ism, the original authors[27] provided no evidence of which isomer was obtained. Apparently, in our hands the synthesis produced a mixture of isomers. This was clearly shown by the ^{13}C NMR spectrum which is fully consistent with a mixture of the trans and cis isomers in the ratio of about 2:1. The trans isomer has the following ^{13}C NMR (δ_{Me_4Si}[26], D_2O): 55.2 (C_6), 39.8 (C_2, C_{10}), 31.0 (C_5, C_7), 24.8 (C_3, C_9), 23.9 (C_4, C_8). ^{1}H NMR (D_2O, 270 MHz): δ 1.5–2.4 (6 H, broad multiplet, β and γ protons), 3.2 (2 H, t, axial α-methylene), 3.3 (1 H, q, α-methyne), 3.6 (2 H, d, equatorial α-methylene). The cis isomer has ^{13}C NMR δ 43.7 (C_6), 31.8 (C_2, C_{10}), 26.6 (C_5, C_7), 20.6 (C_3, C_9), 20.6 (C_4, C_8). ^{1}H NMR δ 1.5–2.4 (6 H, broad m, β and γ protons), 3.3 and 3.5 (5 H, broad m's, α protons).

Attempts to enrich the isomer mixture in the trans isomer (presumably the more stable thermodynamically) by thermal pyramidal inversion[27] were unsuccessful. Fractional crystallization of both the bromide and the hexafluorophosphate did not produce appreciable enrichment. Therefore the exchange was studied directly on the 2:1 isomer mixture. This caused no special difficulty since the α protons of the minor (cis) isomer turned out to exchange more than ten times faster than the more reactive proton of the trans isomer. The exchange of the latter could then be studied without interference.

References and Notes

(1) (a) Laboratorio dei Composti del Carbonio Contenenti Eteroatomi del C.N.R., (b) Università di Bologna.

(2) (a) G. Barbarella, A. Garbesi, and A. Fava, *J. Am. Chem. Soc.*, **97**, 5883 (1975); (b) ref 2–7 in ref 2a.

(3) (a) M. Cinquini, S. Colonna, and F. Montanari, *Chem. Commun.*, 1441 (1970); (b) P. Calzavara, M. Cinquini, R. Fornasier, and F. Montanari, *J. Am. Chem. Soc.*, **95**, 7431 (1973); (c) B. M. Trost and R. Hammen, *ibid.*, **95**, 962 (1973).

(4) S. Wolfe, *Acc. Chem. Res.*, **5**, 102 (1972).

(5) (a) R. R. Fraser, F. J. Schuber, and Y. Y. Wigfield, *J. Am. Chem. Soc.*, **94**, 8794 (1972); (b) G. Barbarella, A. Garbesi, A. Boicelli, and A. Fava, *ibid.*, **95**, 8051 (1973); (c) R. Lett, S. Bory, B. Moreau, and A. Marquet, *Tetrahedron Lett.*, 3255 (1971).

(6) Thianium cations not possessing a strong conformational bias have been previously found to undergo exchange with little stereoselectivity if any.[7]

(7) (a) G. Barbarella, A. Garbesi, and A. Fava, *Helv. Chim. Acta*, **54**, 2297 (1971); (b) O. Hofer and E. L. Eliel, *J. Am. Chem. Soc.*, **95**, 8045 (1973).

(8) The fundamentals of perturbation theory may be found in several quantum

mechanic texts; see, for example, H. Heilbronner and H. Bock, "Das Hückel MO Modell und Seine Anwendung", Verlag Chemie, Weinheim/Bergstr., Germany, 1968; R. Hoffmann, *Acc. Chem. Res.*, **4**, 1 (1971); M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry", McGraw-Hill, New York, N.Y., 1969.

(9) Recently Hunter[10] and Fraser[11] have warned against the possibility that H–D exchange rates may not be directly relatable to carbanion stability, because of internal return.[12] In aqueous solvent, however, internal return is undoubtedly negligible,[13] and Fraser's results themselves stand to prove it.[11]

(10) D. H. Hunter, Y. Lin, A. L. McIntyre, D. J. Shearing, and M. Zvagulis, *J. Am. Chem. Soc.*, **95**, 8327 (1973).

(11) R. R. Fraser and L. K. Ng, *J. Am. Chem. Soc.*, **98**, 4334 (1976).

(12) D. J. Cram, "Fundamentals of Carbanion Chemistry", Academic Press, New York, N.Y., 1965, Chapters 3, 5.

(13) (a) J. Almy, D. C. Garwood, and D. J. Cram, *J. Am. Chem. Soc.*, **92**, 4321 (1970); (b) D. H. Hunter, "Isotopes in Organic Chemistry", E. Buncel and C. C. Lee, Ed., Elsevier, Amsterdam, 1975, p 135.

(14) A similar interaction (n_C–$\sigma^*_{S–H}$) has recently been found to be the major factor responsible for the preferred conformation and relative stability of oxy and thio carbanions.[15]

(15) N. D. Epiotis, R. L. Yates, F. Bernardi, and S. Wolfe, *J. Am. Chem. Soc.*, **98**, 5435 (1976).

(16) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).

(17) All computations have been carried out with the Gaussian 70 system of programs: W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, Program No. 236, Quantum Chemistry Program Exchange, University of Indiana, Bloomington, Ind.

(18) E. L. Eliel and R. L. Willer, *J. Am. Chem. Soc.*, **96**, 3021 (1974).

(19) G. Barbarella, unpublished.

(20) G. Barbarella, P. Dembech, A. Garbesi, and A. Fava, *Tetrahedron*, 1045 (1976).

(21) V. I. Dronov and V. P. Krivonogov, *Khim. Geterotsikl. Soedin.*, 622, 1186 (1972).

(22) D. K. Dalling, D. M. Grant, and E. G. Paul, *J. Am. Chem. Soc.*, **95**, 3718 (1973).

(23) (a) G. Barbarella, P. Dembech, A. Garbesi, and A. Fava, *Org. Magn. Reson.*, **8**, 108, 469 (1976); (b) R. L. Willer and E. L. Eliel, *J. Am. Chem. Soc.*, **99**, 1925 (1977).

(24) E. L. Willer and E. L. Eliel, *Org. Magn. Reson.*, in press. We thank Professor Eliel for letting us know of their results before publication.

(25) R. H. Eastman and G. Kritchevsky, *J. Org. Chem.*, **24**, 1428 (1959).

(26) The internal standard was $(CH_3)_3SiCD_2CD_2Na$ (Me_3SiPNa); the shieldings have been converted to the Me_4Si scale using the value δ_{Me_4Si}, −1.8 ppm for the methyl carbon of Me_3SiPNa.[23a]

(27) D. Darwish and G. Tourigny, *J. Am. Chem. Soc.*, **88**, 4303 (1966); R. Scartazzini and K. Mislow, *Tetrahedron Lett.*, 2719 (1967); A. Garbesi, N. Corsi, and A. Fava, *Helv. Chim. Acta*, **53**, 1499 (1970).

Electronic Structure of the π Donor Naphthalene 1,8-Disulfide[1]

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Abstract: Naphthalene 1,8-disulfide (**1**) was synthesized via known methodology and rigorously purified. TCNQ reacts with **1** to give a new donor–acceptor complex with a charge-transfer maximum at 925 nm and the electrical properties of an insulator. Ultraviolet photoelectron spectroscopy (UV PES) in the gas phase and solid state was used to study the molecular electronic structure of **1**; vertical ionization energies of 7.15 and 5.75 eV are observed in the gas and solid, respectively. The UV PES results are interpreted by means of perturbation molecular orbital (PMO) and CNDO/S2 calculations. It is found that the highest occupied molecular orbital structure is determined by π interactions between sulfur lone pairs and naphthalene π levels. The present work confirms an earlier suggestion that coplanar sulfur–sulfur lone pair interactions in disulfides should be ~2.0 eV.

Introduction

The present study of the electronic structure of naphthalene 1,8-disulfide (**1**), a compound first isolated from the reaction of naphthalene and sulfur vapors in a hot iron tube,[2] was carried out in connection with our continuing interest in the chemical and physical properties of novel organochalcogen compounds, particularly with respect to relationships between

their molecular properties and novel solid-state phenomena.[3-6] Physical properties of **1** studied previously include its dipole moment,[7] the solution electron spin resonance of its cation radical[8,9] and its anion radical,[8] charge-transfer spectra,[8] and both solution and solid state Raman spectra.[10] Recently, the synthesis of the selenium and tellurium analogues of **1** has been reported;[11] the tellurium compound was reported to form a

Table I. Comparison between Measured Vertical Ionization Potentials and Calculated Orbital Energies (eV)

Band	I_v	PMO, ϵ	CNDO/S2, ϵ
1	7.15	−7.1 (a₂)	−7.3 (a₂)
2	8.95	−8.9 (b₁)	−8.6 (b₁)
3	9.30	−9.0 (b₁)	−9.1 (b₁)
4	9.44	−9.1 (a₂)	−9.5 (a₂)
5	11.18	−11.0 (b₁)	−11.4[a] (b₁)

[a] Three σ levels are predicted to lie higher in energy than this level at −10.5, −10.6, and −11.1 eV, respectively.
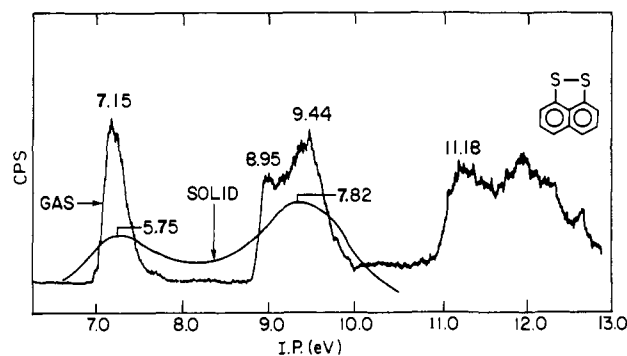

Figure 1. Gas phase (21.2 eV, heavy line) and solid (9.18 eV, thin line) photoemission spectra for naphthalene 1,8-disulfide. The solid spectrum has been shifted by 1.43 eV (the polarization energy) to align the peaks with those of the gas phase spectrum. Actual ionization energies are indicated on the curve.

conducting compound with 7,7,8,8-tetracyanoquinodimethan (TCNQ, 2). Moreover, TCNQ is known to form conducting salts with 1,4,5,8-tetrathianaphthalene[12] (3) and tetrathiotetracene[13,14] (4), two organosulfur donors with structural features in common with 1. Clearly, the electronic structure of 1 is a matter of current interest.
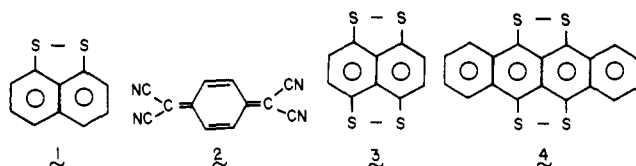
In the present work, 1, synthesized according to known methodology,[8] was rigorously purified. The improved purity of our samples is manifested in a higher melting point than previously observed and by the absence of low intensity maxima previously reported[8,15] in the visible spectrum of 1 (see Experimental Section). TCNQ reacts with 1 to give an insulating donor–acceptor complex. The molecular electronic structure of 1 was studied by ultraviolet photoelectron spectroscopy (UV PES) in the gas phase and solid state and the results of these experiments are used to estimate the polarization energy of the crystal. The photoelectron spectroscopy data is interperted by the use of a perturbation molecular orbital (PMO) scheme and a CNDO/S2 calculation with mutually consistent results.

Experimental Section

General. Melting points are uncorrected. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. The mass spectrum was obtained from Shrader Analytical Laboratory, Detroit, Mich. Ultraviolet–visible spectra were obtained on a Cary 15 spectrophotometer and the charge-transfer spectrum was obtained on a Cary 17D spectrophotometer, both in 1-cm cells.

UV PES. The high resolution gas phase photoelectron spectrum of 1 was obtained on a VG ESCA-2 photoelectron spectrometer using HeI radiation. The energy scale was calibrated using the photoelectron lines of the rare gases, which were run concurrently with the sample. The HeI spectrum is shown in Figure 1 and ionization energies are given in Table I.

Compound 1 was also sublimed in a vacuum of 1 × 10⁻¹⁰ Torr onto a polycrystalline-gold-coated substrate at ∼100 K, in a photoemission apparatus previously described.[16] The inelastic scattering length of electrons 5.7 eV above the vacuum level of 1 was determined by observing the decrease in electrons emitted form the gold substrate as small amounts of 1 were deposited. The transmission had the expected exponential decrease with increasing deposit, and the 1/e scattering length was 3.04 × 10¹⁴ molecules cm⁻². This value is somewhat larger than those obtained earlier[17] for TNCQ and tetrathiafulvalene (TTF, 5), 1.9 and 2.0 × 10¹⁴ molecules cm⁻², respectively. Photoemission spectra of condensed films were obtained at various photon energies between 7.7 and 10.2 eV; the spectrum at 9.18 eV of a 12.5 × 10¹⁴ molecules cm⁻² deposit is shown as the thin line in Figure 1. This spectrum has been shifted before plotting by 1.43 eV so that corresponding peaks of gas and solid spectra are aligned—the actual ionization energies of the peak centers are marked in the figure. The curve amplitude was adjusted so that the area under the peak at 7.15 eV was the same for gas and solid. The area under the curve, between 8.1 and 10.6 eV, is 2.10 times the area under the first peak in both gas and solid.

Naphthalene 1,8-Disulfide (1). Naphthalene 1,8-disulfide was synthesized according to the method of Zweig and Hoffman.[8] The crude product was purified either by chromatography on silica gel with hexane elution followed by vertical sublimation or by gradient sublimation[18] at 50 °C (10⁻⁶ mm), mp 120–121 °C (lit. mp 118.5,[2] 116,[8,19] 118,[15] 119 °C[7,20]). The infrared spectrum of 1 (Nujol) between 2000 and 625 cm⁻¹ is in agreement with that reported.[21] The mass spectrum shows parent and base peak at m/e 190. The absorption spectrum obtained in methylcyclohexane exhibited the following: λ_{max} 460 nm (sh, ε 70), 376 (sh, 11 000), 371 (15 000), 357 (12 000), 292 (sh, 400), 286 (500), 253 (26 000), 222.5 (sh, 11 000), 216 (sh, 14 000), 206 (33 000). This data is in satisfactory quantitative agreement with that reported earlier[15] between 200 and 400 nm. The absence of maxima reported earlier[8,15] and reduced intensity between 400 and 600 nm are consistent with improved purity in our samples. No evidence of the maxima reported earlier could be found in cyclohexane, dichloromethane, ethanol, and pyridine solutions. Anal. Calcd for C₁₀H₆S₂: C, 63.12, H, 3.18; S, 33.70. Found (performed in triplicate): C, 63.15 ± 0.07, H, 3.18 ± 0.11; S, 33.64 ± 0.20.

Complex of 1 with TCNQ. To a solution of gradient-sublimed TCNQ (0.10 g, 0.49 mmol) in acetonitrile was added solid 1 (0.15 g, 0.79 mmol) and the mixture was heated to boiling. Since no precipitation occurred when the solution cooled to room temperature, the solvent was slowly evaporated with nitrogen gas. In this manner, a greenish black crystalline solid, 0.09 g (47% yield), mp 229–231 °C dec, was obtained. In dichloromethane solution at a concentration of 1.2 × 10⁻² M in both 1 and TCNQ, an absorption maximum assigned to a charge-transfer transition was observed at 925 nm. Anal. Calcd for C₂₂H₁₀N₄S₂: C, 66.98; H, 2.56; N, 14.20; S, 16.26. Found: C, 66.92; H, 2.58; N, 14.39; S, 16.01.

Results and Discussion

A. Donor–Acceptor Complex of 1 and TCNQ. TCNQ reacts with 1 in acetonitrile solution to give a greenish black crystalline complex of 1:1 stoichiometry. This complex exhibited a resistivity of 10¹⁰ Ω-cm, measured as a compressed pellet. The resistivity of this new complex is comparable with that reported[22] for complexes of TCNQ with the 2,3- 1,5-diamino derivatives of naphthalene, 10¹⁰ and 10⁹ Ω-cm, respectively. The tetracyanoethylene (TCNE) complex of 1 was reported to have a resistivity of 7.2 × 10¹¹ Ω-cm.[8] In dichloromethane solution 1 and TCNQ show a charge transfer maximum at 925 nm. The TCNE and 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ, 6) complexes of 1 show maxima at 790 and 970 nm in the same solvent.[8]
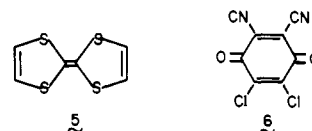
B. Gas Phase and Solid-State UV PES of 1. The 21.2-eV gas phase ultraviolet photoelectron spectrum of **1**, shown in Figure 1, shows the first vertical ionization of **1** at 7.15 eV. Earlier work[8] reported values of 7.06 eV from electron impact mass spectrometry and 7.20 eV from charge-transfer spectra for the ionization energy of **1**. For comparison, 1,8-diaminonaphthalene and 1,8-bis(dimethylamino)naphthalene are reported[23] to have vertical ionization energies, obtained by photoelectron spectroscopy, of 7.10 and 7.05 eV, respectively.

Also shown in Figure 1 is the 9.18-eV photoemission spectrum of a film of **1** evaporated onto a gold substrate. The threshold for photoemission is 5.12 eV and the vertical ionization energy of the solid is 5.75 eV.

The solid-state polarization energy, P, is the energy obtained by subtracting the solid-phase orbital ionization energies (I_C) from those of the corresponding peaks in the gas phase spectrum (I_G); i.e., $P = I_G - I_C$.[24] Using the centroid of the first gas phase peak, we find a value of $P \simeq 1.43$ eV for **1**. Values of P for anthracene,[3,25] TCNQ,[4] and TTF[4] are 1.0, 1.1, and 0.9–1.2 eV, respectively. However, it has been found[26] that, for certain organic compounds, e.g., dibenzotetrathiafulvalene (DBTTF, **7**), P depends on the orientation of molecules in the
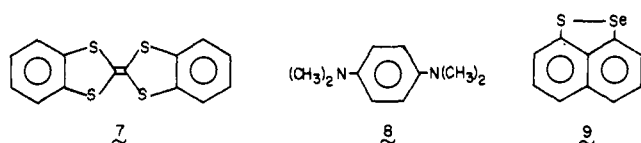
condensed phase and is controlled by the substrate material. We have studied **1** only on gold and emphasize that the value of P obtained is not necessarily substrate independent.

C. Donor–Acceptor Complexes, Ion-Radical Salts, and Molecular Parameters. In the present work, we have found that **1** reacts with TCNQ to give a donor–acceptor complex, while it has been reported that the tellurium analog of **1** reacts with TCNQ to give a material with the properties expected of an ion-radical salt.[11] The physical basis for the occurrence of charge-transfer between neutral organic donors and acceptors can be understood[5,27] in terms of a charge-transfer interaction energy, ΔE_{C-T}.

$$\Delta E_{C-T} = (I_G - A_A) - (E_M + E_{ex} + E_{pol} + \dots) \quad (1)$$

In eq 1, charge transfer will occur when the energy cost of ionizing a donor–acceptor pair ($I_G - A_A$, where I_G is the gas phase ionization energy of the donor and A_A is the gas phase electron affinity of the acceptor) is adequately compensated for by Madelung forces (E_M), exchange forces (E_{ex}), polarization forces (E_{pol}), etc. The relationship of the physical parameters in the second set of parentheses in eq 1 to molecular structure and parameters such as I_G and A_A may be quite complex, as illustrated below.

The formation of the donor–acceptor complex between **1** and TNCQ in the present work is neither surprising nor difficult to rationalize, since I_G for **1** (7.15 eV) is greater than that observed for TTF ($I_G = 6.81–6.83$ eV[4,28]) or N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD, **8**, $I_G = 6.84$ eV),[29] both of which react with TCNQ to give ion-radical salts in acetonitrile solution.[22,30–32] Further it has been reported[8] that **1** gives donor–acceptor complexes with TCNE and DDQ, acceptors with electron affinities comparable with or greater than that of TCNQ.[34] Additionally, the cation radical of **1** would be less polarizable[9] than that of its tellurium analogue.[11]

To illustrate the potential intricacy of complex vs. salt formation, we choose the example of DBTTF and TCNQ. Both the gas phase and solid-state (I_c) ionization energies (6.81[35] and 5.74 eV[26] (gold substrate), respectively) and polarizability[36] of the cation radical of DBTTF are comparable with those of TTF ($I_c = 5.96$ eV (gold substrate).[26] It might therefore be

expected that an ion-radical salt should result from interaction of DBTTF and TCNQ. Instead, reaction of these compounds in acetonitrile leads to a donor–acceptor complex.[37–39] Further since the oxidation potential of DBTTF is significantly higher than that of TTF in acetonitrile (0.72 and 0.47 V, respectively, vs. SCE),[36] we accordingly attempted reaction of DBTTF and TCNQ by cosublimation (140 °C (10^{-6} mm)) onto Kapton or Teflon films.[18] In these experiments, reaction must take place either in the vapor or on a substrate where DBTTF and TTF have comparable ionization energies, and reaction between TTF and TCNQ to give a salt has been observed.[17,40] The product obtained in these experiments had an infrared spectrum and x-ray powder diffraction pattern identical with those of the donor–acceptor complex obtained in solution synthesis. Further spectroscopic experiments with DBTTF–TCNQ are in progress.[41]

The status of the donor–acceptor complex vs. ion-radical salt problem may be summarized as follows. Choosing conservative limits, it is unlikely that organic compounds with I_G greater than 7.5 eV or A_A less than 2.2 eV will be involved in ion-radical salt formation in reactions with each other. It is further apparent from the above discussion that even in compounds with $I_G < 7.0$ eV and $A_A > 2.5$ eV an a priori knowledge of both I_G and A_A may not be sufficient information to allow prediction of ion-radical salt formation.

D. PMO and CNDO/S2 Calculations. To interpret the UV PES of **1**, shown in Figure 1, PMO[42–44] and CNDO/S2[45] calculations were carried out. In the PMO calculations we construct the π-molecular orbital structure of **1** from the interaction of disulfide lone paris with naphthalene π orbitals. The parameters that are needed for the PMO calculations are the basis orbital energies for napthalene and disulfide lone pairs, the ZDO (zero differential overlap) π-molecular orbital wave functions for naphthalene and the disulfide moiety, which are determined by symmetry, and relevant overlap integrals.

Throughout this work, the validity of Koopman's theorem is assumed:

$$\epsilon_i = -IP_{v,i}$$

thus permitting the extraction of orbital energies directly from UV PES. Basis orbital energies for naphthalene obtained from its UV PES[46,47] are given in Table II for the relevant π orbitals together with the corresponding ZDO molecular orbital wave functions. Orbital assignments are based on the recent CNDO/S2 calculations of Lipari and Duke.[45] Through-bond interactions between the sulfur lone pairs causes these levels to split into a bonding (n_+) and antibonding (n_-) combination with ZDO wave functions given by

$$n_+ = \frac{1}{\sqrt{2}} (P_{S1} + P_{S2}) \qquad b_1$$

$$n_- = \frac{1}{\sqrt{2}} (P_{S1} - P_{S2}) \qquad a_2$$

From ionization potential data obtained on organic disulfides,[48,49] the basis orbital energies for n_+ and n_- are estimated to be at 8.1 and 10.1 eV, respectively, assuming the sulfur lone pairs to be orthogonal to the naphthalene plane. That this geometry is reasonable is supported by x-ray diffraction data obtained on **3**,[50] **4**[51] and the mixed sulfur–selenium compound **8**[52] which show the chalcogen atoms to be coplanar with the aromatic ring.[53] Raman studies on **1**, furthermore, indicate that maximum possible distortion from planarity is of the order of 20°.[10] Since overlap integrals vary as $\cos \vartheta$, the effect of small changes from planarity would be insignificant. Larger changes, however, would be reflected in the agreement between the PMO results and the photoelectron spectral data.

Since only orbitals of the same symmetry can interact, n_-

Table II. Basis Energies and Orbitals for Naphthalene π Levels

MO	Orbital energy[a]	ZDO wave function[b]
$D_{2h}(C_{2v})$		
$1a_u(a_2)$	−8.13	$0.425\,(P_1 - P_4 + P_5 - P_8)$ $+ 0.263\,(P_2 - P_3 + P_6 - P_7)$
$2b_{1u}(b_1)$	−8.88	$0.408\,(P_2 + P_3 + P_6 + P_7)$ $- 0.408\,(P_9 + P_{10})$
$1b_{3g}(b_1)$	−10.01	$0.400\,(P_1 - P_4 - P_5 + P_8)$ $+ 0.174\,(P_2 - P_3 - P_6 + P_7)$ $+ 0.347\,(P_9 - P_{10})$
$1b_{2g}(a_2)$	−11.37	$0.263\,(P_1 + P_4 - P_5 - P_8)$ $+ 0.425\,(P_2 + P_3 - P_6 - P_7)$
$1b_{1u}(b_1)$	−13.80	$0.301\,(P_1 + P_4 + P_5 + P_8)$ $+ 0.231\,(P_2 + P_3 + P_6 + P_7)$ $+ 0.461\,(P_9 + P_{10})$

[a] References 42–44. [b] E. Heilbronner and H. Bock, "The HMO-Model and Its Application", Vol. 3, Wiley, New York, N.Y., 1976.

belonging to the a_2 irreducible representation in C_{2v} interacts only with the a_u and b_{2g} (both of a_2 in C_{2v}) orbitals of naphthalene. Similarly n_+ can interact only with the b_{1u} and b_{3g} orbitals. The $2b_{1u}$ orbital remains nonbonding with respect to sulfur substitution since in the PMO approximation only nearest neighbors interact. The $2b_{1u}$ which contains no electron density at the 1- and 8-substitution sites, thus, remains unperturbed by disulfide substitution. Figure 2 summarizes all of the orbital interactions in the form of an orbital correlation diagram. Since the electronegativity of the sulfur atom is nearly equal to that of carbon, inductive shifts of the basis orbital energies are ignored.

To predict the extent of interaction, a perturbation Hamiltonian matrix is set up. Diagonal matrix elements H_{ii} are taken to be equal to the basis orbital energies. Off-diagonal elements H_{ij} due to π–n overlap are evaluated within the PMO prescription that only nearest neighbors interact. This then yields

$$H_{ij} = \langle \text{naphthalene} \,|\, \mathcal{H} \,|\, n \rangle = \sqrt{2}\, c_i\beta$$

where c_i is the coefficient at the C-8 position of naphthalene for the ith molecular orbital and β_{CS} is the carbon–sulfur resonance integral. For the a_2–n_- interaction the following 3 × 3 secular determinant results.

$$\begin{vmatrix} -8.13 - \epsilon & 0.60\beta_{CS} & 0 \\ 0.60\beta_{CS} & -8.10 - \epsilon & 0.37\beta_{CS} \\ 0 & 0.37\beta_{CS} & -11.37 - \epsilon \end{vmatrix} = 0$$

In a similar manner the b_1–n_+ interaction yields

$$\begin{vmatrix} -10.01 - \epsilon & 0.57\beta_{CS} & 0 \\ 0.57\beta_{CS} & -10.10 - \epsilon & 0.43\beta_{CS} \\ 0 & 0.43\beta_{CS} & -13.80 - \epsilon \end{vmatrix} = 0$$

The C-S resonance integral β_{CS} is taken to equal −1.8 eV.[54] Solving these cubic equations then yields the following spectra of orbital eigenvalues: $\epsilon(a_2) = -7.1, -9.1, -11.5$; $\epsilon(b_1) = -9.0, -11.0, -14.0$. As shown in Table I the calculated values are in excellent agreement with experimental results.

CNDO/S2[45] calculations provide further confirmation of the validity of these results. The CNDO/S2 is a new parameterization of the CNDO method which has been developed in this laboratory for the interpretation of photoelectron and UV absorption data.[55-57] It differs from earlier parametrizations primarily in its simplicity and its treatment of atomic orbital exponents as variable parameters to describe the range of the one-electron overlap integrals.
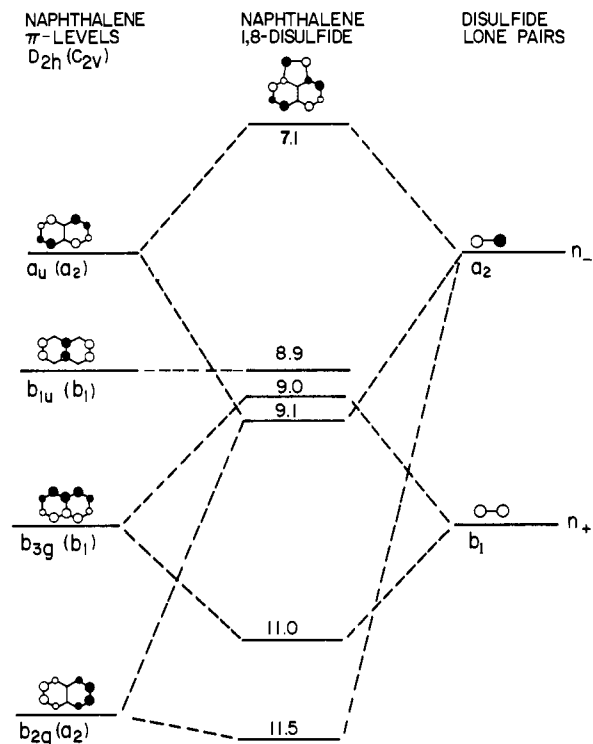

Figure 2. π-Orbital correlation diagram and calculated (PMO) energy eigenvalues for naphthalene 1,8-disulfide.

Since the extension of the CNDO/S2 method to organosulfur compounds is discussed in detail in another paper,[58] we present here only a summary of the results of these calculations. As shown in Table I, calculated CNDO/S2 ionization potentials agree with experiment to within ±0.3 eV. The four highest levels are of π character and are followed by three σ levels with the fifth π level predicted at 11.4 eV. The CNDO/S2 ordering and assignments of π orbitals agrees completely with that shown in the PMO orbital correlation diagram in Figure 2. The first ionization arises from a molecular orbital due to the $a_u\pi$–n_ interaction. The broad collection of peaks observed between 8.8 and 10.0 eV are predicted by the calculation to be due to ionization from three π orbitals of b_{1u}, b_{3g}, and a_u naphthalene parentage. Deconvolution of the second band in the experimental spectrum gives three peaks at 8.95, 9.30, and 9.44 eV, respectively. The second π level at 8.6 eV in the CNDO/S2 calculation is completely devoid of sulfur character with a sulfur orbital population $<3 \times 10^{-3}$ and is of b_{1u} naphthalene parentage. It is only in the diffuse band starting at $\sim$10.8 eV that σ levels are predicted to occur. The results of the CNDO/S2 calculations, thus, confirm in every respect the predictions made via the PMO scheme.

All of these data indicate that the highest occupied molecular orbital structure is determined by π interactions between sulfur lone pairs and naphthalene π levels. The carbon–sulfur π interaction (PMO $\beta_{CS} \sim -1.8$ eV) in **1** is substantial when compared with that observed in alphatic disulfides or when even contrasted with C–Cπ overlap ($\beta_{C-C} \sim -2.5$ eV).[59,60] The good agreement between the above calculations and experiment places the suggestion of Bock and Wagner[48] that coplanar sulfur–sulfur lone-pair interactions should be large[61] ($\sim$2.0 eV) on a firm experimental basis, since the output of the PMO calculations depends critically on the n_+ and n_- basis orbital energies.

peri-Disulfide substitution is found to provide a viable mechanism for lowering the first ionization potential of polyacenes due to the large sulfur–sulfur interaction and the strong carbon–sulfur overlap. This effect, it should be noted,

is comparable with that produced by amino substitution. The first ionization for **1**, 7.15 eV, is nearly equal to that reported for 1,8-diaminonaphthalene (7.10 eV) and 1,5-diaminonaphthalene (7.18 eV).[23] More detailed analysis of the UV PES spectra of these derivatives and those of amino-substituted benzenes[62] indicates that π lone pair overlap, measured by β, is of the same order of magnitude for disulfide and amino substituents ($\beta_{C-S} = -1.8$ eV vs. $\beta_{C-N} = -2.4$ eV).[23,63] On this basis it is anticipated that the first vertical ionization of **3**[12] in the gas phase should be less than the 7.15-eV value observed for **1** in this work. PMO calculations, using the prescription in this work, in fact, yield a value of 6.6 eV for the first ionization potential of **3**, in good agreement with a recent UV PES measurement of 6.75 eV, and 6.5 eV for **4**,[64] significantly lower than the value of 7.04 eV reported for tetracene in the gas phase.[65]

References and Notes

(1) Portions of this work were presented at the 10th Middle Atlantic Regional Meeting of the American Chemical Society, Philadelphia, Pa., Feb 23–26, 1976, Abstracts of Papers, K33.
(2) M. Lanfry, *C. R. Hebd. Seances Acad. Sci.*, **152**, 92 (1911).
(3) P. Nielsen, A. J. Epstein, and D. J. Sandman, *Solid State Commun.*, **15**, 53 (1974).
(4) D. J. Sandman, P. Nielsen, A. J. Epstein, N. O. Lipari, and G. P. Ceasar, 169th National Meeting of the American Chemical Society, Philadelphia, Pa., April 6–11, 1975, Abstracts of Papers, ORGN 46, and unpublished work.
(5) A. J. Epstein, N. O. Lipari, D. J. Sandman, and P. Nielsen, *Phys. Rev. B.*, **13**, 1569 (1976).
(6) D. J. Sandman, A. J. Epstein, and J. S. Chickos, paper presented at the 172nd National Meeting of the American Chemical Society, San Francisco, Calif., Aug 29–Sept 3, 1976, Abstracts of Papers, PHYS 88, and unpublished work.
(7) H. Lumbroso and C. Marschalk, *J. Chim. Phys.*, **48**, 123 (1951).
(8) A. Zweig and A. K. Hoffmann, *J. Org. Chem.*, **30**, 3997 (1965).
(9) B. I. Stepanov, W. Ya. Rodinov, A. Ya. Zheltov, and V. V. Orlov, *Tetrahedron Lett.*, 1079 (1971).
(10) H. E. VanWart and H. A. Scheraga, *J. Phys. Chem.*, **80**, 1823 (1976).
(11) J. Meinwald, D. Dauplaise, F. Wudl, and J. J. Hauser, *J. Am. Chem. Soc.*, **99**, 255 (1977).
(12) F. Wudl, D. E. Schafer, and B. Miller, *J. Am. Chem. Soc.*, **98**, 252 (1976).
(13) R. C. Wheland and J. L. Gillson, *J. Am. Chem. Soc.*, **98**, 3916 (1976).
(14) L. I. Buravov, O. N. Eremenko, R. B. Lyubovskii, L. P. Rozenberg, M. L. Khidekel, R. P. Schibaeva, I. F. Schegolev, and E. B. Yagubskii, *JETP Lett. (Engl. Transl.)*, **20**, 208 (1974).
(15) H. S. Desai and B. D. Tilak, *J. Sci. Ind. Res., Sect. B*, 19, 390 (1960).
(16) P. Nielsen, *Phys. Rev. B.*, **10**, 1673 (1974).
(17) P. Nielsen, D. J. Sandman, and A. J. Epstein, *Solid State Commun.*, **17**, 1067 (1975).
(18) A. R. McGhie, A. F. Garito, and A. J. Heeger, *J. Crystal Growth*, **22**, 294 (1974).
(19) W. B. Price and S. Smiles, *J. Chem. Soc.*, 2372 (1928).
(20) Our melting point of 120–121 °C for 1 has also been observed on samples prepared by an independent method:[11] J. Meinwald and D. Dauplaise, private communication.
(21) N. N. Vorozhtsov, Jr., and V. Ya. Rodinov, *Dokl. Akad. Nauk SSSR*, **134**, 1085 (1960).
(22) L. R. Melby, R. J. Harder, W. R. Mahler, R. E. Benson, and W. E. Mochel, *J. Am. Chem. Soc.*, **84**, 3374 (1962).
(23) J. P. Maier, *Helv. Chim. Acta*, **57**, 994 (1974).
(24) F. Gutman and L. E. Lyons, "Organic Semiconductors", Wiley, New York, N.Y., 1967.
(25) W. Schmidt, *J. Chem. Phys.*, **66**, 828 (1977).
(26) P. Nielsen, unpublished work.
(27) H. M. McConnell, B. M. Hoffman, and R. M. Metzger, *Proc. Natl. Acad. Sci. U.S.A.*, **53**, 46 (1965).
(28) R. Gleiter, F. Schmidt, D. O. Cowan, and J. P. Ferraris, *J. Electron Spectrosc.*, **2**, 207 (1973).
(29) R. Edgell, J. C. Green, and C. N. R. Rao, *Chem. Phys. Lett.*, **33**, 600 (1975).
(30) L. B. Coleman, M. J. Cohen, D. J. Sandman, F. G. Yamagishi, A. F. Garito, and A. J. Heeger, *Solid State Commun.*, **12**, 1125 (1973).
(31) J. P. Ferraris, D. O. Cowan, V. Walatka, and J. Perlstein, *J. Am. Chem. Soc.*,

95, 948 (1973).
(32) Recently, A. Yamagishi, F. Watanabe, and T. Masui, *J. Chem. Soc., Chem. Commun.*, 273 (1977), reported the observation of a donor–acceptor complex between TMPD and TCNQ in chloroform solution and discuss the possibility of electron transfer taking place via such a complex. The possibility of a thermal transition from a donor–acceptor complex to an ion-radical salt in a solid has been mentioned,[33a] and, recently,[33b] it has been suggested that certain solids obtained from reaction of TCNQ and dialkyl-dihydrophenazines may be near the neutral–ionic transition.
(33) (a) Z. G. Soos, *Ann. Rev. Phys. Chem.*, **25**, 121 (1974); (b) Z. G. Soos, H. J. Keller, W. Moroni, and D. Nöthe, *J. Am. Chem. Soc.*, **99**, 5040 (1977).
(34) E. M. C. Chen and W. E. Wentworth, *J. Chem. Phys.*, **63**, 3183 (1975), report the following ranges of electron affinity values: TCNE, 2.73–2.90 eV; TCNQ, 2.77–2.88 eV; DDQ, 3.00–3.13 eV.
(35) J. Spanget-Larsen, R. Gleiter, and S. Hünig, *Chem. Phys. Lett.*, **37**, 29 (1976).
(36) S. Hünig, G. Kiesslich, H. Quast, and D. Scheutzow, *Justus Liebigs Ann. Chem.*, 310 (1973).
(37) L. B. Coleman, Ph.D. Thesis, University of Pennsylvania, Philadelphia, Pa., 1975.
(38) J. P. Ferraris, Ph.D. Thesis, Johns Hopkins University, Baltimore, Md., 1974.
(39) R. N. Lyubovskaya, M. Z. Aldoshina, V. Ya. Rodinov, T. A. Chilbisova, and M. L. Khidekel, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 177 (1975).
(40) (a) A. F. Garito, private communication. (b) We have also observed salt formation of the new conducting salt BTP–TCNQ on Kapton: D. J. Sandman, A. J. Epstein, T. J. Holmes, and A. P. Fisher, III, *J. Chem. Soc., Chem. Commun.*, 177 (1977).
(41) D. J. Sandman, C. H. Griffiths, T. J. Holmes, et al., unpublished work.
(42) E. Heilbronner and H. Bock, "The HMO Model and Its Applications. Vol. 1: Basis and Manipulations", Verlag Chemie, Weinheim, 1976, and references therein.
(43) G. P. Ceasar, J. Green, L. A. Paquette, and R. E. Wingard, Jr., *Tetrahedron Lett.*, 1721 (1973).
(44) D. G. Streets and G. P. Ceasar, *Mol. Phys.*, **26**, 1037 (1973).
(45) N. O. Lipari and C. B. Duke, *J. Chem. Phys.*, **63**, 1748 (1975).
(46) D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy", Wiley, New York, N.Y., 1970, Chapter 11.
(47) C. R. Brundle, M. B. Robin, and N. A. Kuebler, *J. Am. Chem. Soc.*, **94**, 1466 (1972).
(48) H. Bock and G. Wagner, *Angew. Chem., Int. Ed. Engl.*, **11**, 150 (1972).
(49) M. Guimon, C. Guimon, and G. Pfister-Guillouzo, *Tetrahedron Lett.*, 441 (1975).
(50) F. Wudl, private communication, and unpublished work.
(51) O. Dideberg and J. Toussaint, *Acta Crystallogr., Sect. B*, **30**, 2481 (1974).
(52) J. Meinwald and D. Dauplaise, private communication.
(53) In collaboration with Professor I. Bernal and Dr. J. Korp (University of Houston), we have attempted to obtain the crystal and molecular structure of 1 using crystals grown from ethanol solution. From 28 high-angle reflections, the following data were obtained: monoclinic crystals; space group $P2_1/h$; $a = 7.971$ (2), $b = 10.890$ (4), $c = 10.633$ (3)Å; $\beta = 109.86$ (2)°; $V = 868.1$ Å³; $Z = 4$; $\rho_c = 1.46$, $\rho_m = 1.43$ g/cm³. A total of 2811 unique reflections were collected. After several unsuccessful attempts to refine various structures and recollection of data on new crystals, the reciprocal space lattice was examined in detail to see if there existed any evidence of halving along the lattice rows which would reveal the presence of a superlattice. This is precisely what was found. Two–three dozen reflections which fell exactly between points along one or more of the sublattice rows were noted. Peak scans indicated that the cell dimensions were doubled in all three dimensions. The superlattice has the same space group, $P2_1/n$, as the simple lattice noted above. Additional work on the origin of the superlattice is in progress. Earlier, I. Bernal and J. Ricci, Jr., collected two set of film data on two independently grown crystals of 1 and encountered the difficulties noted above in attempts to refine the structure. We wish to thank Professor Bernal and Dr. Korp for permission to cite their unpublished results.
(54) R. Gleiter, M. Kobayashi, J. Spanget-Larsen, J. P. Ferraris, A. N. Bloch, K. Bechgaard, and D. O. Cowan, *Ber. Bunsenges. Ges. Phys. Chem.*, **79**, 1218 (1975).
(55) N. O. Lipari and C. B. Duke, *J. Chem. Phys.*, **63**, 1748 (1965).
(56) C. B. Duke, K. L. Yip, G. P. Ceasar, A. W. Potts, and D. G. Streets, *J. Chem. Phys.*, **66**, 256 (1977).
(57) W. R. Salaneck, J. W.-p. Lin, A. Paton, C. B. Duke, and G. P. Ceasar, *Phys. Rev. B.*, **13**, 4517 (1976).
(58) G. P. Ceasar et al., unpublished work.
(59) J. H. D. Eland and C. J. Handy, *Z. Naturforsch, A*, **23**, 355 (1968).
(60) E. Heilbronner, R. Gleiter, H. Hopf, V. Hornung, and A. de Meyere, *Helv. Chim. Acta*, **54**, 783 (1971).
(61) J. P. Snyder and L. Carlsen, *J. Am. Chem. Soc.*, **99**, 2931 (1977), also discuss this point.
(62) D. G. Streets, W. E. Hall, and G. P. Ceasar, *Chem. Phys. Lett.*, **17**, 90 (1972).
(63) G. P. Ceasar, paper presented at the 5th Northeast Regional Meeting of the American Chemical Society, Rochester, N.Y., Oct 14–17, 1973, Abstract 207.
(64) F. Wudl and R. Gleiter, unpublished work. We thank Dr. Wudl for a private communication of these results.
(65) R. Boschi, E. Clar, and W. Schmidt, *J. Chem. Phys.*, **60**, 4406 (1974).