time 32 min) collected. It was a white, crystalline solid, mp 30°. The infrared carbonyl absorptions occurred at 1745 (s) and at 1780 cm^{-1} (w). The nmr spectrum in $CHCl_3$ consisted of a doublet at τ 7.53, multiplet at 8.05, singlet at 8.66, and multiplet at 8.88. The integrated areas are 0.9, 1.0, 2.9, and 15.0, respectively.

Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27; O, 16.30. Found: C, 73.55; H, 10.31; O, 16.50.

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Intramolecular Hydrogen Bonding in *o*-Methylmercapto Derivatives of N-Methylaniline and N-Methyl-4-aminoazobenzene[1]

JOHN D. SCRIBNER[2] AND JAMES A. MILLER

McArdle Laboratory for Cancer Research, Medical Center, University of Wisconsin, Madison, Wisconsin 53706

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The recent report of Szmant and Rigau[3] on the intramolecular hydrogen bonding in *cis*-2-phenylmercaptoindanol prompted us to report our observations on the strong hydrogen bonding present in derivatives of 2-methylmercaptoaniline. This came to our attention during the isolation of 3-methylmercapto-N-methyl-4-aminoazobenzene (**1**) from cold, alkaline digests of livers from rats fed the hepatocarcinogen, N,N-dimethyl-4-aminoazobenzene (**2**).[4] At the time when the identity of **1** was still unknown to us, we were struck by the disparity between its behavior on alumina chromatography (similar to that of tertiary aminoazo dyes) and its chemical behavior (as a secondary amine). Upon chromatography on carboxymethylcellulose in citric acid–ethanol, it proved to be considerably less basic than **2**.[4] Lithium aluminum hydride reduction of the N-acetyl or N-benzoyl derivative of **1** cleaved the amide linkage, regenerating **1**.[4] Similar treatment of the N-acetyl derivative of 3-methyl-N-methyl-4-aminoazobenzene (**3**) yielded the expected N-ethyl derivative.

The infrared spectra of **1** also indicated hydrogen bonding of the N hydrogen to the *ortho* substituent, as shown in Table I. The appropriate frequencies for **3** are shown for comparison. A similar contrast in the effects of the different *ortho* substituents is found in the spectra of the parent amines, 2-methylmercapto-N-methylaniline and N-methyl-*o*-toluidine. In the spectrum of **3**, the area of the peak at 3344 is twice that of the peak at 3442 cm^{-1}, which is at the same frequency as the single peak shown by neat N-methyl-*o*-toluidine. These data permit the interpretation that the higher frequency band in the KBr medium may be ascribed to intermolecular hydrogen bonding between dye molecules, while the lower frequency, more intense band is due to the much more likely hydrogen bonding of dye molecules to the KBr matrix.

TABLE I

EFFECTS OF AN *o*-MeS GROUP ON SPECTRA AND pK_a VALUES OF AROMATIC AMINES

Compd	N–H stretching frequency, cm^{-1}	pK_a
1	3386[a,b]	2.03[e]
3	3344, 3442,[a] 3468[b]	2.94[e]
2-MeS-N-Me-aniline	3386[c,d]	3.71[f]
N-Me-*o*-toluidine	3442,[c] 3460[d]	4.58[f]

[a] KBr pellet. [b] CCl_4 solution, 2 mg/ml. [c] Pure liquid. [d] CCl_4 solution, 0.2% (v/v). [e] 23°, 1% ethanol in 0.1 *M* HCl–KCl buffers. [f] 23°, 1% ethanol in 0.05 *M* citrate buffers.

The previous qualitative observation of the weakly basic character of **1** was confirmed by determination of its pK_a value, which is shown in Table I. Whether this base-weakening effect is actually due to hydrogen bonding is uncertain. The difference in pK_a values between those for 2-methylmercapto-N-methylaniline and N-methyl-*o*-toluidine is only slightly greater than the difference of the pK_a values reported for 4-methylmercaptoaniline and *p*-toluidine[5] and thus appears to be due in large part to inductive and resonance effects.

The *o*-methylmercapto group confers a high specificity on reactions of 1,4-phenylenediamine. 3-Methylmercapto-4-aminoazobenzene could be synthesized readily by condensation of nitrosobenzene and 2-methylmercapto-1,4-phenylenediamine in acetic acid–ethanol. The unhindered amino group was preferred to the hydrogen-bonded amino group by a ratio of 21:1. Similarly, condensation of nitrosobenzene with 2-methylmercapto-5-methyl-1,4-phenylenediamine favored compound **4** over compound **5** by a ratio of 11:1 (Chart I).

The evidence cited makes it clear that, if favored by a rigid configuration, sulfide sulfur can serve effectively as an electron donor in hydrogen bonding to amines.

Experimental Section

Infrared spectra were taken on a Beckman IR-10 spectrophotometer, set on the slow scanning speed (100 cm^{-1}/min, uncertainty in reading 3 cm^{-1}). The pK_a values were determined by the method of Sawicki and Ray.[6] The melting points were estimated to ±1° from the slopes of the melting curves obtained with the Accumelt apparatus (American Instrument Co.).

N-Methyl-2-methylmercaptoaniline.—2-Methylmercaptoaniline (Aldrich, 21.7 g, 0.156 mole) was dissolved in a mixture of 100 ml of 90% formic acid and 500 ml of benzene and the mixture was refluxed on a steam bath until no more water and formic acid could be collected in a water trap. The remaining solvent was removed under vacuum, and the residual oil was shaken with 250 ml of 5% Na_2CO_3 and drawn off. The carbonate solution was washed with 50 ml of ether, the ether was added to the oil, and the combined organic material was dried over Na_2SO_4. The ether was removed under vacuum and the residue was dried further by dissolving it in benzene and boiling off the solvent at atmospheric pressure until a clear distillate was obtained. The remaining solvent was removed under vacuum to give 25 g of crude N-formyl-2-methylmercaptoaniline (96% yield, single N–H band in infrared spectrum). This product was dissolved in 200 ml of ether and added over a 45-min period to a mixture of 11.4 g (0.3 mole) of $LiAlH_4$ in 500 ml of anhydrous ether. The mixture was stirred for another hour, and then refluxed for another

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(2) National Science Foundation Cooperative Graduate Fellow, 1965–1966.

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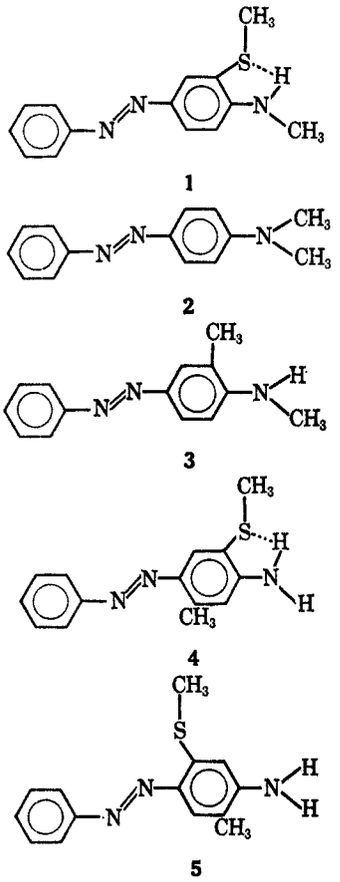
CHART I



1 2 3 4 5

3 hr. Ethyl acetate was added carefully; then 300 ml water was added. The layers were separated and the ether layer was dried over Na_2SO_4. The residue from the ether layer was fractionally distilled to yield 17.0 g (75%) of N-methyl-2-methylmercaptoaniline: bp 64° (0.06 mm); infrared spectrum 3386 s, 3066 m, 2984 m, 2920 s, 2865 m, 2812 m, 1591 s, 1500 s, 1454 s, 1427 s, 1317 s, 1286 m, 1166 m, 1017 w, 1031 m, 966 w, 740 m cm^{-1} (pure liquid); nmr spectrum (Varian A-60, hexamethyldisiloxane internal reference, pure liquid) δ 2.20 (3 H), 2.82 (3 H), 4.8 (1 H), 6.49 (triplet, 2 H), 7.1 (multiplet, 2 H).

3-Methylmercapto-N-methyl-4-aminoazobenzene (1).—2-Methylmercaptoaniline was converted to its ω-methyl sulfonate by the procedure of Miller, *et al.*[7] This product was coupled with diazotized *p*-aminobenzoic acid to give 4′-carboxy-3-methylmercapto-4-aminoazobenzene ω-methylsulfonate, which was hydrolyzed in alcoholic alkali[7] to yield 4′-carboxy-3-methylmercapto-4-aminoazobenzene, mp 219°. Acetic acid was added to the hydrolysis mixture to complete precipitation of the dye, which was filtered and washed with water. Recrystallization from acetic acid gave a sample for analysis. *Anal.* Calcd for $C_{14}H_{13}N_3O_2S$: C, 58.53; H, 4.56; N, 14.63; S, 11.14. Found: C, 58.27; H, 4.89; N, 14.03; S, 11.06. This compound (102 g) was dissolved in 1500 ml of 10% KOH and heated on a steam bath. When the temperature reached 60°, 225 g of $Na_2S_2O_4$ was added in 50-g portions. The mixture was heated for another 0.5 hr, 1000 ml of 11 *N* KOH was added, and the mixture was cooled and extracted with three 500-ml portions of a 1:1 mixture of ether and benzene. The extract was dried over Na_2SO_4 and evaporated to give 40.5 g of solid 2-methylmercapto-1,4-phenylenediamine, mp 93°. This diamine (7.7 g, 0.05 mole) was coupled with 5.5 g of nitrosobenzene.[8] The product was chromatographed on alumina with 30% benzene in hexane (Skellysolve B); 7.8 g of 3-methylmercapto-4-aminoazobenzene (64%) was obtained. Only 0.37 g of presumed 2-methylmercapto-4-aminoazobenzene was found. Rechromatography of the 3-methylmercapto-4-aminoazobenzene on a longer column with 15% benzene in hexane, followed by evaporation of solvent and removal of the last traces of solvent in a vacuum desiccator over mineral oil gave an oil which was analyzed. *Anal.* Calcd for $C_{13}H_{13}N_3S$: C, 64.19; H, 5.39; N, 17.27; S, 13.15. Found: C, 64.08; H, 5.29; N, 17.24; S, 12.94. This compound was formylated by the procedure described above. When the benzene was removed from the reaction product, treatment of the residue with ether effected instantaneous crystallization to a solid mass. This was filtered, washed with ether, and air dried to give beautiful, orange crystals in yields of 60–70%, mp 139°. The N-formyl-3-methylmercapto-4-aminoazobenzene was methylated with methyl iodide and KOH by the procedure of Ishikawa, *et al.*,[8] to give 1 in 80% yield after alumina chromatography. *Anal.* Calcd for $C_{14}H_{15}N_3S$: C, 65.36; H, 5.88; N, 16.33; S, 12.44. Found: C, 65.56; H, 5.95; N, 16.38; S, 12.47. Compound 1 was a thick oil which, when highly purified and cooled at −20° for several days, solidified to crystals which melted at 46°; for the infrared spectrum see ref 4.

2-Methylmercapto-5-methyl-4-aminoazobenzene (4).—Potassium hydroxide (6.5 g) was dissolved in 100 ml of absolute ethanol. Methanethiol (4.8 g) was added, followed by 3-nitro-4-chlorotoluene (Aldrich, 17.2 g, 0.10 mole). The mixture was refluxed for 3 hr, then diluted to 500 ml with water. The product was extracted with two 200-ml portions of 20% benzene in hexane. Removal of the solvent left a dark red-black mass, which was leached with boiling hexane. Upon cooling, yellow, oily crystals separated from the hexane. Recrystallization from 30 ml of 95% ethanol gave 6.4 g (34%) of 3-nitro-4-methylmercaptotoluene, mp 75°. This was reduced by Kuhn's procedure[9] in quantitative yield (5.4 g) to 2-methylmercapto-5-methylaniline. The ω-methylsulfonate was prepared as for 2-methylmercaptoaniline, coupled in the same way with diazotized *p*-aminobenzoic acid, and the coupling product was similarly hydrolyzed to give a 40% yield of 4′-carboxy-2-methylmercapto-5-methyl-4-aminoazobenzene. This compound (2.0 g) was reduced with $Na_2S_2O_4$ as before to give 2-methylmercapto-5-methyl-1,4-phenylenediamine (0.49 g, 44%, mp 89°). The diamine (0.42 g, 0.0025 mole) was dissolved in a mixture of 2.3 ml of absolute ethanol and 0.45 ml of glacial acetic acid. Nitrosobenzene (0.27 g) was added, and the mixture was allowed to stand for 3 days at room temperature, then made alkaline with 2% NaOH and extracted with ether. The residue from the ether extract was chromatographed on alumina. Compound 4 (0.35 g, 55%, mp 67°) was eluted first, followed by compound 5 (0.03 g, 5%). *Anal.* Calcd for N-methyl derivative of 4 ($C_{15}H_{17}N_3S$): C, 66.40; H, 6.32; N, 15.49; S, 11.79. Found: C, 66.45; H, 6.36; N, 15.42; S, 11.70.

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Cerium(IV) Oxidation of Organic Compounds. III. Preparation of Cyclopropanecarbaldehyde from Cyclopropanemethanol[1a-c]

L. BREWSTER YOUNG[1d] AND WALTER S. TRAHANOVSKY

Department of Chemistry, Iowa State University, Ames, Iowa 50010

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We wish to report a convenient and efficient oxidative synthesis of cyclopropanecarbaldehyde (1). We have found that an aqueous solution 1 *N* in ceric ammonium nitrate oxidizes cyclopropanemethanol (2) to 1 in 64% isolated yield. The reaction occurs rapidly (5–15 min) under mild conditions (75°) and affords a simple,

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