[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY, LAFAYETTE, IND.]

Sulfur in Amine Solvents[1]

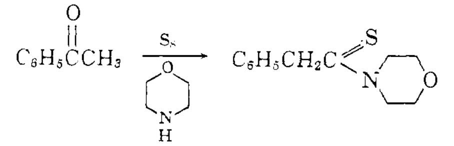
BY ROBERT EARL DAVIS AND HISHAM F. NAKSHBENDI

RECEIVED NOVEMBER 15, 1961

When yellow octatomic sulfur is dissolved in amine solvents, unusual colors are observed ranging from deep yellow, to orange and even green. Solutions in aliphatic primary and secondary amines conduct current quite well. It is suggested that ionic ammonium polythioamine salts are produced. Solutions in tertiary amines and pyridine bases contain very few ions, but sulfur is much more yellow than expected. This has been explained in terms of a contact charge transfer process occurring during excitation. A cubic relationship between the extinction coefficient and the refractive index of the solvent has been obtained from quantum theory. This relationship holds quite well for sulfur in inert solvents. However, sulfur solutions in amines do not fit this curve, suggesting strong chemical interaction. The significance of the data is discussed in terms of two important areas of sulfur chemistry: the Willgerodt reaction and the interaction between an amino nitrogen and a thiol sulfur in the aminothiols which are radio-protective compounds.

Introduction

The Willgerodt reaction[2] originally referred to the conversion of an aryl alkyl ketone to a terminal carboxamide with reduction of the ketone carbonyl using ammonium polysulfide. Kindler[3] introduced the use of dialkylamines and sulfur in which case thioamides are formed. Morpholine is a very convenient solvent[4] and the thiomorpholide is usually obtained. Typical is the reaction of acetophenone



(1)

Such modifications usually are classified together as the Willgerodt–Kindler reaction. A total conspectus[5–8] of this reaction is available in the writings of several authors. Pryor[7] has considered this reaction as a typical example of one type of sulfur oxidation.

Emphasis upon understanding this reaction always has been placed upon the organic substrate. Davis[8] placed strong emphasis on the nature of the interaction between the sulfur and the amine and reviewed this rather neglected area of research. Before judgment can be made upon the mechanisms of the Willgerodt reaction, the nature of the interaction of sulfur and the amine must be more clearly understood. It is the purpose of this investigation to provide some insight into this area. Several physical techniques have been used to obtain information.

Results

Ultraviolet Spectrum of Octatomic Sulfur.—The ultraviolet spectrum of octatomic sulfur in a hydrocarbon solvent as methylpentane, cyclohexane or *n*-hexane is characterized by a gentle maximum between 260 and 280 mμ, a gentle minimum at 251 mμ and a maximum at 225 mμ at room temperature. A long wing extends above 300 mμ and this is responsible for the familiar canary-yellow color. At low temperatures (130°K.) in methylpentane the broad band between 260 and 280 mμ is split into two bands at 263 mμ (38020 cm.$^{-1}$) and 278 mμ (35970 cm.$^{-1}$). It is a general phenomenon that absorption bands sharpen with decreasing temperature. As a consequence of the Franck-Condon principle, a change in distribution of molecules over the various vibrational levels of the ground state leads to sharpening of the absorption bands with lowering the temperature. At low temperatures the vibrational quantum numbers of the absorbing molecules will be zero in accordance with the Boltzmann exponential distribution law. The most probable electronic transitions for these molecules then involve excitation from the lowest level.

If sulfur is now dissolved in a different solvent, the extinction coefficient will change. If the solvent does not interact with sulfur and only exerts a bulk solvent effect due to an internal electric field, one would expect that the extinction coefficient (ϵ) should increase with the increase in the refractive index (n) of the medium.[9] The relationship

$$\epsilon = C(n^3 + 4n + 4/n) \quad C \text{ a constant} \qquad (2)$$

has been derived from the quantum theory and this derivation is described in the Appendix. The equation accurately correlates ϵ and n for sulfur in inert solvents[13]; however, deviations occur for basic solvents (Fig. 1).

Sulfur in Amines.—The color of sulfur in amine solvents is much more intense than predicted

---

(1) Part III. Studies on the Willgerodt Reaction.

(2) (a) C. Willgerodt, *Chem. Ber.*, **20**, 2467 (1887); (b) **21**, 534 (1888); (c) *J. prakt. Chem.*, **80**, 183 (1909); (d) C. Willgerodt and F. H. Merk, *ibid.*, **81**, 74 (1910); (e) C. Willgerodt and T. Schlotz *ibid.*, **81**, 382 (1911); (f) C. Willgerodt and B. Albert, *ibid.*, **83**, 383 (1911).

(3) (a) K. Kindler, *Ann.*, **431**, 187 (1923); (b) K. Kindler and T. Li, *Chem. Ber.*, **74B**, 321 (1941); (c) K. Kindler, *Arch. Pharm.*, **265**, 389 (1927); (d) K. Kindler and W. Peschke, *ibid.*, **270**, 340 (1932).

(4) E. Schwenk and E. Bloch, *J. Am. Chem. Soc.*, **64**, 3051 (1942).

(5) M. Carmack and M. A. Spielman, "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946, pp. 83-107.

(6) R. Wegler, E. Kuhle and W. Schafer, *Angew. Chem.*, **70**, 351 (1958).

(7) W. A. Pryor, monograph in preparation, McGraw-Hill Book Co., Inc., New York, N. Y.

(8) R. E. Davis, "Organic Sulfur Compounds. Vol. II. A Critique of Some Reactions of Elemental Sulfurs," Chapter 1, N. Kharasch, ed., Pergamon Press, New York, N. Y., 1962, paper 1 in this series.

(9) Friedman and Kerker[10] studied the ultraviolet absorption of sulfur in methanol, ethanol, chloroform, hexane and water and presented an empirical relationship which was nearly linear between the extinction coefficient and the refractive index. They also observed a small shift toward higher wave length in the position of maximum and minimum of the curves with increase in refractive index (Kündt's rule).[11,12]

(10) H. L. Friedman and M. Kerker, *J. Colloid Sci.*, **8**, 80 (1953).

(11) A. Kündt, *Ann. Phys. Chem.*, **4**, 34 (1878).

(12) A. L. Le Rosen and C. E. Reid, *J. Chem. Phys.*, **20**, 233 (1952).

(13) R. E. Davis, *Proc. Indiana Aca. Sci.*, **71**, paper II (1962).

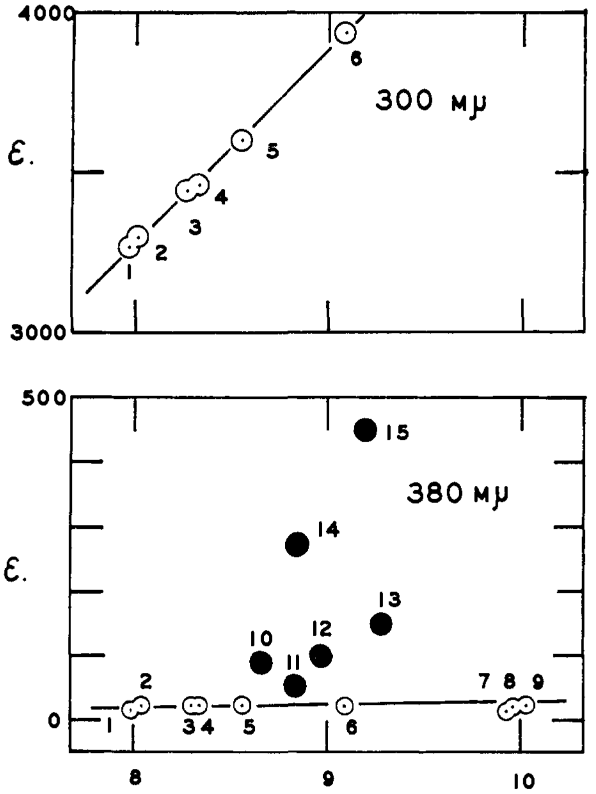


Fig. 1.—Ultraviolet spectrum of sulfur. Extinction coefficient, ε, *versus* $n^3 + 4n + 4/n$ for sulfur in: 1, methanol; 2, water; 3, 95% ethanol; 4, ethanol; 5, *n*-hexane; 6, chloroform; 7, 2,6-lutidine; 8, 4-picoline; 9, pyridine; 10, triethylamine; 11, di-*n*-butylamine; 12, tri-*n*-butylamine; 13, ethylenediamine; 14, *n*-butylamine; and 15, morpholine. Plot A, solvents 1-6 at 300 mμ; plot B, all solvents at 380 mμ. A solid line joins the points which satisfy the conditions of the cubic equation.

by either the empirical or theoretical relationships. The sulfur sample initially contains less than 10^{-8} *M* sulfur dioxide and hydrogen sulfide. Thus there is no hydrogen sulfide or sulfur dioxide initially present due to contamination of the sulfur. Both materials will enhance the color of sulfur by forming open-chain ionic polysulfur compounds.[14-16]

The extinction coefficients of sulfur have been measured in various solvents (Table I). There are three classes of behavior. The first class includes amines in which the sulfur spectrum is initially only slightly affected. The amines in this class are tertiary amines and pyridine bases as 2,6-lutidine, pyridine,[8] 4-picoline, tri-*n*-butylamine and triethylamine[8] in order of their increasing effect. The series 2,6-lutidine < pyridine < 4-picoline < triethylamine ≅ tri-*n*-butylamine indicates the basicity of the nitrogen is important but that sterically hindered amines as 2,6-lutidine are much less effective in enhancing the color. All of these solutions (except in pyridine) change color slowly with time. The rate of change is first order

TABLE I: ULTRAVIOLET SPECTRUM OF SULFUR, S_8, AT 25.00°

λ, mμ	A[a]	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R
400								291	21.5					10.9	65.8	62.5	448	75
390								278	36.2					17.9	97.9	92.1	450	112
380	25.6	20.8	18.4	18.4	17.6	17.9	18.5	282	61.9	98	91	32	17.4	35.9	142	144	468	150
370	46.4	40.6	37.6	37.6	36.0	44.0	43.2	296	111	180	181	62	44.2	67.5	221	214	539	225
360	89.6	87.2	83.2	80.8	78.4	94.4	80.2	321	223	409	355	120	98.2	129	354	326	661	290
350	166	167	172	170	168	200	164	386	422	668	666	251	220	260			902	370
340	329	330	346	343	343	415	345	473	786	968	1124	488	445	498			1209	445
330	645	645	658	663	660	816	630	601	1240	1880	1920	875	861	925			1580	504
320	1190	1200	1230	1232	1250	1488	1220	775	1830	3000	3034	1580	1570	1670				510
310	2050	2060	2110	2100	2200	2512	2140	978	2250	3380	3390	2740	2730					502
300	3288	3312	3420	3410	3610	3950	3540	1140	2390	5970	6060							481
290	5100	5120	5190	5260	5600	5816	5320	1180	2390	7700	7690							439
280	6310	6330	6320	6450	6750	6910	6400	1130	2350	8350	8460							440
270	6490	6520	6620	6640	6912	7160	6620	1280	2130									482
260	6500	6530	6560	6640	6870	7232	6600											
250	5380	5390	5580	5520	5740	6580	5610											
240	7210	7260	7490	7480	7920		7900											
230	10800	10800	10900	11800	11480													

[a] A, methanol[b]; B, water[b]; C, ethanol[b]; D, 95% ethanol[b]; E, *n*-hexane[b]; F, chloroform[b]; G, cyclohexane; H, *n*-butylamine; I, di-*n*-butylamine; J, tri-*n*-butylamine; K, triethylamine; L, pyridine; M, 2,6-lutidine; N, 4-picoline; O, 1% *n*-butylamine in tri-*n*-butylamine; P, 1% di-*n*-butylamine in tri-*n*-butylamine; Q, morpholine; R, ethylenediamine. [b] Data of Friedman and Kerker; ε recalculated on the basis of S_8.

---

(14) P. D. Bartlett, E. F. Cox and R. E. Davis, *J. Am. Chem. Soc.*, **83**, 103 (1961).

(15) P. D. Bartlett, A. K. Colter, R. E. Davis and W. R. Roderick, *ibid.*, **83**, 109 (1961).

(16) R. E. Davis, Dissertation, Harvard Univ., 1958.

in initial concentration of sulfur (Table II). It is not known what detailed processes are responsible for the observed changes.

The next class of amines is secondary amines like di-*n*-butylamine and morpholine. The dilute solutions in di-*n*-butylamine are deep orange-yellow and tend to be orange-red at high concentration. Dilute solutions in morpholine sometimes show transient greenish hues. The solutions are unstable and the colors change with time. The color increases with time in di-*n*-butylamine but decreases in morpholine. Thus no simple generalization can be made. The products of these reactions have been discussed in paper I of this series[8] and will not be reviewed in this paper.

The third class is primary amines. The spectra are highly abnormal in *n*-butylamine and in ethylenediamine.[8] *In ethylenediamine, dilute solutions of sulfur are beautifully emerald green.* This color has been used routinely in this laboratory as a sensitive, rapid spot test of elemental sulfur.[17] At higher concentrations the color becomes dark orange-red. *An effluvium emanates* (*vide infra*). These solutions are unstable and the color changes rapidly with time. Passage of moist air or oxygen through the solution produces a straw-yellow solution containing a white precipitate of ethylenediammonium thiosulfate

$$H_2NCH_2CH_2NH_2 \xrightarrow[\substack{O_2\\H_2O}]{S_8} H_3{}^+NCH_2CH_2{}^+NH_3\ S_2O_3{}^{-2} \quad (3)$$

The addition of 1% by weight of mono-*n*-butylamine to tri-*n*-butylamine produces a much more yellow solution. In this case the optical density increases with time for the first five hours and then decreases. Addition of di-*n*-butylamine to tri-*n*-butylamine also produces a more intense color and a more rapid color change. The spectrum of sulfur in secondary and primary amines resembles the spectrum of sulfur in tertiary amines to which hydrogen sulfide has been added.[19] We therefore can conclude that *open chain polysulfide ions* can be responsible for the color in secondary and primary amines.

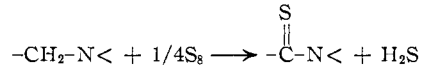
Conductance Data.—Examination of the conductivity of solutions of sulfur in amine solvents further confirms the suggestion that polysulfide ions are present. Sulfur in primary and secondary amines produces many ions. The conductivity is comparable to that of salts such as potassium iodide and tetra-*n*-butylammonium perchlorate at comparable concentration (Table III). However, the mobilities of the ions in the amines are not known so an accurate estimate of the amount of ions cannot be made. The conductivity of sulfur solutions also changes slowly with time. In ethylenediamine the rate of loss of conductivity is about that of the rate of loss of the green color. When the color is gone, the ethylenediamine still contains ions and the conductance now changes very slowly. In all of the amine solutions except pyridine, there is a slow production of hydrogen sulfide. This would account for the final conductance of the solutions as the amine salt of hydrogen sulfide is formed. The salt can be isolated and the hydrogen sulfide liberated by reaction with acid.

TABLE II
FIRST-ORDER RATE CONSTANTS FOR COLOR CHANGES OF SULFUR SOLUTIONS AT 25.00°

Amine	λ, mμ	k_1, sec.$^{-1}$
Ethylenediamine	320	1.9×10^{-4}
n-Butylamine	310	2.4×10^{-4}
Di-*n*-butylamine	340	1.4×10^{-5}
Tri-*n*-butylamine	340	1.0×10^{-6}
Pyridine	340	$<1 \times 10^{-8}$[a]
4-Picoline	340	1×10^{-6}
2,6-Lutidine	330	$<1 \times 10^{-7}$[b]
Morpholine	370	6×10^{-5}

[a] No change observed after several days in total darkness. [b] Change in optical density was only 0.021 unit in 2 days. As an infinity reading was not recorded, a rate constant cannot be estimated unless an assumption is made concerning O.D$_\infty$. Estimates are based upon an optical change of 0.100 unit.

Production of Hydrogen Sulfide.—All the amines except pyridine produce hydrogen sulfide at a slow but nevertheless measurable rate. Ethylenediamine produces about 0.54 ± 0.03 mole of hydrogen sulfide for each gram atom of sulfur after one month at 25°. The most common reaction of sulfur and amines is replacement of active methylene hydrogens with sulfur


$$-CH_2-N< + 1/4S_8 \longrightarrow -\overset{\overset{S}{\|}}{C}-N< + H_2S \quad (4)$$

The ratio of hydrogen sulfide to gram atoms of sulfur is 0.50 in reaction 4.

However, the reaction of amines with sulfur is not fully understood. Some of the thioamide may have hydrolyzed during the analytical procedure. Ethylenediamine also produces 0.30 mole of ammonia per gram atom of sulfur. The odors of these solutions have already received comment.

Heats of Solution (Reaction).—The heat of solution of sulfur in amine solvents is currently being considered. The heats of solution of sulfur in inert solvents and tertiary amines are quite small. The heat of solution (and reaction) of sulfur in ethylenediamine is very large. Expressed in more realistic manner: upon addition of one gram atom of sulfur to 170 ml. of ethylenediamine at room temperature, the solution immediately refluxed of its own accord and ammonia was evolved. The odor of the residue is so foul as to hinder research. The nature of the interaction of sulfur and amines will probably continue to be a neglected area of research.

Recovery of Octatomic Sulfur.—Octatomic sulfur can be quantitatively recovered from *all* the solutions in amine solvents immediately after preparation. Rapid solution of sulfur even in ethylenediamine followed by rapid dilution with aqueous hydrochloric acid reprecipitates octatomic sulfur. Upon long standing the sulfur can be recovered in quantitative yield only from pyridine. All other

---

(17) For example, cymenes react with a sulfur in the presence of a base to produce 4-aryl-1,2-dithiole-3-thiones.[9] Fields[18] used a copper wire as a test for sulfur in which case a small sample of the solution is heated for 1 hour. If the wire darkens, sulfur is still present. In our work on dithiole-thiones, the ethylenediamine test is immediate.

(18) E. K. Fields, *J. Am. Chem. Soc.*, **77**, 4255 (1955).

(19) See Fig. 6 of an earlier paper.[14]

TABLE III

CONDUCTANCE DATA[a] IN AMINE SOLVENTS AT 25°

Amine	Pure solvent	S_8 (*c*, *M*)	KI (*c*, *M*)	*n*-Bu_4NClO_4[d] (*c*, *M*)
n-Butylamine	3.0×10^{-8}	5.62×10^{-5}[b] (4.71×10^{-3})[c]	1.15×10^{-6} (2.89×10^{-4})	2.20×10^{-5} (7.3×10^{-3})
Di-*n*-butylamine	9.0×10^{-11}	1.5×10^{-9} (2.39×10^{-3})		1.6×10^{-8} (4.50×10^{-3})
Tri-*n*-butylamine	1.0×10^{-10}	1.5×10^{-10} (1.94×10^{-2})		1.0×10^{-7} (7.12×10^{-3})
4-Picoline	1.8×10^{-8}	5.77×10^{-8} (6.55×10^{-3})		10.3×10^{-4} (5.82×10^{-3})
2,6-Lutidine	2.9×10^{-8}	4.0×10^{-8} (3.84×10^{-3})	2.5×10^{-6} (3.2×10^{-4})	4.06×10^{-5} (4.46×10^{-3})
Morpholine	3.4×10^{-8}	6.26×10^{-4} (5.42×10^{-2})		9.96×10^{-4} (5.49×10^{-2})
Pyridine	1.2×10^{-7}	2.8×10^{-7} (1.97×10^{-3})		7.2×10^{-4} (2.01×10^{-3})
Ethylenediamine[e]	5×10^{-7}	1.1×10^{-4} (3.27×10^{-3})		[e]

[a] Mho ± 1%. [b] Mho of solution. [c] Term in parentheses is the molar concentration of material added. [d] Tetra-*n*-butylammonium perchlorate. [e] See ref. 26 and 27.

amines containing labile hydrogens undergo reaction. The rate of reaction is increased by increasing the temperature or by photolysis by light.[16]

Discussion

A theory must now account for the following facts. Sulfur in amines having hydrogens on the nitrogen produces unusual colors and many ions. Sulfur solutions in tertiary amines are somewhat abnormal but very few ions are initially present. Lastly the sulfur can be quantitatively recovered from *all* the amine solutions immediately after preparation by dilution with dilute hydrochloric acid. Thus the initial stages of the processes are completely reversible. Previously[8] the following scheme was postulated

$$R_2NH + S_8 \rightleftharpoons \underset{\text{I}}{R_2N^+H\text{-}S_8^-} \qquad (5)$$

$$R_2N^+H\text{-}S_8^- + R_2NH \overset{\text{fast}}{\rightleftharpoons} R_2N^+H_2 + \underset{\text{II}}{R_2N\text{-}S_8^-} \qquad (6)$$

All of the present data are at least explicable in terms of reactions 5 and 6 for the interaction of primary or secondary amines. Step 3 is somewhat analogous to the postulated initial ring opening of sulfur by triarylphosphines.[14-16,19a] However, the order of electronegativities (P = 2.1, S = 2.5, N = 3.0) indicates that nitrogen would not donate its electrons to sulfur to any great extent unless the proton could be removed. An analogous statement would be that the protonated octathioamine (I) would be an extremely strong acid and the thioamine II an extremely weak base. Perhaps two amine molecules react with the sulfur in an over-all third-order reaction. Under the present conditions the order in amine cannot be determined because the amine is the solvent and in large excess. Steps 5 and 6 must be reversible because the removal of the amine (with aqueous acid) produces octatomic sulfur. Sulfur can even be recovered from the interesting solution it produces in liquid ammonia (nitrogen tetrasulfide, N_4S_4, and ammonium polysulfides) by evaporation.[8] Even if the octathioamine had been degenerated to $R_2NS_x^-$ ($x < 8$), it is conceivable that a sulfur chain ring could be constructed in a stepwise manner. Such construction of a sulfur ring has been previously discussed.[8,16,20,21]

Tertiary amines also produce enhancement of the sulfur spectrum. However few ions are present (Table II). The direct ring opening of octatomic[14,16] and or hexatomic[15] sulfur by a very pure tertiary amine as triethylamine has been *conclusively proved not to occur.*

$$R_3N\colon + S_8 \not\longrightarrow R_3N^+\text{—}S_8^- \qquad (7)$$

$$R_3N\colon + S_6 \not\longrightarrow R_3N^+\text{—}S_6^- \qquad (8)$$

However, the effect of the tertiary amines depends upon base strength (trialkylamines > 4-picoline > pyridine) and steric requirements can reverse the basicity order (pyridine > 2,6-lutidine). The most consistent explanation would involve a *contact charge transfer complex*

$$R_3N + S_8 \xrightarrow{h\nu} (R_3N^+S_8^-)^* \qquad (9)$$

in which the excited state would have partial ionic character. Increasing the basicity of the nitrogen would increase availability of the electrons to be promoted into the sulfur ring. The sulfur atom and an octatomic sulfur molecule are large. Therefore a contact charge transfer process would be very sensitive to the size of the amine. 2,6-Lutidine certainly has a sterically shielded nitrogen.[22]

Subsequent Reactions.—The mechanisms of reactions which finally lead to irreversible oxidation–reduction cannot be described from the present data or from extant literature data.[8] The rate of loss of conductivity is somewhat less than the rate of change in color for all the amines except ethylenediamine.

The important point to be made is that mechanisms exist which open the octatomic sulfur ring and

---

[19a] P. D. Bartlett and G. Meguerian, *J. Am. Chem. Soc.*, **78**, 3710 (1956).

[20] R. E. Davis, *ibid.*, **80**, 3565 (1958).

[21] R. E. Davis, *Proc. Indiana Aca. Sci.*, **70**, 100 (1962).

[22] H. C. Brown and R. B. Johannesen, *J. Am. Chem. Soc.*, **75**, 16 (1953), and earlier papers.

produce linear polysulfur chains. In previous investigations,[14–16,19,23] it has been found that the open-chain sulfur species react much faster than cyclic octatomic sulfur.

The present data are of importance in understanding the Willgerodt reaction. Numerous mechanisms have been proposed, reviewed[5–8] and critisized.[7,8] No single mechanism will explain the extant data[8] and no mechanism discusses the role of inorganic sulfur, for the emphasis has always been upon the organic substrate.

The present study has discussed the intermolecular action of a basic amine nitrogen and a sulfur molecule. This will serve as a foundation upon which we will later discuss the intramolecular interaction that occurs in aminoethanethiols. These compounds are somewhat unique in that they render some degree of protection to mammalian tissue against radiation damage.

Acknowledgment.—The present study was supported by grants from the Walter Reed Army Institute of Research and the National Science Foundation.

Experimental[24]

Materials.—Sublimed U.S.P. grade (Mallinckrodt) sulfur was recrystallized three times from reagent grade benzene in total darkness and dried *in vacuo* at 40° for 2 days over phosphorus pentoxide.

Analysis for sulfur dioxide–hydrogen sulfide was made using the kinetic system of triethylamine catalysis of the reaction of sulfur with triphenylphosphine in moist benzene.[14] Sulfur dioxide can be detected at 10^{-8} *M* and hydrogen sulfide at 10^{-7} *M*. The sulfur sample was free from these impurities. A sample of sulfur used in our earlier investigation[16] gave identical results.

Tetra-*n*-butylammonium perchlorate was prepared by metathesis of the iodide salt (7.3116 g., 1.989×10^{-2} mole) with anhydrous silver perchlorate (4.1041 g., 1.989×10^{-2} mole) in anhydrous ethanol. The silver iodide was removed by filtration and washed with hot ethanol. The filtrate was then evaporated *in vacuo*, giving a quantitative yield (99%) of the perchlorate salt.[25] The salt was recrystallized from 50 ml. of purified ethyl acetate and 10 ml. of purified isoöctane. Long needles were obtained, m.p. 202–203°, reported 203–204°. The material was then recrystallized four times (m.p. 202–203°) and dried *in vacuo*.

Potassium iodide (Mallinckrodt AR) was dried *in vacuo* at 55°. Methylpentane (commercial grade of an isomeric hexane mixture obtained from Phillips Petroleum Co.) was passed through a long column of activated silica gel. The solvent was transparent to 200 mμ.

Cyclohexane (Eastman white label) was repeatedly shaken with concentrated sulfuric acid until the acid layer remained nearly colorless. The cyclohexane was washed with water and then dilute aqueous sodium hydroxide, dried over sodium sulfate and then phosphorus pentoxide and distilled through a 17-plate column; b.p. 80.5° at 752 mm. Upon passage through a long column packed with Davison 200 mesh silica gel, the solvent was transparent to 212 mμ.

Triethylamine (Eastman white label) was refluxed with 0.05 part of benzoic anhydride and then distilled. The amine was then refluxed from calcium hydride (ammonia free) for 20 hours. Distillation under dry nitrogen gave a center cut (b.p. 89.1° at 742 mm., $n^{25}\text{D}$ 1.4003) which was homogeneous by gas chromatography.

Tri-*n*-butylamine (Eastman white label) was treated with one-eighth of its weight of benzenesulfonyl chloride in aqueous sodium hydroxide (15%) at 0–5°. The mixture was shaken intermittently and allowed to warm to room temperature. After 1 day the amine layer was washed with aqueous sodium hydroxide and then with water and dried over potassium carbonate. The amine was finally dried over calcium hydride and then distilled *in vacuo*. The center cut (b.p. 64.1 to 64.4° at 2.0 mm., $n^{25}\text{D}$ 1.4261) was homogeneous to V.P.C.

Di-*n*-butylamine (Eastman) was shaken with potassium hydroxide pellets and distilled *in vacuo*. The samples were gas chromatographed. The purest cut was then redistilled (b.p. 158–159 at 740 mm., $n^{25}\text{D}$ 1.4095); V.P.C. demonstrated the presence of 2–3% of isomeric di-butylamines.

Mono-*n*-butylamine was treated with potassium hydroxide and carefully fractionally distilled; b.p. 76.4–76.5° at 742 mm., $n^{25}\text{D}$ 1.3986. The material was 99% homogeneous on V.P.C. analysis.

Pyridine (Merck C.P.) was refluxed over calcium hydride and then distilled through a 25-plate column; b.p. 114° at 740 mm., $n^{25}\text{D}$ 1.5091.

4-Picoline was shaken with solid potassium hydroxide and then distilled; b.p. 143° at 742 mm.

2,6-Lutidine was treated in like manner; b.p. 142° at 744 mm. All the pyridines were homogeneous on V.P.C. analysis.

Morpholine was refluxed from sodium and then distilled; b.p. 128° at 742 mm.

Ethylenediamine was purified in a manner previously described.[26,27]

Ultraviolet Spectra.—The low temperature cell was constructed of quartz to fit into the light path of a Cary model 14 spectrophotometer. A small quartz Dewar held the coolant in an evacuated space made of optical quartz flats. The solution in the 1.00-cm. cell was cooled by conduction and convection. The temperature difference between the solution and the coolant was less than 0.5° as measured by a thermocouple.

Spectra of sulfur in solvents were measured at 25.00 ± 0.01° using a thermostated cell compartment[23] for a calibrated Beckman[28] DU spectrophotometer. A Cary model 14 recording spectrophotometer was also used to record the spectra. Spectra were recorded as quickly as possible.

Measurement of the Conductance.—The measurements on the ethylenediamine solutions were performed using a Jones bridge as previously described.[26]

More recently an inductively coupled ratio arm bridge has been used which was constructed by N. Koizumi. A ratio arm transformer with a winding ratio of exactly 1:1 is the heart of the instrument. A General Radio type 1210C R-C oscillator operating at 1 kc. was applied across the transformer. The admittance of a ratio arm can be expressed as $Y_{\text{R}} = g_{\text{k}} + i\omega c_{\text{R}}$ where g_R is the conductance and c_R the capacitance, and $\omega = 2\pi f$. The null condition of the bridge is given by

$$\frac{Y_{\text{L}}}{Y_{\text{R}}} = \frac{g + i\omega(C_{\text{L}})}{g_{\text{r}} + g_{\text{x}} + i\omega(C_{\text{R}} - C_{\text{X}})}$$

where x refers to the unknown. A General Radio type 1231-B amplifier and null detector with a 1 kc. filter was used to indicate the null. The instrument reads directly in conductance, $g = 1/R$. The direct reading range of 10^{-10} to 10^{-1} mho can be covered with an accuracy of 1%. Several conductivity cells were used with cell constants of 0.1077, 0.1087 and 0.3451.

Analysis for Hydrogen Sulfide.—Solutions of sulfur in amines were allowed to stand in a dark cupboard. The solutions were acidified with aqueous hydrochloric acid and steam distilled under nitrogen into a dilute zinc chloride solution containing aqueous ammonia. The distillate was then acidified and titrated with 0.100 *N* iodine in potassium iodide.

Appendix[29,30]

The Relationship Between ε and *n*.—The extinction coefficient, ε, is related to the oscillator

---

[23] P. D. Bartlett and R. E. Davis, *J. Am. Chem. Soc.*, **80**, 2513 (1958).

[24] All temperatures are taken from calibrated thermometers.

[25] E. D. Hughes, C. K. Ingold, S. K. Mok, S. Patai and Y. Pocker, *J. Chem. Soc.*, 1220 (1957).

[26] J. Peacock, F. C. Schmidt, R. E. Davis and W. B. Schaap, *J. Am. Chem. Soc.*, **77**, 5829 (1955).

[27] B. B. Hibbard and F. C. Schmidt, *ibid.*, **77**, 225 (1955).

[28] Beckman manual.

[29] A more detailed derivation of the relationships between ε and *n* was presented before the Indiana Academy of Science Meeting, Oct., 1961; ref. 13.

[30] The reader is referred to W. Kauzmann, "Quantum Chemistry," Academic Press, Inc., New York, N. Y., 1957, pp. 546–725, for an excellent discussion of the nature of the interaction of light and matter.

strength, f_i, of a normal electric dipole transition between states k and o with wave functions ϕ_k and ϕ_o. The oscillator strength is given by

$$f_i = \frac{8\pi^2 \nu_{ko} m_e |\vec{M}_{ko}|^2}{3he^2} \tag{1}$$

where

$$|\vec{M}_{ko}|^2 = |\int \phi_k^* M \phi_o \mathrm{d}t|^2 \tag{2}$$

where M_{ko} is a Hermitian dipole operator between states, ϕ_k and ϕ_o.

The value of f_i is a function of the refractive index of the medium (n). The equation

$$f_i = \frac{2303\ m_e c}{\pi\ Ne^2} \frac{9n}{(n^2+2)^2} \int \epsilon\ \mathrm{d}\nu \tag{3}$$

can be derived from theory and includes a small internal electric field correction $(9n/(n^2 + 2)^2)$ due to the application of an Lorentz–Lorenz field.[31,32]

The extinction coefficient, ϵ_i can be expressed as

$$\epsilon_i = \frac{Ne^2}{2303\ cm_e} f_i \phi(\nu) \tag{4}$$

where $\phi(\nu)$ determines the shape of the absorption band. Using the Lorentz formula for the line shape with a half-band width of δ cm.$^{-1}$ and the normalization of $\phi(\nu)$

$$\int \phi(\nu)\ \mathrm{d}\nu = 1 \tag{5}$$

the equation

$$\epsilon = \frac{f_i \pi N e^2}{9\delta 2303\ m_e c} \left(n^3 + 4n + \frac{4}{n}\right) \tag{6}$$

can be derived which expresses the functional dependence of ϵ upon n. The first term will remain constant to a good degree of approximation for sulfur which has an allowed band ($f_i \rightarrow 1$) and a zero dipole moment such that

$$\int \phi_0^* m \phi_0 \mathrm{d}t = 0$$

The restrictions on eq. 6 are discussed in detail in another paper.[27] Thus

$$\epsilon \propto n^3 + 4n + \frac{4}{n} \tag{7}$$

To a higher approximation

$$\epsilon \propto n \quad (n \approx 1) \tag{8}$$

Friedman and Kerker[10] suggested a linear relationship between ϵ and n for sulfur in inert solvents with n between 1.3 and 1.5. The more exact relationship is the cubic equation 7.

[31] N. Chako, *J. Chem. Phys.*, **2**, 644 (1934).

[32] R. S. Mulliken and C. A. Rieke, *Rep. Prog. Phys.*, **8**, 231 (1941).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA, PHILADELPHIA 4, PA.]

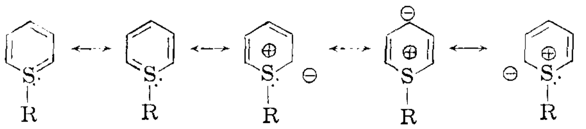
Thiabenzene. II. Rearrangement of 1-Alkyl-2,4,6-triphenylthiabenzenes to 2- and 4-Alkyltriphenylthiopyrans

BY GEORGE SULD[1] AND CHARLES C. PRICE

RECEIVED JANUARY 20, 1962

Whereas phenyllithium reacted with 2,4,6-triphenylthiopyrylium ion (I) to give deep purple 1,2,4,6-triphenylthiabenzene,[2] reaction with methyl, ethyl and butyl Grignard reagents gave only transiently deep red or purple solutions from which the colorless 2- or 4-alkyltriphenylthiopyrans were isolated. The structures of the 2- and 4-methyl homologs were established by desulfurization to 1,3,5-triphenylhexane and 3-methyl-1,3,5-triphenylpentane, respectively. Reaction of I with cyclopentadienyllithium gave the 2-cyclopentadienylthiopyran, while reaction with lithium aluminum hydride formed the 4H-triphenylthiopyran, which was reconverted to I on attempted S-alkylation with methyl iodide, methyl sulfate or triethyloxonium fluoroborate.

The possibility of double bond character for sulfur ylids[3] has interested us in the possible benzenoid conjugation which might be observed in a heterocyclic ring system we have called "thiabenzene."[2]



While there seems to be ample support for the view that sulfur can stabilize an adjacent unshared electron pair by resonance involving the 3d-orbitals on sulfur in some way, there have been arguments advanced against such resonance permitting through conjugation at sulfur or phosphorus.[4] The argument against through conjugation is based on the non-interaction between orthogonal 3d-orbitals. This non-interaction, however, is dependent on the symmetrical nature of the 3d-orbitals. Since two 3d-orbitals involved in overlap with adjacent 2p-orbitals become distorted in the process of 2p–3d π-bonding, their interaction no longer vanishes. Thus, the hybrid $3d_{xz}$ and $3d_{yz}$ orbitals involved in such π-bonding to adjacent $2p_z$-orbitals can be viewed as "pseudo-π" rather than normal 3d-orbitals for the purpose of constructing a cyclic conjugated aromatic system.

There is an alternative scheme which might also provide through conjugation in thiabenzene. This would involve rehybridization of the sulfur bonding electrons so that the σ-bonds become sp^2 rather than p^3, the unshared electrons are promoted to 3d-orbitals and the $3p_z$-orbital is left open for conjugation with the electrons from the adjacent $2p_z$-orbitals on carbon.[5]

[1] Abstracted from the doctoral dissertation of George Suld, 1960. Supported in part by National Science Foundation Grant No. G-6270.

[2] G. Suld and C. C. Price, *J. Am. Chem. Soc.*, **83**, 1770 (1961).

[3] See, *e.g.*, W. v. E. Doering and A. K. Hoffman, *ibid.*, **77**, 521 1955).

[4] See, *e.g.*, M. J. S. Dewar, E. A. C. Lucken and M. A. Whitehead, *J. Chem. Soc.*, 2423 (1960).