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Physical and Inorganic Chemistry

Ground States of Conjugated Molecules. XX.[1] SCF MO Treatment of Compounds Containing Bivalent Sulfur[2]

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Abstract: The semiempirical SCF MO π approximation described in earlier papers of this series has now been extended to conjugated compounds of bivalent sulfur. Calculations are reported for a number of thiophene derivatives, the results being in good agreement with experiment. Calculations are also reported for some thiepine derivatives.

Although a number of papers have appeared in recent years describing theoretical studies of heterocyclic sulfur compounds,[4] not one of them has been primarily concerned with ground state properties. While some attempts have been made to calculate bond lengths (*e.g.*, in thiophene[5,6] or 1,4-thiophthene[7,8]), these investigations have been primarily concerned with calculations of light absorption, using the Pople[9] or Pariser–Parr[10] methods, and the parameters, in particular the one-electron resonance integrals, have been chosen accordingly.

In the first papers of this series,[11,12] it was pointed out that calculations of ground state properties, in particular heats of formation, cannot logically be carried out using parameters determined from excitation energies, for the two problems are quite distinct. Techniques were developed for determining parameters in the Pople treatment appropriate to the calculation of heats of formation, and in its most recent forms[13–15] this approach has proved remarkably successful for conjugated molecules derived from carbon, hydrogen, nitrogen, and oxygen, giving estimates of heats of formation and bond lengths that rarely differ from experiment by more than the limits of likely experimental error. The purpose of the present paper is to describe an extension of this treatment to compounds (*e.g.*, thiophene) containing sulfur in a formally bivalent state.

Theoretical Procedure

The principles of our semiempirical SCF MO π approximation have been discussed in detail in earlier papers[11–14] of this series and need not be repeated. In the original version, the key parameter, *i.e.*, the one-electron core resonance integral (β_{ij}^c), was estimated by the thermocycle method of Dewar and Schmeising.[16] Although successful in the applications described there, this approach is limited in scope since it requires a knowledge of the properties of a

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[1] Part XIX: N. Bodor, M. J. S. Dewar, and A. J. Harget, *J. Amer. Chem. Soc.*, in press.

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[11] A. L. H. Chung and M. J. S. Dewar, *ibid.*, 42, 756 (1965).

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[13] M. J. S. Dewar and C. de Llano, *ibid.*, 91, 789 (1969).

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"pure" double bond between the elements in question, and such data are not available for bonds formed by elements other than carbon, nitrogen, and oxygen.

Recently[15] it has been shown that at least equally good results can be obtained by using the Mulliken approximation, *i.e.*

$$\beta_{ij}^{c} = KS_{ij} \qquad (1)$$

where K is a constant characteristic of the bond in question, and S_{ij} the corresponding overlap integral, calculated using Slater–Zener AO's. The value of the one parameter K can be found by fitting the observed properties, in particular the heat of formation, of a single suitable molecule containing the bond in question, assuming of course that the parameters for the remaining bonds have already been determined. Previous studies[1,15] have established suitable values for the parameters for bonds formed by C, N, and O. It is of course also necessary to know the bond energies and force constants of corresponding σ bonds in order that their contribution to the overall heat of atomization may be estimated; this, however, can be achieved without recourse to data for double bonds.

Extensive studies by others have established the unimportance of contributions by 3d AO's of sulfur on properties such as dipole moments,[17] polarographic reduction potentials,[18] spin densities,[19] and electronic spectra;[20] similar conclusions have also been reached by *ab initio* SCF MO calculations.[21] The 3d AO's of bivalent sulfur apparently have too high energy to contribute to the ground state. It is true that contrary opinions have been expressed on the basis of semiempirical calculations;[22] here, however, the role of 3d AO's depends on the choice of parameters. For the present purpose it seems more logical to neglect such contributions, the new parameters to be determined then referring only to the 3p AO of sulfur.

The valence state ionization potential (W_s) and one-center repulsion integral $(ii,ii)_s$ for sulfur were determined as before[13,15] by the Pariser–Parr method[10] using the promotion energies of Hinze and Jaffé.[23] The values used here were as follows

$$W_s = -22.88 \text{ eV}; \ (ii,ii)_s = 11.90 \text{ eV} \qquad (2)$$

The values for carbon were those used previously[13,15] ($W_c = -11.16$ eV; $(ii,ii)_c = 11.13$ eV). The two-center repulsion integrals were calculated, as before, by Ohno's[24] method, *i.e.*

$$(ii,jj) = e^2[(R_i + R_j)^2 + r_{ij}]^{-1/2} \qquad (3)$$

where r_{ij} is the internuclear distance and R_i and R_j are defined in terms of the corresponding one-center repulsion integrals by

$$R_i = e^2/(ii,ii) \qquad R_j = e^2/(jj,jj) \qquad (4)$$

The contribution of σ bonds to the heat of atomization is written[13–15] as a sum of bond energies and compression energies, the latter being calculated from a Morse potential function. For the C(sp^2)–S σ bond energy, the value suggested by Mackle and Mayrick (75.6 kcal/mol or 3.2783 eV[25]) was used, and for SH the value (81.4 kcal/mol or 3.5298 eV) estimated by Johns and Ramsay.[26]

The equilibrium length of a C(sp^2)–S σ bond was deduced from that of the corresponding C(sp^3)–S bond (1.817 Å)[27] by assuming the difference to be half that between a C(sp^3)–C(sp^3) σ bond and a C(sp^2)–C(sp^2) σ bond (0.030 Å);[16] *i.e.*, C(sp^2)–S = 1.802 Å. The Morse constant (a) for a C(sp^2)–S bond was likewise deduced from that[28] (1.8085 Å^{-1}) for a C(sp^3)–S bond, by assuming the difference to be the same as for corresponding C–C bonds; *i.e.*, for C(sp^2)–S

$$a = 1.9663 \text{ Å}^{-1} \qquad (5)$$

In our procedure,[13–15] bond lengths are estimated from an assumed linear relation between bond order (p) and bond length (r). With the value derived above for a C(sp^2)–S σ bond (*i.e.*, $p = 0$), the relation is[29]

$$r = 1.802 - 0.229p \qquad (6)$$

The corresponding quantities for CC and CH bonds were taken from the preceding papers.[13,15] The only remaining quantities to be determined are those in eq 1, *i.e.*, the constants K, and the values for the effective nuclear charges of the Slater–Zener orbitals used in the calculation of the overlap integrals. The values for carbon–carbon bonds ($K = 6.9270$ eV; $Z = 3.18$) were those used previously;[15] for sulfur

$$K = 15.7265 \text{ eV} \qquad Z = 4.551 \qquad (7)$$

Resonance Energies

Previous papers of this series[13–15] have shown that the heats of atomization of classical conjugated molecules[30] derived from carbon, hydrogen, nitrogen, and oxygen can be written as sums of corresponding "classical" or "polyene" bond energies. This led to the definition of resonance energy for analogous nonclassical systems as the difference between the actual heat of atomization and the value calculated for one possible classical structure using appropriate bond energies. This treatment has now been extended to sulfur compounds by calculating several classical conjugated sulfides derived from polyenes by replacement of –CH═CH– units by bivalent sulfur. The results are shown in Table I. Using the "polyene" bond energies deduced previously,[15] *i.e.*

$$\begin{gathered} \text{C═C} = 5.4648 \text{ eV} \qquad \text{C—C} = 4.3860 \text{ eV} \\ \text{C—H} = 4.4375 \text{ eV} \end{gathered} \qquad (8)$$

one arrives at the following value for the CS polyene

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[29] The same expression was earlier reached by Clark (see ref 7).

[30] A classical conjugated molecule is one for which only a single classical (unexcited resonance) structure can be written.

bond energy

$$\text{vinyl-S bond energy} = 3.4860 \text{ eV} \qquad (9)$$

The last column of Table I shows heats of atomization calculated for classical structures, using eq 8 and 9. It will be seen that the values agree very well with those given by the SCF MO π approximation (penultimate column in Table I). Note that the polyene CS bond energy is greater than that estimated for a "pure" C(sp^2)–S σ bond by 0.208 eV (4.79 kcal/mol), and that the polyene CS bond is also correspondingly shorter (by 0.049 Å); this of course runs parallel to the behavior of the "single" bonds in polyenes.[13,15]

Results and Discussion

A. Heats of Atomization and Ionization Potentials. Table II shows the results of calculations by the SCF MO π approximation, using the parameters indicated, for the compounds listed in Figure 1. The second and third columns of the table compare calculated and observed heats of atomization, the fourth column lists the calculated resonance energies, and the fifth and sixth columns compare calculated and observed vertical ionization potentials, the "calculated" values being obtained from Koopmans' theorem.

It is unfortunate that so few data are available to check these predictions quantitatively. The two heats of formation that have been reported agree with calculated values, but of course the parameter K in eq 1 was chosen to fit one of them (thiophene). However the agreement between the calculated and observed ionization potentials is also good. As a further check, the adiabatic ionization potential of thiophene was calculated by the "half-electron" method;[31] the value so obtained (8.68 eV) is, as expected, less than the value given by Koopmans' theorem and is in reasonable agreement with the spectroscopic value (8.91 eV) of Price and Walsh,[32] and with photoionization spectroscopy results of Watanabe, *et al.* (8.86 ± 0.005 eV),[33] and of Eland (8.87 eV).[34]

The calculated heats of atomization and resonance energies also seem to correspond well in a qualitative sense to the known chemistry of these compounds.

(A) The calculated resonance energy of thiophene (6.5 kcal/mol) is similar to that of pyrrole (5.3 kcal/mol)[35] and greater than that of furan (4.3 kcal/mol).[35] Thiophene derivatives undergo Diels–Alder reactions only with difficulty, unlike corresponding derivatives of furan, but somewhat less easily than analogous derivatives of pyrrole.

(B) The calculated resonance energy of 2,3-benzothiophene (III) (24.8 kcal/mol) is greater than that (22.6 kcal/mol)[15] of benzene, implying that both rings in III are aromatic, whereas the resonance energy of 3,4-benzothiophene (IV) (9.3 kcal/mol) is not only much less than that of III but also much less than that of benzene. Thus the extra ring in IV is predicted to destroy the aromaticity of the benzene moiety. This difference is certainly reflected in the chemistry of III and IV. Thus, while III was first prepared in 1893[36] and shows normal aromatic behavior and stability,[37] IV has only very recently been synthesized[38,39] and is clearly much more reactive than III. For example, IV, unlike III, undergoes Diels–Alder addition of maleic anhydride.[40] Similar differences are of course also observed in the analogous oxygen and nitrogen compounds. Thus while the analogs of III (benzofuran and indole) are well known, isobenzofuran has not yet been reported, and isoindole, which has only recently been synthesized,[41] is far more reactive than indole.

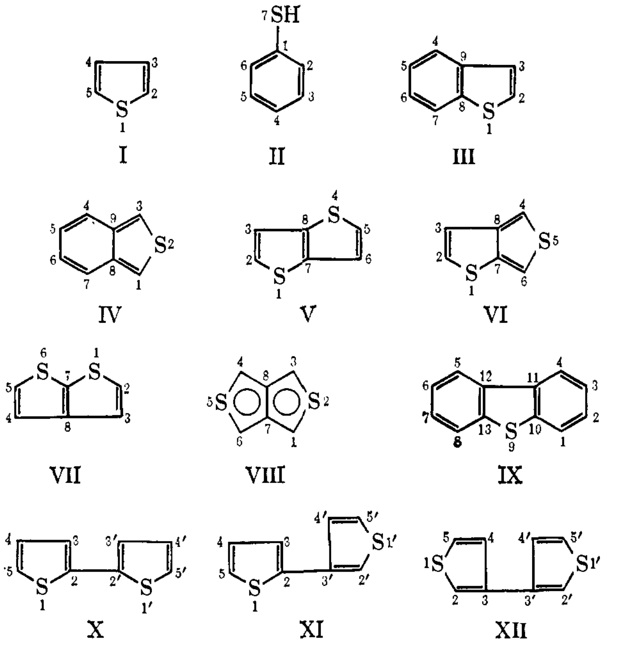

Figure 1. Numbering of compounds for which calculations are reported.

(C) Similar conclusions follow for the thiophthenes V–VIII. The predicted resonance energies of the 1,4 (V) and 1,6 (VII) isomers are much greater than that for thiophene (I), the ratios of resonance energies for thiophthene/thiophene being similar to that[13,15] for naphthalene/benzene. Both these compounds should therefore behave as bicyclic heteroaromatics; both have indeed been known for some time[42,43] and are chemically stable, showing, as predicted, a relationship to naphthalene similar to that shown by thiophene to benzene. The 1,5 isomer (VI) on the other hand is predicted to be much less stable, bearing the same relationship to V and VII that 3,4-benzothiophene (IV) bears to 2,3-benzothiophene (III). The synthesis of VI has only recently been achieved after repeated failures[44] and its properties show it to be much less

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Table I. Bond Lengths and Heats of Atomization of Unsaturated Thioethers

Compound	Calculated bond lengths, Å C═C	C—S	Heats of atomization, eV Calculated	Classical value[a]
$CH_2{=}CH{-}S{-}CH{=}CH_2$	1.341	1.753	44.540	44.527
$CH_2{=}({=}CH{-}S{-}CH{=})_2{=}CH_2$	1.341	1.753	65.833	65.828
$CH_2{=}({=}CH{-}S{-}CH{=})_3{=}CH_2$	1.341	1.753	87.125	87.100

[a] Calculated with the "polyene" C═C bond energy and the C(sp^2)–H bond energy, from ref 13 and 15, presented in eq 8, and with the C–S bond energy of eq 9.

Table II. Heats of Atomization, Resonance Energies, and Vertical Ionization Potentials of Thiophene Derivatives

Compound	−(Heat of atomization), eV Calcd	Obsd	Resonance energy, kcal/mol	Vertical ionization potential,[a] eV Calcd	Obsd
Thiophene (I)	40.321	40.32[b]	6.5	8.93	9.0 ± 0.05[c]
Benzenethiol (II)	59.712	59.71[d]	22.1	8.75	
Benzo[*b*]thiophene (III)	74.076		24.8	8.57	8.47[e]
Benzo[*c*]thiophene (IV)	73.404		9.3	7.92	
1,4-Thiophthene (V)	57.351		11.3	8.31	
1,5-Thiophthene (VI)	57.115		5.9	8.05	
1,6-Thiophthene (VII)	57.316		10.5	8.48	
2,5-Thiophthene (VIII)	55.390		−33.9[f]	6.46	
Dibenzothiophene (IX)	107.896		44.6	8.53	8.35[e]
2,2′-Bithienyl (X)	76.137		12.7	8.13	
2,3′-Bithienyl (XI)	76.112		12.1	8.17	
3,3′-Bithienyl (XII)	76.064		11.0	8.23	

[a] From Koopmans' theorem. [b] G. Waddington, J. W. Knowlton, D. W. Scott, G. D. Oliver, S. S. Todd, W. N. Hubbard, J. C. Smith, and H. M. Huffmann, *J. Amer. Chem. Soc.*, **71**, 797 (1949); S. Sunner, *Acta Chem. Scand.*, **9**, 847 (1955). [c] H. D. Hartough in "The Chemistry of Heterocyclic Compounds," Vol. 3, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1952, p 94. [d] D. W. Scott, J. P. McCullough, W. N. Hubbard, J. F. Messerly, I. A. Hossenlopp, F. R. Frow, and G. Waddington, *J. Amer. Chem. Soc.*, **78**, 5463 (1956). [e] G. Tröger, Diplomarbeit, Technical University, Dresden, 1967. [f] Relative to the classical structures used for V, VI, and VII.

Table III. Bond Lengths and π-Electron Densities in Thiophene Derivatives

Compound	Bond[a]	Bond length, Å Calcd	Obsd	Atom[a]	π-Electron density
I	1–2	1.721	1.718,[b] 1.723[b]	1	1.8477
	2–3	1.357	1.352, 1.360	2	1.0476
	3–4	1.442	1.455, 1.430	3	1.0285
II	1–2	1.398		1	0.9824
	2–3	1.396		2	1.0300
	3–4	1.396		3	0.9877
	1–7	1.752		4	1.0191
				7	1.9631
III	1–2	1.731		1	1.8810
	2–3	1.352		2	1.0274
	3–9	1.454		3	1.0317
	8–9	1.398		4	0.9906
	1–8	1.735		5	1.0156
	4–9	1.410		6	0.9954
	4–5	1.386		7	1.0243
	5–6	1.406		8	1.0149
	6–7	1.387		9	1.0190
	7–8	1.407			
IV	1–2	1.711		1	1.0621
	1–8	1.369		2	1.8127
	8–9	1.442		4	0.9979
	4–9	1.455		5	1.0108
	4–5	1.357		8	1.0229
	5–6	1.447			
V	1–2	1.724	1.72[c]	1	1.8629
	1–7	1.729	1.74	2	1.0406
	2–3	1.356	1.36	3	1.0390
	3–8	1.445	1.41	7	1.0574
	7–8	1.372	1.36		
VI	1–2	1.743		1	1.9165
	1–7	1.750		2	1.0234
	2–3	1.349		3	1.0286
	3–8	1.464		4	1.0493
	7–8	1.443		5	1.8378
	4–8	1.365		6	1.0847
	4–5	1.716		7	1.0261
	5–6	1.720		8	1.0337
	6–7	1.361			

Table III (*Continued*)

Compound	Bond[a]	Bond length, Å		Atom[a]	π electron density
		Calcd	Obsd		
VII	1-2	1.728		1	1.8666
	1-7	1.727		2	1.0575
	2-3	1.355		3	1.0174
	3-8	1.448		7	1.0653
	7-8	1.370		8	1.0517
VIII	1-2	1.687		1	1.1348
	1-7	1.402		2	1.7188
	7-8	1.446		7	1.0115
IX	1-2	1.391		1	1.0253
	2-3	1.402		2	0.9918
	3-4	1.390		3	1.0154
	4-11	1.406		4	0.9893
	10-11	1.399		9	1.9035
	1-10	1.403		10	1.0040
	9-10	1.742		11	1.0224
	11-12	1.461			
X	1-2	1.721	1.70[a]	1	1.8442
	2-3	1.364	1.43	2	1.0334
	3-4	1.439	1.43	3	1.0455
	4-5	1.358	1.37	4	1.0281
	1-5	1.717	1.70	5	1.0487
	2-2′	1.464	1.49		
XI	1-2	1.723		1	1.8502
	2-3	1.363		2	1.0280
	3-4	1.441		3	1.0429
	4-5	1.358		4	1.0262
	1-5	1.722		5	1.0541
	1′-2′	1.720		1′	1.8467
	2′-3′	1.362		2′	1.0426
	3′-4′	1.445		3′	1.0297
	4′-5′	1.356		4′	1.0354
	1′-5′	1.721		5′	1.0443
	2′-3′	1.466	1.445[d]		
XII	1-2	1.721	1.71[d]	1	1.8489
	2-3	1.361	1.36	2	1.0541
	3-4	1.444	1.43	3	1.0191
	4-5	1.357	1.38	4	1.0264
	1-5	1.722	1.67	5	1.0515
	3-3′	1.470	1.48		

[a] For numbering, see Figure 1. [b] Two structures consistent with the microwave spectrum: B. Bak, D. Christensen, J. Rastrup Andersen, and E. Tannenbaum, *J. Chem. Phys.*, **25**, 892 (1956). [c] E. G. Cox, R. J. H. Gillot, and G. A. Jeffrey, *Acta Cryst.*, **2**, 356 (1949). [d] G. J. Visser, G. J. Heeres, J. Wolters, and A. Vos, *ibid.*, **B25**, 467 (1968).

stable than V or VII. The fourth possible isomer, 2,5-thiophthene (VIII), is predicted to be a very unstable antiaromatic compound, with a heat of atomization less than even that of VI by 1.72 eV or 40 kcal/mol. This of course is not surprising, for only unsatisfactory zwitterionic structures for VIII can be written unless 3d AO's are involved, and as we have seen, the 3d AO's of bivalent sulfur seem to be too high in energy to be of much importance in bonding. Until very recently VIII eluded all attempts of synthesis; it has now been obtained by Cava and Pollack[45] but only as a transient and very reactive intermediate.

(D) The bithienyls X, XI, and XII are interesting compounds. X-Ray studies have shown all three to be planar in the solid state with the thiophene rings in a *trans* orientation.[46] Our calculations imply that there should be little interaction between the rings, the calculated resonance energies being about double that for thiophene itself; this of course might have been expected in view of the parallel between bithienyl–thiophene and biphenyl–benzene (see ref 13 and 15). As one might also have anticipated on this basis, the calculated heats of atomization of the *cis* and *trans* isomers differ little, the *trans* isomers being the more stable but only by *ca.* 0.3 kcal/mol. If the difference were indeed as small as this, one might have expected the crystal to be a random *cis–trans* mixture, for the gain in entropy (R log 2) would outweigh the energy difference. However, calculation of nonbonded interactions by the method of Bartell[47] indicates that these differ very considerably for the two isomers, favoring *trans;* thus in the case of X, the calculated difference in the nonbonded interactions amounts to 5.6 kcal/mol. Admittedly this is probably an overestimate, for while the *trans* isomer does predominate, there is enough disorder in the crystal to make the estimated bond lengths subject to large possible errors.

B. Bond Lengths and Charge Densities. Our procedure automatically leads to predictions of bond lengths;[13–15] predicted and observed bond lengths and π charge densities are listed in Table III. The agreement between the calculated and observed bond lengths is satisfactory, the larger deviations occurring only in cases when the experimental values are less accurately known.

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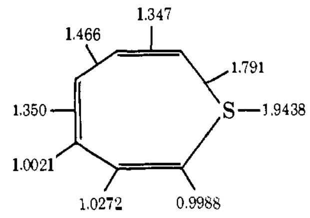
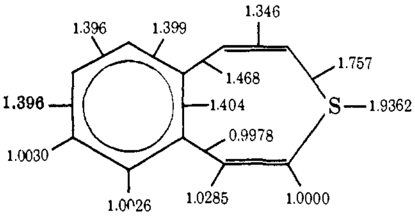
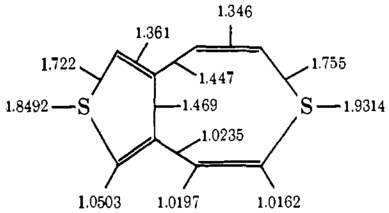


XIII
ΔH_a, -58.700 eV
E_R, −1.45 kcal/mol
I_v, 8.01 eV



XIV
ΔH_a, -92.591 eV
E_R, 19.9 kcal/mol
I_v, 8.04 eV



XV
ΔH_a, -75.739 eV
E_R, 3.5 kcal/mol
I_v, 8.03 eV

Figure 2. Heats of atomization (ΔH_a), resonance energies (E_R), and vertical ionization potentials (I_v) for thiepine (XIII), benzo[*d*]thiepine (XIV), and thieno[*c*,*d*]thiepine (XV).

The structure of 2,2′-bithienyl (X) has also been determined by electron diffraction in the gas phase by Almenningen, Bastiansen, and Svendsås.[48] They found the configuration to be *trans*, but with the rings twisted out of coplanarity by 34°. In part XVII,[15] a procedure for treating such situations was described. It is assumed that the one-electron resonance integral follows a cosine law

$$\beta_{ij}^c = \beta_{ij}^c(0°) \cos \theta \tag{10}$$

where θ is the angle of twist from coplanarity about the *ij* bond. The two-center integrals are still given by eq 3, and nonbonded interactions are calculated by Bartell's[47] method. The results obtained in this way for biphenyl were very satisfactory, the calculated angle of twist agreeing closely with experiment. In the case of X, the same procedure gave too low a value for the angle of twist (10° instead of 34°); however, the bond lengths calculated for a 34° twist (Table IV) are in excellent agreement with experiment (mean difference, ±0.003 Å). Note that the bond lengths calculated for X are almost identical for the planar (Table III) and twisted (Table IV) forms, apart from the interannular bond, which is correctly predicted to be larger in the latter.

Table IV. Bond Lengths in Nonplanar 2,2′-Bithienyl

Bond		1–2	2–3	3–4	4–5	5–1	2–2′
Length, Å	obsd[a]	1.717	1.357	1.433	1.357	1.717	1.480
	calcd	1.720	1.361	1.440	1.357	1.720	1.477

[a] See ref 48.

The π-electron densities in the last column of Table III also seem reasonable. The densities of sulfur are significantly less in the aromatic thiophene derivatives than in open chain ones, where values of 1.93–1.94 are calculated. Note the low values for sulfur in IV, and for the sulfur in position 5 of VI; any aromaticity of the second ring depends, in resonance terminology, on the contribution of structures in which these sulfur atoms are present in the form $\geqslant S^+$. The same factor also accounts of course for the exceptionally low π-electron densities on sulfur in VIII; if 3d AO's are neglected, VIII is a mesoionic compound.

All these compounds, other than IX, are distinguished by having relatively negative carbon atoms; this might tend to suggest that they should undergo electrophilic substitution readily, as indeed is the case. Moreover the most favored point of attack is the position of maximum π-electron density; thus whereas I substitutes preferentially in the 2 position rather than the 3 position, the reverse is true of III. In the case of I, the proton nmr spectrum also seems to suggest that the π-electron density is greater in the 2 than in the 3 position,[49] in agreement with our calculations.

Our calculations lead to a π dipole moment for thiophene of 1.22 D; in order to calculate the overall dipole moment, we need to estimate the contribution of the σ electrons. The dipole moment of tetrahydrothiophene is 1.87 D;[5] that of the σ skeleton in thiophene might be expected to be less, due to the greater electronegativity of sp^2 carbon compared with sp^3 carbon. On the other hand the polarization of the σ electrons gives sulfur in thiophene a positive charge; this will tend to increase the σ moment. Since it is impossible to assess the relative magnitude of these two opposing effects, it seems reasonable to assume as a first approximation that the σ moment in thiophene is the same as in tetrahydrothiophene.

Clark[50] has reported CNDO/2 calculations for thiophene using three models for sulfur: (I) including 3s and 3p AOs only; (II) adding to this 3d; (III) adding 4s and 4p as well as 3d. His estimated π-electron distributions agree with ours, while Table V compares his three estimates of the overall dipole moment with ours and with experiment.

Table V. Calculated and Observed Dipole Moments (μ) for Thiophene

	Model I[a]	Model II[a]	Model III[a]	This paper	Experiment[b]
μ, D	0.895	2.258	1.836	0.65	0.550 ± 0.040

[a] CNDO/2 calculations by Clark;[50] see text. [b] B. Harris, R. J. W. LeFevre, and E. P. A. Sullivan, *J. Chem. Soc.*, 1622 (1953).

C. Thiepine Derivatives. In view of the current interest in potentially heteroaromatic compounds con-

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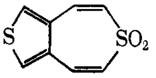
taining seven-membered rings, we also carried out calculations for thiepine (XIII), benzo[*d*]thiepine (XIV), and thieno[*c*,*d*]thiepine (XV). The heats of atomization, resonance energies, ionization potentials (from Koopmans' theorem), bond lengths (in Å), and calculated charge densities are indicated in Figure 2. Thiepine (XIII) is predicted to be antiaromatic; as in the case of other antiaromatic systems (*e.g.*, pentalene,[13,15] heptalene,[13,15] and the 5,4,5, 5,4,7, and 7,4,7 tricyclic polyenes[51]), the negative resonance energy is minimized by bond alternation, the CC bond lengths being close to those predicted[13,15] for polyene single and double bonds. The same is true of the sulfur-containing ring in XIV; the predicted resonance energy is close to that (22.6 kcal/mole[15]) of benzene. Neither of these compounds has as yet been reported, and the behavior of the corresponding nitrogen and oxygen compounds (azepine and oxepine) certainly seems to indicate that neither is aromatic.[52,53]

The thieno[*c*,*d*]thiepine (XV) is predicted to have a small positive resonance energy, less than that of thiophene (I), and the bond lengths in the thiophene ring also give some indication of departure from a classical polyene structure; thus the predicted length of the 2,3 bond (1.361 Å) is significantly greater than normal polyene value (1.345 Å),[15] and that of the CS bond (1.722 Å) less than in XIV (1.757 Å). The π-electron densities in the thiophene ring are also close to those in I itself (Table III) and imply a greater degree of charge transfer from sulfur to carbon than would be expected in a classical sulfide; *cf.* the π-electron densities on sulfur in XV (1.8492), XIII (1.9438), XIV (1.9362), and I (1.8477). On both counts, however, the thiepine ring should not be aromatic.

Recently XV has been synthesized[54] and studied by X-ray crystallography.[55] The molecule is planar and the crystal structure seems to be similar to that of azulene, showing a similar disorder; this indeed hindered attempts to determine bond lengths. The only bond length reported, *i.e.*, that of the central bond (1.46 ± 0.02 Å), is in good agreement with our calculated value (1.469 Å). Schlesinger, *et al.*,[55] argued that XV is probably aromatic because, unlike the corresponding sulfone XVI, it is planar. This argument is, however, a weak one because the SO_2 group in XVI is much thicker than the sulfur atom in XV. The thiophene rings in both compounds must in any case be planar; if the thiepine ring in XV is also planar, the molecule should resemble that of azulene in forming a roughly elliptic disk of more or less uniform thickness. On this basis one might expect XV, if planar, to form disordered crystals—as indeed it does. The gain in entropy through this disorder could well counter the (possibly small) energy needed to flatten the thiepine ring. In XVI the situation is of course different since the oxygen atoms of the SO_2 group project above and below the π nodal plane; one would not therefore expect crystals of planar XVI to be disordered since the two ends of the molecule are so different in thickness. According to our calculations, XV should be analogous to benzo[*d*]thiepine (XIV) in having an aromatic ring attached to a nonaromatic, or weakly aromatic, thiepine moiety. The reported chemistry of XV seems to be consistent with this picture.



XVI

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