the structure is different in the gas phase and in the crystal. Crystal lattice forces (intermolecular van der Waals forces) are sufficient to flatten out biphenyl (about 5 kcal/mol). To flatten out [18]annulene ($D_3 - D_{3h}$) is calculated to require 8.9 kcal, an amount that might be available. Once the molecule is flat, the D_{3h} structure is favored over the D_{6h} by only 1.16 kcal/mol.

Conclusions

The method formulated here appears to be a convenient adaptation for the application of the force field method to the determination of structures of molecules containing delocalized systems. While previous *ad hoc* calculations have treated many individual systems, each as a special case, this method is general and of wide applicability, as shown by good results with a diversity of structures. The general limitations of force field methods remain.[5,87]

[87] J. E. Williams, Jr., P. J. Stang, and P. v. R. Schleyer, *Annu. Rev. Phys. Chem.*, 19, 531 (1968).

Hückel Molecular Orbital π-Resonance Energies. Heterocycles Containing Divalent Sulfur

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Abstract: Coulombic and resonance integrals have been evaluated for divalent sulfur from thermodynamic data. These were used in Hückel calculations to obtain resonance energies for a large number of sulfur heterocycles. An excellent correlation between the experimental properties and calculated resonance energies was found for the known compounds.

We have shown that the lack of correlation between Hückel delocalization energies and experimental aromaticity of cyclic conjugated hydrocarbons, especially nonalternant hydrocarbons, is due to an inappropriate choice of reference structure rather than to an inherent fault of the Hückel wave functions.[1] When, in place of isolated double bonds, the reference structure proposed by Dewar[2] in his Pariser–Parr–Pople calculations is used, an excellent correlation between experimental aromaticity and Hückel resonance energies is found for a wide range of cyclic hydrocarbons.[1,3–5] Dewar's reference structure, based on his discovery that the energies of acyclic polyenes are additive, allows the comparison of the calculated π energy of a cyclic compound with the energy of a "localized" cyclic reference structure. The major difference between this "localized" reference structure and the earlier delocalization energy reference is that the contribution of the π part of the carbon–carbon "single" bonds is included in addition to the π contribution of the carbon–carbon double bonds. Hückel π-resonance energies obtained in this manner range from positive (aromatic) to zero (nonaromatic) to negative (antiaromatic).

We have also found that the Hückel method can be used in a very simple manner to calculate heats of atomization accurately for both acyclic and cyclic hydrocarbons.[6] Since the resonance energy of a system equals the difference between its heat of atomization and that of the reference structure,[2,6] this discovery potentially allows the comparison of our calculated resonance energies directly with experimentally determined resonance energies obtained from heats of combustion. Unfortunately, thermochemical data are not yet available for sufficient acyclic polyenes to determine the necessary bond energy terms and to decide whether the π energies of these reference systems are indeed additive.

Recently, we have extended our method of calculation to cyclic systems containing the amine nitrogen, ether oxygen and carbonyl oxygen.[7,8] The results for these are as impressive as those for the hydrocarbons. Sulfur heterocycles show a more varied behavior than their oxygen or nitrogen analogs, and in this paper we present results for conjugated systems containing sulfur atoms each of which donates two electrons to the π system. Predictions will be shown to agree well with observed behavior, including cases where simple rule-of-thumb methods such as counting resonance structures or use of the $4n + 2$ rule fail. In this respect the Hückel method is as least as satisfactory as the more sophisticated Pariser–Parr–Pople work of Dewar and Trinajstić[9] on sulfur heterocycles.

Evaluation of Integrals

Hückel calculations on sulfur heteromolecules require a choice of sulfur atom Coulombic integral (eq 1)

$$\alpha_{\mathrm{S}:} = \alpha_{\mathrm{C}} + \beta_{\mathrm{C-C}} h_{\mathrm{S}:} \qquad (1)$$

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[1] B. A. Hess, Jr., and L. J. Schaad, *J. Amer. Chem. Soc.*, **93**, 305 (1971).

[2] (a) M. J. S. Dewar and C. de Llano, *ibid.*, **91**, 789 (1969); (b) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969.

[3] B. A. Hess, Jr., and L. J. Schaad, *Tetrahedron Lett.*, 17 (1971).

[4] B. A. Hess, Jr., and L. J. Schaad, *J. Amer. Chem. Soc.*, **93**, 2413 (1971).

[5] B. A. Hess, Jr., and L. J. Schaad, *J. Org. Chem.*, **36**, 3418 (1971).

[6] L. J. Schaad and B. A. Hess, Jr., *J. Amer. Chem. Soc.*, **94**, 3068 (1972).

[7] B. A. Hess, Jr., L. J. Schaad, and C. W. Holyoke, Jr., *Tetrahedron*, **28**, 3657 (1972).

[8] B. A. Hess, Jr., L. J. Schaad, and C. W. Holyoke, Jr., *ibid.*, **28**, 5299 (1972).

[9] M. J. S. Dewar and N. Trinajstić, *J. Amer. Chem. Soc.*, **92**, 1453 (1970).

and of the resonance integral for the carbon–sulfur bond (eq 2). We have found that these corrections can

$$\beta_{C-S:} = k_{C-S:}\beta_{C-C} \qquad (2)$$

be evaluated in a very systematic manner using experimental heats of atomization of heteroatom containing systems.[7,8] This is an especially appropriate experimental property for the evaluation of these integrals since, like the resonance energy, it is a ground-state property.

The heat of atomization (ΔH_a) of a conjugated system containing sulfur may be expressed as

$$\Delta H_a = -[n_{CC}E_{CC} + n_{CH}E_{CH} + n_{CS}E_{CS} + P\cdot\beta] \quad (3)$$

where E_{CH} is the energy of each of the n_{CH} C–H bonds, E_{CC} is the σ energy of each of the n_{CC} C–C bonds, and E_{CS} is the σ energy of each of the n_{CS} C–S bonds. $P\cdot\beta$ is the π-binding energy. π-Binding energies and therefore heats of atomization are a function of $h_{S:}$ and $k_{C-S:}$. The best values of these integral corrections were obtained as follows. By choosing some initial pair of $h_{S:}$ and $k_{C-S:}$, Hückel π-binding energies were calculated, and with the previously determined values of E_{CH} and E_{CC} the linear least-squares method was used to determine E_{CS} and β. The parameters $h_{S:}$ and $k_{C-S:}$ were varied systematically and the above process repeated until the error, Δ

$$\Delta = \sum_i[\Delta H_a^{\mathrm{expt}}(i) - \Delta H_a^{\mathrm{calcd}}(i)]^2 \qquad (4)$$

was minimized.

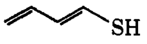
Unfortunately, there are only three compounds for which thermochemical data are available: thiophene, diphenyl sulfide, and thianthrene.[10] Nevertheless, they are sufficiently different in structure that we thought the determination of $h_{S:}$ and $k_{C-S:}$ was worth carrying out. No single minimum was found, but for each $h_{S:}$ chosen a $k_{C-S:}$ was found which gave essentially the same Δ. This is not surprising since we are adjusting four parameters to fit three heats of atomization. On the other hand, the shape of the Δ surface in the space of these four parameters is not known and such behavior is not guaranteed. With $h_{S:} = 1.0$, the value $k_{C-S:} = 0.68$ minimized Δ. These values together with the resulting $E_{CS} = -3.0340$ eV and $\beta = -1.3143$ eV reproduced the observed heats of atomization to within 0.005 eV. All of the resonance energy calculations which follow were done using these integral corrections. We emphasize that the evaluation of these parameters is based strictly on the experimental ground-state property, heat of atomization, and that the calculated resonance energies follow automatically. The integral values *were not* judiciously manipulated to give agreement between calculated resonance energies and experimental aromaticity.

Resonance Energies

In order to obtain the energies of the localized sulfur reference structures to be used in the calculation of resonance energies, the π-bond energy terms listed in Table I must be evaluated from conjugated acyclic polyenes which contain sulfur. This was done in the same manner as for the two-electron nitrogen and oxygen systems[7] using the sulfur acyclics **1–27**. Summing

Table I. Empirical π-Bond Energies of Carbon-Sulfur Bonds

Designation	Bond type	π-bond energy (β)
$\ddot{\mathrm{S}}$2	CH–SH	0.1934
$\ddot{\mathrm{S}}$1	CH–S	0.1934
$\ddot{\mathrm{S}}$1	C–SH	0.2128
$\ddot{\mathrm{S}}$0	C–S	0.2165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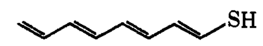
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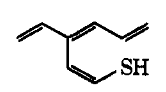
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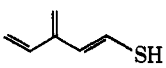
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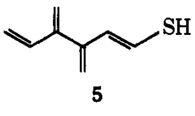
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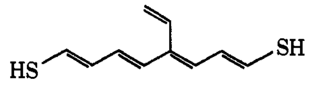
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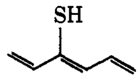
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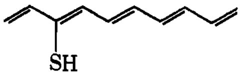
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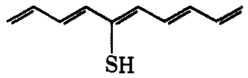
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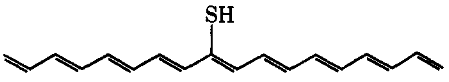
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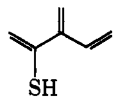
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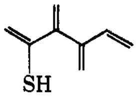
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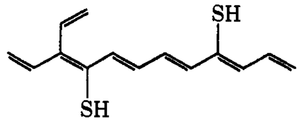
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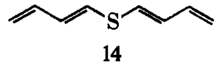
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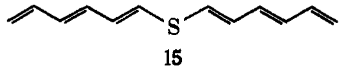
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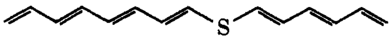
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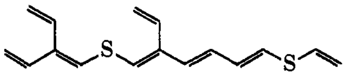
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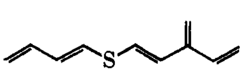
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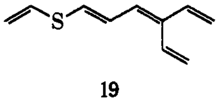
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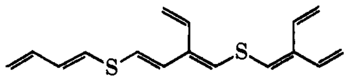
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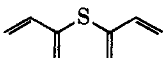
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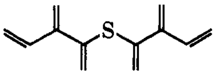
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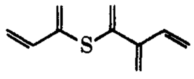
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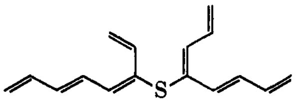
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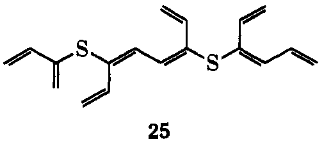
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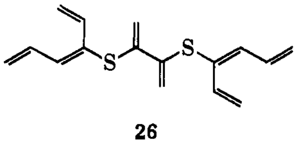
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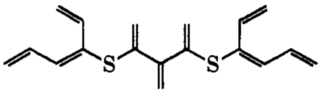
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(10) J. D. Cox and G. Pilcher, "The Thermochemistry of Organic and Organometallic Compounds," Academic Press, New York, N. Y., 1970.

Table II. Resonance Energies of Heterocycles Containing Divalent Sulfur

Compd	π-Binding energy (β)	Additive energy (β)	Resonance energy (β)	REPE (β)
Thiirene (**28**)	2.000	2.457	−0.457	−0.114
Thiophene (**29**)	5.186	4.993	0.193	0.032
Thiepin (**30**)	7.296	7.528	−0.232	−0.029
Thia[9]annulene (**31**)	10.182	10.064	0.118	0.012
Thia[11]annulene (**32**)	12.457	12.600	−0.144	−0.012
Thia[13]annulene (**33**)	15.236	15.136	0.100	0.007
Thia[15]annulene (**34**)	17.584	17.672	−0.088	−0.006
Thia[17]annulene (**35**)	20.307	20.208	0.099	0.006
Thia[19]annulene (**36**)	22.697	22.744	−0.047	−0.002
Thia[21]annulene (**37**)	25.387	25.280	0.107	0.005
Benzo[*b*]thiophene (**38**)	11.011	10.568	0.443	0.044
Benzo[*c*]thiophene (**39**)	10.764	10.517	0.247	0.025
1-Benzothiepin (**40**)	13.300	13.104	0.196	0.016
2-Benzothiepin (**41**)	12.820	13.053	−0.233	−0.019
3-Benzothiepin (**42**)	13.260	13.051	0.209	0.017
Dibenzo[*b,f*]thiepin (**43**)	19.094	20.423	0.671	0.042
Dibenzo[*b,e*]thiepin (**44**)	18.855	18.629	0.226	0.014
Dibenzo[*b,d*]thiepin (**45**)	19.227	18.656	0.571	0.036
Dibenzo[*c,e*]thiepin (**46**)	18.597	18.603	−0.006	0.000
Thieno[3,2-*b*]thiophene (**47**)	8.247	8.004	0.243	0.024
Thieno[3,4-*b*]thiophene (**48**)	8.101	7.955	0.146	0.015
Thieno[2,3-*b*]thiophene (**49**)	8.224	8.004	0.220	0.022
Thieno[2,3-*b*]thiepin (**50**)	10.451	10.540	−0.089	−0.007
Thieno[2,3-*c*]thiepin (**51**)	10.222	10.491	−0.269	−0.022
Thieno[2,3-*d*]thiepin (**52**)	10.440	10.487	−0.047	−0.004
Thieno[3,2-*c*]thiepin (**53**)	10.223	10.491	−0.268	−0.022
Thieno[3,2-*b*]thiepin (**54**)	10.474	10.540	−0.066	−0.006
Thieno[3,4-*b*]thiepin (**55**)	10.484	10.491	−0.007	−0.001
Thieno[3,4-*d*]thiepin (**56**)	10.446	10.438	0.008	0.001
Thiepino[2,3-*b*]thiepin (**57**)	12.677	13.075	−0.398	−0.028
Thiepino[3,4-*b*]thiepin (**58**)	12.775	13.027	−0.252	−0.018
Thiepino[4,5-*b*]thiepin (**59**)	12.632	13.022	−0.390	−0.028
Thiepino[4,3-*b*]thiepin (**60**)	12.768	13.027	−0.259	−0.019
Thiepino[3,2-*b*]thiepin (**61**)	12.642	13.075	−0.433	−0.031
Thiepino[4,5-*c*]thiepin (**62**)	12.739	12.974	−0.235	−0.017
Thiepino[4,5-*d*]thiepin (**63**)	12.593	12.969	−0.376	−0.027
Cyclopenta[*b*]thiopyran (**64**)	10.748	10.570	0.178	0.018
Cyclopenta[*c*]thiopyran (**65**)	10.718	10.517	0.201	0.020
Cyclohepta[*b*]thiopyran (**66**)	13.030	13.106	−0.076	−0.006
Cyclohepta[*c*]thiopyran (**67**)	12.925	13.053	−0.128	−0.011
Thiopyrano[3,2-*b*]thiopyran (**68**)	10.489	10.544	−0.055	−0.005
Thiopyrano[3,4-*b*]thiopyran (**69**)	10.399	10.491	−0.092	−0.008
Thiopyrano[4,3-*b*]thiopyran (**70**)	10.298	10.438	−0.140	−0.012
1,4-Dithiin (**71**)	4.775	4.913	−0.139	−0.017
1,4-Dithiocin (**72**)	7.444	7.449	−0.005	−0.001
73	32.386	31.328	1.058	0.038
74	19.500	19.085	0.415	0.026
75	13.156	13.637	−0.481	−0.040
76	16.421	16.173	0.248	0.018
77	18.554	18.709	−0.155	−0.010
78	13.753	13.531	0.222	0.019
79	11.186	11.022	0.164	0.014
80	11.197	11.022	0.175	0.015
81	14.141	14.040	0.101	0.007
82	17.001	16.574	0.427	0.027
83	16.934	16.572	0.362	0.023
84	13.947	14.146	−0.199	−0.014
85	18.820	19.006	−0.186	−0.010
86	14.216	14.067	0.149	0.009
87	14.259	13.988	0.271	0.017

the appropriate bond energy terms from Table I reproduces the Hückel π-binding energy per electron of compounds **1**–**27** to within 0.001β on the average, and never worse than to 0.005β. Thus, as in the hydrocarbons, acyclic systems form an appropriate reference for the computation of resonance energy. As has been pointed out,[7] the fact that it is impossible to construct compounds with arbitrary numbers of our various bond types implies an arbitrariness in the bond energy terms. No particular physical interpretation of the bond energies should be attempted; therefore, they are to be used only in the computation of resonance energies. For a cyclic system, resonance energy is obtained by subtracting the energy of the reference structure, computed with the C–S bond energies of Table I and the previously obtained C–C bond energies (Table II, ref 1), from the Hückel π-binding energy. Results for 60 compounds (**28**–**87**) are tabulated in Table II. As previously, both the resonance energy and resonance energy per π electron (REPE) are listed. The latter is particularly suitable when comparing compounds of different size.


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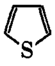
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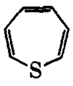
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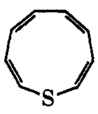
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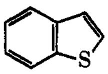
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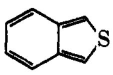
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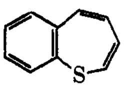
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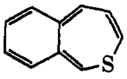
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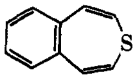
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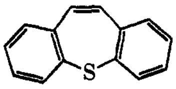
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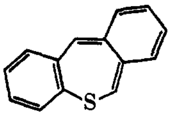
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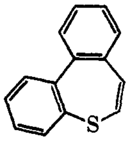
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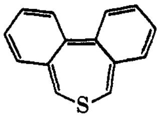
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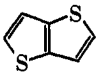
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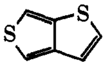
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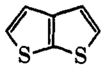
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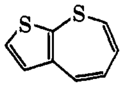
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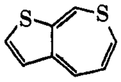
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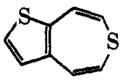
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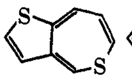
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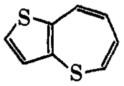
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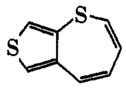
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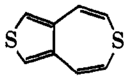
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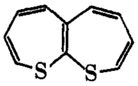
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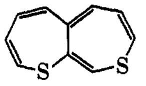
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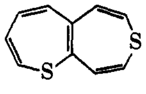
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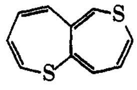
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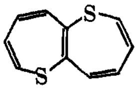
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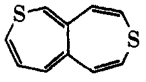
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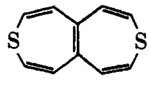
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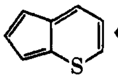
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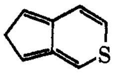
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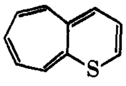
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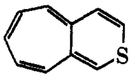
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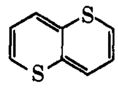
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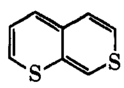
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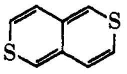
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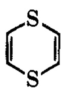
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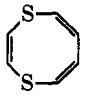
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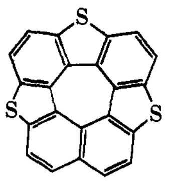
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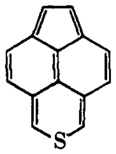
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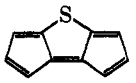
The Thiaannulenes. The most striking aspect of the REPE's of these compounds is their initial strong alternation between aromaticity and antiaromaticity. This alternation decreases as ring size increases and approaches nonaromaticity for large rings. These results are very similar to the azaannulenes[7] and the annulenes.[1,11] The strongly antiaromatic thiirene is as yet unknown and the likelihood of its preparation seems remote.[12] On the other hand, thiophene has a positive REPE about one-half that of benzene. This appears to be in line with its well-known properties. It is interesting to make a comparison of the three five-membered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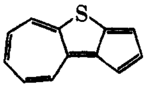
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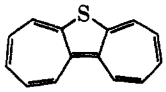
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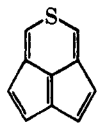
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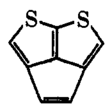
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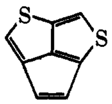
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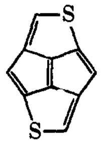
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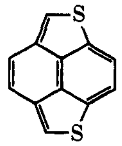
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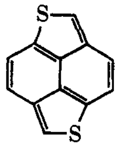
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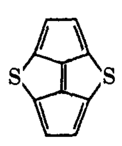
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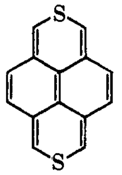
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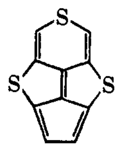
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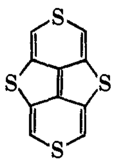
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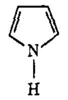
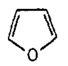
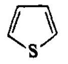
heterocycles, pyrrole, furan, and thiophene (see Table III). Pyrrole and thiophene are predicted to be similarly aromatic while furan is predicted to be only slightly aromatic. Their chemistry appears to be in accord with these predictions since, for example, furan undergoes Diels–Alder reactions readily, while pyrrole and thiophene do not.

Table III. A Comparison of Resonance Energies of Pyrrole, Furan, and Thiophene

Compd	Resonance energy (β)	REPE (β)
	0.233	0.039
	0.044	0.007
	0.193	0.032

The next member of the series, thiepin, is predicted to be antiaromatic. In agreement with this is the absence of a successful synthesis despite numerous attempts.[13] Even an approach modeled after the successful synthesis of azepine and oxepine met with failure.[14] No simple unsubstituted members of the higher thiaannulenes have been reported.

A number of benzo-substituted thiaannulenes have been synthesized. Of the two possible benzothiophenes, benzo[*b*]thiophene is calculated to have considerable resonance stabilization. Its chemistry is that of a typical aromatic heterocycle.[15] On the other hand, benzo[*c*]thiophene has about only one-half the resonance stabilization of benzo[*b*]thiophene. Although it has been successfully prepared, its stability is not high presumably due to readily accessible path-

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[11] B. A. Hess, Jr., and L. J. Schaad, *Tetrahedron Lett.*, 5113 (1972).

[12] The synthesis of substituted mono- and dioxide derivatives of thiirene have been reported; however, their properties would be expected to be quite different from thiirene itself: L. A. Carpino, L. V. McAdams, III, R. H. Rynbrandt, and J. W. Spiewak, *J. Amer. Chem. Soc.*, **93**, 476 (1971); L. A. Carpino and H. W. Chen, *ibid.*, **93**, 785 (1971).

[13] L. Field and D. L. Tuleen, *Heterocycl. Compounds*, **26**, 574 (1972).

[14] T. J. Barton, M. D. Martz, and R. G. Zika, *J. Org. Chem.*, **37**, 552 (1972).

[15] B. Iddon and R. M. Scrowston, *Advan. Heterocycl. Chem.*, **11**, 177 (1970).

ways leading to benzene derivatives, for example, Diels–Alder additions.[16]

There are three possible benzo derivatives of thiepin, **40**–**42**. It is apparent from their REPE's that **40** and **42** should be isolable, while **41**, 2-benzothiepin, is predicted to be antiaromatic. Traynelis has recently reported the synthesis and characterization of 1-benzothiepin.[17] Several stable derivatives of this system have also recently been synthesized.[18] Although **42** has not been reported, several stable derivatives have been.[19] Neither 2-benzothiepin (**41**) nor any of its derivatives are known.[20] Its predicted antiaromaticity and potential conversion to naphthalene by sulfur explusion indicate that its isolation under normal conditions is extremely unlikely.

Of the four possible dibenzothiepins, **43** and **45** appear to be the best candidates for synthesis. In agreement with this is the reported preparation of dibenzo[*b*,*f*]thiepin (**43**) by Bergmann and Rabinovitz.[21] The other three dibenzothiepins are unknown.[22]

Several derivatives of the higher thiaannulenes have been reported[23,24] but none simple enough (for example, without benzo substitution) to allow a fair assessment of the aromaticity of the parent compounds.

The Thienothiophenes. All three thienothiophenes have been prepared. Compounds **47** and **49** are reported to be quite stable and do undergo electrophilic substitution[25] in agreement with their positive REPE's. Thieno[3,4-*b*]thiophene (**48**) is also known but is apparently not as stable as **47** and **49** since it is reported to undergo air oxidation relatively easily.[26] Interestingly, its calculated REPE is somewhat less than **47** and **49**.

The Thienothiepins. The fusion of the aromatic thiophene ring to the antiaromatic thiepin ring leads to seven compounds, **50**–**56**. One might have anticipated all of them to be similar in stability or REPE. However, they range from -0.028β to $+0.001\beta$. The only known compound, thieno[3,4-*d*]thiepin (**56**),[27] is the one predicted to have the greatest stability, although its REPE (0.001β) indicates that it should be nonaromatic rather than aromatic. Reasoning from the stability and crystal structure of **56**, Schlessinger[28] has suggested that it is aromatic. This interpretation, however, has recently been questioned by Dewar and Trinajstić.[9]

The Thiepinothiepins. The fusion of two thiepin rings gives seven possible compounds (**57**–**63**). All are calculated to be moderately antiaromatic. The likelihood of their being stable isolable compounds would therefore appear to be small.

The Cyclopentathiopyrans. The cyclopentathiopyran ring system may be considered as a sulfur analog of azulene in which the seven-membered ring of azulene is replaced by the thiopyran ring. Both **64** and **65** are predicted to be similar to azulene in their REPE's and hence aromatic. Anderson and Harrison have reported not only the synthesis of cyclopenta[*c*]thiopyran (**65**) but also that it undergoes typical aromatic electrophilic substitution.[29] The chemistry of cyclopenta[*b*]thiopyran (**64**) has been found to be very similar to **65**.[30]

Other Systems. Compounds **66**–**70** all are calculated to be slightly antiaromatic. Neither the parent compounds nor any of their derivatives have been reported.

1,4-Dithiin is computed to have a negative REPE and hence should be antiaromatic. However, it has been isolated, although its properties do not appear to be those of an aromatic system.[31] Its stability is most certainly due to its ability to assume a nonplanar conformation. This nonplanarity has been confirmed by X-ray diffraction.[31] Cyclooctatetraene's stability, even though it is a Hückel $4n$ system, is normally explained in a similar manner.

1,4-Dithiocin (**72**) is a particularly interesting compound. It has been considered to be a $4n + 2$ system with ten π electrons and hence thought to be potentially aromatic.[32] However, our calculation predicts 1,4-dithiocin to be a nonaromatic (REPE $= 0.001\beta$), showing the hazard in applying Hückel's rule to systems other than the monocyclic hydrocarbons. **72** is unknown, although a dihydro derivative has been reported.[32] No mention was made of attempts to convert the dihydro-1,4-dithiocin to 1,4-dithiocin. Several derivatives of 1,4-dithiocin have been reported[33,34] but none appear to have any aromatic character associated with the 1,4-dithiocin ring.

Compound **73** has recently been synthesized.[35] It is a hetero derivative of a [7]circulene and appears to be extremely stable as indicated by its very high melting point. Our calculated REPE (0.038β) is in good accord with this.

Schlessinger has synthesized two derivatives of acenaphtho[5,6-*cd*]thiopyran (**74**)[36,37] and claimed it to be an example of a stable tetravalent sulfur heterocycle. While three resonance structures (**74a**, **74b**, and **74c**) can be written while include the sulfur as tetravalent, a fourth (**74**) shows divalent sulfur as pointed out by Cava.[38] We have calculated the REPE of **74** to be 0.026β. The relatively high REPE of **74** raises the question of whether the tetravalent resonance structures need be invoked to explain the stability of this system.

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(17) V. J. Traynelis and Y. Yoshikawa, Abstracts, 164th National Meeting of the American Chemical Society, New York, N. Y., 1972, No. ORGN-56.

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(19) V. J. Traynelis, *Heterocycl. Compounds*, **26**, 714 (1972).

(20) Reference 19, p 709.

(21) E. D. Bergmann and M. Rabinovitz, *J. Org. Chem.*, **25**, 828 (1960).

(22) Reference 19, p 727ff.

(23) P. J. Garratt, A. B. Holmes, F. Sondheimer, and K. P. C. Vollhardt, *J. Amer. Chem. Soc.*, **92**, 4492 (1970).

(24) A. B. Holmes and F. Sondheimer, *ibid.*, **92**, 5284 (1970).

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(26) H. Wynberg and D. J. Zwanenburg, *Tetrahedron Lett.*, 761 (1967).

(27) R. H. Schlessinger and G. S. Ponticello, *J. Amer. Chem. Soc.*, **89**, 7138 (1967).

(28) T. D. Sakore, R. H. Schlessinger, and H. M. Sobell, *ibid.*, **91**, 3995 (1969).

(29) A. G. Anderson, Jr., and W. F. Harrison, *Tetrahedron Lett.*, No. 2, 11 (1960).

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(31) W. E. Parham, H. Wynberg, W. R. Hasek, P. A. Howell, R. N. Curtis, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, 76, 4957 (1954).

(32) W. Schroth, W. Kiessling, J. Peschel, and U. Schmidt, *Z. Chem.*, **4**, 302 (1964).

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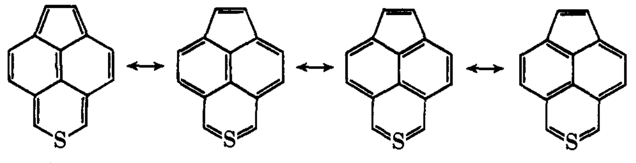
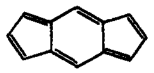


74 74a 74b 74c

Additional experiments need to be carried out to determine the contribution of tetravalent sulfur resonance structures, since in light of our findings stability of the system alone does not require their inclusion.

Compounds **75**–**87** are all unknown but represent interesting sulfur heterocycles. While a number appear to be potentially aromatic systems, for example, **82** and **83**, others with negative REPE's should be antiaromatic in their behavior. Of the antiaromatics **75** is particularly interesting. Although it is isoelectronic with *s*-indacene (**88**) (REPE = 0.009β) and similar in structure, it is predicted to be quite antiaromatic (−0.040β).



88

The above results are further evidence that the Hückel method as presently employed is an extremely useful tool not only in its predictive power but also, and perhaps potentially more important, in gaining a more basic understanding of the nature of aromaticity of cyclic conjugated systems. While earlier treatments of sulfur compounds based on the Hückel method were often helpful,[39] the use of the reference structure as proposed by Dewar greatly increases the reliability of predictions of aromatic character of sulfur heterocycles.

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Relative Nucleophilicity of Common Nucleophiles toward Sulfonyl Sulfur. II. Comparison of the Relative Reactivity of Twenty Different Nucleophiles toward Sulfonyl Sulfur *vs.* Carbonyl Carbon[1a,b]

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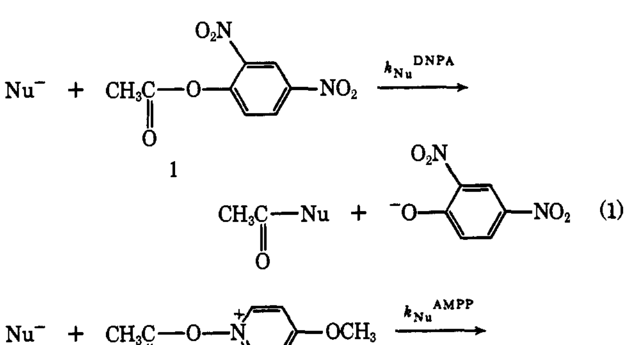
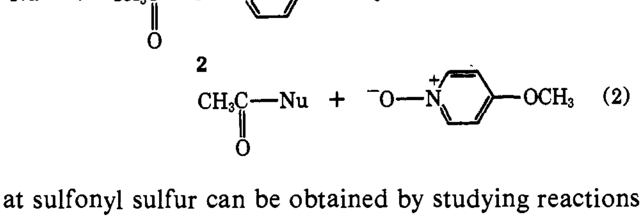
Abstract: The rate of reaction of 20 different nucleophiles with phenyl α-disulfone (**3**) at 25° in 60% dioxane has been determined, mainly by stopped-flow techniques. Comparison of the rate constants with those for reaction of the same nucleophiles with 2,4-dinitrophenyl acetate (**1**) or 1-acetoxy-4-methoxypyridinium perchlorate (**2**) reveals that, except for fluoride ion, the relative reactivity of all the nucleophiles toward sulfonyl sulfur can be predicted quite accurately from a knowledge of their relative reactivity toward carbonyl carbon in a substitution involving a leaving group of similar character and p*K*. Since the nucleophiles studied cover a wide range of nucleophile types, this suggests that in general sulfonyl sulfur is very similar to carbonyl carbon as an electrophilic center. The reactivity of HO_2^-, CH_3CONHO^-, and hydrazine indicates that α-effect nucleophiles of all types show enhanced reactivity (an α effect) toward **3** comparable to that which they exhibit in substitutions with **1** and **2**. The reactivity of fluoride ion toward sulfonyl sulfur is greater than would be predicted from its reactivity toward carbonyl carbon by a factor of about 20.

In 1968 Jencks and Gilchrist[2] reported data on the reactivity of about 40 different nucleophiles toward each of a series of four esters, including 2,4-dinitrophenyl acetate (**1**) and 1-acetoxy-4-methoxypyridinium perchlorate (**2**). Because the data for eq 1 and 2 encompass a wide range of types of nucleophiles and were all obtained under a single set of reaction conditions, they offer an unusually comprehensive and reliable storehouse of information on the relative reactivity of nucleophiles in a substitution reaction at a carbonyl carbon bearing a good leaving group (p*K* = 2–4).



(1)



(2)

Kice, Kasperek, and Patterson[1b] have shown that data on the reactivity of nucleophiles in a substitution at sulfonyl sulfur can be obtained by studying reactions of phenyl α-disulfone (**3**) of the type shown in eq 3.

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[1] (a) This research supported by the National Science Foundation, Grant No. GP-25799; (b) previous paper: J. L, Kice, G. J. Kasperek, and D. Patterson, *J. Amer. Chem. Soc.*, 91, 5516 (1969); (c) National Science Foundation Undergraduate Research Participant, summer 1972.

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