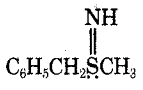
5


$\mathrm{C_6H_5CH_2}\underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle NH}{\|}}{S}}\mathrm{CH_3}$

6


$\mathrm{C_6H_5CH_2}\underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle NTs}{\|}}{S}}\mathrm{CH_3}$

7


$\mathrm{C_6H_5CH_2}\underset{\cdot\cdot}{\overset{\overset{\displaystyle NH}{\|}}{S}}\mathrm{CH_3}$

8

Results and Discussion

The photoelectron spectra were induced with aluminum K_α X-radiation with a quantum energy of 1486.6 eV. All measurements were made on solid samples prepared by crushing the powders onto an aluminum support. The spectra were recorded at −100° to prevent sublimation and were calibrated by reference to the C(1s) line at 285.0 eV (see Experimental Section). Binding energies with respect to the Fermi level (BE_f) may be calculated for each nucleus from the energy of the exciting radiation ($h\nu$), the measured kinetic energy of the ejected electrons (KE_{sp}), and the work function of the spectrometer (φ_{sp} = 4.6 eV) (eq 1). In practice, the BE for the nucleus of interest was derived from eq 2, which is obtained by subtracting the eq 1 that contains the C(1s) values for BE and KE from the analogous equation with parameters for the desired nucleus. The parameters $h\nu$ and φ_{sp} thereby drop out.

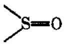
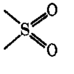
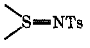
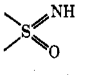
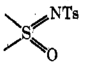
$$BE_f = h\nu - KE_{sp} - \varphi_{sp} \qquad (1)$$

$$BE_f = KE_{C(1s)} - KE + 285.0 \qquad (2)$$

The O(1s), N(1s), and S(2p) binding energies for compounds **3–7** are listed in Table I. The oxygen and sulfur binding energies are in excellent agreement with published results on other compounds containing the sulfoxide and sulfone functionalities.[4] A difference between line positions of 0.2 eV is easily discernible. The nonequivalent S(VI) sulfurs and the nonequivalent oxygens in the sulfoximide **7** display identical chemical shifts. In the sulfimide **5**, however, the imide sulfur [S(IV)] and the sulfonyl sulfur [S(VI)] have chemical shifts that differ by 1.4 eV.

TABLE I

BINDING ENERGIES FOR DERIVATIVES OF BENZYL METHYL SULFIDE[a,b]

Compd	O(1s)	N(1s)	S(2p)
 (**3**)	532.0		166.2
 (**4**)	532.2		168.2
 (**5**)	532.1	398.7	166.6,[c] 168.0[d]
 (**6**)	532.2	398.7	168.1
 (**7**)	532.2	399.1	168.4[d,e]

[a] Units of eV; absolute values are probably ±0.5 eV, depending on the reliability of the reference peak, but relative values are ±0.1 eV. [b] Relative to a C(1s) value of 285.0 eV (reference peak). [c] Binding energy for S(IV). [d] Binding energy for S(VI). [e] There are two nonequivalent S(VI) sulfurs in this molecule, with identical binding energies.

In our discussion of these results, we shall first approach the problem in a qualitative fashion, and then make a brief quantitative examination of some of the data. The S(2p) binding energies offer the most useful set of data, since sulfur is present as the central atom in all members of the series under consideration (**3–8**). In the qualitative approach, the BE is taken simply as a measure of the charge on the atom of interest.[4] Thus the increase of 2 eV on going from the sulfoxide **3** to the sulfone **4** indicates a greater amount of positive charge on the sulfur atom in the latter molecule.

The BE for S(IV) in the *N*-tosylimide **5** is clearly larger (0.4 eV) than that in the sulfoxide. The increase in binding energy corresponds to a more pronounced positive charge on sulfur and to a greater contribution from the semipolar form 2. This increase in importance of the semipolar form is primarily due to the presence of the *N*-tosyl group, which stabilizes a negative charge on nitrogen by induction, if not by resonance. Although we could not obtain measurements on the unsubstituted sulfimide **8**, the sulfoximides **6** and **7** provide a useful comparison. In this pair of compounds, replacement of N–H with N–Ts results in an increase in the S(2p) BE of ∼0.3 eV. Thus an *N*-tosyl group raises the

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[4] B. J. Lindberg, K. Hamrin, G. Johansson, U. Gelius, A. Fahlman, C. Nordling, and K. Siegbahn, *Phys. Scripta*, **1**, 286 (1970).

[5] J. B. Lambert, C. E. Mixan, and D. S. Bailey, *J. Amer. Chem. Soc.*, **94**, 208 (1972); J. B. Lambert, D. S. Bailey, and C. E. Mixan, *J. Org. Chem.*, **37**, 377 (1972).

polarity of the S–N bond, placing a larger positive charge on sulfur. Furthermore, the S(2p) BE of the sulfone **4** (168.2) is essentially the same as that for the sulfoximide **6** (168.1). The oxide group and the unsubstituted imide group (NH) therefore place similar charges on sulfur. From these observations, we can conclude that the S–NTs bond is more polar than the S–O bond (larger contribution from **2**), but there is little difference in polarity between the S–NH and S–O bonds.

Some information can also be obtained from the N(1s) binding energies.[6] The amount of negative charge on the nitrogen atom in the *N*-tosylsulfoximide **7** is lower (BE 0.4 eV higher) than that in the parent sulfoximide **6**. Despite the higher polarity of the S–N bond in **7**, the electron-withdrawing nature of the attached tosyl group leaves a smaller negative charge on nitrogen. A comparison of the sulfimide **5** and the sulfoximide **7** shows that introduction of the oxygen atom on sulfur reduces the negative charge on nitrogen.

To analyze the nature of the S(IV)–N bond quantitatively, the atomic charge parameter (q) must be calculated for sulfur in the two extreme structures **1** and **2**, and compared with the value derived from experiment.[4] The charge parameter is the sum of the formal charge (Q) on the atom in question and the contribution (I) from the partial ionic character of all the attached bonds (eq 3). The ionic bond component is expressed

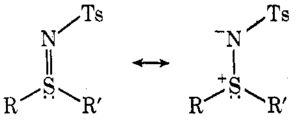
$$q = Q + \Sigma I \tag{3}$$

as a function of the electronegativity difference, adjusted for formal charge, between the atoms of the bond (eq 4).[4] These quantities are available from the

$$I = 1 - e^{-0.25(\chi_A - \chi_B)^2} \tag{4}$$

work of Siegbahn, *et al.*,[4,6] following Pauling. Calculations for the *N*-tosylsulfimides[7] give an atomic charge q at S(IV) of +0.12 for the covalent form **1** and +0.97 for the semipolar form **2**. Reference to Siegbahn's correlation between atomic charge and the S(2p) binding energy[4] indicates that the observed value of 166.6 eV corresponds to a q of +0.6. By comparison of this value with the two extremes, the bond can be described as about 45% covalent. Analogous calculations for sulfoxides[4] gave an estimate of 60% covalency for the S–O bond. The quantitative approach therefore is in agreement with the qualitative approach that the S–NTs bond has a higher polarity than the S–O bond of sulfoxides.

Summary.—Photoelectron studies of *N*-tosylsulfimides have indicated that the S–NTs bond is more polar than the S–O bond in sulfoxides. The dual structures of eq 5, however, provide the best representation. Withdrawal of negative charge from nitrogen into the tosyl group is probably the most important factor contributing to the enhancement of the semipolar nature of the S–NTs bond. Oae and coworkers[2c] have found that *N*-tosylsulfimides racemize considerably more rapidly than sulfoxides. Their explanation of the higher barrier to sulfur inversion, in agreement with our conclusions, is that the sulfoxide bond has greater covalency than the *N*-tosylsulfimide bond. The photoelectron spectra have also demonstrated that the sulfimide bond (S–NH) and the sulfoxide bond (S–O) are very similar in polarity.



(5)

Experimental Section

Melting points were determined in a Hershberg apparatus and are uncorrected. ESCA (electron spectroscopy for chemical analysis) spectra were induced with aluminum K_α X-radiation with a quantum energy of 1486.6 eV and were recorded on an AEI ES-100 electron spectrometer.[8] Binding energies were calculated by means of eq 2. The value of BE_f for the C(1s) reference peak (285.0 eV) has been established previously.[9] The close agreement between our values for the O(1s) and S(2p) binding energies and those measured previously for similar sulfoxides and sulfones[4] indicates that the reference materials used in the two studies must have similar C(1s) binding energies. Because the carbon constitution of molecules **3–7** is constant (phenyl, methylene, methyl), the C(1s) binding energy is probably identical for all members of the series. Therefore, reliability of the reported values (Table I) is limited not by differences in referencing but by the standard deviation of the measurement (0.1 eV). We therefore consider that the relative values reported in Table I are reliable to ±0.1 eV, but the absolute values, which depend on the accuracy of the 285.0-eV figure, may be reliable only to ±0.5 eV. The significant conclusions of this study are based on relative values. Elemental analyses were carried out by Miss H. Beck, Analytical Services Laboratories, Department of Chemistry, Northwestern University. The preparation of the derivatives of benzyl methyl sulfide paralleled those previously reported for thiane derivatives.[5] Therefore experimental details are omitted, and only physical properties are reported herein. The nmr data are collected in Table II.

TABLE II

NMR DATA FOR THE DERIVATIVES OF BENZYL METHYL SULFIDE[a]

Compd	Arom[b]	CH_2[b]	CH_3	$ArCH_3$	NH
3	7.35	4.00 (13.0)	2.45		
5	7.20, 7.32 (8.0)	4.10 (12.0)	2.50	2.33	
6	7.37	4.30 (13.0)	2.90		2.65
7	7.40, 7.50 (8.0)	4.70[c]	3.03	2.40	

[a] Chemical shifts are in δ in parts per million from TMS values; coupling constants (in parenthesis) are in hertz; the solvent is CCl_4. [b] The δ values correspond to centers of multiplets. [c] J_{AB} was not observable.

Benzyl methyl sulfide was obtained from Aldrich Chemical Co.

Benzyl methyl sulfoxide (**3**) had mp 57–58°. *Anal.* Calcd for $C_8H_{10}OS$: C, 62.34; H, 6.49. Found: C, 62.40; H, 6.50.

Benzyl methyl sulfone (**4**) was obtained as a gift from Dr. F. G. Bordwell of Northwestern University.

***N*-Tosylbenzylmethylsulfimide** (**5**) had mp 167–168°. *Anal.* Calcd for $C_{15}H_{17}NO_2S_2$: C, 58.63; H, 5.54; N, 4.56. Found: C, 58.29; H, 5.46; N, 4.57.

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(6) R. Nordberg, R. G. Albridge, T. Bergmark, U. Ericson, J. Hedman, C. Nordling, K. Siegbahn, and B. J. Lindberg, *Ark. Kemi*, **28**, 257 (1968).

(7) For details of the calculation, see C. E. Mixan, Ph.D. Dissertation, Northwestern University, 1972.

(8) We are grateful to the National Science Foundation for an equipment grant that aided the purchase of this instrument.

(9) W. E. Morgan, W. J. Stec, R. G. Albridge, and J. R. Van Wazer, *Inorg. Chem.*, **10**, 926 (1971); U. Gelius, P. F. Hedén, J. Hedman, B. J. Lindberg, R. Manne, R. Nordberg, C. Nordling, and K. Siegbahn, *Phys. Scripta*, **2**, 70 (1970).

Benzylmethylsulfoximide (6) had mp 81–82°. *Anal.* Calcd for $C_8H_{11}NOS$: C, 56.80; H, 6.51; N, 8.28. Found: C, 56.41; H, 6.35; N, 8.32.

***N*-Tosylbenzylmethylsulfoximide** (7) had mp 128–130°. *Anal.* Calcd for $C_{15}H_{17}NO_3S_2$: C, 55.73; H, 5.26; N, 4.33. Found: C, 56.06; H, 5.29; N, 4.21.

Benzylmethylsulfimide (8) was prepared by the method used previously[5] for thiane 1-imide, but the compound decomposed under X-radiation.

Registry No.—3, 824-86-2; **4,** 3112-90-1; **5,** 38401-37-5; **6,** 38401-38-6; **7,** 38401-39-7.

Substituted Ammonium Salts of Benzothiazoline-2-thione. Nuclear Magnetic Resonance Studies of Ion Pairs in Polar and Nonpolar Media[1]

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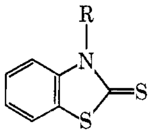
Received May 18, 1972

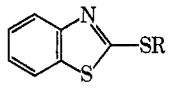
The primary and secondary ammonium salts of benzothiazole-2-thiol exist mainly in the benzothiazoline-2-thione structure. In nonpolar aprotic solvents the substituted ammonium salts of benzothiazoline-2-thione exist in intimate ion pairs. In polar solvents these salts dissociate into solvent-separated ion pairs. The effect of charge separation increases the electron densities around the thiazoline ring, as indicated by the chemical shifts of the aromatic ring hydrogens.

A previous paper[2] described the nmr shifts for the aromatic protons of S- and N-substituted derivatives of benzothiazoline-2-thione and benzothiazole-2-thiol.

This paper reports recent nmr and uv absorption studies on several primary and secondary alkylammonium salts of benzothiazole-2-thiol (Ib), the so-called 2-mercaptobenzothiazole or "MBT" of the rubber industry, which, however, are shown to be salts of benzothiazoline-2-thione, structure Ia.



Ia, R = H
IIa, R = alkylammonium



Ib, R = H
IIb, R = alkylammonium

The uv absorption spectra of the ammonium salts showed a strong absorption band at 320 mμ attributed to the thione structure (Ia) and a band which was present when the spectra were recorded in either polar or nonpolar solvents (Table I). It is concluded, then, that these compounds are salts of benzothiazoline-2-thione, not salts of benzothiazole-2-thiol as traditionally conceived.

The nmr spectra of the primary ammonium salts (IIa, IIb) (example, R = H; R′ = isopropyl) of benzothiazoline-2-thione in a relatively nonpolar medium, such as deuteriochloroform, showed a strong absorption peak at about 265 Hz (4.41 ppm), which was attributed to the ammonium protons of the alkylammonium ion. In addition, a single envelope, AB type splitting pattern at 438 Hz (7.30 ppm) was attributed to the 4, 5, 6, 7 aromatic protons (see Figure 1), indicating the benzothiazoline-2-thione structure by analogy with the earlier results.[3,4] The nmr spectra of the secondary ammonium salts (IIa) (examples, R = ethyl; R′ = ethyl and R = isopropyl; R′ = cyclohexyl) in relatively nonpolar media ($CDCl_3$ or C_6D_6) exhibited a pattern similar to that of the primary ammonium salts, except for the peak position of the ammonium protons of the alkylammonium ion, which appeared at about 516 Hz (8.60 ppm). The values are independent of the concentration. The aromatic protons of the anion again gave the single envelope pattern at the same position, 7.30 ppm.

In a more polar protic solvent, methanol, the nmr spectra of both primary and secondary ammonium salts showed peaks for the ammonium protons at positions 300–320 Hz (5.08–5.20 ppm) (Figure 2). In addition, the pattern for the 4, 5, 6, 7 aromatic protons was noted to separate into the two-envelope A_2B_2 type splitting pattern.[5] Here again the uv absorption at 320 mμ indicates that the thione structure of the benzothiazoline salt is retained.

The chemical shifts caused by the stepwise addition of methanol to solutions of primary and secondary ammonium salts in $CDCl_3$ are in the direction of the results obtained in pure methanol, 5.08 ppm. However, addition of more than 4 equiv of methanol to the solution resulted in little further change in the chemical shift of the ammonium protons.

For example, in the case of the secondary alkyl ammonium salts (R = ethyl; R′ = ethyl; R = methyl or isopropyl; R′ = cyclohexyl), the ammonium proton chemical shift is at 8.60 ppm in pure $CDCl_3$.

Even more striking was the change in the nature of the nmr spectra of the aromatic protons of the anion of Ia. The addition of only 1 mol of methanol per mole of either primary or secondary alkylammonium salt resulted in a change from the single-envelope AB type splitting observed in pure $CDCl_3$ solution to the double-envelope A_2B_2 type splitting observed in pure methanol solution. As shown in Table II, some of this effect is due to dilution, but the major effect is the polarity of the medium. This change was reversed by adding $CDCl_3$. The demonstrated reversibility indicates the existence of equilibrium conditions for both anions and cations in the solutions of these salts, as shown in Scheme I.

In deuteriochloroform, the salts appear to exist

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[1] Presented before the Division of Organic Chemistry at the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968.

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