

π -ELECTRON STRUCTURE OF HETEROCYCLIC MOLECULES CONTAINING SULFUR

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(Received in USA 13 September 1979)

Abstract—The π -electron structure of sulfur containing heterocyclic molecules is approached from the point of view of correlating the degree of sulfur participation with the ability to propose resonance structures involving the whole of the hydrocarbon part of a molecule. If this is possible, there is a relatively low degree of sulfur participation. Any bond rigidity introduced into proposed resonance structures to avoid charge isolation or multiple C-S bonding correlates with a higher degree of sulfur participation. The results were obtained within the method originally proposed by Dewar and Harget with a new parameterization for sulfur as reported herein.

In recent years Dewar *et al.*¹ have reported a series of studies of ground state properties of conjugated systems, including heterocyclic molecules. We have used their methods to study some nonbenzenoid hydrocarbons² and have found that the methods give excellent predictions of aromatic behaviour. For those molecules containing N and O we have again found the parameters given by Dewar *et al.*¹ to be dependable.

In the present work on sulfur compounds we attempted to use the parameters reported by Dewar and Trinajstić^{1b} but could not obtain reasonable values for known heats of atomization. The next

section of this paper therefore reports a parameterization for sulfur containing molecules.

The molecules studied in this report are given diagrammatically in Fig. 1. Thiophene, V, was used for the parameterization with molecule I used as a check. The only other suitable sulfur containing molecule which has its heat of atomization reported in the literature is thianthrene, LIV, but it is a non-planar species, rendering it suspect for a check on the parameterization. Molecules II, III and IV are included for comparison with the results of Dewar and Trinajstić. Molecules V to LVIII are reported upon in the following sections with particular reference to the

Table 1. Values of parameters

Parameter	Present Value	Value of Dewar <i>et al.</i> ^{1b} (*)
w_C	11.16 eV	
w_S	23.74 eV	22.63 eV
$\gamma_{1,C}$	11.134 eV	
$\gamma_{1,S}$	12.095 eV	11.90 eV
z_C	3.18	
z_S	6.957	4.551
n_C	2	
n_S	3	2
ζ_C	1.59	
ζ_S	2.319	2.276
$K(C-S)$	10.7665	15.7265
A	1.802(C-S), 1.512(C-C)	
B	0.229(C-S), 0.174(C-C)	

*Value of the parameters not shown in this column is the same as that of the present work.

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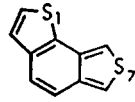
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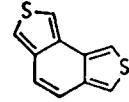
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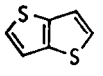
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XXIX



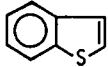
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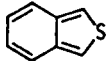
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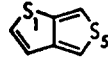
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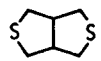
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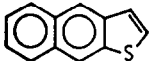
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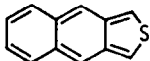
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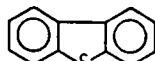
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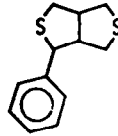
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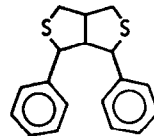
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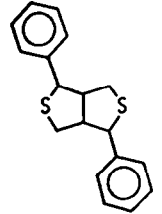
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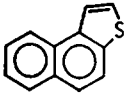
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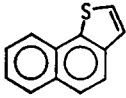
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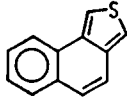
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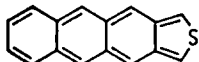
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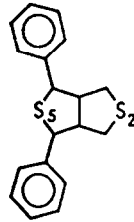
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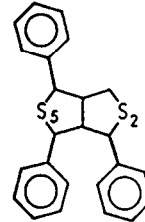
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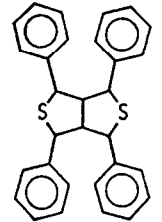
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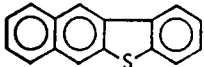
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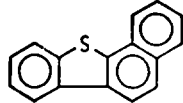
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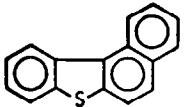
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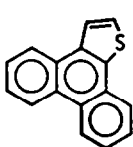
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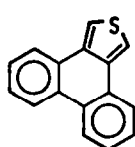
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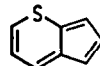
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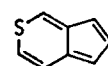
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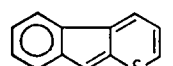
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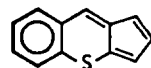
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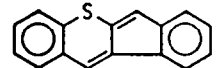
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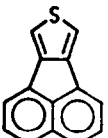
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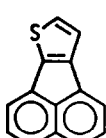
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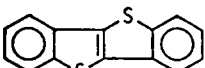
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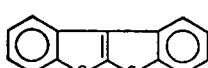
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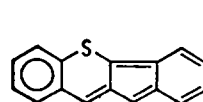
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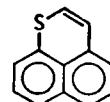
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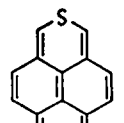
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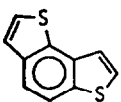
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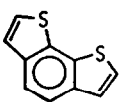
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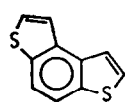
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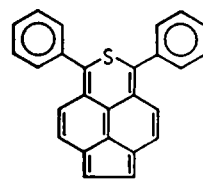
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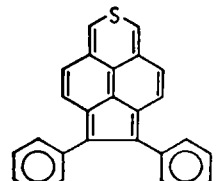
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XXVII



XLVIII



XLIX

Table 2. Heat of atomization, ΔH_a , (e.v.)

	Molecule	Heat of Atomization		
		Present Work	Dewar-Trinajstić	Difference
V	Thiophene	40.320 (40.32)*	40.321	0.001
I	Benzenethiol	59.670 (59.71)*	59.712	0.042
VI	Benzo[b]thiophene	74.078	74.076	-0.002
VII	Benzo[c]thiophene	73.398	73.404	0.006
XXX	1,4-Thiophthene	57.355	57.351	-0.004
XXXI	1,5-Thiophthene	57.113	57.115	0.002
XXXII	1,6-Thiophthene	57.316	57.316	0
XXXIII	2,5-Thiophthene	55.332	55.390	0.058
X	Dibenzothiophene	107.898	107.896	-0.002
II	2,2'-Bithienyl	76.137	76.137	0
III	2,3'-Bithienyl	76.089	76.112	0.023
IV	3,3'-Bithienyl	76.065	76.064	-0.001
LIV	Thianthrene	110.392 (110.16)**		
LV		58.717	58.700	-0.017
LVIII		75.734	75.739	0.005

Figures in the parantheses are the experimental value. *Taken from Ref. (1b). **Calculated from the heat of formation value (Ref. 7).

(7) S. Sunner, Acta Chem. Scand. 9, 847 (1955).

Dewar and Morita⁶ have argued that the valence state ionization energy should be proportional to Z^2 . Z the effective nuclear charge. This argument, however, does not take into account the differences in the principal quantum number, n , of the orbitals involved. Assuming the p atomic orbitals to be hydrogenlike, the valence state ionization energy should be proportional to Z^2/n^2 . Following this premise we obtain

$$Z_X = Z_C n_X / n_C (W_X / W_C)^{1/2}$$

Although this distinction in method of obtaining Z_S disappears when one calculates Z_S , the orbital exponent, still the distinction in the method is critical when calculating the overlap integral to be used in the Mulliken approximation. Using the approach of Dewar and Morita, one should logically use a $2p-2p$ overlap formula. The modified method logically requires use of a $2p-3p$ overlap formula with the same sulfur orbital exponent. The values of the parameters used in this paper are included in Table 1.

Table 2 contains the results obtained with our parameterization, along with the reported values of Dewar *et al.*^{1b} The striking feature in this table is the agreement between these sets of results.

COMPOUNDS WITH FUSED THIOPHENE AND HYDROCARBON RINGS (V-XXIX)

The molecules of this type can be readily grouped into two classes which we choose to call thiophenic and non-thiophenic (in place of the more usual quinonoid and benzenoid) to call attention to the dominant characteristics in the 5-membered ring. Table 3 gives some of the results of our calculations and we have assembled into Table 4 some properties which serve to distinguish the two classes.

In these Tables, $E_R^{b, \text{calc}}$ is the resonance energy of the hydrocarbon nuclei in which delocalization may still occur when we consider structures, as in Fig. 1, in which the S atom is not involved in any double bond formation. E_R^{-S} is the resonance energy of the artificial hydrocarbon species derived from the heterocyclic systems by deleting the C-S bonds, retaining the same initial geometry. In Table 4, R_i-R_i and R_i-R_h are the differences between the predicted lengths of the hydrocarbon-heterocyclic fusion bond and the corresponding bond in thiophene and the hydrocarbon, respectively. Finally, q_S is the calculated sulfur charge density which is related to $E_R-E_R^{-S}$ by

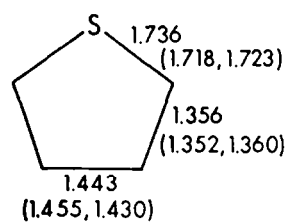
$$q_S = 1.926 - 0.279(E_R - E_R^{-S}),$$

Table 3. Heat of atomization (e.v.), resonance energies (e.v.) and charge density on sulfur atom

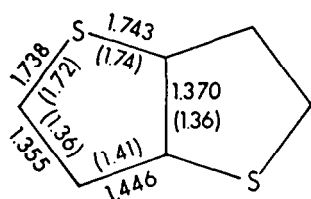
Molecule	$-\Delta H_a$	E_R	E_R^{-S}	$E_R - E_R^{-S}$	E_R^{basic}	q_S
V	40.320	0.283	0.081	0.202	0	1.87
VI	74.078	1.078	0.977	0.101	0.980	1.90
VII	73.398	0.398	0.123	0.275	0	1.85
VIII	107.469	1.506	1.445	0.061	1.457	1.91
IX	106.500	0.538	0.237	0.301	0	1.84
X	107.898	1.935	1.902	0.033	1.960	1.92
XI	107.587	1.624	1.449	0.175	1.457	1.89
XII	107.581	1.618	1.475	0.143	1.457	1.89
XIII	107.187	1.224	0.981	0.243	0.980	1.86
XIV	140.728	1.802	1.758	0.044	1.774	1.91
XV	139.610	0.684	0.372	0.312	0	1.84
XVI	141.313	2.388	2.379	0.009	2.437	1.92
XVII	141.377	2.451	2.389	0.062	2.437	1.91
XVIII	141.382	2.457	2.398	0.059	2.437	1.91
XIX	141.254	2.329	2.160	0.169	2.125	1.88
XX	141.033	2.108	1.882	0.226	1.960	1.86
XXI	121.814	1.614	1.411	0.203	1.464	1.87
XXII	121.891	1.691	1.513	0.178	1.464	1.88
XXIII	124.898	2.112	1.945	0.167	1.960	1.90
XXIV	124.876	2.091	1.911	0.180	1.960	1.90
XXV	91.022	1.199	0.975	0.224	0.980	1.89
XXVI	91.009	1.186	0.980	0.206	0.980	1.90
XXVII	91.021	1.198	0.984	0.214	0.980	1.90
XXVIII	90.427	0.604	0.161	0.443	0	1.88(1), 1.85(7)
XXIX	90.253	0.430	0.008	0.422	0	1.87

Table 4. Properties used for classification

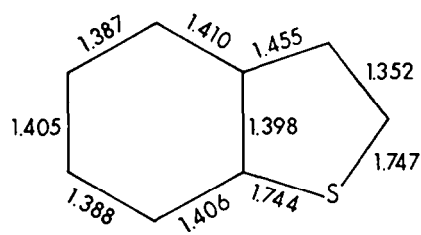
	Thiophenic	Non-Thiophenic
$E_R - E_R^{basic}$	0.283 to 0.684	-0.025 to 0.219
$E_R - E_R^{-S}$	0.202 to 0.312	0.009 to 0.178
$ R_f - R_t _{ave}$	0.002	0.039
$ R_f - R_h _{ave}$	0.048	0.005
q_S	1.84 - 1.87	1.88 - 1.92



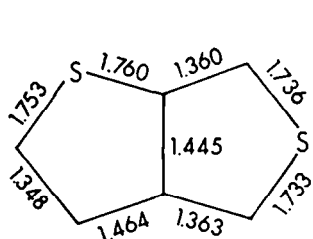
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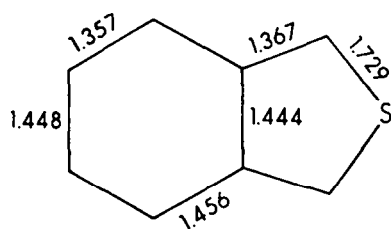
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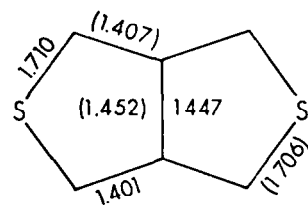
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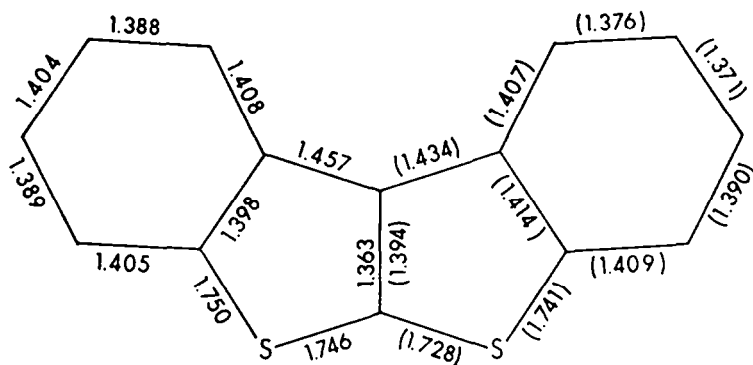
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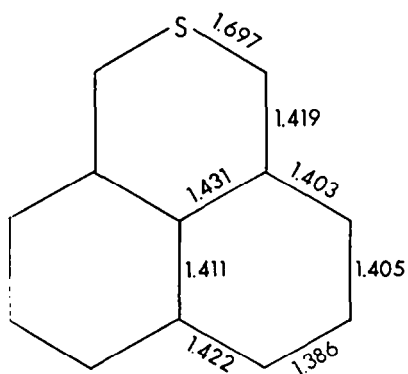
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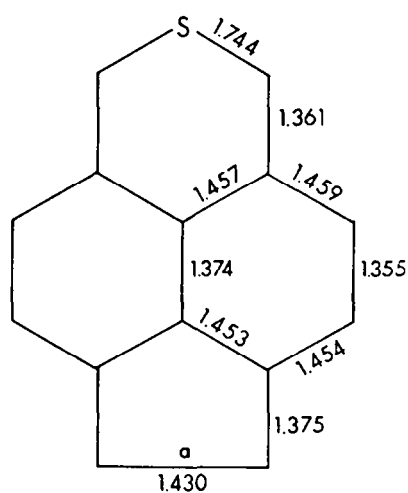
XXXIII



XXIV



LI



XLVI

Fig. 3. Bond length diagrams. Experimental values, given in parentheses, were obtained from V. B. Bak, D. Christensen, J. Rastrup Andersen and E. Tannenbaum, *J. Chem. Phys.* **25**, 892 (1956). XXIV: I. Goldberg and U. Shmueli, *Acta Cryst.* **27**, 2165 (1971). XXX: E. G. Cox, R. J. H. Gillot and G. A. Jeffrey, *Acta Cryst.* **2**, 356 (1949). XXXIII: Ref. 15, for derivative XXXIX.

which yields a standard deviation from the calculated sulfur charge density of 0.003.

All of the properties in Table 4 point towards the degree of sulfur participation in π -bonding as the feature distinguishing the two classes. In the non-thiophenic molecules the hydrocarbon part can develop nearly its full resonance stabilization without such participation. This is reflected in the higher sulfur charge density and in the minor departure of the fusion bond length from the normal hydrocarbon value. This is not the case in the thiophenic systems where the greater participation is shown by the reduced sulfur charge density and lower C-S bond length. (Fig. 3). This is accompanied by a greater enhancement of the resonance energy above the E_R^{basic} and E_R^S values as well as a minor departure of the fusion bond length from the thiophenic value.

The predicted bond lengths in thiophene (V) and the benzthiophenes (VI and VII), which are typical of all molecules discussed in this section, are given in Fig. 3. In addition to the features discussed above, one clearly sees the characteristics of "bond rigidity" which have been carried to their extreme in giving the diagrams for the dominant resonance structure in Fig. 1.

The low resonance energy for the thiophenic molecules (VII, IX, XIII, XV, XX, XXI, XXIX) compared to that of similar iso-electronic non-thiophenic systems suggests that these molecules have a tendency to instability; this is in agreement with experiment. Thus the molecule, VII, is highly reactive, and is obtained in poor yield in synthesis.⁸ The molecule, IX, has not yet been synthesized but is only generated as a transient intermediate and trapped as a mixture of adducts.⁹ From the resonance energy it is expected that compound XIII is more stable than VII or IX because E_R^{basic} for XIII is not zero as in VII or IX. This too is in agreement with experiment.¹⁰

The common structural feature of the non-thiophenic molecules, having the sulfur adjacent to the hydrocarbon ring, leads one to propose that both classes of rings are present in XXVIII. This structural indication is borne out by the calculated properties: the sulfur charge densities are 1.85 and 1.88 in the thiophenic and non-thiophenic rings; the resonance energy is above that of the corresponding purely

thiophenic XXIX but well below that of the purely non-thiophenic XXV-XXVII.

Thiophthenes and derivatives (XXX-XXXIX)

The thiophthenes are of particular interest to theoretical and synthetic chemists and have been studied theoretically by many workers.^{16,11} The pattern of sulfur charge densities and of resonance energies given in Table 5 are consistent with the classification into thiophenic and non-thiophenic nuclei given in the previous section.

Molecules XXX-XXXII have been synthesized: XXX and XXXII, which are purely non-thiophenic in character, display relatively greater stability than XXXI, which is of mixed character.¹² In the case of XXXIII, where both sulfurs are in thiophenic positions, the negative resonance energy indicates a complete lack of stability in the planar conformation, consistent with the experimental evidence of the highly transient nature of this species and its methyl substituted derivatives.¹³

Tetraphenyl derivatives of XXXIII are stable.¹⁴ We have carried out calculations on its hypothetically planar phenyl substituted derivatives molecules XXXIV-XXXIX. Upon single substitution the resonance energy rises sharply from -1.53 to 0.59 e.v. Further substitution enhances the resonance energy by about 1.04 e.v. per phenyl group. This value is, of course, close to the resonance energy of benzene, 0.98 e.v. This suggests that the observed stability of the tetra-substituted derivative is not due to major resonance enhancement by the additional phenyl groups, particularly since steric crowding requires the phenyl groups to be out of the plane.¹⁵

Compounds with sulfur in non-5-membered rings (XL-LVIII)

The charge densities on the sulfur and the resonance energies of XL-LVIII, given in Table 6, permit one to establish a classification parallel to that used for the 5-membered ring systems. Those molecules with low resonance energies and zero "basic" resonance energies have charge densities of 1.90 or lower on the sulfur. The others have resonance energies close to the

Table 5. Heat of atomization (e.v.), resonance energy (e.v.) and charge density on sulfur atom

Molecule	$-\Delta H_a$	E_R	q_S
XXX	57.355	0.494	1.88
XXXI	57.113	0.252	1.93 (1), 1.87 (5)
XXXII	57.316	0.456	1.89
XXXIII	55.332	-1.529	1.77
XXXIV	108.063	0.593	1.78
XXXV	160.779	1.621	1.78
XXXVI	160.791	1.633	1.78
XXXVII	160.804	1.646	1.78 (5), 1.79 (2)
XXXVIII	213.519	2.672	1.78 (5), 1.79 (2)
XXXIX	266.244	3.709	1.79

"basic" values and sulfur charge densities consistently above 1.90.

The molecule XLI is a peculiar one. It is stable and has been classified as aromatic which can not be accounted for from its calculated resonance energy which is less than that of XL which is unstable.¹⁶ Moreover it can not be represented by more than one Kekule structure without involving charge isolation or multiple C-S bonding.

Compound XLV is a somewhat special case in that the bond rigidity extends into the benzene ring attached to the 5-membered ring. Thus the "basic" resonance is 0.980 e.v., due to the other benzene ring. This is reflected in the low resonance energy 1.195 e.v., compared to the similar molecule XLIV which has a resonance energy of 1.985 e.v., close to twice that of benzene. Nevertheless the sulfur charge density in XLV is 1.91 consistent with the ability to propose a "basic" structure which does not have complete bond rigidity.

The resonance energy of XLVII is 0.220 e.v., consistent with the experimentally observed high reactivity of the species.¹⁷ The phenyl derivatives XLVIII and L have been prepared and found to be relatively stable.¹⁸ The resonance energies of these molecules and of XLIX may be very closely predicted by assuming additivity of the resonance energies of the parent, XLVII, and the requisite number of benzene nuclei. This contrasts with the behaviour of the thiophthene (XXXIII) case discussed above where substitution of a single phenyl group raised the resonance energy by over two electron volts with subsequent phenyl substitution being close to additive in the sense used here.

Although the resonance energies in the present case are nearly additive, considerable perturbation of the sulfur containing nucleus is observed upon phenyl substitution, particularly in XLVIII and L. In XLVIII the bond order of every bond except the C-S bond of the S containing nucleus is decreased from high values or increased from low values, consistent with improved delocalization. The same is found in XLIX except for the C-C bond labelled 'a' in Fig. 3, but the changes are not as pronounced as in XLVIII.

Since steric hindrance certainly forces the two phenyl groups in positions shown in XLIX out of the molecular plane, and since the perturbation of the sulfur containing nucleus by the phenyl groups is small compared to those in positions shown in XLVIII, it is suggested that the stability of the tetraphenyl species has, in large part, the same origin as the stability of the diphenyl species XLVIII.

The molecule LII is highly unplanar.¹⁹ Hence the calculations might not be so much meaningful. However, under planar configuration the molecule is predicted to be very much reactive. The low resonance energies and the "zero basic" resonance energies of LII, LV and LVII are consistent with their high reactivity or instability.²⁰ On the other hand, molecules LIII, LIV and LVI are stabilized²¹ by the addition of benzene rings to the corresponding structures LII, LII, and LV. Once again the resonance energies of the compounds are close to the "basic" resonance energies attributed to the benzene rings. Molecule LVIII is another curious case since the low resonance energy is inconsistent with the remarkable observed stability.²² We suggest that, although the molecule is observed to

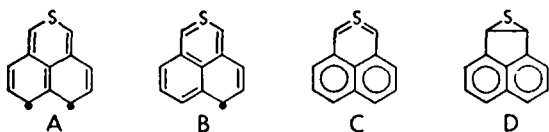
Table 6. Heat of atomization (e.v.), resonance energies (e.v.) and charge density on sulfur atom

Molecule	$-\Delta H_a$	E_R	E_R^S	$E_R - E_R^S$	E_R^{basic}	q_S
XL	73.191	0.191	0.133	0.058	0	1.90
XLI	73.124	0.124	0.053	0.071	0	1.90
XLII	106.985	1.022	0.990	0.032	0.98	1.91
XLIII	107.012	1.049	1.044	0.005	0.98	1.92
XLIV	140.820	1.895	1.704	0.191	1.96	1.92
XLV	140.120	1.195	1.167	0.028	0.98	1.91
XLVI	107.393	1.430	1.445	-0.015	1.457	1.93
XLVII	120.420	0.220	0.093	0.129	0	1.88
XLVIII	225.786	2.210	2.090	0.120	1.960	1.88
XLIX	225.706	2.129	2.002	0.127	1.960	1.88
L	331.081	4.128	4.006	0.122	3.920	1.88
LI	105.215	0.331	-0.302	0.633	0	1.71
LII	42.570	-0.053	-0.056	-0.003	0	1.94
LIII	76.483	0.897	1.008	-0.111	0.980	1.94
LIV	110.392	1.843	1.959	-0.116	1.960	1.94
LV	58.717	-0.047	0.058	-0.105	0	1.95
LVI	126.520	1.832	1.902	-0.070	1.960	1.94
LVII	73.006	0.006	0.035	-0.029	0	1.93
LVIII	75.734	0.148	0.005	0.143	0	1.87 (2), 1.94 (6)

be planar in the crystal, it may gain stability in other phases by departing from planarity. This is consistent with the view of Dewar and Trinajstić^{1b} who also report results similar to ours. A suggestion that the electronic structure might have a strong contribution from a charge-separated structure (similar to azulene) is not consistent with the calculated π -dipole moment of 0.4 D.

MULTIPLE C-S BONDING

In Fig. 1 we have left the "basic" structures of molecules XXXIII and LI unspecified because it is not possible to involve every centre in double bond formation without involving the sulfur in multiple C-S bonding. For example



It should be noted that the model used in this paper is that of bivalent sulfur under the definition of valency as the number of unpaired electrons in the orbitals of an atom in its valence state. Since we do not provide for d orbital participation, any π bonding by the sulfur in our model must arise from sulfur p orbital participation. This is consistent with recent *ab initio* and CNDO type calculations²³ on sulfur compounds of this type considered in this paper in which it is found that d orbital participation is unimportant for the prediction of ground state properties.

Even though only p-orbitals are taken into account it is possible to propose valence bond structures of the type given in diagrams B and C above. There has been a tendency in the literature to speak of the sulfur in diagram C as being tetravalent. We do not like to use this term in the present context, reserving tetravalency to refer to situations where the model is one in which the valence shell has been expanded to include d orbitals as in, e.g. the sulfate ion. In this vein it should be observed that, because of the requirement that the two electrons attributed to the sulfur p orbital must be a singlet pair, structure C can be equivalently written as structure D.

Among all of the compounds studied in this paper XXXIII, and its derivatives, and LI are clearly different in several properties. The sulfur charge densities are distinctly low, 1.71–1.79 compared with 1.84–1.95 for all other compounds. The C-S bond orders are distinctly high, 0.40 in XXXIII and 0.46 in LI. Typical C-S bond orders in the other compounds are 0.25–0.30. This clearly indicates that there is a higher degree of sulfur participation in the π -bonding of those molecules for which classical Kekulé structures cannot be written without involving forms of the type of diagram C. Even though there is significant participation, the resonance energies remain low, consistent with the experimental evidence of instability and transient nature.²⁴

Structures of type C can also be written for the other molecules considered and this has been done in particular for XLVII.¹⁷ However, the pattern of predicted bond lengths, given in Fig. 3, shows a striking similarity to the "basic" resonance structures

given in Fig. 1 so that we regard the contribution of structures of type C as being minimal in all cases other than LI and XXXIII and its derivatives.

CONCLUSION

In this work we have delineated a relation between the "basic" resonance structures of a molecule and the degree of sulfur participation in the π -bonding. In general, the ability to propose structures which indicate delocalization in the whole of the purely hydrocarbon portion of the molecule correlates with a total molecular resonance energy which is close to that for the hydrocarbon part. At the same time the sulfur charge density is relatively high and the C-S bond orders low, indicating a generally low degree of sulfur participation. Such molecules are generally stable.

The other category consists of molecules for which one cannot propose more than one (and in some cases, none) resonance structure without invoking charge isolation or multiple C-S bonding. If one forgoes these possibilities there is a consequent bond rigidity in the structure which extends into at least the hydrocarbon ring neighbouring to the heterocyclic nucleus. This correlates with resonance energies for the total molecule which are distinctly greater than the "basic" resonance energies, with relatively lower sulfur charge densities and higher C-S bond orders. This indicates that there is greater sulfur participation with consequent enhancement of delocalization. In this type of molecule, the use of the resonance energy as indicator of stability appears to be less certain. The case of XL and XLI is an example, as is, to some extent, thiophene itself.

These molecules for which charge isolation or multiple C-S bonding occur in proposing resonance structure exhibit significantly greater participation of the sulfur p orbital in the π -bonding. We argue that this case should nevertheless not be attributed to tetravalent sulfur.

Thiophene resembles benzene more closely than furan and pyrrole. The resonance energy of thiophene, pyrrole and furan are 0.283, 0.250¹ and 0.186¹ eV calculated by this method. Hence the aromaticity of these molecules is in the order thiophene > pyrrole > furan and this is also in agreement with the experimental results. Thiophene derivatives undergo Diels-Alder reactions with much difficulty, unlike corresponding derivatives of furan, but less easily than similar derivatives of pyrrole. The high stability of thiophene is mainly due to more complete equilibration of the π -electron density in the thiophene molecule as compared with the pyrrole and furan molecules. Since in thiophene delocalization is likely to involve the d orbitals of the sulfur atom and this can not be taken into account in the case of pyrrole or furan because nitrogen or oxygen are not capable of expanding their outer electronshell beyond the octet (they are in the minor group).

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