Thiabenzenes. V. 1-Phenylthiabenzene[1]

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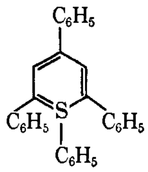
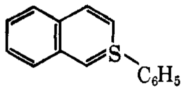
Abstract: 1-Phenylthiabenzene, prepared by the reaction of thiopyrylium iodide or perchlorate with phenyllithium, is much more stable to heat, oxygen, and light than 1,2,4,6-tetraphenylthiabenzene. The low dipole moment (0.8 D) and the proton resonance only near τ 2.8 support the earlier view of aromatic conjugation in this ring system, with the remarkable color and amorphous character due to extremely low barriers to bending at the S–phenyl bond.

The preparations of 1,2,4,6-tetraphenylthiabenzene (I), 2-phenyl-2-thianaphthalene (II), 1-phenyl-1-thianaphthalene (III), 10-phenyl-10-thiaanthracene (IV), and 9,10-diphenyl-10-thiaanthracene (V) have already been reported.[4,5] All are highly colored amorphous solids, I being thermally and oxygen reactive at room temperature, in marked contrast to the other less hindered and more stable analogs. Now 1-phenylthiabenzene (VI), the primary ring system of the "thiabenzenes," has been prepared in two ways and we wish to report on its properties.


I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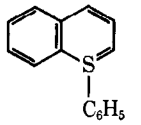
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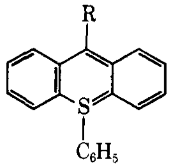
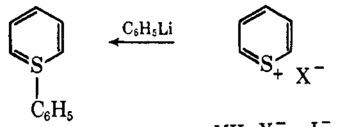

IV, R = H
V, R = C_6H_5


VI

VII, $X^- = I^-$
VIII, $X^- = ClO_4^-$

1-Phenylthiabenzene (softening point 68–73°) is a red-brown amorphous solid more similar in properties to the thianaphthalenes and the thiaanthracenes than to I. Unlike I, the compound was stable to light and oxygen. The absorption in the nmr spectrum at τ 2.8 is characteristic of aromatic protons and indicates that a cyclic π-electron system is present in VI. This supports the existence of aromatic type through conjugation in the molecule also supported by the low dipole moment of 0.8 D. The ultraviolet spectrum of 1-phenylthiabenzene in ethyl alcohol shows λ_{max} (log ϵ) at 202 (4.01) and 246 (3.63) mμ. The spectrum is similar to that of biphenyl which shows λ_{max} (log ϵ) at 205 ($\sim$4.50) and 250 mμ (4.26).[6] Like the other thiabenzenes reported earlier,[5] the spectra seem to resemble closely the analogous carbon aromatic systems, superimposed on a long "tail" out into the visible which gives these compounds their color. This characteristic "tail" absorption remains essentially unchanged down to −77°, according to an experiment performed here by Professor Robin Hochstrasser. The remarkable amorphous character and color of these compounds still seem best explained by an extremely low barrier to bending at the sulfur–phenyl bond. With little or no variation in energy of the ground state with bending, but an excitation energy (to an excited state we believe must involve considerable electron transfer from the phenyl ring to the thiabenzene ring) differing continuously with bending angle, one can rationalize both the amorphous character and unusual spectra of these compounds.

The marked difference between the properties of I and VI is further evidence for the theory that the bonding in I is different from that in the other thiabenzenes due to steric hindrance to the coplanar geometry for the S-phenyl group by the two *o*-phenyl groups in I. As suggested earlier,[5] I must therefore make greater use of the p^3 orbitals of sulfur for σ bonding, the d orbitals for cyclic conjugation, and the 3s orbital for the unshared pair. The lack of such steric hindrance to coplanarity in VI and the other thiabenzenes allows the rings to be coplanar, or at least coaxial. This permits the structures of II–VI to involve more effective rehybridization of the sulfur atom to utilize sp^2 orbitals for σ bonds, the 3d orbital for the unshared pair of electrons and the 3p orbital for cyclic aromatic conjugation. The second structure would be expected to provide better overlap and as a result a more stable molecule. This interpretation is indeed supported by the markedly lower stability reported by Markl[7] for the analogous phosphorabenzenes, whose electronic structure could only be that analogous to the nonplanar arrangement in I, *i.e.*, involving only 3d orbitals for π bonding.

1-Phenylthiabenzene (VI) was prepared[3] from 1.00 g (5.86 mmol) of VIII[8,9] suspended in 100 ml of anhydrous ether. The white reaction mixture was

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[1] Supported in part by a grant from the National Science Foundation, NSF GP-5269.

[2] Doctoral Dissertation, University of Pennsylvania, 1964.

[3] Doctoral Dissertation, University of Pennsylvania, 1968.

[4] (a) G. Suld and C. C. Price, *J. Am. Chem. Soc.*, **83**, 1770 (1961); (b) *ibid.*, **84**, 2090 (1962); (c) *ibid.*, **84**, 2094 (1962).

[5] C. C. Price, M. Hori, T. Parasaran, and M. Polk, *ibid.*, **85**, 2278 (1963).

[6] R. A. Friedel, M. Orchin, and L. Reggel, *ibid.*, **70**, 202 (1948).

[7] G. Markl, *Angew. Chem.*, **25**, 168, 669, 1121 (1963).

[8] I. Degani, R. Fochi and C. Vincenzi, *Tetrahedron Letters*, 1167 (1963); *Gazz. Chim. Ital.*, **94**, 203 (1964).

[9] J. Strating, J. H. Keiger, E. Molenaar, and L. Brandsma, *Angew. Chem.*, **74**, 465 (1962).

stirred at -70° under a nitrogen atmosphere and phenyllithium[10] (16 ml, 1.5 *N* in ether, 4 equiv) was added over a 5-min period, forming a dark red solution. After quenching with an excess of cold aqueous ammonium chloride, a red-brown organic layer was formed to which 25 ml of benzene was added. The two layers were filtered to remove 0.347 g of an insoluble dark brown solid, and the organic layer was then separated and washed with cold distilled water. The dark brown oily residue left on evaporation was taken up in 100 ml of dry benzene and filtered to remove insoluble material. After drying over sodium sulfate and evaporating, the residual brown oil was dried overnight at 0.004 mm and 18.4 mg of biphenyl distilled over into the trap. Anhydrous ether (20 ml) was added to the oily residue. The red solution was filtered from some insoluble material and cooled in an ice–water bath before adding 100 ml of cold petroleum ether (bp 30–60°). The brown solid which precipitated was collected by filtration, washed with petroleum ether, and then freeze dried from benzene to yield 121.5 mg (14%) of 1-phenylthiabenzene, softening point 68–73°.

1-Phenylthiabenzene (VI) was also prepared[2] by treating 1.0 g of VII[11] suspended in 50 ml of ether under nitrogen in a separatory funnel capped with a rubber serum cap with 15 ml of 2 *M* phenyllithium in ether–benzene (Lithium Corp. of America, New York, N. Y.) added by a syringe slowly with shaking. After 15 min additional shaking, it was worked up as above to give 72 mg of a brown solid, softening point 68–72°.

Anal. Calcd for $C_{11}H_{10}S$: C, 75.81; H, 5.78; S, 18.40; mol wt, 174. Found: C, 75.71; H, 5.92; S, 18.22; mol wt, 173 (Rast method).

The nmr showed only a single absorption centered at τ 2.8. The ultraviolet spectrum in ethanol showed λ_{max} (log ϵ) 202 (4.01) and 246 mμ (3.64), and major infrared absorption bands occurred at 3050 (35), 3020 (45), 1600 (40), 1580 (45), 1474 (35), 1437 (30), 1020 (40), 740 (60), and 685 cm^{-1} (65) (% abs).

The dipole moment and molecular refractivity were measured at 30 ± 0.002° using a General Radio Co. frequency capacitance bridge, oscillator, and null detector[12] to measure the dielectric constant of various concentrations of VI in benzene. The corresponding refractive indices were measured by a Pulferich refractometer. The Halverstadt–Kumler[13] equation was then used to calculate the molar polarization (142.67 cc), the molar refraction (130.28 cc), and the dipole moment (0.79 ± 0.2 D).

Mass Spectra of VI run at various inlet temperatures showed very low intensity parent peaks at 174 amu. The major peak at temperatures above 100° was biphenyl (154 amu), while at 90°, the major peak was the thiopyrylium ion (97 amu). In all spectra, there was a moderately intense peak at 186 amu, corresponding to diphenyl sulfide. These observations indicate that VI is very unstable to electron impact, decomposing readily to phenyl radical and thiopyrylium ion. The phenyl radical (or ion) must then rapidly attack another molecule of VI to form diphenyl sulfide and a $C_5H_4^+$ fragment, also very abundant in all the mass spectra. We believe the biphenyl is formed mainly by thermal decomposition in the inlet.

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Evidence and Hypothesis for a "Taube Bridge Electron Transfer" Propagating to a Remote Site through σ Bonding. The Formation of Ethylene from Monoethyl Sulfate

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Abstract: Ethylene has been produced from monoethyl sulfate by a reaction with a free radical or oxygen in the presence of a reduced metal ion, ferrous. A "Taube Bridge" mechanism involving electron activity at a remote site is proposed for this process.

The requirement for the close physical location of nuclei within molecular dimensions for redox processes was elegantly and conclusively taught by Westheimer[2a] in his ester mechanism for the two-electron chromic acid oxidation of alcohols, and this same kind of spatial requirement was established by Taube[2b] for many inorganic one-electron transfer reactions. This type of molecular arrangement can now be taken as a model frame of reference from which one should view all redox processes and is understood as a consequence of the molecular orbitals needed to transmit electrons across space.[3] The conduction of

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[1] Predoctoral Fellow, National Institute of Health Training Grant 1-T01-ES-84 from Division of Environmental Sciences.

[2] (a) F. H. Westheimer, *Chem. Rev.*, **45**, 419 (1949); (b) H. Taube and H. Meyers, *J. Amer. Chem. Soc.*, **76**, 2103 (1954).

[3] D. W. Urry and H. Eyring, *J. Theoret. Biol.*, **8**, 198 (1965).