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]

ADEL F. HALASA* AND G. E. P. SMITH, JR.

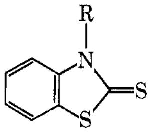
Central Research Laboratories, The Firestone Tire and Rubber Company, Akron, Ohio 44317

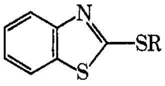
Received May 18, 1972

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.

[2] A. F. Halasa and G. E. P. Smith, Jr., *J. Org. Chem.*, **36**, 636 (1971).

[3] H. P. Koch, *J. Chem. Soc.*, 401 (1949).

[4] C. G. Moore and E. S. Wright, *ibid.*, 4237 (1952).

[5] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, p 147.

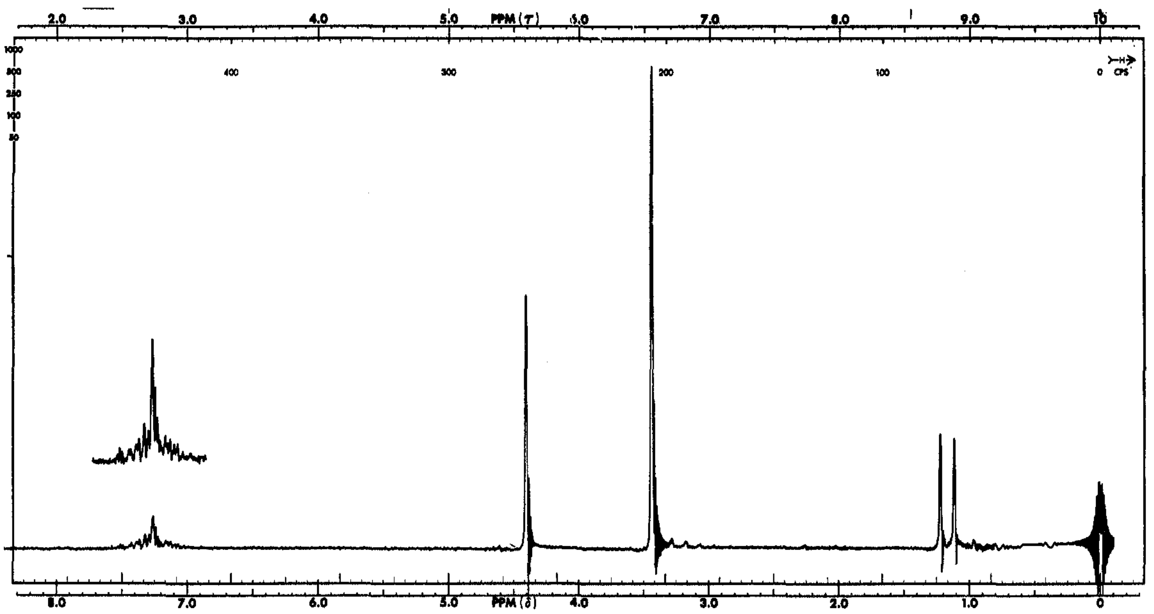
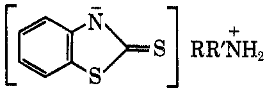


Figure 1.—Nmr spectrum of secondary ammonium salt of benzothiazoline-2-thione in pure $CDCl_3$. One mole of MeOH added.

TABLE I

UV AND NMR SPECTRA OF AMINE SALTS I OF BENZOTHIAZOLINE-2-THIONE



I

Registry no.	I: R	I: R'	Uv max, mμ[a]: CHCl₃	Uv max, mμ[a]: MeOH	Nmr of RR'NH₂⁺, ppm: CDCl₃	CDCl₃ with added methanol: 1 mol	2 mol	3 mol	4 mol	5 mol	100% MeOH
38456-42-7	H	$CH(CH_3)_2$	245 (m)	238 (m)							
			293 (m)	253 (w)							
			320 (vs)	320 (vs)	4.41	4.58	4.66	4.80	4.70	4.93	5.08
38456-43-8	Cyclohexyl	$CH(CH_3)_2$	240 (m)	240 (m)							
			290 (w)	250 (w)							
			320 (vs)	320 (vs)	8.60	7.50	6.59	5.83	4.86	4.86	4.86
38456-44-9	Cyclohexyl	CH_3	240 (m)	238 (m)							
			245 (w)	249 (w)							
			320 (vs)	320 (vs)	8.33	7.30	6.72	5.95	5.01	5.01	5.01
38456-45-0	CH_2CH_3	CH_2CH_3	245 (m)	240 (m)							
			296 (w)	255 (w)							
			320 (vs)	320 (vs)	8.60	7.23	6.46	5.88	5.36	5.20	5.20

[a] m = medium; w = weak; vs = very strong.

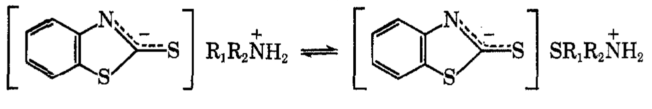
TABLE II

EFFECT OF CONCENTRATION CHANGES ON THE NMR OF $RR'N^+H_2$[a]

I: R	I: R'	1 ml	2 ml	3 ml	4 ml	5 ml
H	CH_2CH_3	5.35	4.91	4.63	4.43	4.23
CH_2CH_3	CH_2CH_3		5.08	4.70	4.25	

[a] 0.001 mol of amine salt and 0.05 mol of MeOH in $CDCl_3$.

SCHEME I



(Scheme I) as intimate ion pairs[6] in which the cation causes localization of the negative charge resulting in little influence of the negative charge on the aromatic protons. This effect results in the typical AB splitting pattern (Figure 1).

In more polar solvents (*e.g.*, CD_3OD, DMSO-d_6, MeOH–$CDCl_3$), the intimate ion pairs are dissociated, resulting in delocalization of the negative charge into the aromatic ring (Scheme II). This effect produces the typical A_2B_2 splitting pattern (Figure 2).

The changes in chemical shifts of the ammonium ion protons noted when methanol is added to $CDCl_3$ solutions of the salts may be explained by an equilibrium solvation–ion[7] separation effect (Scheme III). This phenomenon reaches a limiting value of $\Delta\delta = 1.7 \pm 0.2$ ppm at 3–4 equiv of the polar solvent.

Some preliminary dilution studies (see Table II) indicate that the ion-pair aggregates of the more soluble salts of this study dissociate and solvate in polar, as dis-

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(6) S. Winstein, P. E. Klinedienst, and G. C. Robinson, *J. Amer. Chem. Soc.*, **83**, 885 (1961).

(7) T. E. Hagen Esch and J. Smid, *J. Amer. Chem. Soc.*, **88**, 307, 318 (1966).

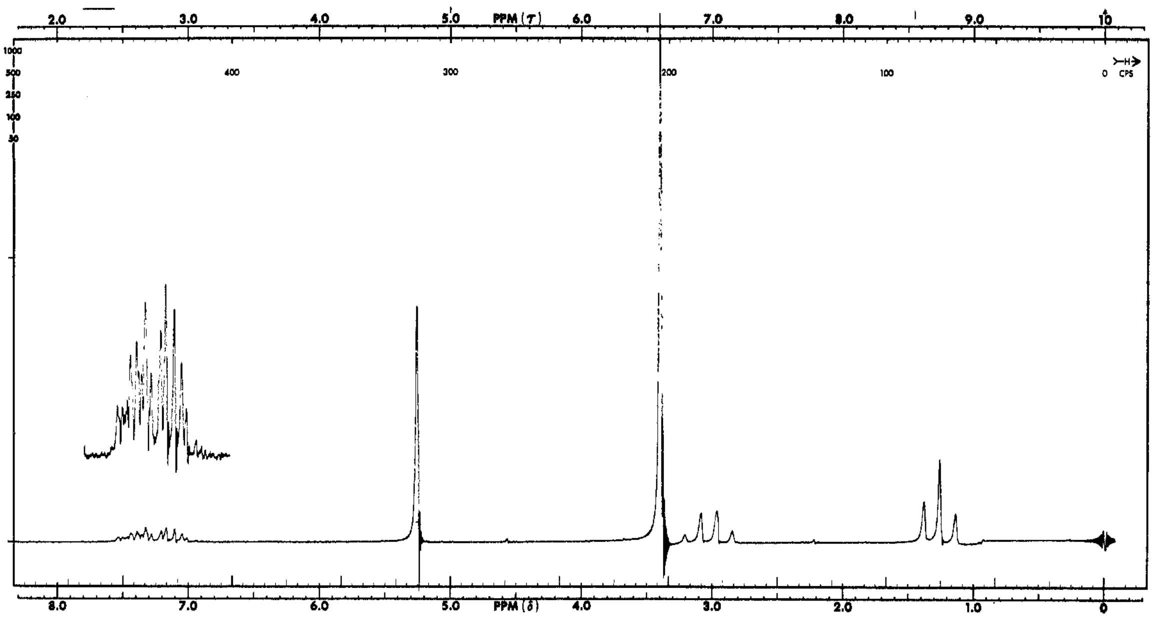
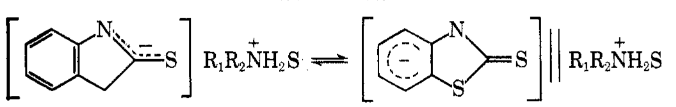
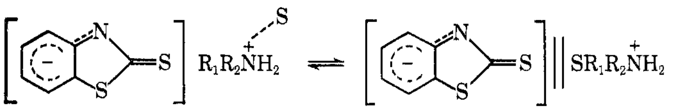


Figure 2.—Nmr spectrum of primary ammonium salt of benzothiazoline-2-thione in $CDCl_3$. Five moles of MeOH added.

SCHEME II



SCHEME III



tinct from nonpolar, solvents, with ion separation as the environment changes from concentrated to very dilute solutions. In the primary ammonium salts, Ia (R = H; R′ = alkyl), a chemical shift from 5.35 ppm at 11% concentration to 4.23 ppm at 0.5% concentration is produced. A similar chemical shift was noted in the nmr spectra of secondary ammonium salts Ia (R = ethyl; R′ = ethyl) in changing the concentration. Thus the dilution effect, in the case of the secondary ammonium cations, is smaller, distinct, and separable from the effect produced by changing from a nonpolar, aprotic to a polar, protic environment.[8,9]

Experimental Section

Reagents.—Benzothiazoline-2-thione was recrystallized several times from benzene solution. The amines used were purified by distillation.

Ammonium salts of benzothiazoline-2-thione were prepared in anhydrous ether by the addition of the appropriate amine to an ether slurry of 2-benzothiazole-2-thiol. The white salts formed immediately. The salts were filtered and washed several times with ether and dried in a vacuum oven. The nmr spectra were run on the salts in nmr grade $CDCl_3$, C_6D_6, CD_3OD, and DMSO-d_6 and methanol distilled from Mg metal.

Registry No.—Ia, 4464-58-8; Ib, 149-30-4.

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(8) G. Fraenkel, *J. Chem. Phys.*, **39**, 1614 (1963).

(9) G. Fraenkel and J. P. Kim, *J. Amer. Chem. Soc.*, **88**, 4203 (1966).