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Naphthalene 1,8-Disulfide

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A re-examination of the synthesis of naphthalene 1,8-disulfide (I) has been made. The polarographic oxidation and reduction potentials of I and related compounds were investigated as well as their charge-transfer absorption maxima with tetracyanoethylene and *p*-chloranil. The electron spin resonance (e.s.r.) spectra of the anion and cation radicals generated by one-electron reduction and oxidation of I were also obtained. The results are interpreted in terms of the highest filled molecular orbital of I belonging to a π system delocalized over the entire molecule, while its lowest unfilled orbital is indicated to be perpendicular to the π system and localized predominantly on the sulfur atoms.

Molecules containing seven electrons delocalized in a planar ring may be expected to have exceptionally low ionization potentials and stable cationic derivatives. This consequence of the Hückel $4n + 2$ rule[1] is exemplified by the cycloheptatrienyl radical, which has been reported to have the extremely low ionization potential of 6.60 e.v. (electron impact)[2] or 6.24 e.v. (photoionization),[3] and whose cation, tropylium, is quite stable under a wide variety of conditions.[4] Neutral molecules without unpaired electrons but with seven delocalized electrons in a ring should be capable of existing in at least two stable oxidation states. Few oxidation–reduction systems involving such aromatic cations are known, and those that have been studied are mostly nitrogen compounds.[5] A possible nitrogen-free example of such a system is the red compound, naphthalene 1,8-disulfide (I), and its cation.

Geometric considerations indicate a planar structure for I. Thus, the distance between the *peri* positions in naphthalene is virtually identical with the S–S bond distance in aryl disulfide[3] (2.4 Å.) and the normal C–S–S disulfide bond angles agree closely with the 90° anticipated for planar I.[7,8] Delocalization of the electrons in the sulfur containing ring of I is indicated by its ultraviolet spectrum[9] which is markedly different from that of naphthalene, the normal disulfide linkage, or naphthalene-1,8-dithiol.

Results

Synthetic.—From the results of Desai and Tilak,[9] it appears that naphthalene 1,8-disulfide (I) was first prepared by Lanfrey,[10] who caused naphthalene and sulfur to interact in a hot iron tube. Price and Smiles[11] also reported the preparation of I, starting with 1-aminonaphthalene-8-sulfonic acid.

Our initial attempts to repeat the work of Price and Smiles were rather confusing. Characterization of the intermediates, however (*cf.* Experimental Section), indicated that, despite some unnecessary steps, these workers had indeed prepared I. The route reported by Price and Smiles (broken lines) and the reactions which we have found to occur (full lines) are depicted in Chart I. Thus, the disulfide–bissulfonic acid salt (IV) is obtained directly from copper–sulfur dioxide treatment of the diazonium salt (II) and further treatment with hydrogen iodide[11] is unnecessary. Treatment of IV with phosphorus pentachloride does not give the disulfonyl chloride as previous workers had assumed[9,11] but rather the cyclic thiosulfone (V) (a new compound) is formed. This, on zinc–hydrochloric acid reduction, followed by air oxidation of the resulting dithiol (VI), gives I. Naphthalene-1,8-dithiol (VI) is also readily methylated to give 1,8-bis(methylthio)-naphthalene (VII).[11]

Polarographic Oxidation.—The first polarographic half-wave oxidation potential of I occurs at 0.95 v. (*vs.*

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(1) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, Chapter 10.

(2) A. G. Harrison, L. R. Honnen, H. J. Dauben, Jr., and F. P. Lossing, *J. Am. Chem. Soc.*, **82**, 5593 (1960).

(3) B. A. Thrush and J. J. Zwolenik, *Proc. Chem. Soc.*, 339 (1962).

(4) W. E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **76**, 3203 (1954).

(5) Examples of molecules which have stable cation radicals are N,N,-N′,N′-tetramethyl-*p*-phenylenediamine, triarylamines, and phenothiazine derivatives.

(6) A. K. Kitaigorodskii, "Organic Chemical Crystallography," translated by Consultants Bureau, New York, N. Y., 1961, p. 403.

(7) However, the azimuthal angle around aryl disulfide linkages is usually 103° (ref. 8) and would be 0° here.

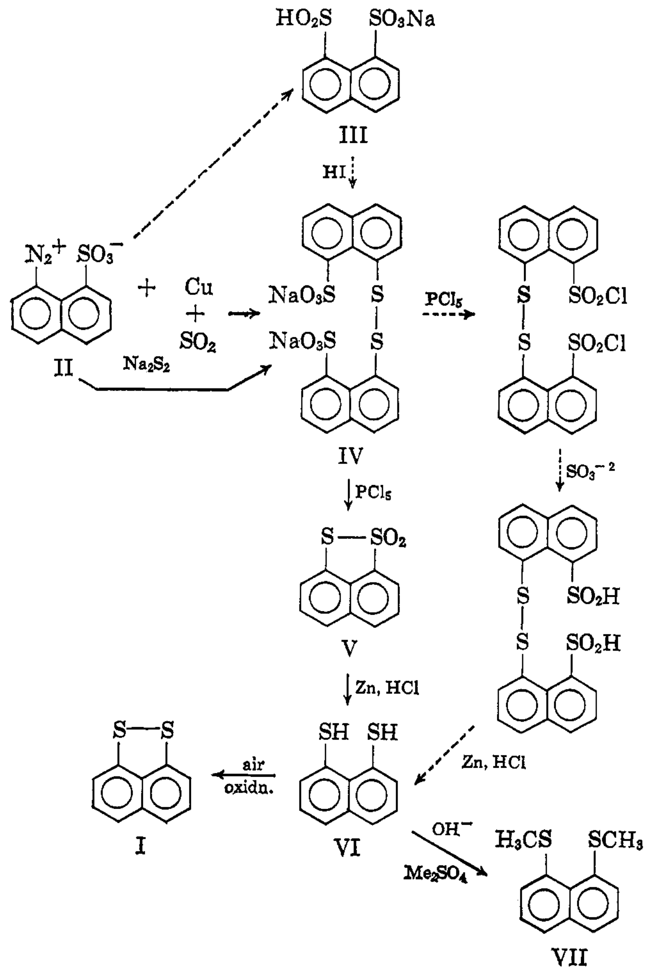
(8) C. C. Price and S. Oae, "Sulfur Bonding," Ronald Press, New York, N. Y., 1962, p. 42.

(9) H. S. Desai and B. D. Tilak, *J. Sci. Ind. Res.* (India), **19B**, 390 (1960).

(10) M. Lanfrey, *Compt. rend.*, **152**, 92 (1911).

(11) W. B. Price and S. Smiles, *J. Chem. Soc.*, 2372 (1928).

CHART I



s.c.e.) in acetonitrile at a rotating platinum electrode. The diffusion current for this wave corresponds to a one-electron transfer under the conditions employed.[12] Cyclic voltammetry in acetonitrile indicates that the one-electron oxidation product is stable at least to the limits that diffusion imposes on the measuring procedure (10–15 sec.). In 1,2-dimethoxyethane (DME), however, the cation has a lifetime of only *ca.* 2 sec. as estimated by the cyclic voltammogram. The first half-wave oxidation potentials of I and five related molecules, all apparent one-electron waves, are listed in Table I.

Charge-Transfer Complexes.—In methylene chloride solution naphthalene 1,8-disulfide forms colored charge-transfer complexes with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone, tetracyanoethylene (TCNE), and *p*-chloranil. The longest wave-length absorption maxima for these complexes occur at 970, 790, and 695 mμ, respectively.

A lustrous blue solid 1:1 complex of I and TCNE could be isolated. A pressed pellet of this complex had $\rho_{25} = 7.2 \times 10^{11}$ ohm-cm. A comparison of the positions of their longest wave-length absorption maxima with TCNE is given for I and related compounds in Table I.

Polarographic Reduction.—At a dropping mercury electrode, I undergoes one-electron reduction (I_D = 2.63)[12] at −0.98 v. (*vs.* s.c.e.) in dimethylformamide (DMF). Cyclic voltammetry indicates that this reduction species is stable under the conditions employed. A further reduction takes place at −2.65 v., but the nearness to background discharge precludes an *n*-value estimation for this process.

TABLE I

OXIDATION AND REDUCTION POTENTIALS AND CHARGE-TRANSFER MAXIMA FOR I AND RELATED COMPOUNDS

	$E_{1/2}$(oxidn.), v.[b]	C.t. max.,[a] cm.$^{-1}$ × 10^3	$E_{1/2}$(redn.), v.[b]
Naphthalene 1,8-disulfide (I)	+0.95	12.7	−0.98
1,8-Bis(methylthio)-naphthalene	+1.09	14.0	−2.22
9,10-Dithiophenanthrene	+1.47	18.2	−0.72
2,2′-Bis(methylthio)-biphenyl	+1.39	. . .[c]	−2.58
Thianthrene	+1.28	16.5	−2.59[d]
Naphthalene	+1.54	18.2	−2.50

[a] With TCNE in methylene chloride solution. [b] In acetonitrile *vs.* aqueous s.c.e. electrode unless otherwise indicated. [c] C.t. absorption is extremely weak and a maximum could not be assigned. [d] In dimethylformamide solution.

The reduction potentials of I and of 9,10-dithiophenanthrene are considerably lower than that of the other compounds in Table I,[13] but are similar to the reduction potential of diphenyl disulfide (−0.79 v.) in aprotic solvents.[14] The latter, however, undergoes two-electron transfer at its first reduction wave, while I and 9,10-dithiophenanthrene both undergo one-electron transfer.

E.s.r. of the Cation Radical of I.—Dissolution of I in concentrated sulfuric acid, or electrolytic oxidation of I in DME at its first oxidation wave relative to s.c.e., produces a paramagnetic species whose e.s.r. hyperfine coupling structure could be unambiguously assigned to interaction with three pairs of equivalent protons. The coupling constants are 5.30, 4.44, and 0.88 gauss in both solvents and the g value is 2.0081. When 1,8-bis(methylthio)naphthalene is dissolved in sulfuric acid, an e.s.r. spectrum identical with that derived from I was obtained after several minutes.

E.s.r. of the Anion Radical of I.—When I is reduced with sodium in DME in the e.s.r. microwave cavity, a single line, 1.04 gauss peak to peak, with g = 2.0110, is seen. Electrochemical reduction of I at its first reduction wave in the same solvent partially resolves this line into an overlapped 1:2:1 triplet, $a_H \cong 0.4$ gauss. Attempts to deuterate I selectively, to aid in the assignment of this triplet to the responsible pair of protons, have been unsuccessful (*cf.* Experimental Section).

Calculations and Discussion

Polarographic oxidation potentials and the energies of charge-transfer maxima with common acceptors have both been shown to be measures of the ionization potentials of aromatic hydrocarbons.[15] As both measurements are approximately linearly related to the ionization potential, they should bear a similar relationship to each other. This has been found to be the case

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(12) One cannot place too great a reliance on diffusion currents as a measure of Δn: *cf.* T. A. Miller, B. Prater, J. K. Lee, and R. N. Adams, *J. Am. Chem. Soc.*, **87**, 121 (1965).

(13) In 75% aqueous dioxane: G. J. Hoijtink and J. Van Schooten, *Rec. trav. chim.*, **71**, 1089 (1952).

(14) Unpublished results of W. H. Jura.

(15) See ref. 1, p. 188.

TABLE II

ENERGIES AND ELECTRON DISTRIBUTIONS IN THE HFMO AND LUMO OF I

	HFMO		LUMO	
	SCF	Hückel[a]	SCF	Hückel[a]
Energy	7.05 e.v.	−0.3434 (β)	+0.48 e.v.	+0.6689 (β)
Electron distribution[b]				
Positions 2, 7	0.062		0.053	
	(0.074)	0.077	(0.061)	0.052
3, 6	0.017		0.061	
	(0.022)	0.012	(0.075)	0.076
4, 5	0.085		0.183	
	(0.106)	0.099	(0.164)	0.017

[a] Parameters employed: $\alpha_s = \alpha_c + \beta_{cc}\ \beta_{cs} = \beta_{ss} = 0.5\beta_{cc}$ (*cf.* ref. 23). [b] Closed-shell SCF results are in parentheses.

in the aromatic hydrocarbon studies, and the linearity observed between the two types of measurements for the sulfur compounds listed in Table I suggests that the oxidation potentials and charge-transfer maxima of these compounds are similarly related to their ionization potentials. As ionization potentials are a measure of orbital energy levels and as e.s.r. hyperfine coupling constants are a measure of spin distribution, information is thus experimentally available on some fundamental molecular characteristics for I.

Such experimental data can be correlated and compared with highly approximate molecular orbital methods, such as the Hückel method, but they are also of importance for more rigorous quantum mechanical treatment. This is particularly interesting in the case of I which offers an apparently planar rigid structure, C_{2v} symmetry, and low molecular weight in a sulfur derivative of naphthalene, itself a much theoretically studied hydrocarbon. For these reasons closed-shell SCF calculations of the type developed by Pariser and Parr[16] and Pople[17] (PPP) were performed.

The matrix elements of the SCF Hamiltonian which include the assumption of zero differential overlap,[16] can be expressed as

$$H_{rs} = \delta\omega_r + (R_{rr}\gamma_{rr} - {}^1/_2\gamma_{cc}{}^\circ) + \sum_{s(\neq r)}(2R_{ss} - Z_s)\gamma_{rs}$$

$$H_{rs} = \beta_{rs} - R_{rs}\gamma_{rs}$$

using the notation of McWeeny,[18] where $\delta\omega_r$ is defined as $\omega_r - \omega_c$, the difference in ionization potential of atom r under consideration and a 2p orbital on a carbon atom in an alternant hydrocarbon. The carbon–carbon resonance integrals were calculated by the method of Pariser and Parr[16]; however, the repulsion integrals were evaluated by the method of Mataga and Nishimoto[19] assuming planar geometry (*vide infra*). The valence-state ionization potentials and electron affinity of divalent sulfur as suggested by Sappenfield and Kreevoy[20] were employed and the resulting SCF eigenvalues were adjusted assuming that $\omega_c = 9.50$ e.v., an empirical value obtained from alternate hydrocarbon studies.[21] The adjacent carbon–sulfur resonance integral was taken as −1 e.v., and the sulfur–sulfur resonance integral was taken as −0.8 e.v. The ionization potential and electron affinity of I calculated in this manner, and corrected for the McWeeny $\delta\omega_c - {}^1/_2\gamma_{cc}{}^\circ$, are reported in Table II.

Open-shell SCF calculations by the method described by Roothaan[22] were also made. The closed-shell SCF density matrix was used to construct the starting Hamiltonian matrix. The spin density thus calculated for the three proton-bearing sites in the cation radical and anion radical of I are reported in Table II. These values were found to be relatively unchanged from the charge distributions that had been calculated at the same sites in the highest filled (HFMO) and lowest unfilled molecular orbitals (LUMO) of I by the closed-shell procedure. The latter values are reported in parenthesis in Table II.

Insight into the molecular orbital structure of I with only two heteroatom parameters can be achieved by the Hückel method. This is because symmetry transformations couple the sulfur core integrals (α_s) and the sulfur–sulfur bond integral ($\beta_{s\text{-}s}$) in the submatrix containing the highest filled and lowest unfilled molecular orbital—the orbitals for which experimental evidence is available. Table II also reports the energies of the highest filled and lowest unfilled molecular orbitals of I and the unpaired electron distribution in the ion radicals of I as calculated by the Hückel method. The Hückel parameters that were employed are indicated in the table.[23] These parameters were also used to generate the starting *R* matrix for the closed-shell SCF procedure, using the assumption that the Hückel β_{cc} has a value of −4.8 e.v.

Both the closed-shell SCF calculations and the Hückel treatment give values for the energy of the HFMO of I which are in reasonably good agreement with the values which can be estimated from the oxidation potential and charge-transfer data. The polarographic oxidation potential of I is close to that of anthracene (+1.09 v.)[24] which has a measured electron-impact ionization potential of 7.55 e.v.[25] Similarly, the energy of the charge transfer maxima of I with *p*-chloranil[26] and with TCNE[27] correspond to an ionization potential of 7.2 e.v. From the Hoijtink relation-

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(16) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953).

(17) J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).

(18) R. McWeeny and T. E. Peacock, *Proc. Phys. Soc.* (London), **A70**, 41 (1957); R. McWeeney, *ibid.*, **A70**, 593 (1957).

(19) N. Mataga and K. Nishimoto, *Z. Physik. Chem.* (Frankfurt), **13**, 140 (1957).

(20) D. S. Sappenfield and M. M. Kreevoy, *Tetrahedron, Suppl. 2*, **19**, 157 (1963).

(21) N. S. Hush and J. A. Pople, *Trans. Faraday Soc.*, **51**, 600 (1955).

(22) C. C. J. Roothaan, *Rev. Mod. Phys.*, **32**, 179 (1960).

(23) Values for α_s and β_{cs} are similar to those suggested by A. Kuboyama [*J. Am. Chem. Soc.*, **86**, 164 (1964)]. The value used for β_{ss} is somewhat lower than that calculated for 3pπ–3pπ overlap at 2.4 Å. using Slater orbitals [R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949)] and the Mulliken "Magic Formula" relating overlap and resonance integrals.

(24) E. S. Pysh and N. C. Yang, *J. Am. Chem. Soc.*, **85**, 2124 (1963).

(25) M. E. Wacks and V. H. Dibeler, *J. Chem. Phys.*, **31**, 1557 (1959).

(26) G. Briegleb and J. Czekalla, *Z. Elektrochem.*, **63**, 6 (1959).

(27) G. Briegleb, J. Czekalla, and G. Reuss, *Z. Physik. Chem.* (Frankfurt), **30**, 333 (1961).

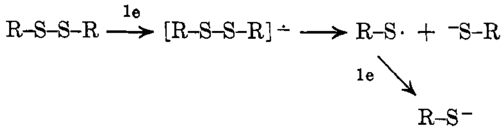
ship[28] of the Hückel HFMO and polarographic oxidation potentials of alternant hydrocarbons, the energy of the HFMO of I might be expected to be $\cong 0.45\beta$. Similarly, the relationship between HFMO energies and $\lambda_{\max}$ of hydrocarbon complexes with tetracyanoethylene[29] suggests a HFMO for I of $\sim 0.4\beta$. Both results are slightly more negative than the value calculated by the Hückel procedure (0.34β), using ordinary parameters. The ionization potential of naphthalene 1,8-disulfide as measured directly, by electron impact, in the mass spectrometer was found[30] to be 7.06 e.v. Although there are some uncertainties associated even with this direct ionization potential method of measurement,[31] the agreement with the calculations is found to be good.

In sharp contrast to the oxidation potential relationship, the reduction potential of I suggests[31] a Hückel LUMO of 0.08β instead of the calculated 0.67β. The SCF calculations also predict that I should be considerably more difficult to reduce than would be indicated by the reduction potential.[31]

Thus, the ease of reduction of I, relative to that of naphthalene, cannot be anticipated from ordinary π molecular orbital calculations. The apparently anomolous character of the LUMO of I is further indicated by a comparison of the e.s.r. spectra of its ion radicals with calculated unpaired electron densities. On both a theoretical[32] and experimental[33] basis aryl proton hyperfine coupling constants have been shown to be proportional to the spin density on the contiguous ring carbon atoms. Therefore, the 5.30-, 4.44-, and 0.88-gauss couplings in the cation radical of I may be assigned to the 4,5, 2,7, and 3,6 protons, respectively, based on Hückel unpaired electron distribution. The SCF calculations for the cation of I gave eigenvectors whose square bore no resemblance to the observed e.s.r. spectra. Parameters for SCF calculations which are adequate in accounting for several molecular properties seem to be difficult to find.[34,35]

Both Hückel and SCF calculations, however, suggest that the anion radical of I will have an e.s.r. spectrum similar to that of the cation with perhaps a somewhat narrower over-all spread. Reduction of the spread of the spectrum is anticipated from the smaller proportion of unpaired electron at the π sites adjacent to ring protons and because cation radicals are known[36,37] to have a larger σ–π interaction than the corresponding anion radicals. These effects do not account for the extremely narrow spectrum that is observed for the anion radical of I. The limited spread of the e.s.r. spectrum of this radical together with its g value higher than that of the cation radical indicates that the unpaired spin is highly localized on sulfur and interacts only weakly with the ring protons.

The polarographic potentials and e.s.r. spectra are thus consistent with the conclusion that the LUMO of I is not in a delocalized π system but in an orbital localized on sulfur. From the apparent geometry of I, the framework of sulfur bonding may be assumed to be essentially p^2. The four remaining third-shell electrons on each sulfur must then be divided between a 3s orbital and the $3p_z$ orbital perpendicular to the molecular plane. Molecular orbitals constructed from the 3s orbitals will be filled and over-all nonbonding. The $3p_z$ orbitals are those which interact with the aromatic π system. The remaining possibilities for the lowest acceptor orbitals of I are molecular orbitals constructed from 3d orbitals on sulfur, or the antibonding orbital associated with the sulfur–sulfur p_σ–p_σ bond. A pure d orbital seems unlikely since it would not be orthogonal to, and hence would be expected to interact strongly with, the π system. The sulfur–sulfur p–p antibonding orbital (a σ orbital), perhaps with some d orbital hybridization, can well account for the unique one-electron reduction of I.[38] Noncyclic aryl disulfides investigated undergo two-electron reduction.[14] Presumably, the one-electron adduct undergoes S–S bond cleavage to give a thiol anion and a sulfenyl radical. The latter undoubtedly has an electron affinity higher than that of the disulfide resulting in over-all two-electron transfer.



$$\begin{array}{l} \text{R–S–S–R} \xrightarrow{\text{1e}} [\text{R–S–S–R}]^{\cdot-} \longrightarrow \text{R–S}\cdot + {}^{-}\text{S–R} \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad \searrow^{\text{1e}} \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \text{R–S}^{-} \end{array}$$

In the monoanion of compound I sulfur atoms are retained within bonding distance because of the rigid naphthalene backbone, and further reduction is made difficult by electronic repulsion. Exceptional cyclic disulfide dianion stabilization is neither anticipated nor observed for I in aprotic solvents, although such stabilization has been reported for aqueous solutions of "aromatic" 1,2-dithiete derivatives.[39]

The red color of I may be accounted for as a result of having the lowest unfilled molecular orbital perpendicular to the π system. Absorption maxima, mμ (log ϵ), are observed at 425 (2.18), 460 (2.01), and 490 (1.85). These extinction coefficients are reminiscent of symmetry forbidden n → π^* transitions, and the bands may possibly be due to a $\pi \rightarrow \sigma^*$ transition in this instance.

Experimental Section[40]

Naphtho[1,8-*cd*]-1,2-dithiol 1,1-Dioxide.—1-Aminonaphthalene-8-sulfonic acid (Eastman Kodak Co.), 60 g. (0.27 mole), finely powdered, was mixed to a paste with water in a mortar. The paste was transferred to a flask containing 200 ml. of water. Sulfuric acid (50 ml.) was added followed by sufficient ice to

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(28) G. J. Hoijtink, *Rec. trav. chim.*, **77**, 555 (1958).

(29) M. J. S. Dewar and H. Rogers, *J. Am. Chem. Soc.*, **84**, 395 (1962)

(30) We wish to thank T. E. Mead of these laboratories for this measurement.

(31) G. Briegleb, *Angew. Chem. Intern. Ed. Engl.*, **3**, 617 (1964).

(32) M. Karplus and G. K. Fraenkel, *J. Chem. Phys.*, **35**, 1312 (1961), and references therein.

(33) *Cf.* M. C. R. Symons in "Advances in Physical Organic Chemistry," V. Gold, Ed., Academic Press Inc., New York, N. Y., 1963, p. 283.

(34) T. Nakajima, *Bull. Chem. Soc. Japan*, **38**, 83 (1965).

(35) A pertinent discussion on "Parameters in Advanced M.O. Methods" can be found in the article by R. D. Brown in "Molecular Orbitals in Chemistry, Physics, and Biology—A Tribute to R. S. Mulliken," P. O. Lowdin and B. Pullman, Ed., Academic Press Inc., New York, N. Y., 1964, p. 502.

(36) A. Carrington, F. Dravnieks, and M. C. R. Symons, *J. Chem. Soc.*, 947 (1959).

(37) J. R. Bolton and G. K. Fraenkel, *J. Chem. Phys.*, **40**, 3307 (1964).

(38) Professor R. Hoffmann has informed us that these conclusions are in excellent agreement with molecular orbital calculations made by the extended Hückel method [*cf.* R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963)]. Professor Hoffmann finds that the 3d orbitals on sulfur included the calculations σ^* is the LUMO. In addition, σ^* is predominantly S_{3p_y} (~75%) with an appreciable admixture of $S_{3d_{x^2-y^2}}$ (~11%) and quite localized on *S* (92% in terms of Mulliken gross atomic populations).

(39) H. E. Simmons, D. C. Blomstrom, and R. D. Vest, *J. Am. Chem. Soc.*, **84**, 4756 (1962).

(40) All melting points are uncorrected.

make a volume of 800 ml. A solution of 30 g. (0.43 mole) of sodium nitrite in 100 ml. of water was added with stirring over 0.5–0.75 hr. The internal temperature of the reaction mixture was maintained at −10 to −15° throughout the addition. After stirring the reaction mixture for 1.5 hr. further at −10 to −15°, the solid, pale brown diazonium sulfonate was filtered and washed with 100 ml. of ice–water. The still-wet, pasty diazonium salt was added to 200 ml. of sodium sulfide solution[41] at 0 to −10°, and the foamy mass was allowed to stand at room temperature for 3 hr. The pH of this material was brought to 7.5 by addition of concentrated hydrochloric acid, and the hot reaction mixture was filtered to remove sulfur. On cooling crude disulfide disulfonic acid (IV) precipitated. A further quantity could be obtained by saturating the reaction mixture with sodium chloride. The total yield of crude dried disodium 8,8'-dithiodi-1-naphthalenesulfonate was 45 g. The infrared spectrum (with sulfonate ion absorption at 1060 and 1200 cm.$^{-1}$) was fully consistent with this structure. Polarography confirmed the presence of the disulfide linkage.

The crude, anhydrous disodium salt (47 g.) was powdered, cooled in ice, and treated with 30 g. (0.14 mole) of phosphorus pentachloride, added slowly so that the reaction mixture did not warm. During the addition the reaction mixture became pasty and partially fluid. This mixture was allowed to warm to room temperature and stand for 0.5 hr. and then was triturated with 100 ml. of benzene and filtered. The product was repeatedly extracted with benzene until the extract was essentially colorless.

After treatment with ice, the combined benzene extracts were concentrated and the residue was taken up in methanol treated with charcoal and crystallized. The yield was 18 g. (45%) of pale yellow needles, m.p. 148–149°. This compound had infrared absorption maxima at 1130 and 1310 cm.$^{-1}$ characteristic of thiosulfones.

Anal. Calcd. for $C_{10}H_6O_2S_2$: C, 54.03; H, 2.72; S, 28.85; O, 14.56. Found: C, 54.14; H, 2.79; S, 28.85; O, 14.56.

Naphthalene-1,8-dithiol, Naphthalene 1,8-Disulfide, and 1,8-Bis(methylthio)naphthalene.—These compounds were prepared by the method of Price and Smiles,[11] using the zinc–hydrochloric acid procedure on the above dioxide. Over-all, from several similar experiments, 62 g. (69%) of pure naphthalene 1,8-disulfide, m.p., 116°, was obtained from 123 g. of disodium 8,8'-dithiodi-1-naphthalenesulfonate.

9,10-Dithiophenanthrene and 2,2'-Bis(methylthio)biphenyl.—These compounds were prepared by literature methods[42] from 2,2'-dithiobiphenyl. The latter compound was prepared by lithium aluminum hydride reduction of the corresponding disulfonyl chloride.[43]

Deuterium Exchange Experiments.—A potassium *t*-butoxide solution was prepared by dissolution of 0.20 g. (0.053 g.-atom) of potassium in 11.25 g. of 80–90% deuterio-*t*-butyl alcohol. To this solution was added 1.0 g. (0.0052 mole) of naphthalene-1,8-dithiol, and the mixture was stirred overnight. Naphthalene 1,8-disulfide was obtained in quantitative yield by air oxidation. The infrared spectrum of the product was identical with that of undeuterated disulfide indicating that little or no aromatic proton exchange had occurred.

Two exchange experiments were run in acid media. In the first, 3.0 g. (0.016 mole) of naphthalene-1,8-dithiol was treated with 15 ml. of deuterioacetic acid and 0.3 g. of dideuteriosulfuric acid and in the second 1.0 g. (0.0053 mole) of naphthalene 1,8-disulfide was treated with 10 ml. of deuterioacetic acid and 0.2 g. of dideuteriosulfuric acid. Both runs were made at 108° for 30 hr. In each case the isolated naphthalene 1,8-disulfide contained appreciable deuterium as indicated by the infrared spectrum. Both the infrared and n.m.r. spectra, however, indicated unspecific deuteration. There was no suggestion of an emerging AB pattern in the n.m.r. spectrum. Such a pattern would be seen if deuterium exchange at specific ring sites occurred at a rate appreciably greater than at other sites.

Charge-Transfer Complex.—TCNE, 0.095 g., was dissolved in 25 ml. of methylene chloride (warmed slightly and shaken to effect solution) and filtered into a stirred solution of 0.141 g. of naphthalene 1,8-disulfide dissolved in 10 ml. of methylene chloride. The resulting green solution was concentrated to 10 ml. and the mixture was filtered cold to give 0.11 g. (47%) of blue needles, m.p. 138–140°.

Anal. Calcd. for $C_{16}H_6N_4S_2$: C, 60.36; H, 1.90; N, 17.60; S, 20.14. Found: C, 60.43; H, 2.21; N, 17.26; S, 20.13.

Measurements. Charge-Transfer Maxima.—These were obtained by mixing concentrated methylene chloride (spectral grade) solutions of the thiosubstituted aromatics and the acceptors in equimolar proportions, then diluting, if necessary. All spectral measurements were made on a Cary 14 spectrophotometer at 22°. Since only charge-transfer maxima were relevant to this investigation, no attempt was made to measure equilibria and extinction coefficients for the complexes. Quantitative ultraviolet spectra were also obtained in the Cary 14 instrument.

Polarography.—The polarographic data were obtained at room temperature on a Leeds and Northrup Electrochemograph, Type E. Oxidations were carried out in dry (<0.01% water) acetonitrile at a rotating platinum electrode with 0.1 *M* tetra-*n*-propylammonium perchlorate as supporting electrolyte. Reductions were performed at a dropping mercury electrode. An aqueous saturated calomel reference electrode (s.c.e.) was used throughout. The electrochemical cell used to carry out controlled potential electrolyses in the e.s.r. cavity was essentially the same as that described in the literature.[44,45]

E.s.r. Spectra.—The e.s.r. spectrometer was a Varian Model V-4502 with 100 kc./sec. modulation and a Varian 6-in. magnet. Sulfuric acid solutions were prepared by dissolving a few milligrams of material in 96% sulfuric acid and then transferring to the Varian V-4548 flat quartz cell. The spectra were calibrated against the hyperfine splitting of 13.0 gauss of an aqueous solution of peroxylamine disulfonate which was contained in a melting point capillary placed in the cavity along with the solution of the radicals under investigation.

Molecular orbital calculations were made by a Burroughs Model 205 computer using programs especially written for this machine.

N.m.r. Spectra.—The proton magnetic resonance spectra were measured in carbon tetrachloride containing a small amount of tetramethylsilane as an internal standard. The spectra were obtained either on a Varian Model DP60 spectrophotometer at 56.4 Mc./sec. or on a Varian A-60 spectrophotometer.

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