

AROMATICITY IN HETEROCYCLIC MOLECULES CONTAINING DIVALENT SULFUR

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Dedicated to Dr R. Zahradník on the occasion of his 60th birthday.

The conjugated circuits model is applied to heterocycles containing divalent sulfur. A novel parametrization is introduced for $4n + 2$ and $4n$ conjugated circuits containing a single sulfur atom. The relative aromatic stabilities of a number of heterocyclic systems containing divalent sulfur are studied. Comparison is made whenever possible with earlier reported resonance energies of these compounds, obtained by using Hückel MO and SCF π -MO models, and appropriate reference structures. Special attention is given to positional isomers. An explanation of the differences amongst such isomers is given.

In the present work we wish to report an application of the conjugated circuits model^{1,2} to heterocyclic molecules containing divalent sulfur. Such an application will allow us to predict their aromatic stabilities.

The chemistry of heterocycles containing divalent sulfur is still a very active area of research judging from the reports appearing in the current chemical literature (e.g.³⁻⁹). In addition, these heterocyclics exhibit some interesting biological properties such as anticancer activity (e.g.^{10,11}). Rudolf Zahradník was amongst the first to study this rich class of sulfur-containing π -electronic systems using quantum chemical methods (e.g.¹²⁻¹⁷).

The aromatic stability of a conjugated system is its intrinsic stability towards decomposition.¹⁸⁻²⁰ Resonance energy, RE , is a theoretical quantity which serves as an indicator of aromatic stability.^{21,22} RE is defined as that part of the molecular binding energy which denotes deviation from simple bond additivity.^{23,24} This extra stability, present in some polycyclic conjugated structures but absent in others,

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is associated with the aromatic character of the compound, or the lack of it. Hence one may speak of the aromatic stability of polycyclic (heterocyclic) conjugated systems.²⁵

The conjugated circuits model is a graph-theoretical model which allows one to calculate the *RE*'s of conjugated molecules in a simple way and to produce reliable predictions on the aromatic stability of a given class of conjugated compounds. This model has already been successfully tested on a wide range of conjugated systems such as benzenoid and non-benzenoid hydrocarbons,^{1,26-30} their ions^{31,32} and excited states of benzenoids,³³ Möbius systems³⁴ and heterocycles.³⁵⁻³⁷ In addition, recent discussions on the aromatic stability of buckminsterfullerene (a soccerball-like structure C_{60}) support the conjugated circuits model as the most convenient theoretical model for predicting the aromatic stabilities of conjugated carbon cages.³⁸⁻⁴¹

THEORETICAL

The Conjugated Circuits Model

The conjugated circuits model was introduced for the study of conjugation and aromaticity in polycyclic conjugated molecules.¹ Graph-theoretical analyses of Kekulé valence structures revealed that each Kekulé structure may be partitioned into several conjugated circuits. A conjugated circuit is defined as a circuit within an individual Kekulé valence structure in which there is a regular alternation of formal carbon-carbon single and double bonds.^{1,2} Thus, the conjugated circuits are necessarily of even length.

The circuit decomposition of an individual Kekulé structure belonging to a given polycyclic conjugated molecule leads to $4n + 2$ ($n = 1, 2, \dots$) and/or $4n$ ($n = 1, 2, \dots$) linearly independent, linearly dependent and disconnected circuits. The total number of all conjugated circuits within a single Kekulé valence structure is equal to $K - 1$ (ref.⁴²), where K is the number of Kekulé structures (the Kekulé number) for a conjugated polycyclic molecule. Linearly independent circuits are those that cannot be represented by a superposition of conjugated circuits of smaller size.

The $4n + 2$ circuits are denoted by R_n , and the $4n$ circuits by Q_n . The resonance energy of a polycyclic conjugated molecule, within the conjugated circuits model, may be expressed in terms of the quantities R_n and Q_n (ref.²):

$$RE = \frac{1}{K} \sum_{n \geq 1} (a_n R_n + b_n Q_n), \quad (1)$$

where K is the number of Kekulé structures for the conjugated molecule, R_n and Q_n are, respectively, the parametric values for the conjugated circuits of size $4n + 2$ and $4n$ containing only carbon atoms, whilst a_n and b_n represent the number of R_n

and Q_n circuits, respectively, for a given value of n . The sum is over all R_n and Q_n in all Kekulé structures. The R_n quantities contribute towards the aromatic stability of a conjugated system, whilst the Q_n quantities have a destabilizing effect on the aromatic stability of a system. We have truncated the set of conjugated circuits at those of size fourteen ($n = 3$). In considering only the smallest three conjugated circuits of types R_n and Q_n , we have followed the empirical findings that only the smallest circuits make appreciable contributions to the resonance energy.⁴³ In principle, one could include higher terms, but the data needed for establishing the parameters are very scarce, especially for heterocyclic structures. This then limits the extent of parametrization to the dominant conjugated circuits.

The numerical values of the R_n ($n = 1, 2, 3$) parameters are obtained¹ from the parametrization procedure based on the SCF π -MO resonance energies of Dewar and de Llano.⁴⁴ The numerical values of the Q_n ($n = 1, 2, 3$) parameters are obtained from the SCF π -MO RE of cyclobutadiene (-0.781 eV^*)⁴⁴ by utilizing the approximations:^{1,43,45}

$$Q_2 = R_2 Q_1 / R_1 \quad (2)$$

$$Q_3 = R_3 Q_1 / R_1. \quad (3)$$

The values of the R_n and Q_n ($n = 1, 2, 3$) parameters are given in Table I.

As an illustration of the conjugated circuit approach we consider benzo(a)pyrene and biphenylene. The Kekulé valence structures of benzo(a)pyrene are given in Fig. 1 and those of biphenylene in Fig. 2. The circuit decomposition of one of the Kekulé structures of benzo(a)pyrene is shown in Fig. 3 and of one of the Kekulé structures of biphenylene in Fig. 4. The total decomposition of the Kekulé structures of benzo(a)pyrene in terms of its conjugated circuits (see Table II) is given by:

$$22R_1 + 14R_2 + 10R_3 + 6R_4. \quad (4)$$

The total circuit decomposition of the Kekulé structures of biphenylene (see Table III) is given by:

$$8R_1 + 2Q_1 + 4Q_2 + 2Q_3 + 4R_1R_1. \quad (5)$$

TABLE I

Numerical values for the R_n and Q_n parameters (in eV)

$R_1 = 0.869$	$Q_1 = -0.781$
$R_2 = 0.247$	$Q_2 = -0.222$
$R_3 = 0.100$	$Q_3 = -0.090$

* $1 \text{ eV} = 96.4853 \text{ kJ mol}^{-1}$.

The resonance energies of benzo(*a*)pyrene and biphenylene are given as follows (linearly independent and linearly dependent conjugated circuits are used):

$$RE(\text{benzo}(a)\text{pyrene}) = (22R_1 + 14R_2 + 10R_3)/9 = 2.619 \text{ eV} \quad (6)$$

$$RE(\text{biphenylene}) = (8R_1 + 2Q_1 + 4Q_2 + 2Q_3)/5 = 0.864 \text{ eV} . \quad (7)$$

It is found that a larger molecule has, as a rule, a larger *RE*, because the deviations

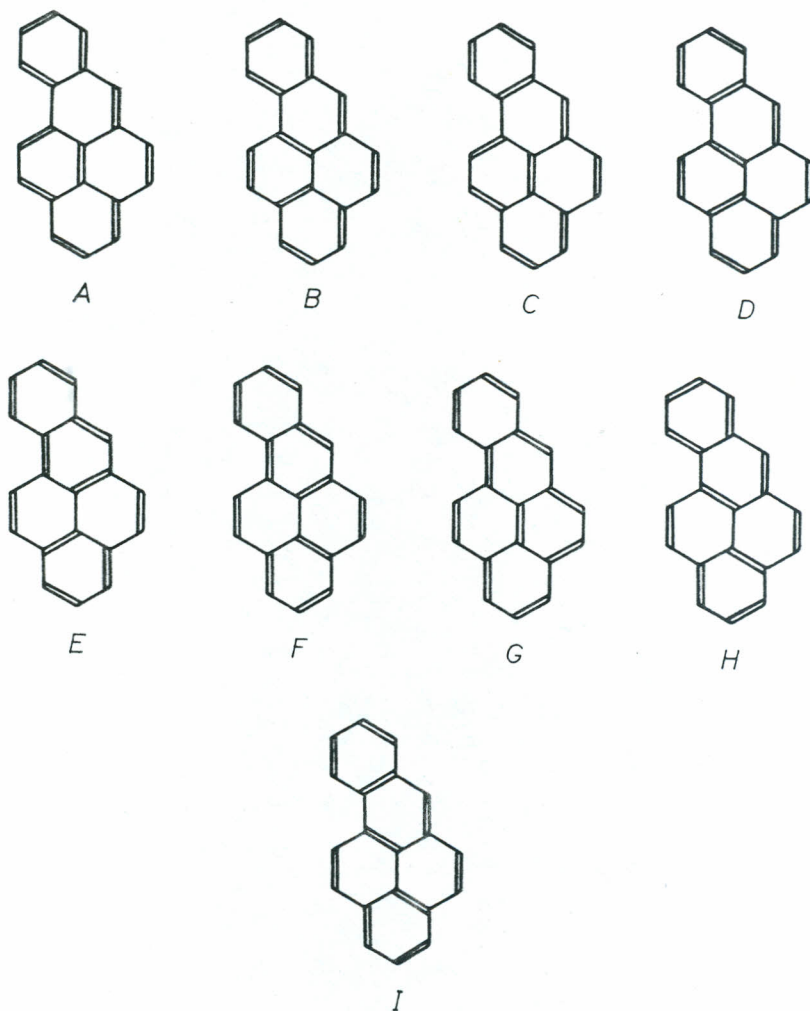


FIG. 1
Kekulé valence structures of benzo(*a*)pyrene

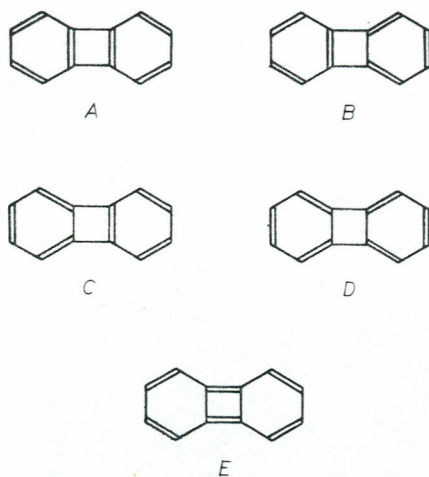


FIG. 2
Kekulé valence structures of biphenylene

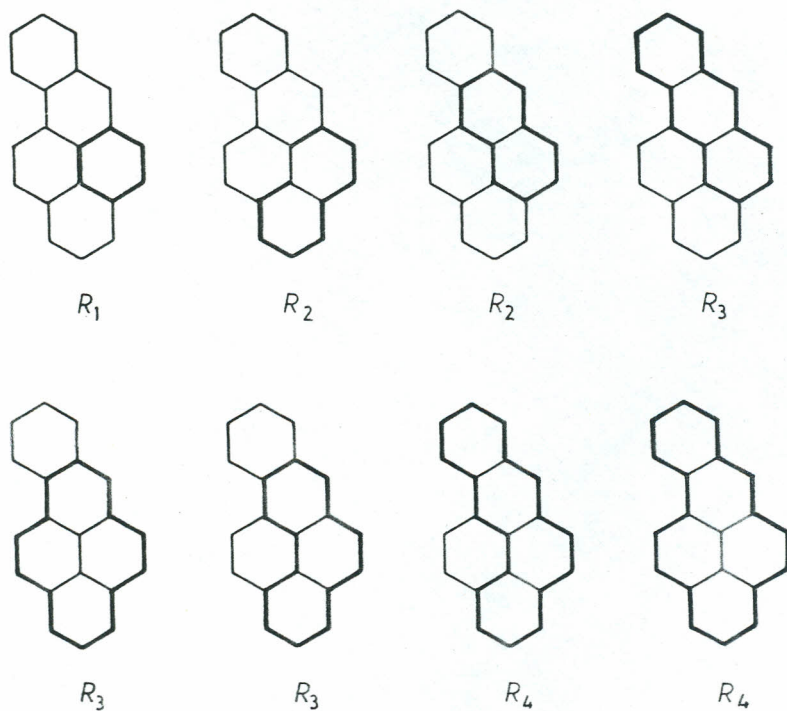


FIG. 3
Conjugated circuits belonging to the Kekulé structure G of benzo(a)pyrene

TABLE II

The circuit decomposition of the Kekulé structures of benzo(a)pyrene. Disjoint circuits are denoted by $R_n \cdot R_n$

Kekulé structures	Conjugated circuits count					
	R_1	R_2	R_3	R_4	$R_1 \cdot R_1$	$R_1 \cdot R_2$
A	2	1	1	2	1	1
B	3	1		1	2	1
C	2	2	2		1	1
D	4		1		3	
E	2	3	1		1	1
F	3	1	1	1	1	1
G	1	2	3	2		
H	2	2	1		1	2
I	3	2			2	1

TABLE III

The circuit decomposition of the Kekulé structures of biphenylene. Disjoint circuits are denoted by $R_n \cdot R_n$

Kekulé structure	Conjugated circuits count				
	R_1	Q_1	Q_2	Q_3	$R_n \cdot R_n$
A	2	1			1
B	2		1		1
C	2		1		1
D	2			1	1
E		1	2	1	

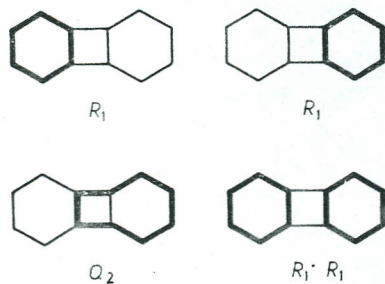


FIG. 4

Conjugated circuits belonging to the Kekulé structure B of biphenylene

from bond additivities accumulate.²⁴ To eliminate the size effect we consider RE per π electron, RE/e , which is defined as:^{24,46,47}

$$RE/e = RE/N, \quad (8)$$

where N is the number of π electrons in the molecule.

For example, comparison of the RE/e values of benzo(*a*)pyrene (0.131 eV) and biphenylene (0.086 eV) indicates that benzo(*a*)pyrene is more aromatic than biphenylene. This prediction is in agreement with experiment.^{48,49}

Extension of the Conjugated Circuits Model to Heterocycles Containing Divalent Sulfur

A divalent sulfur, to some extent, interrupts conjugation in heterocyclic systems, because it only partly contributes its electrons to the pool of π electrons delocalized over the entire skeleton of a conjugated molecule. Since we consider only heterocyclic systems containing divalent sulfur, the bonds adjacent to sulfur, i.e., the carbon–sulfur bonds, are formally single bonds. We can therefore imagine sulfur with its two π electrons as formally equivalent to an isolated double bond “contracted” to a single atomic site. Actually we can always formally generate a heterocyclic structure containing divalent sulfur from a polycyclic conjugated hydrocarbon by replacing the fragment $-\text{CH}=\text{CH}-$ with $-\ddot{\text{S}}-$. Illustrative examples are shown in Fig. 5.

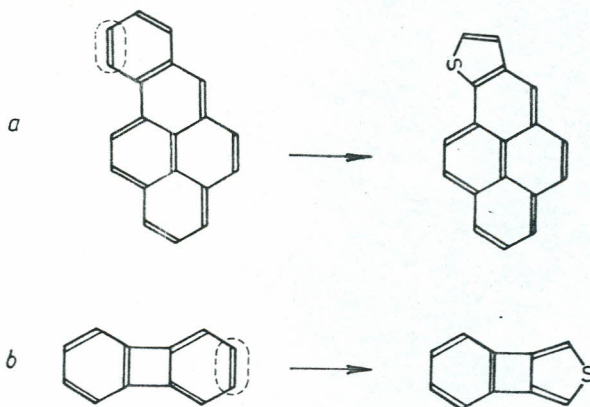


FIG. 5

Formal generation of pyreno(1,2-*b*)thiophene (a) and 2-thianorbiphenylene (b) by intrusion of the divalent sulfur instead of the double bond fragment into the appropriate position of benzo(*a*)-pyrene (a) and biphenylene (b)

Inspection of the Kekulé valence structures of benzo(a)pyrene in Fig. 1 indicates that only 6 Kekulé structures (C, D, E, F, G, I) can formally produce the Kekulé structures of pyreno(1,2-*b*)thiophene by the above process. Thus, there are only six Kekulé structures which belong to pyreno(1,2-*b*)thiophene and these are shown in Fig. 6. Similarly, only two Kekulé structures (B, D) of biphenylene can formally produce the Kekulé structures of 2-thianorbiphenylene (benzo(3,4)cyclobuta(1,2-*c*)-thiophene). These are shown in Fig. 7.

In general, the parent conjugated hydrocarbon always possesses more Kekulé structures than the derived heterocyclic molecule containing a divalent heteroatom.

In order to illustrate the conjugated circuits of S-containing polycycles, we will consider pyreno(1,2-*b*)thiophene and 2-thianorbiphenylene. The circuit decomposition of Kekulé structures A and F of pyreno(1,2-*b*)thiophene is given in Fig. 8. The circuit decomposition of the Kekulé structures of 2-thianorbiphenylene is given

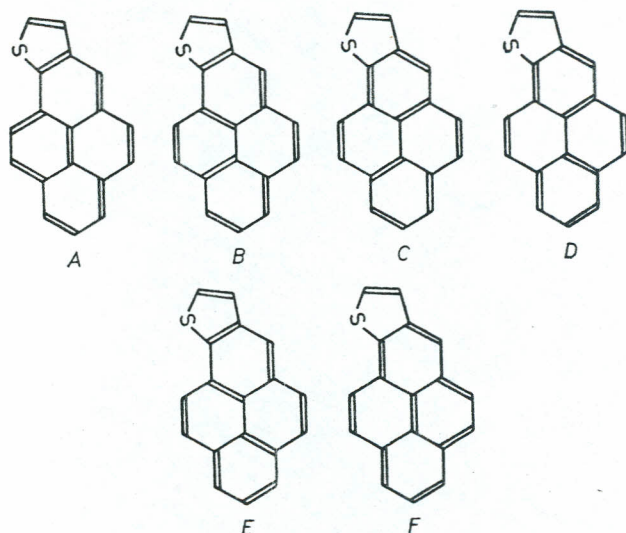


FIG. 6

Kekulé structures of pyreno(1,2-*b*)thiophene

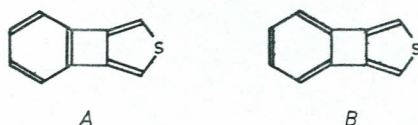


FIG. 7

Kekulé structures of 2-thianorbiphenylene

in Fig. 9. We denote $4n + 2$ conjugated circuits containing a single sulfur atom by S_n ($n = 1, 2, 3$) and $4n$ conjugated circuits containing a single sulfur atom by T_n

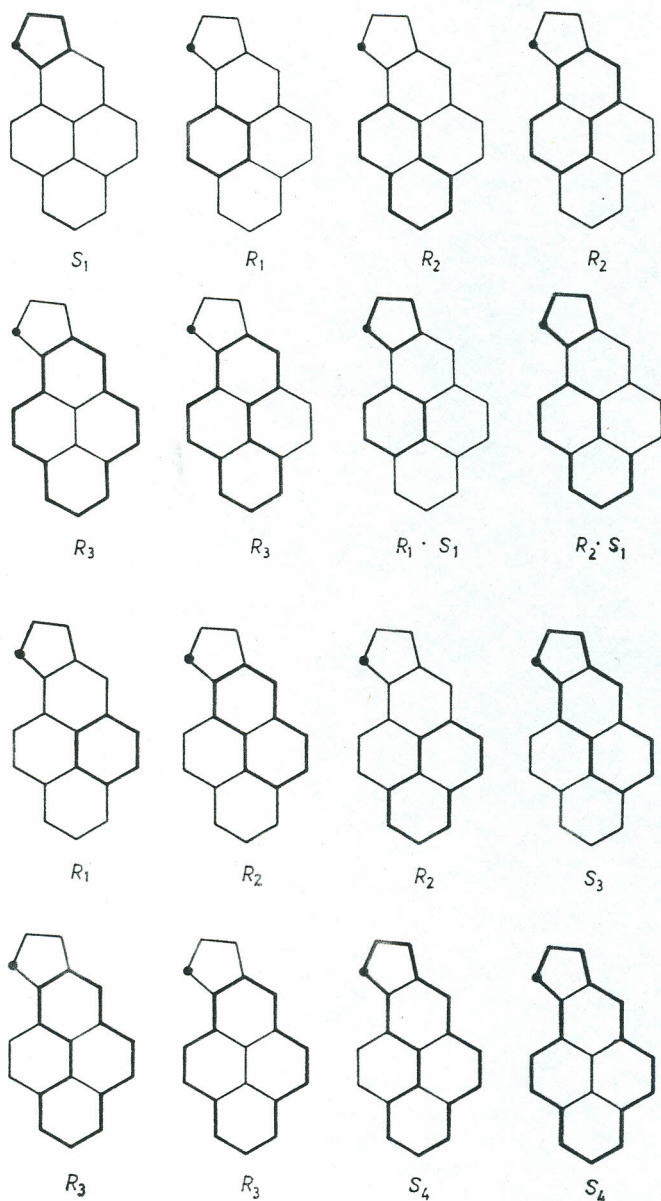


FIG. 8

Conjugated circuits belonging to the Kekulé structures A (a) and F (b) of pyreno(1,2-*b*)thiophene. The position of the sulfur is denoted by a black dot

($n = 1, 2, 3$). The enumeration of the conjugated circuits belonging to the Kekulé structures of pyreno(1,2-*b*)thiophene is given in Table IV. Note that the total number of conjugated circuits for a given Kekulé structure of a heterocyclic compound containing divalent sulfur is also equal to $K - 1$, where K is the Kekulé number of the parent conjugated hydrocarbon. Therefore, each Kekulé structure of pyreno(1,2-*b*)thiophene must be decomposable into 8 conjugated circuits (see Fig. 8).

The total circuit decomposition of the Kekulé structures of pyreno(1,2-*b*)thiophene is given by:

$$12R_1 + 8R_2 + 6R_3 + 3S_1 + 2S_2 + 3S_4 + \\ + 4R_1R_1 + 5R_1S_1 + 2R_1S_2 + R_2S_1. \quad (9)$$

TABLE IV

The circuit decomposition of the Kekulé structures of pyreno(1,2-*b*)thiophene. Disjoint circuits are denoted by $R_n \cdot R_n$ or $R_n \cdot S_n$

Kekulé structures	Conjugated circuits count										
	R_1	R_2	R_3	S_1	S_2	S_3	S_4	$R_1 \cdot R_1$	$R_1 \cdot S_1$	$R_1 \cdot S_2$	$R_2 \cdot S_1$
A	1	2	2	1					1		1
B	3		1	1				1	2		
C	2	2			1	1		1		1	
D	3		1		1		1	1		1	
E	2	2		1				1	2		
F	1	2	2			1	2				

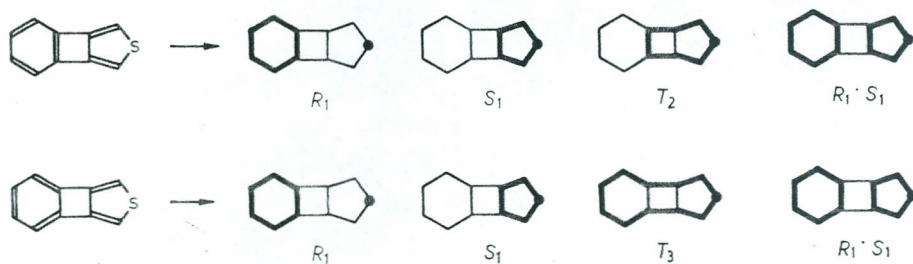


FIG. 9

Conjugated circuits belonging to the Kekulé structures of 2-thianorbiphenylene. The position of the sulfur is denoted by a black dot

Similarly, the total circuit decomposition of the Kekulé structures of 2-thianorbi-phenylene is given by:

$$2R_1 + 2S_1 + T_2 + T_3 + 2R_1S_1 \quad (10)$$

To inject some chemistry into the formalism of the conjugated circuits model, we need the parametric values for S_n and T_n . The parameters must be selected in such a way that they are in accordance with experimental observations. Thus, we may hope that such a set of parameters will be useful for predicting the aromatic stabilities of unknown compounds. However, extensive work is needed before a reliable set of parameters can be established within the framework of any theoretical model. The set of parameters for S_n and T_n is derived rather approximately. However, in due course, this set may undergo revision when better and more extensive SCF π -MO calculations and more experimental work on S-containing conjugated molecules become available.

Our basic assumption is that the ratios of various $(4n + 2)$ contributions with a heteroatom will not change. Hence, from relatively reliable ratios for R_n approximate values for S_n can be derived.

The numerical values for S_n ($n = 1, 2, 3$) are obtained from SCF π -MO resonance energy of thiophene (0.282 eV)⁵⁰ and by making use of the approximations:^{35,45}

$$S_2 = R_2S_1/R_1 \quad (11)$$

$$S_3 = R_3S_1/R_1 \quad (12)$$

In order to obtain T_n we utilized the following analogous relationships:

$$T_1 = Q_1S_1/R_1 \quad (13)$$

and its generalization:

$$T_n = Q_nS_n/R_n \quad (14)$$

The assumptions that the ratios Q_n/R_n and S_n/T_n are similar are based on empirical observations for benzene and cyclobutadiene, in the case of conjugated hydrocarbons,^{49,51,52} and similarly for thiophene and thiirene, in the case of heterocycles containing a single divalent sulfur.⁵³⁻⁵⁶ These molecules represent the extreme cases of aromaticity and antiaromaticity in each class of compounds. Thiophene has been known for a long time to be a stable compound,^{5,53} whilst thiirene has only recently been observed in an argon matrix at 8 K and is an antiaromatic species.⁵⁴⁻⁵⁷ Theoretical calculations also support relationship (14). For example, Hess and Schaad produced the following set of RE/e values (in β units) for the above molecules:^{24,58} 0.065 (benzene), -0.268 (cyclobutadiene), 0.032 (thiophene), and

-0.114 (thiirene). The ratios benzene/cyclobutadiene (-0.242) and thiophene/thiirene (-0.281) are indeed similar within the framework of the Hess-Schaad approximations.

The S_n and T_n ($n = 1, 2, 3$) parameters, used in this work, are given in Table V.

The resonance energies of heterocycles containing divalent sulfur can be calculated from the following expression:

$$RE = (1/K) \sum_{n \geq 1} (a_n R_n + b_n Q_n + c_n S_n + d_n T_n), \quad (15)$$

where S_n and T_n are, respectively, the parametric values for the $4n + 2$ and $4n$ conjugated circuits containing carbon atoms and a single sulfur atom. c_n and d_n represent the number of S_n and T_n circuits, respectively, for a given value of n , whilst the other symbols have their previous meanings.

We can now calculate the RE for pyreno(1,2-*b*)thiophene. The RE is given by:

$$RE = (12R_1 + 8R_2 + 4R_3 + 3S_1 + 2S_2 + 2S_3)/6 = 2.311 \text{ eV}. \quad (16)$$

This value is close to the RE of benzo(*a*)pyrene (2.586 eV) and indicates that pyreno(1,2-*b*)thiophene should be considered an aromatic species. This molecule, indeed, is an aromatic compound, known for some time.^{59,60}

The resonance energy of 2-thianorbiphenylene is similarly given by:

$$RE = (2R_1 + 2S_1 + T_2 + T_3)/2 = 1.100 \text{ eV}. \quad (17)$$

This molecule is also predicted to be aromatic and it has been prepared as a stable white crystalline solid with characteristic properties of an aromatic compound.⁶¹

Positional Isomers Containing Divalent Sulfur

Heterocyclic molecules that differ only in the position of the heteroatom are called positional isomers. They differ in their chemical and physical properties and the

TABLE V

Numerical values for the S_n and T_n ($n = 1, 2, 3$) parameters (in eV)

$S_1 = 0.282$	$T_1 = -0.253$
$S_2 = 0.080$	$T_2 = -0.072$
$S_3 = 0.032$	$T_3 = -0.029$

differences have to be attributed to local structural variations. The pair of molecules: benzo(*b*)thiophene and benzo(*c*)thiophene may be used to illustrate the positional isomerism in organo-sulfur chemistry. Their structures and the corresponding circuit counts are shown in Fig. 10. For the following discussion, it is convenient to express the R_2 , R_3 , S_1 , S_2 , and S_3 parameters in terms of the R_1 parameter:

$$\begin{aligned} R_2 &= 0.284R_1 & S_1 &= 0.325R_1 \\ R_3 &= 0.115R_1 & S_2 &= 0.092R_1 \\ & & S_3 &= 0.037R_1 . \end{aligned}$$

Considering only the *RE* expressions in Fig. 10 without using the numerical values for the graph theoretical parameters, we can immediately deduce that benzo(*b*)thiophene is aromatic (and more stable) than its positional isomer benzo(*c*)thiophene. This agrees fully with experiment.^{5,53,62} Chemists have been interested in these compounds from the last century^{5,53,62-68} and experimental work on them continues to appear, even to this day.⁷ Both compounds, benzo(*b*)thiophene and benzo(*c*)thiophene, are, of course, less stable than the parent hydrocarbon naphthalene, whose resonance energy is given by:

$$RE = (4R_1 + 2R_2)/3 = 1.523R_1 = 1.323 \text{ eV} . \quad (18)$$

Other theoretical models of aromaticity such as the Hess-Schaad REPE model⁵⁸ or the Zagreb Group TRE model⁶⁹ also agree with the above predictions.

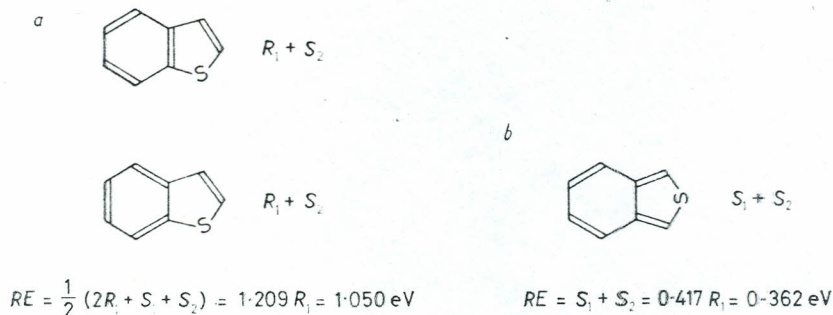


FIG. 10

The circuit counts and resonance energies for benzo(*b*)thiophene (*a*) and benzo(*c*)thiophene (*b*)

RESULTS AND DISCUSSION

Heterocyclic Compounds with a Single Divalent Sulfur and $4n + 2$ Rings

Diagrams of the selected heterocyclic molecules containing a single divalent sulfur and only $4n + 2$ rings are given in Fig. 11. Their resonance energy expressions and numerical results are given in Table VI.

There are several points worth noting in Table VI. The resonance energy of the heterocyclic molecule containing a divalent sulfur and $4n + 2$ rings can be partitioned into (i.e., can be given as a sum of) the *RE* of the hydrocarbon part and the *RE* due to S_n ($n = 1, 2, 3$) circuits:

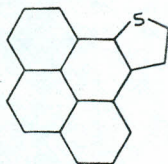
$$RE(\text{sulfur molecule}) = RE(\text{hydrocarbon part}) + RE(\text{sulfur part}) \quad (19)$$

The *RE*'s (and the *RE* expressions) of many conjugated hydrocarbons are available in literature.^{1,26-30} The *RE* of the sulfur part of a molecule which involves only S_n ($n = 1, 2, 3$) circuits is given by:

$$RE(\text{sulfur part}) = (1/K) \sum_{n \geq 1} c_n S_n, \quad (20)$$

where the symbols have their previous meaning.

For example, to obtain the *RE* of pyreno(4,5-*b*)thiophene (26A), which is a positional isomer of pyreno(1,2-*b*)thiophene, we add to the *RE* of pyrene the value for $RE(\text{sulfur part}) = (5S_1 + S_2 + 2S_3)/6$.



26A

$$RE(26A) = RE(\text{pyrene}) + (5S_1 + S_2 + 2S_3)/6 = 2.133 + 0.259 = 2.392 \text{ eV} \quad (21)$$

If we compare the *RE* values or the *RE* expressions $\{RE(26A) = (12R_1 + 8R_2 + 4R_3 + 5S_1 + S_2 + 2S_3)/6\}$ for pyreno(4,5-*b*)thiophene and pyreno(1,2-*b*)thiophene, we see that the difference is equal to $(2S_1 - S_2)/6$ or 0.081 eV in favour of 26A. Both compounds are known and exhibit properties similar to the parent hydrocarbons.^{59,60}

All compounds in Table VI except 10, 16, and 19 are known. These three compounds are representative of heterocyclic molecules in which the carbon part has

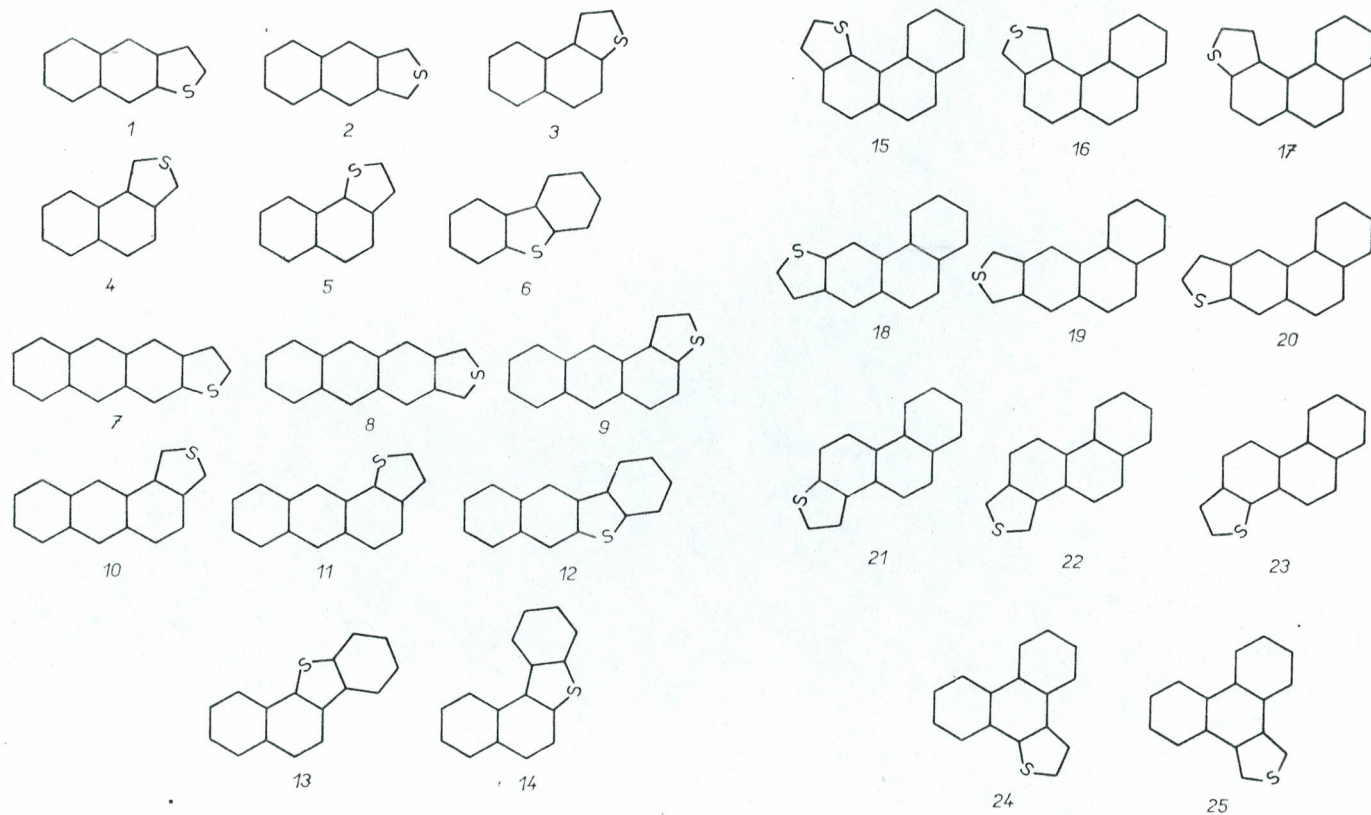


FIG. 11

Diagrams of randomly selected conjugated molecules with a single divalent sulfur and $4n + 2$ rings

TABLE VI
The resonance energies of selected molecules with a single divalent sulfur and $4n + 2$ rings

Molecule ^a	Resonance energy			RE/e (in eV)	Reference to the preparative work
	in terms of conjugated circuits	in terms of the R_1 parameter	numerical value (in eV)		
1	$(4R_1 + 2R_2 + S_1 + S_2 + S_3)/3$	1.674	1.455	0.104	104—106
2	$S_1 + S_2 + S_3$	0.454	0.394	0.028	107
3	$(4R_1 + 2R_2 + 2S_1 + S_2 + S_3)/3$	1.782	1.549	0.111	104, 108
4	$(2R_1 + 2S_1 + S_2 + S_3)/2$	1.390	1.207	0.086	109, 110
5	$(4R_1 + 2R_2 + 2S_1 + S_2 + S_3)/3$	1.782	1.549	0.111	111, 112
6	$(8R_1 + S_1 + 2S_2 + S_3)/4$	2.136	1.856	0.133	113, 114
7	$(6R_1 + 4R_2 + 2R_3 + S_1 + S_2 + S_3)/4$	1.955	1.699	0.094	115
8	$S_1 + S_2 + S_3$	0.454	0.394	0.022	116—120
9	$(6R_1 + 4R_2 + 2R_3 + 3S_1 + S_2 + S_3)/4$	2.117	1.840	0.102	115, 121
10	$(4R_1 + 2R_2 + 3S_1 + S_2 + S_3)/3$	1.891	1.643	0.091	—
11	$(6R_1 + 4R_2 + 2R_3 + 3S_1 + S_2 + S_3)/4$	2.117	1.840	0.102	115, 121
12	$(14R_1 + 4R_2 + S_1 + 2S_2 + 2S_3)/6$	2.620	2.277	0.126	115, 122—124
13	$(14R_1 + 4R_2 + 2S_1 + 3S_2 + 2S_3)/6$	2.689	2.337	0.130	106, 115, 124—128
14	$(14R_1 + 4R_2 + 2S_1 + 3S_2 + 2S_3)/6$	2.689	2.337	0.130	106, 115, 129—132
15	$(10R_1 + 4R_2 + 2R_3 + 3S_1 + 2S_2 + S_3)/5$	2.512	2.183	0.121	133
16	$(4R_1 + 2R_2 + 3S_1 + S_2 + S_3)/3$	1.891	1.643	0.091	—
17	$(10R_1 + 4R_2 + 2R_3 + 3S_1 + 2S_2 + S_3)/5$	2.512	2.183	0.121	133
18	$(10R_1 + 4R_2 + 2R_3 + 2S_1 + 2S_2 + S_3)/5$	2.447	2.127	0.118	133, 134
19	$(2R_1 + 2S_1 + 2S_2 + S_3)/2$	1.435	1.247	0.069	—
20	$(10R_1 + 4R_2 + 2R_3 + 2S_1 + 2S_2 + S_3)/5$	2.447	2.127	0.118	133, 134
21	$(10R_1 + 4R_2 + 2R_3 + 3S_1 + 2S_2 + S_3)/5$	2.512	2.183	0.121	133, 135—137
22	$(4R_1 + 2R_2 + 3S_1 + S_2 + S_3)/3$	1.891	1.643	0.091	138
23	$(10R_1 + 4R_2 + 2R_3 + 3S_1 + 2S_2 + S_3)/5$	2.512	2.183	0.121	133, 139
24	$(10R_1 + 4R_2 + 2R_3 + 4S_1 + S_2 + 2S_3)/5$	2.566	2.230	0.124	133, 140
25	$(8R_1 + 4S_1 + S_2 + 2S_3)/4$	2.366	2.056	0.114	116—120, 141—147

^a Labels correspond to compounds in Fig. 11.

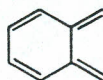
a quinoid structure. Linear quinoid structures possess only *one* Kekulé valence structure. In the case of fused benzenoid hydrocarbons (or more generally systems built from $4n + 2$ rings), it has been established that the quinoid structure is always less stable than the corresponding delocalized structure.⁷⁰ The same appears to hold in the chemistry of heterocyclic compounds. Molecules having delocalized bonds always possess at least two Kekulé valence structures and simple resonance-theoretical arguments suggest an increase of stability with increasing K , thus preferring positional isomers which do not have quinoid structures.

To illustrate the above point let us compare the hydrocarbon parts of benzo(*b*)-thiophene and benzo(*c*)thiophene: styrene (27) and *o*-xylylene (28).



27

$$K = 2$$



28

$$K = 1$$

Other theoretical indices of aromaticity^{24,69} predict 27 to be more aromatic (and more stable) than 28. This is also verified by experiment.⁷¹⁻⁷⁵ In early graph-theoretical studies of heterocyclic compounds, the data on the stability of the hydrocarbon parts of isomeric molecules have been used to predict the stabilities of the molecules as a whole.⁷⁶⁻⁷⁸ Now, it is confirmed that the earlier approach was essentially correct: *in all studied cases we always obtain the quinoid structure to be less stable than the delocalized structure.*

The stability of quinoid structures *decreases* with the size of the linearly annelated systems. Compare, for example, 2 ($RE/e = 0.028$ eV) and 8 ($RE/e = 0.022$ eV). The stability of *bent* quinoid structures *increases* with size. Compare, for example, 4 ($RE/e = 0.086$ eV) and 10 ($RE/e = 0.091$ eV). The reason for the difference between the linear and bent quinoid structures is that the bent structures allow an increase in delocalization in the parts remote from the localized portion of the molecule. This is clearly seen from the hydrocarbon parts of the studied quinoid structures (see Fig. 12).

A simple resonance-theoretical criterion of aromatic stability^{38,43,79} is the number of Kekulé structures divided by the number of π electrons (K/e). The ordering of the structures in Fig. 12 using this index is: 25a (0.25) > 10a (0.19) $\approx$ 16a (0.19) $\approx$ 22a (0.19) > 4a (0.17) > 19a (0.13) > 2a (0.08) > 8a (0.06). The same ordering parallels the ordering of heterocyclic structures obtained by the conjugated circuits criterion RE/e : 25 ($RE/e = 0.114$ eV) > 10 ($RE/e = 0.091$ eV) $\approx$ 16 ($RE/e = 0.091$ eV) $\approx$ 22 ($RE/e = 0.091$ eV) > 4 ($RE/e = 0.086$ eV) > 19 ($RE/e = 0.069$ eV) > 2 ($RE/e =$

$= 0.028 \text{ eV}) > 8 (RE/e = 0.022 \text{ eV})$. Limited available experimental data are supportive of the above qualitative results.⁶²

*Heterocyclic Compounds with Two or More Non-Adjacent
Divalent Sulfur Atoms and $4n + 2$ Rings*

Diagrams of the selected heterocycles with two or more non-adjacent divalent sulfur atoms and only $4n + 2$ rings are given in Fig. 13. Their resonance energy expressions and numerical results are given in Table VII. The conjugated circuits containing two (or more) non-adjacent sulfur atoms, denoted by $(SS)_n$, are neglected. For this class of molecules only $(SS)_3$ or larger circuits arise. They appear to have a negligible contributions to the resonance energy.³⁶ Hence, the RE of the heterocyclic systems with two (or more) non-adjacent sulfur atoms and with $4n + 2$ rings

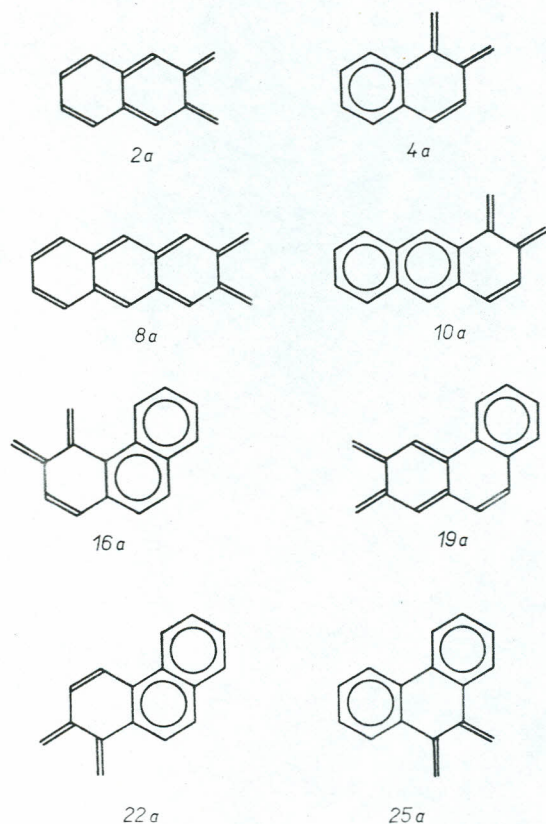


FIG. 12

The hydrocarbon parts of the heterocycles with quinoid structures containing divalent sulfur

only is given by the expression:

$$RE = (1/K) \sum_{n \geq 1} (a_n R_n + c_n S_n + e_n (SS)_n + f_n (SSS)_n + \dots) \quad (22)$$

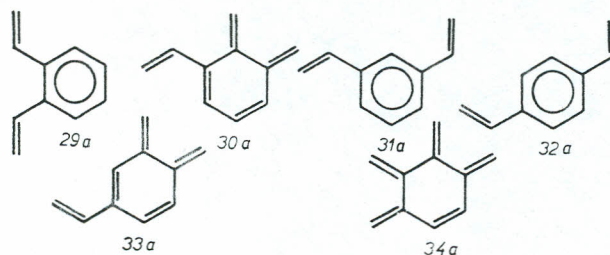
which is approximated to:

$$RE = (1/K) \sum_{n \geq 1} (a_n R_n + c_n S_n). \quad (23)$$

The compounds in Fig. 13 have been less extensively studied experimentally than the compounds in Fig. 11, and consequently only a few of them are known. The observations that we made in the previous section also hold for these compounds. We will only briefly summarize them below:

1. The resonance energy of the compounds in Fig. 13 may be partitioned as in expression (19) and expressed by Eq. (23). For example, the resonance energy of 52 is just the sum of $RE(\text{benzene})$ and $(3/2)(S_1 + S_2)$, i.e. $RE(52) = 0.869 + 0.543 = 1.412 \text{ eV}$.

2. It is enough to investigate the underlying carbon skeleton of the heterocycle, and predictions can then be made about the relative aromatic stability of the compound. This is because the quinoid structures are always less aromatic than the related delocalized structures. Consider, for example, the tricyclic structures 29–34. Their underlying carbon skeletons are given below.



Inspection of these structures allows one immediately to group them into three subclasses based on (i) the number of Kekulé structures, and, in the case of equal K 's, (ii) on the types of the unsaturated fragments within the localized structure of the hexagonal ring (the butadiene fragment is considered to be less reactive than the ethylene fragment):

- a) 29a, 31a, 32a
- b) 30a, 33a
- c) 34a.

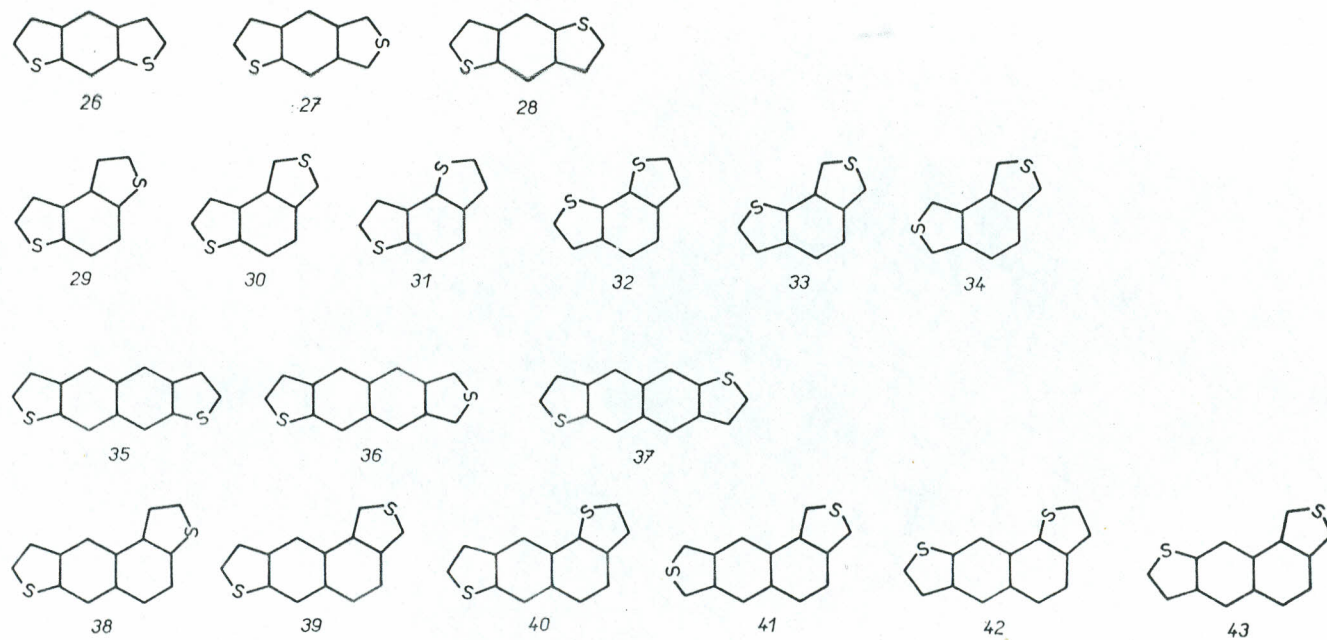


FIG. 13

Diagrams of randomly selected heterocyclic molecules with two or more non-adjacent divalent sulfur atoms and $4n + 2$ rings

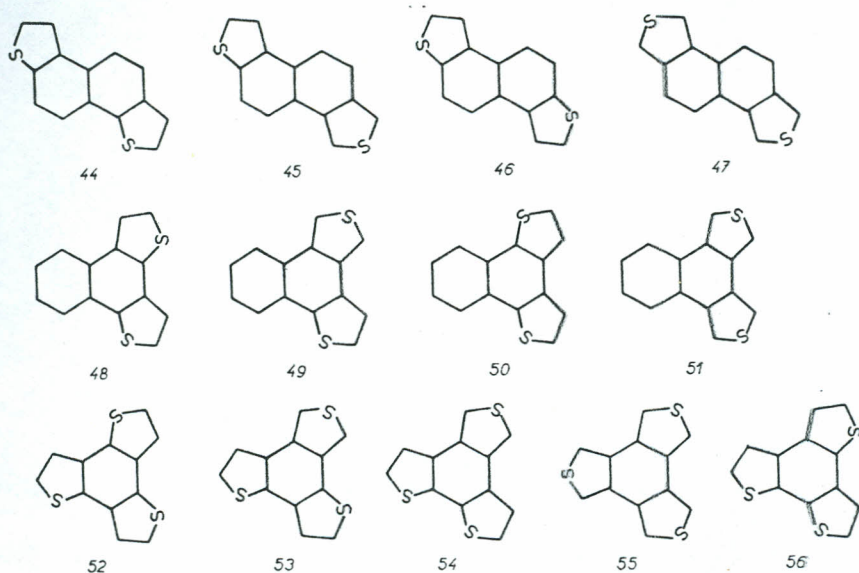


FIG. 13
(Continued)

This is also the stability order; the first group being the most stable and the last the least stable. The RE 's obtained by the conjugated circuits model produce the same stability pattern for the corresponding heterocycles:

- a) $RE(29) = RE(31) = RE(32) = 1.231 \text{ eV}$
- b) $RE(30) = RE(33) = 0.645 \text{ eV}$
- c) $RE(34) = 0.564 \text{ eV}.$

3. Angularly fused ring structures are always more stable than linearly fused ring structures. Compare, for example, 35 and 38. The bent structure 38 is more aromatic by $(1/3)S_1$ (0.094 eV). However, within the approximation used in the case of the smallest pair of linear-bent isomers in Fig. 13, i.e., 26 and 29, the RE 's are identical. If we write down the complete RE expressions:

$$RE(26) = (2R_1 + 2S_1 + 2S_2)/2 \quad (24)$$

$$RE(29) = (2R_1 + 2S_1 + 2S_2 + (SS)_3 + S_1S_1)/2 \quad (25)$$

then 29 appears to be more aromatic for a negligible amount of $((SS)_3 + S_1S_1)/2$.

4. Aromatic stability of linear quinoid systems decreases with size, but increases with size for bent quinoid systems.

TABLE VII

The resonance energies for selected heterocyclic molecules with two or more non-adjacent divalent sulfur atoms and $4n + 2$ rings

Molecule ^a	Resonance energy			RE/e (in eV)	Reference to the preparative work
	in terms of conjugated circuits	in terms of the R_1 circuit	numerical value (in eV)		
26	$(2R_1 + 2S_1 + 2S_2)/2$	1.417	1.231	0.088	
27	$S_1 + S_2$	0.417	0.362	0.026	
28	$(2R_1 + 2S_1 + 2S_2)/2$	1.417	1.231	0.088	
29	$(2R_1 + 2S_1 + 2S_2)/2$	1.417	1.231	0.088	148—150
30	$2S_1 + S_2$	0.742	0.645	0.046	150
31	$(2R_1 + 2S_1 + 2S_2)/2$	1.417	1.231	0.088	150—152
32	$(2R_1 + 2S_1 + 2S_2)/2$	1.417	1.231	0.088	150, 153
33	$2S_1 + S_2$	0.742	0.645	0.046	150
34	$2S_1$	0.650	0.564	0.040	150, 154—156
35	$(4R_1 + 2R_2 + 2S_1 + 2S_2 + 2S_3)/3$	1.825	1.586	0.088	
36	$S_1 + S_2 + S_3$	0.454	0.394	0.022	
37	$(4R_1 + 2R_2 + 2S_1 + 2S_2 + 2S_3)/3$	1.825	1.586	0.088	
38	$(4R_1 + 2R_2 + 3S_1 + 2S_2 + 2S_3)/3$	1.934	1.680	0.093	
39	$(2R_1 + 3S_1 + 2S_2 + S_3)/2$	1.598	1.389	0.077	
40	$(4R_1 + 2R_2 + 3S_1 + 2S_2 + 2S_3)/3$	1.934	1.680	0.093	

41	$2S_1 + S_2$	0.742	0.645	0.036	
42	$(4R_1 + 2R_2 + 3S_1 + 2S_2 + 2S_3)/3$	1.934	1.680	0.093	
43	$(2R_1 + 3S_1 + 2S_2 + S_3)/2$	1.598	1.389	0.077	
44	$(4R_1 + 2R_2 + 4S_1 + 2S_2 + 2S_3)/3$	2.042	1.774	0.099	
45	$(2R_1 + 3S_1 + 2S_2)/2$	1.580	1.373	0.076	
46	$(4R_1 + 2R_2 + 4S_1 + 2S_2 + 2S_3)/3$	2.042	1.774	0.099	
47	$2S_1 + 2S_2$	0.834	0.725	0.040	
48	$(4R_1 + 2R_2 + 4S_1 + 2S_2 + 2S_3)/3$	2.042	1.774	0.099	157
49	$(2R_1 + 4S_1 + S_2 + S_3)/2$	1.714	1.489	0.083	157
50	$(4R_1 + 2R_2 + 4S_1 + 2S_2 + 2S_3)/3$	2.042	1.774	0.099	158
51	$(2R_1 + 4S_1)/2$	1.650	1.434	0.080	159, 160
52	$(2R_1 + 3S_1 + 3S_2)/2$	1.626	1.412	0.078	161
53	$3S_1 + S_2$	1.067	0.927	0.052	
54	$3S_1 + S_2$	1.067	0.927	0.052	
55	$3S_1$	0.975	0.847	0.047	161, 162
56	$(2R_1 + 3S_1 + 3S_2)/2$	1.626	1.413	0.078	

^a Labels correspond to diagrams in Fig. 13.

Heterocyclic Compounds with One or Two Divalent Sulfur Atoms, and $4n + 2$ and $4n$ Rings

Diagrams of an ad hoc selection of heterocycles containing divalent sulfur, and $4n + 2$ and $4n$ rings are shown in Fig. 14. The resonance energies of the structures in Fig. 14 are given in Table VIII. Resonance energies are calculated using expression (15). Contributions from the $4n$ conjugated circuits containing two sulfur atoms, denoted by $(TT)_n$, are neglected as negligible.

Most of the studied compounds are not as yet prepared. This fact may be expected from our predictions that many of the structures in Fig. 14 are anti-aromatic species and as such difficult to prepare.

Some results are of interest. For example, 58 is predicted more stable than 59. The greater stability of 58 is related to the quinoid structure of its carbon skeleton. In the case of systems containing $4n$ rings, the quinoid structures are more stable than the corresponding delocalized structures.^{76,77} This empirical observation may be rationalized by means of the concept of the algebraic structure count, ASC.⁸⁰

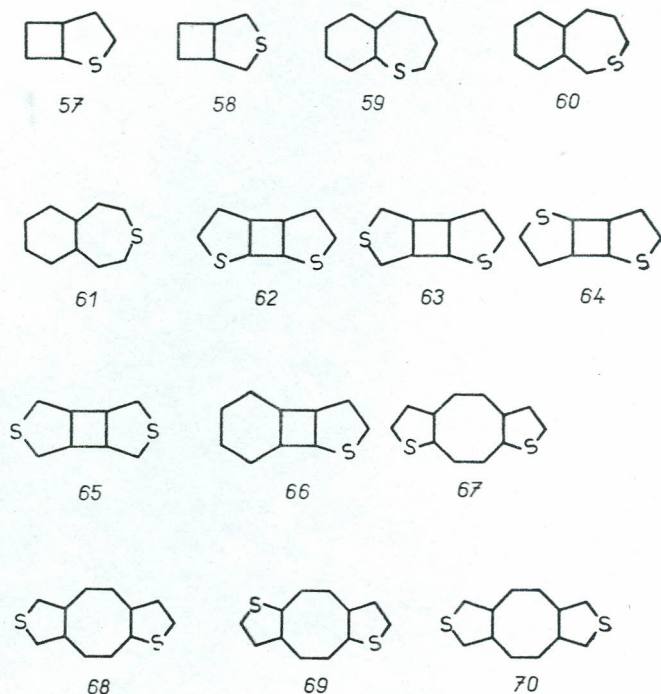


FIG. 14

Diagrams of randomly selected heterocycles with one or two divalent sulfur atoms, and $4n + 2$ and $4n$ rings

The *ASC* is defined for alternants only as

$$ASC = |K^+ - K^-|, \quad (26)$$

where K^+ and K^- are the Kekulé structures of opposite parity.⁸¹⁻⁸³ The Kekulé structures of opposite parity appear only in the conjugated systems containing $4n$ rings. Note that the number of Kekulé structures is given by:

$$K = K^+ + K^-. \quad (27)$$

In the case of conjugated structures with only $4n + 2$ rings, $K^- = 0$, $K = K^+$, and $ASC \equiv K$.⁸⁴ The concept of the *ASC* in connection with the stability of conjugated systems containing $4n$ rings has been explored systematically by the Zagreb Group⁸²⁻⁸⁴ and by Herndon.^{43,85}

It has been established that *ASC* (quinoid structure) is always higher than *ASC* (delocalized structure). The underlying structures corresponding to 57 and 58 are

TABLE VIII

The resonance energies of selected heterocycles with a single divalent sulfur atom and $4n + 2$ and $4n$ rings

Molecule ^a	Resonance energy		<i>RE/e</i> (in eV)	Reference to the prepara- tive work
	in terms of conjugated circuits	numerical value (in eV)		
57	$(2Q_1 + S_1 + T_2)/2$	-0.676	-0.085	
58	$S_1 + T_2$	0.210	0.026	163, 164
59	$(2R_1 + T_2 + T_3)/2$	0.819	0.068	165, 166
60	$T_2 + T_3$	-0.101	-0.008	
61	$(2R_1 + T_2 + T_3)/2$	0.819	0.068	167, 168
62	$(2Q_1 + 2S_1 + 2T_2)/2$	-0.571	-0.048	
63	$2S_1 + T_2$	0.492	0.041	
64	$(2Q_1 + 2S_1 + 2T_2)/2$	-0.571	-0.048	
65	$2S_1$	0.564	0.047	
66	$(2R_1 + Q_1 + Q_2 + 2S_1 + T_2 + T_3)/3$	0.399	0.033	
67	$(2Q_2 + 2S_1 + 2T_3)/2$	-0.571	-0.036	
68	$2S_1 + T_3$	0.492	0.031	
69	$(2Q_2 + 2S_1 + 2T_3)/2$	-0.571	-0.036	
70	$2S_1$	0.564	0.035	

^a Labels correspond to compounds in Fig. 14.

vinylcyclobutadiene (57a) with $ASC = 0$ and 3,4-dimethylenecyclobutene (58a) with $ASC = 1$.



57a



58a

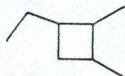
The experimental facts are in agreement with predictions based on the ASC values, that 58a should be more stable than 57a: The synthesis of 58a has been reported^{86,87} whereas the preparation of 57a as yet has not. However, 3,4-dimethylenecyclobutene readily polymerizes in the presence of air, but it is stable for long periods at room temperature when stored under nitrogen. Other theoretical indices of aromaticity such as REPE of Hess and Schaad^{24,88} support our prediction of 58a being more stable than 57a.

Based on the prediction that $58a > 57a$, we prognosticate that the parent structures 57 and 58 will behave similarly: $58 > 57$. This prognosis is supported by other theoretical models, including the conjugated circuits model (and as such supports the present selection of parameters) and also by experiment. The derivatives of 3-thiabicyclo(3.2.0)heptatriene (57) have been reported,^{89,90} whilst as far as we know, a compound containing the 2-thiabicyclo(3.2.0)heptatriene (57) moiety has not yet been synthesized.

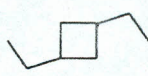
A similar case can be presented for the four isomeric dithienylenes 62–65. The stability prediction is $65 > 63 > 62 \approx 64$. There are no experimental data available to check this prediction. However, the above prediction agrees with the expectations based on the considerations of only the underlying carbon skeletons. The stability criterion is their ASC values, and when these are the same the stability is related to the number of vinyl groups which are reactive functional groups and act destabilizingly on the structure to which they are attached. The stability prediction is as follows: $65a > 63a > 62a \approx 64a$.



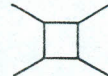
62a



63a



64a

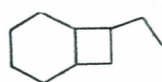


65a

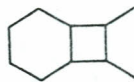
ASC	0	1	0	1
No. of vinyls	2	1	2	0

For the stability of isomeric dithienylenes it is, of course, also important to consider the strain in the 4-membered moiety, which is not included in our study. Wynberg⁹¹ attempted to prepare 65, but without success. He attributed the preparative difficulties to the presence of a highly strained 4-membered ring system.

Additional interesting examples are thianorbiphenylenes. There are two possible isomeric thianorbiphenylenes: 1-thianorbiphenylene (66) and 2-thianorbiphenylene. The stability prediction is that the 2-isomer ($RE/e = 0.092$ eV) is more stable than the 1-isomer ($RE/e = 0.033$ eV). This nicely parallels experimental facts. 2-Thianorbiphenylene was prepared 18 years ago⁶¹ whereas 1-thianorbiphenylene is still unknown. Again the prediction on stability of isomeric thianorbiphenylenes was reached by considering only their underlying carbon skeletons 66a and 66b.



66a



66b

ASC

1

2

The stability prediction is $66b > 66a$. This prediction is again in agreement with the available experimental evidence: The derivatives of 66b are known,^{92,93} whilst neither 66a nor its derivatives are presently available.

CONCLUSIONS

The conjugated circuits model, which is a simple structural model,^{94,95} has been extended to heterocyclic molecules containing divalent sulfur. The conjugated circuits model parallels intuitive ideas of chemists such as Clar's aromatic sextets,^{48,96} it can be rigorously related to graph-theoretical cluster expansions and resonance-theoretical arguments.^{94,95,97-99} The conjugated circuits model introduces a novel superposition principle not recognized before within quantum chemistry.¹⁰⁰⁻¹⁰² We believe the model is worthy of further study and further applications to the chemistry of conjugated structures.

The conjugated circuits model is applicable to *all* cyclic conjugated structures, and in conjunction with recent extensions in the form of the conjugated chains concept,¹⁰³ to all conjugated systems, i.e., cyclic, acyclic and cyclic with exo-cyclic linear and branched fragments. In the area of heterocyclic chemistry, the conjugated circuits model has been applied previously to heterocycles with nitrogen^{35,37} and now to heterocycles with divalent sulfur. The reasons for the limited application of the model to heterocyclic systems is that the experimental and theoretical data necessary for the determination of the numerical values for the graph theoretical parameters for many heterocycles are rather scarce.⁴⁵

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