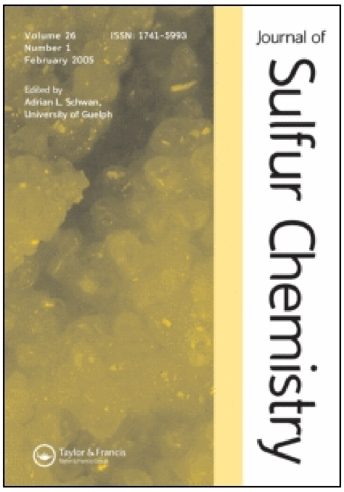

Journal of Sulfur Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926081

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To cite this Article Randić, Milan and Trinajstić, Nenad(1986) 'On the Relative Stabilities of Conjugated Heterocycles Containing Divalent Sulfur', Journal of Sulfur Chemistry, 6: 5, 379 — 426
To link to this Article: DOI: 10.1080/01961778608082499
URL: http://dx.doi.org/10.1080/01961778608082499

Sulfur Reports
Volume 6 (5), September 1986, pp. 379–430

Printed in the United Kingdom

ON THE RELATIVE STABILITIES OF CONJUGATED HETEROCYCLES CONTAINING DIVALENT SULFUR

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(Received August 13, 1985)

We have examined the relative stabilities of a number of heterocyclic systems containing divalent sulfur by applying the conjugated circuit model. Comparison is made with earlier reported resonance energies of these compounds, obtained by employing the HMO and SCF π-MO models and appropriate reference structures, indicating a fair parallelism. The approach is then extended to numerous polycyclic sulfur-containing systems synthesized in the last decade and is used for discussing the relative stabilities of positional isomers producing the qualitative explanation for the differences amongst such isomers. Finally, we made predictions on yet unknown structures with divalent sulfur, extending the study to polycyclic systems involving fused rings other than benzene.

Key Words: Divalent sulfur-containing heterocycles, conjugated circuit model, HMO, SCF.

INTRODUCTION

Graph Theory has opened novel avenues to the investigation of *families* of compounds, dealing with trends and similarities as well as differences amongst apparently related compounds.[1] In their application to conjugated hydrocarbons these developments clarified the concept of aromaticity—to which a clear and simple *structural* definition was given.[2–4] A novel concept—the conjugated circuit model—appears to have a fundamental role in the characterization of conjugated compounds. Compounds having only 4n + 2 conjugated circuits are classified (by definition!) as aromatic, those having only 4n conjugated circuits are antiaromatic, whilst compounds containing both, 4n + 2 and 4n, conjugated circuits possess ambivalent character. In a number of publications the application of this approach has been outlined and discussed, applications including nonbenzenoid systems[4], large benzenoid systems[5–7], anions and cations of conjugated hydrocarbons[8–10], dianionic[11], and even heterocyclic systems[12]. In each case the analysis involves examination of all Kekulé valence

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[‡] Operated for the Department of Energy, US Government, by Iowa State University under Contract No. W-7405-ENG-82. This work was supported in part by the Office of the Director.

structures, and for each structure separately one identifies all conjugated circuits and presents the count. The resonance energies are derived by a suitable selection of parameters defining the count. Whilst there may be some basis for considering some alternative parametrization, much of the conclusions are independent of the details of the numerical values for the parameters. Indeed, this is one of the major advantages of this particular graph theoretical approach, because such deductions are reliable, yet provide an answer to many relative properties.

The conjugated circuit model was also independently introduced by Gomes[13–15] and studied by several people.[16–17] In addition, a number of contributions, by us and others, appeared reporting various associated problems involving conjugated circuits.[18–24] Since the use of the conjugated circuit model introduces a new kind of superposition principle, novel to quantum chemistry,[15] we believe the model is worth of further studies and applications to the chemistry of conjugated structures.

In this paper we consider conjugated heterocyclic compounds containing divalent sulfur. A number of such compounds have been analysed by Hess and Schaad[25] some 10 years ago using the Hückel molecular orbital method *combined* with a suitable reference structure, following the suggestion by Dewar[26] in his Pariser-Parr-Pople-type SCF π-MO calculations regarding the definition of the resonance energy. According to Dewar, the resonance energy (RE) is defined as a departure from the simple bond additivity of energy terms of acyclic structures.

An early graph theoretical approach to conjugated structures containing divalent sulfur in which a graphical method is used to seek differences amongst positional isomers carried over from the parent structures was presented by Knop *et al.*[27] The approach may be outlined on benzo[b]thiophene and benzo[c]thiophene (Fig. 1), following a similar discussion for benzofuran and isobenzofuran, which differ only in the replacement of sulfur by oxygen.[28]

In this approach the authors consider given heterostructures and corresponding hydrocarbon parents derived by exclusion of heteroatoms (and all adjacent heterobonds). If we refer to these as G_k and G'_k, k referring to different isomers, the main result, given in the form of a *postulate*, is that the topological factors which make G_a more stable than G_b are the same factors which make the parent hydrocarbon G'_a more stable than G'_b. Hence from experience we know that the vinyl derivative is less reactive than the quinonoid structure,[29,30] thus the principle suggests benzo[b]-thiophene to be more stable than benzo[c]thiophene—as indeed is the case[31,32]. This prediction is also supported by other theoretical models.[25,33,34] The same models, of course, favor styrene over *o*-xylylene. However, though the graphical approach no doubt captures important structural factors, by the very nature of this reasoning we have excluded sulfur from our considerations. It is possible that the role of sulfur is not negligible and plays a role in addition to the topological factors representing the parent frame (the skeleton without a heteroatom) and that is what we will investigate here.

In a subsequent analysis Gutman and Trinajstić[35] elaborated on factors contributing to the stability of conjugated heterocycles containing a single heteroatom. The algebraic analysis indicated that the stability of conjugated heterocyclics containing a single heteroatom is dependent on the same topological factors which determine the stability of the parent hydrocarbon. In addition, however, there is a term contributing

a) Set of the positional isomers

A_1 A_2

b) Corresponding parent hydrocarbons with Kekulé structure count

	B_1	B_2
	K=2	K=1
REPE	0.046	0.005
TREPE	0.031	0.007

c) Experimental facts about the relative stabilities of the parent hydrocarbons[29,30] B_1 and B_2

$$B_1 > B_2$$

d) Prediction about the relative stabilities of the positional isomers A_1 and A_2

$$A_1 > A_2$$

e) Experimental facts about the relative stabilities of benzo[b]thiophene, A_1, and benzo[c]thiophene, A_2[31,32]

$$A_1 > A_2$$

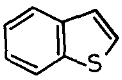
FIGURE 1 Application of the graphical method to the prediction of the relative stabilities of positional isomers such as benzo[b]thiophene and benzo[c]thiophene

to their stability which is related to the underlying hydrocarbon skeleton of the heterocyclic system. We will here look more closely at the partition of the resonance energy into the hydrocarbon part and the heteroatom contribution, and, depending on the topology of the system, we may have positive as well as negative (i.e., destabilizing) contributions.

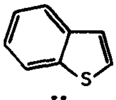
We start by outlining the approach, which in some respect differs in its application from the case of heterocyclic systems in which the heteroatom is participating in conjugation by having single and double bond connections to neighboring atoms, and is formally similar to cases of ions, with the distinction that the site of "charge" is now fixed. Thus, the analysis of heterocyclic compounds containing a divalent heteroatom is simpler than both just mentioned cases. Nevertheless, it requires a differentiation of the contributions involving the heteroatom and those not involving the heteroatom, because, depending on the nature of the heteroatom such formally similar terms may give profoundly different contributions. We will follow with a comparison of our results with those of Hess and Schaad,[25] to see how two different schemes parallel one another. Comparison will also be made with the PPP SCF π-MO results by Dewar and Trinajstić,[33] and the topological resonance energies of Gutman *et al.*,[34] respectively. Finally, after comparing our approach to other theoretical schemes, we will extend the analysis to a number of polycyclic conjugated systems containing divalent sulfur and will end with predictions of some interesting compounds not yet known.

OUTLINE OF THE APPROACH

A divalent heteroatom can in principle "interrupt" the conjugation and act as part of a saturated fragment, or alternatively can contribute its π-electrons to the pool of π-electrons delocalized all over the structure. Divalent sulfur appears to constitute an intermediate case in that it contributes towards overall delocalization of π-electrons, but not with an equal amplitude, so to speak. Let us again consider benzo[b]thiophene, for which we can write down two Kekulé-type valence formulas:

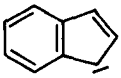


I

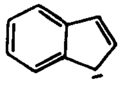


II

The sulfur atom is contributing a pair of electrons to the π-electron system (one of its lone pairs), but since it is divalent the adjacent carbon-sulfur bonds are formally single. We can therefore formally view the sulfur atom as equivalent to an isolated "double bond" contracted to a single atom (sulfur) just as in the case of the corresponding hydrocarbon anion in which the negative charge is located on the carbon at this site taken by sulfur. In the above case, again we have two corresponding Kekulé valence structures:



Ia



IIa

Each Kekulé structure contains conjugated circuits, when this concept is generalized to anions, by formally counting C^- as equivalent to a "contracted" CC double bond.[8] Hence, we obtain immediately for the two structures the following conjugated circuit count:

Structure Ia: $R_1 + X_1^-$

Structure IIa: $R_1 + X_2^-$

Here R_1 represents the conjugated circuits within a benzene ring and X_1^- and X_2^- represent conjugated circuits of the 4n+2 type with n = 1 and n = 2, respectively, incorporating the heteroatom: carbon C^-. In the case of benzo[b]thiophene we do not have a negative charge, and we may therefore write equivalent expressions:

$$\text{Structure I:} \quad R_1 + S_1$$

$$\text{Structure II:} \quad R_1 + S_2$$

where S symbolizes that the heteroatom is sulfur. Thus, there is a full formal (mathematical) similarity between the two cases, the difference being only in the notation and its interpretation. The important difference comes from the fact that the compounds contain divalent sulfur. The additional electrons involved are located on a single atom, while in the case of anions one has to admit other ionic structures in which the negative charge is widely delocalized. Hence, here we have fewer structural formulas to consider, which makes the analysis considerably simpler than in the case of ions, but we cannot speculate on the relative magnitudes of the R_n and S_n terms and consider them to be approximately of similar magnitude, as was possible in the case of ions.[8-11]

We are now ready for the analysis of sulfur-containing conjugated systems. We will start with selected compounds for which there are other computations available. This will allow some comparison to be made, and at the same time we will demonstrate the potential of our approach, which allows some additional deductions related to the relative stability of conjugated systems containing divalent sulfur.

SELECTED SULFUR-CONTAINING COMPOUNDS

In Fig. 2 we show the skeletal forms of a number of cyclic and polycyclic compounds containing divalent sulfur.

We have grouped the compounds into those having a single sulfur, the results for which have been collected in Table 1, and those having two sulfur atoms, which are grouped in Table 2.

All the compounds of Fig. 2 have been studied by other methods, in particular a comparative study has been made by Hess and Schaad[25] using the HMO approach combined with their REPE (resonance energy per electron) criterion. Most of the compounds of Fig. 1 have a single Kekulé valence structure as exemplified by benzo[c]thiophene. In contrast to benzo[b]thiophene and benzo[c]thiophene, with the presence of a seven-membered ring, we come across 4n conjugated (antiaromatic) circuits which we indicate by the symbol T_n. They correspond to Q_n circuits in conjugated hydrocarbons or Y_n^- conjugated circuits in anions, i.e., contributing negatively to the π-electronic energy and destabilizing the system.

The compounds of Table 1 already provide enough variation (and suggest compounds of vastly different character) that we may see how our predictions agree with the accumulated experience. First we notice that in a number of cases we have the same result, the same expression for the molecular resonance energy. Thus, for instance, the following compounds have a single contribution of a conjugated circuit of size 10 involving sulfur (i.e, have S_2 as the expression): thia[9]annulene, cyclopenta[b]thiopyran, and cyclopenta[c]thiopyran. Hence, we predict all three compounds to be of very comparable stability, and if there are differences these are due to

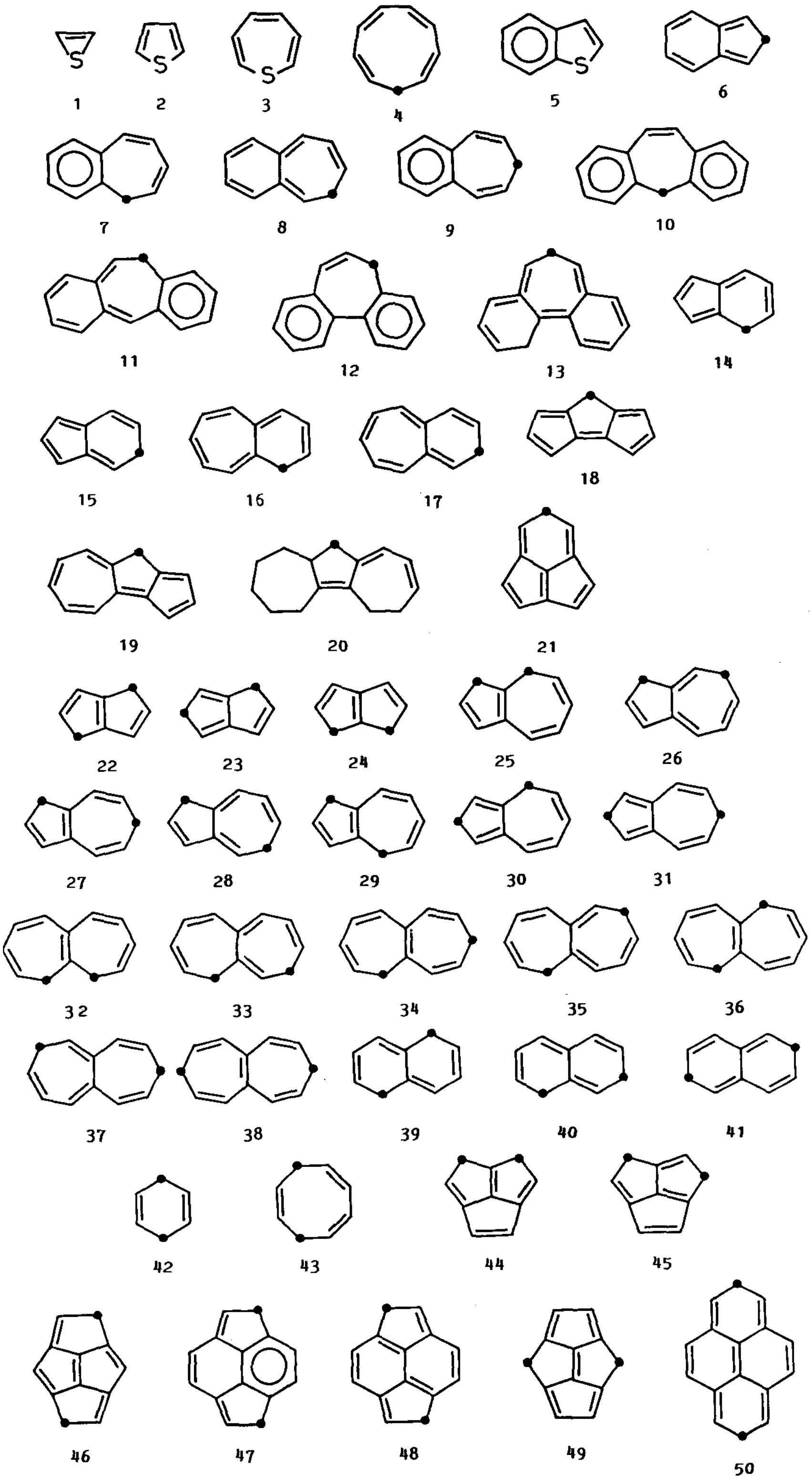


FIGURE 2 Diagrams of the studied heteroconjugated molecules containing divalent sulfur.

TABLE 1

Resonance Energy Expressions for Conjugated Structures Containing a Single Divalent Sulfur Atom (Diagrams 1–21 in Figure 2).

Number in Fig. 2	Name	Resonance energy expression	Resonance energy			Status[d]	Reference to the preparative work
			DREPE[a]	REPE[b]	TREPE[c]		
1	Thiirene	T_1	—	−0.114		—	—
2	Thiophene	S_1	1.48	0.032	0.033	i	e
3	Thiepin	T_2	−0.18	−0.029	−0.023	—	—
4	Thia[9]annulene	S_2	—	0.012	0.012	u	—
5	Benzo[b]thiophene	$(2R_1 + S_1\ S_2)/2$	2.48	0.044	0.035	i	g
6	Benzo[c]thiophene	$S_1 + S_2$	0.93	0.025	0.029	i	h
7	1-Benzothiepin	$(2R_1 + T_2 + T_3)$	—	0.016	0.022	i	i
8	2-Benzothiepin	$T_2 + T_3$	—	−0.019	−0.018	—	—
9	3-Benzothiepin	$(2R_1 + T_2 + T_3)/2$	1.66	0.017	0.008	i	j
10	Dibenzo[b,f]thiepin	$(8R_1 + T_2 + 2T_3 + T_4)/4$	—	0.042	—	i	k
11	Dibenzo[b,e]thiepin	$(2R_1 + T_2 + 2T_3 + T_4)/2$	—	0.014	—	—	—
12	Dibenzo[b,d]thiepin	$(8R_1 + T_2 + 2T_3 + T_4)/4$	—	0.036	—	—	—
13	Dibenzo[c,e]thiepin	$T_2 + 2T_3 + T_4$	—	0.000	—	—	—
14	Cyclopenta[b]thiopyran	S_2	—	0.018	—	i	l
15	Cyclopenta[c]thiopyran	S_2	—	0.020	—	i	m
16	Cyclopenta[b]thiopyran	T_3	—	−0.006	—	—	—

TABLE 1 (*continued*)

Number in Fig. 2	Name	Resonance energy expression	Resonance energy			Status[d]	Reference to the preparative work
			DREPE[a]	REPE[b]	TREPE[c]		
17	Cyclopenta[c]thiopyran	T_3	—	−0.011	—	—	—
18		T_3	—	−0.040	—	—	—
19		S_3	—	0.018	—	—	—
20		T_4	—	−0.010	—	—	—
21		$2S_2$	—	0.019	—	—	—

[a] M. J. S. Dewar and N. Trinajstić, *J. Am. Chem. Soc.*, **92**, 1453 (1970); DREPE = DRE/n, n = number of π-electrons, all values in kcal/mol.

[b] B. A. Hess, Jr., and L. J. Schaad, *J. Am. Chem. Soc.*, **95**, 3907 (1973); REPE = RE/n, all values in β.

[c] I. Gutman, M. Milun, and N. Trinajstić, *J. Am. Chem. Soc.*, **97**, 1092 (1977); TREPE = TRE/n, all values in β.

[d] i = isolated (either parent compound or its derivatives); u = unstable (either parent compound or its derivatives); – = unknown.

[e] H. D. Hartough, "Thiophene and Its Derivatives", Interscience, New York, 1952.

[ee] A. Jurić, A. Sabljić, and N. Trinajstić, *J. Heterocycl. Chem.*, **21**, 273 (1984).

[f] A. Anastassiou, *Pure Appl. Chem.*, **44**, 461 (1975).

[g] L. Gattermann and A. E. Lockhart, *Ber.* **26**, 2808 (1893).

[h] R. Mayer, H. Kleinert, S. Richter, and K. Gewald, *Angew. Chem.*, **74**, 118 (1962).

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[k] E. D. Bergman and M. Rabinovitz, *J. Org. Chem.*, **25**, 828 (1960).

[l] R. Mayer, J. Franke, V. Horak, I. Hanker, and R. Zahradník, *Tetrahedron Lett.*, **1961**, 289.

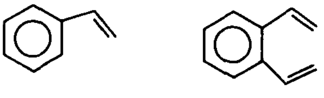
[m] A. G. Anderson, Jr., W. F. Harrison, R. G. Anderson, A. G. Osborne, *J. Am. Chem. Soc.*, **81**, 1255 (1959).

other factors. Compounds having only R_n and S_n contributions qualify according to our definition of aromaticity as fully aromatic. Besides the already mentioned compounds having for the RE expression S_2 the aromatic group includes the benzothiophenes *5* and *6*, as well as the two tricyclic structures *19* and *21*. Fully antiaromatic are compounds *1* (thiirene), *3* (thiepin), *8* (2-benzothiepin), *13* (dibenzo[c,e]thiepin;, and *16* (cyclohepta[b]thiopyran), and these are not known yet. The only compounds showing both aromatic and antiaromatic components are *7* (1-benzothiepin), *9* (3-benzothiepin), and the three dibenzothiepins *10*, *11*, and *12*. If we assume that in general the following inequalities (signifying trends in the relative magnitudes of the various contributing terms) hold:

$$R_n > S_n \quad \text{and} \quad S_n > T_{n+1}$$

we can immediately deduce that all the cases of ambivalent character have a dominant aromatic component, hence all the compounds *7*, *9*, and *10-12* have some inherent stability and positive resonance energy.

We can make a further comparison of compounds having different composition *if* the expression allows a meaningful comparison. For example, a comparison of benzo[b]thiophene $(2R_1 + S_1 + S_2)/2$ with the similar expression for 3-benzothiepin: $(2R_1 + T_2 + T_3)/2$ clearly shows that the latter has reduced (relative) stability, a fact confirmed by the experimental findings.[31,36] Moreover, we see that the difference between the two compounds is solely due to the role of sulfur participation. Examination shows that the contributions of the parent structures:



are in this case the same $(2R_1)$, (while we may have to allow some difference due to the presence of an additional branching carbon (additional vinyl) in the latter structure). This conclusion is at some variance with the general deduction of Gutman and Trinajstic[35] concerning the role of a heteroatom, which requires perhaps some further qualification of the conditions when their approach applies. It may be that the discrepancy is due to their consideration of alternants, and here we allow inclusion of non-alternant systems as well.

In the case of compounds containing two sulfur atoms we can have conjugated circuits involving two sulfurs, one sulfur atom, or none. These we will indicate by the symbols SS_n, S_n, and R_n if of size 4n+2 and by the symbols TT_n, T_n, and Q_n if of size 4n. Most compounds in Table 2 have a single valence structure and allow one to read off the conjugated circuits directly from their structure. In the case of compound *47* (hypothetical) there are two Kekulé valence structures (as shown in Fig. 2 by the inscribed circle). Again the classification of compounds as aromatic and antiaromatic is straightforward. In a few instances we have compounds of "mixed" character, e.g.: *25* (thienol[2,3,-b]thiepin), *27* [thieno[2,3-d]thiepin), *29* (thieno[3,2-b]thiepin), and so on.

TABLE 2

Resonance Energy Expressions for Conjugated Structures Containing Two Non-Adjacent Bivalent Sulfur Atoms (Diagrams 22–50 in Figure 2).

Number in Fig. 2	Name	Resonance energy expression	Resonance energy			Status[d]	Reference to the preparative work
			DREPE[a]	REPE[b]	TREPE[c]		
22	Thieno[3,2-b]thiophene	$2S_1$	1.13	0.024	0.031	i	e
23	Thieno[3,4-b]thiophene	$S_1 + SS_2$	0.59	0.015	0.026	i	f
24	Thieno[2,3-b]thiophene	$2S_1$	1.05	0.022	0.031	i	e
25	Thieno[2,3-b]thiepin	$S_1 + T_2$		−0.007	—	—	—
26	Thieno[2,3-c]thiepin	$T_2 + TT_3$		−0.022	—	—	—
27	Thieno[2,3-d]thiepin	$S_1 + T_2$		−0.004	—	—	—
28	Thieno[3,2-c]thiepin	$T_2 + TT_3$		−0.022	—	—	—
29	Thieno[3,2-b]thiepin	$S_1 + T_2$		−0.001	—	—	—
30	Thieno[3,4-b]thiepin	$S_1 + TT_3$		0.001	—	—	—
31	Thieno[3,4-d]thiepin	$S_1 + TT_3$		0.001	—	i	g
32	Thiepino[2,3-b]thiepin	$2T_2$		−0.028	—	—	—
33	Thiepino[3,4-b]thiepin	$T_2 + SS_3$		−0.018	—	—	—
34	Thiepino[4,5-b]thiepin	$2T_2$		−0.028	—	—	—
35	Thiepino[4,3-b]thiepin	$T_2 + SS_3$		−0.019	—	—	—
36	Thiepino[3,2-b]thiepin	$2T_2$		−0.031	—	—	—

37	Thiepino[4,5-c]thiepin	$T_2 + SS_3$	−0.017	—	—	
38	Thiepino[4,5-d]thiepin	$2T_2$	−0.027	—	—	—
39	Thiopyrano[3,2-b]thiopyran	TT_3	−0.005	—	—	—
40	Thiopyrano[3,4-b]thiopyran	TT_3	−0.008	—	—	—
41	Thiopyrano[4,3-b]thiopyran	TT_3	−0.012	—	—	—
42	1,4-Dithiin	TT_2	−0.017	—	i	h
43	1,4-Dithiocin	SS_2	−0.001	—	i	i
44		$2S_1$	0.014	—	—	—
45		$S_1 + SS_2$	0.015	—	—	—
46		TT_3	0.007	—	—	—
47		$(2R_1 + 2S_1\ 2S_2 + 3SS_3)/2$	0.027	—	—	j
48		$2S_1 + 2S_2$	0.023	—	—	j
49		$2T_3 + TT_3$	−0.014	—	—	—
50		$3TT_4$	−0.010	—	—	—

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[a] M. J. S. Dewar and N. Trinajstić, *J. Am. Chem. Soc.*, **92**, 1453 (1970); DREPE = DRE/n, n = number of π-electrons; all values in kcal/mol.

[b] B. A. Hess, Jr., and L. J. Schaad, *J. Am. Chem. Soc.*, 95, 3907 (1973); REPE = RE/n; all values in β.

[c] I. Gutman, M. Milun, and N. Trinajstić, *J. Am. Chem. Soc.*, **99**, 1692 (1977); TREPE = TRE/n; all values in β.

[d] i = isolated (either parent compound or derivatives); u = unstable (either parent compound or its derivatives); – = unknown.

[e] S. Gronowitz, U. Rudén, and B. Gestblom, *Ark. Kemi*, **20**, 297 (1963).

[f] H. Wynberg and D. J. Zwanenburg, *Tetrahedron Lett.*, **1967**, 767.

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[h] W. E. Parkam, H. Wynberg, W. R. Hasek, P. A. Howell, R. N. Curtis, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **76**, 4957 (1954); non-planar structure.

[i] D. L. Coffen, Y. C. Poon, and M. L. Lee, *J. Am. Chem. Soc.*, **93**, 4627 (1971); 1,6-dibenzodithiocin.

[j] L. H. Klemm, *Adv. Heterocycl. Chem.*, **32**, 127 (1982).

We observe that some of the compounds in Table 2 have their expression for RE given in terms of S_n and/or T_n, while others involve also the parameters (conjugated circuits) SS_n and/TT_n in which both sulfur atoms participate. This means that for the compounds of the former group, e.g.: *22* (thieno[3,2-b]thiophene), *24* (thieno[2,3-b]thiphene), *25* (thieno[2,3-b]thiepin), and so on, one can derive RE using the same parameters as those selected for compounds having a single sulfur. In other words, the presence of two sulfur atoms is purely additive in these compounds, there are no terms that arise from interactive contributions of two heteroatoms. In other compounds of Table 2, such as *23* (thieno[3,4-b]thiophene) or *26* (thieno[2,3-c]thiepin), there are contributions from a sulfur-sulfur interaction. Although we have no numerical estimates on the magnitudes of these contributions due to two sulfur atoms in a single conjugated circuit it is plausible to assume that

$$S_n > SS_n; \quad T_n > TT_n; \quad \text{and} \quad SS_n > TT_{n+1}$$

which is analogous to a similar relationship between R_n and S_n and T_{n+1}, indicating the decreasing trend in the contributions of larger conjugated circuits (in the case of 4n contributions a decrease in absolute values).

COMPARISON WITH THE MO CALCULATIONS

All the compounds of Table 1 and Table 2 have been analyzed using the Hückel MO method by Hess and Schaad.[25] They have found in developing their approach that the Hückel method (although known not to be useful in predicting molecular spectra as elegantly demonstrated by Heilbronner and Jones[37]) can be used in a simple manner to calculate heats of atomization accurately for both acyclic and cyclic hydrocarbons.[25] This may look as an apparent paradox: if a method cannot deliver valid orbital energies, how can one expect useful total energies? But it demonstrates, what has been suspected by many that *Hückel numbers*[38] (which is a more suitable label for Hückel orbital energies in view of the fact that they do not give useful orbital descriptions) compensate mutually some of the errors and produce acceptable overall parameters. In this way we can understand the correlation between the Hückel total energy and log K, K being the number of Kekulé valence structures for the conjugated hydrocarbon,[39] and other similar relationships[40] In the case of divalent sulfur conjugated systems Hess and Schaad[25] have shown that their predictions agree well with the observed behavior and the approach is as satisfactory as the more sophisticated Pariser-Parr-Pople work of Dewar and Trinajstić.[33] DREPE[33] (and TREPE[34]) values are available for only a few of the studied molecules. However, in all these cases there is a fair agreement between the predictions based on REPE and DREPE (TREPE) indices. We wish first to establish that our appoach, with the results summarized in Table 1 and Table 2, gives predictions of the same satisfactory quality. Then we will point to minor differences and additional conclusions that our approach offers over the simple HMO, or alternative MO schemes. One should recall that deductions from HMO are based on a particular *numerical* selection of parameters, and even though one has no reason to expect drastic revision of the input parameters (i.e., revision of the values of molecular integrals) it is by no means clear how sensitive the *minor* differences are to such modifications. In contrast, our deductions are based on *expressions* and few plausible assumptions concerning the relative trends among the graph theoretical parameters R_n, S_n, T_n, etc. Hence our deductions are practically insensitive to minor or even substantial revision of the numerical values for the parameters as long as the above relative trends are preserved—and these appear unlikely to be violated: large conjugated circuits regardless of the nature of the atoms involved will make weaker contributions, as *any* MO theory will tell!

Hence a good test of our approach is to sequence structures, based on their respective RE expressions, and then compare the sequence with the numerical predictions of Hess and Schaad[25] to see if we have an agreement or significant departure. As a first stage of such a comparison we can compare all structures *predicted* according to Table 1 and Table 2 to have the same RE. In Table 3 we have collected compounds predicted to have the same RE and then listed computed RE as given by Hess and Schaad[25]. Immediately it is apparent that the predictions of the two methods agree remarkably well. One has only to think of the *different* nature of the two approaches, and then all sorts of approximations implied in both schemes, particularly in Hückel type computations. One may congratulate the simple Hückel

TABLE 3

Groups of Divalent Sulfur-Containing Heteroconjugated Compounds with the Same RE (Conjugated Circuits) and the Corresponding Hess-Schaad RE Numbers.

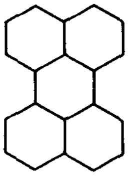
RE (conjugated circuits)	Compounds[a]				RE (numerical)[b]			
S_2	*4*	*14*	*15*		0.118	0.178	0.021	
$(2R_1 + T_2 + T_3)/2$	*7*	*9*			0.196	0.209		
$(8R_1 + T_2 + 2T_3 + T_4)/4$	*10*	*12*			0.671	0.571		
T_3	*16*	*17*	*18*		−0.076	−0.128	−0.481	
$2S_1$	*22*	*24*	*44*		0.243	0.220	0.164	
$S_1 + SS_2$	*23*	*45*			0.146	0.175		
$S_1 + T_2$	*25*	*27*	*29*		−0.089	−0.047	−0.066	
$T_2 + TT_3$	*26*	*28*			−0.269	−0.268		
$S_1 + TT_3$	*30*	*31*			−0.007	0.008		
$2T_2$	*32*	*34*	*36*	*38*	−0.398	−0.390	−0.433	−0.376
$T_2 + SS_3$	*33*	*35*	*37*		−0.252	−0.259	−0.235	
TT_3	*39*	*40*	*41*	*46*	−0.055	−0.092	−0.140	0.101

[a] Numbers correspond to the structures in Figure 2

[b] B. A. Hess, Jr. and L. J. Schaad, *J. Am. Chem. Soc.*, **95**, 3907 (1973)

method (as practiced by Hess and Schaad, i.e., with their parametrization for carbon-carbon terms and their reference structures[25]) in producing so internally consistent results, particularly when one realizes that the selection of parameters was essentially based on thermodynamic data of only three (available) source structures:[41] thiophene, diphenyl sulfide, and thianthrene. We could say, in view of the favorable comparison of Table 3 that the Hückel method passed the test—as we view the concept of conjugated circuits of more fundamental nature. But, of course, those heavily indoctrinated with MO methodology may claim just the opposite: What is important is that two different approaches lead to the same or similar predictions, which gives credibility to both schemes.

Having such a remarkable agreement we may dwell on the differences and seek their explanation, if possible. It is known that MO methods (not only Hückel MO) tend to overemphasize delocalization and in some instances, like perylene, ignore the fact that the central bonds are essentially single bonds[42] and that the molecule is more properly viewed as two weakly interacting naphthalene moieties—the kind of differentiation that the conjugated circuit approach (and the VB method) can handily absorb. On the other hand, in the approach of conjugated circuits we are primarily concerned with circuits structure and do not differentiate bond types although, if one wishes, such contributions can be considered. Hence some differences in the predictions of the two methodologies can be expected, but the nature of the differences is such that in both cases, with appropriate steps, corrections can be implemented. At this stage it is premature to pay attention to such smaller corrections, as we have yet to confirm agreement on the major points over a wider collection of compounds, possibly even other heteroatoms, in order to firmly establish (because such an approach eventually resorts to empirical parametrization) that the frame of the method is immaculate.



Three noticeable exceptions to the harmonious agreements in Table 2 appear to be associated with compound *18* which is predicted by HMO to be strongly antiaromatic and compound *46* which is predicted as aromatic, while in fact they ought to be weakly antiaromatic, as judged in both cases by comparison with other compounds having the same RE expression as compound *4*. At this moment we can neither claim an error nor deficiency of HMO; as yet it remains to be seen what is the possible cause for the disagreement.

Additional comparisons are possible for the compounds in Table 1 and Table 2 which could further clarify the degree of agreement or disagreement between the two approaches: our graph theoretical approach and Hess and Schaad's MO approach. Observe that the expressions for RE are simple arithmetical combinations in many instances, and we can test their arithmetic validity. Let us illustrate this on S_1 and S_2

and their combinations:

S_1	0.193 (*2*)		
S_2	0.118 (*4*)	0.178 (*14*)	0.201 (*15*)
$S_1 + S_2$	0.247 (*6*)		
$2S_1$	0.243 (*22*)	0.220 (*24*)	0.164 (*44*)
$2S_1 + 2S_2$	0.363 (*48*)		
$2S_2$	0.222 (*20*)		

There are here 10 available entries to determine two parameters.

It appears that in a number of cases both S_1 and S_2 derived from HMO are somewhat exaggerated, or alternatively the combinations ($S_1 + S_2$, $2S_1$, $2S_1 + 2S_2$, and $2S_2$) are underestimated. We will leave the comparison at this stage, as our prime goal is not to devise a parametrization for the quantities S_1, S_2 etc., nor to investigate in detail the HMO approach. We mentioned the comparison as of potential interest should one wish to investigate possible alternative parameters, as then the above relations can be of use in selecting amongst alternatives. So despite the above inconsistency (typical of any overdetermined system of equations, to be resolved by a least-squares fitting) we found that simple MO treatment and our graph theoretical approach give similar results, particularly if one uses the numerical data with some care. For instance, we see from Table 3 that *30* and *31*, if the REPE approach of Hess and Schaad is taken too rigidly, would be classified as slightly aromatic and slightly antiaromatic, because the found values for $S_1 + TT_3$ are either positive or negative. The difference of only 0.015 (β) is too small to be given full significance, so we believe the two compounds belong to the same type—which we expect to be slightly aromatic, the compounds being distantly related to azulene. In the case of *31* this statement is supported by experimental facts.[43] In contrast, compounds *27* and *29*, which also have azulene skeletal similarity, are fundamentally different (as is reflected in their expressions for RE: $S_1 + T_2$), even more so compounds *26* and *28* (RE: $T_2 + TT_3$), which are fully antiaromatic. It is this possibility of classifying compounds as aromatic, antiaromatic, and of mixed parentage that makes our approach very attractive for qualitative discussions. But, if one wishes to pursue quantitative comparisons much can be done, as shown in this section, by using the *expressions* for RE. Finally, the last stage in a quantitative study belongs to numerical comparisons for which one would need some reliable parametization—a stage which has yet to await experimental developments and data, or possibly sufficiently accurate SCF MO computations on a sufficiently large body of structures that will result in reliable RE (of an accuracy of a few hundredths of eV at most). So far an insufficient number of molecules with divalent sulfur has been theoretically considered.

A COMPARISON WITH THE GRAPHICAL STUDY OF POSITIONAL ISOMERS[27]

Knop *et al.* have analyzed numerous sulfur compounds using a graphical method already mentioned in the introduction.[27] Their approach amounts formally to interpreting a sulfur atom as fully saturated, i.e., interrupting conjugation. Hence formally one can erase the sulfur atom and consider the remaining carbon fragment, referred to as "parent" structure. It is then proposed that the relative stability of the sulfur compounds will be dominated by the relative stability of the "parent" hydrocarbon skeletons. For the latter one can count the so-called algebraic structure count[44], or corrected structure count[45] in which to individual Kekulé valence structures one assigns parity values of +1 or −1, following the initial work on the parity of conjugated hydrocarbons of Dewar and Longuet-Higgins.[45] Because among the structures considered there are no cases of three odd-membered fused rings, for which the concept of parity was found to be invalid (in fact absurd)[47] the outlined approach can indicate upon the relative stabilities. In addition, the authors consider the branching mode,[48] and were able to derive some empirical rules which further differentiate among different positional isomers. In Table 4 we have summarized the results of Knop *et al.*[27] by adding our own expressions for RE as an additional column. Some of the structures in Table 4 have already appeared in Table 1 or Table 2, but many new ones have been included. For each case we listed conjugated circuits involving carbon atoms only, which correspond to the "parent" structure, and then added conjugated circuits which the simple graphical approach neglected—those with participation of divalent sulfur. Since already data of Knop *et al.*[27] are in agreement with experimental behavior (characterized as "stable"; modestly stable"; "unstable") our supplementing this information with a description of the role of sulfur will hardly change the situation, because the contributing terms of sulfur are expected to make numerically a lesser contribution. There are, however, a number of interesting observations to be seen in Table 4. In the case of bicyclic compounds (the initial entries in Table 4) positional isomers have different "parent" components, but the same sulfur contribution, thus supporting the earlier suggestion of Knop, Trinajstić, and Živković[27] concerning the significance of contributions of the parent structure which also determines the behavior of the sulfur heterocyclic compounds. However, with tricyclic structures we have a greater versatility of situations. Compounds *53* and *55* have a similar "parent" contribution (signified by a single Kekulé valence structure, though different modes of branching and cyclization), but different sulfur contributions: ($2S_1 + T_2$) and ($2S_1 + TT_3$), respectively. Here the sulfur contributions appear to play a dominant discriminatory role, and in view of the fact that we expect TT_3 to be smaller than T_2 the latter compound will be predicted to be slightly more stable. This agrees with the experimental observations which characterize the two compounds as "stable" and "modestly stable", respectively. A similar situation occurs again for the thienobenzothiophenes *62-64* where the sulfur makes a contribution of either ($2S_1 + S_2$) or ($S_1 + SS_2 + SS_3$), while the parent structure gives a constant term (R_1). Additional illustrations are found among the benzodithiophenes, such as *69* and *72* as compared to *73*. Variations in the contributions from sulfur conjugated circuits are not likely to upset the major relative contributions of the parent hydrocarbon, which, for instance, in the case of the benzodithiophenes *68-73* is either R_1 or 0. Nevertheless, the sulfur contributions should not be ignored as they can further differentiate among positional isomers that have the same "parent" contributions. Therefore, we undertook to examine a number of polycyclic sulfur-containing conjugated systems (most of which are experimentally known) and offer our analysis as an assistance for a finer discussion of minor differences among such compounds.

TABLE 4

Relative Stabilities Obtained by the Use of the Graphical Method of Knop *et al.*[27] and RE (Conjugated Circuits) Expressions for a Number of Bicyclic and Tricyclic Conjugated Molecules Containing Either One Sulfur Atom or Two Non-Adjacent Sulfur Atoms.

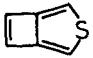
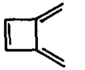
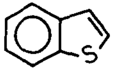
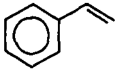
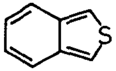
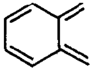
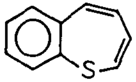
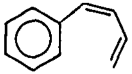
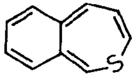
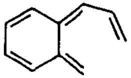
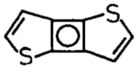
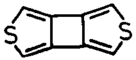
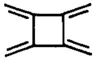
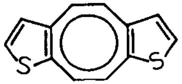
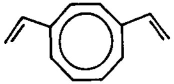
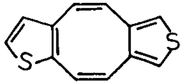
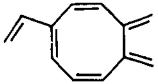
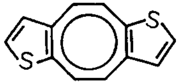
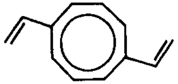
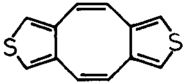
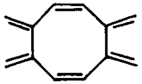
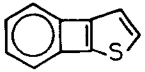
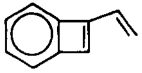
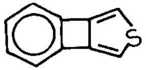
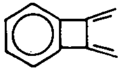
No.	Compound	"parent" hydrocarbon	Essential topological factors	Stability predicted* Stability observed	RE (conjugated circuits)
51			single branching ASC = 0	unstable —	$(2Q_1 + S_1 + T_1)/2$
52			double branching ASC = 1	modestly stable unstable under oxygen and room temp^{a,b}	$S_1 + T_2$
5			single branching ASC = 2	stable stable^{c}	$(S_1 + S_2 + 2R_1)/2$
6			double branching ASC = 1	unstable reactive compound^{d,e}	$S_1 + S_2$
7			single branching ASC = 2	stable stable^{f,g}	$(2R_1 + T_2 + T_3)/2$
8			double branching ASC = 1	unstable —	$T_2 + T_3$
52a			double branching ASC = 0	unstable —	$(2Q_1 + 2S_1 + 2T_2 + TT_3)/2$

TABLE 4 (*continued*)

No.	Compound	"parent" hydrocarbon	Essential topological factors	Stability predicted* Stability observed	RE (conjugated circuits)
53			triple branching ASC = 1	modestly stable —	$2S_1 + T_2$
54			double branching ASC = 0	unstable —	$(2Q_1 + 2S_1 + 2T_2 + TT_3)/2$
55			quadruple branching ASC = 1	stable —	$2S_1 + TT_3$
56			double branching ASC = 0	unstable —	$(2Q_2 + 2S_1 + 2T_3 + TT_4)/2$
57			triple branching ASC = 1	modestly stable —	$2S_1 + T_3$
58			double branching ASC = 0	unstable —	$(2Q_2 + 2S_1 + 2T_3 + TT_4)/2$
59			quadruple branching ASC = 1	stable —	$2S_1 + TT_4$
60			single branching ASC = 1	unstable —	$(2R_1 + Q_1 + Q_2 + S_1 + T_2 + T_3)/3$
61			double branching ASC = 2	stable stable white crystalline solid[h,i]	$(2R_1 + S_1 + T_2 + T_3)/2$

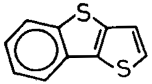
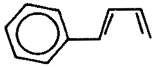
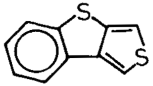
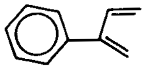
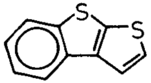
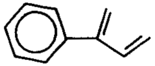
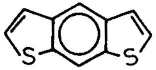
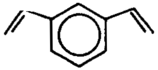
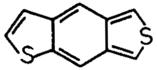
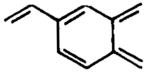
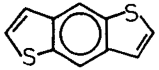
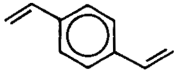
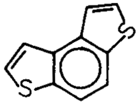
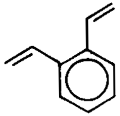
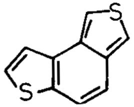
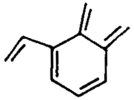
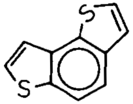
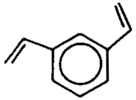
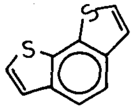
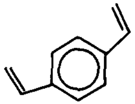
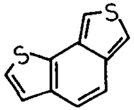
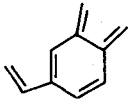
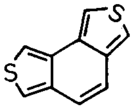
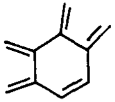
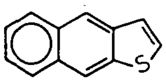
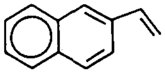
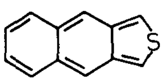
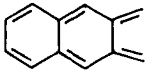
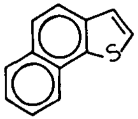
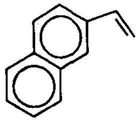
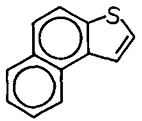
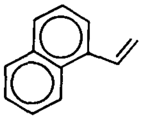
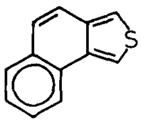
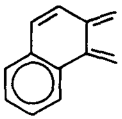
62			single branching ASC = 2	stable stable[j]	$(2R_1 + 2S_1 + S_2)/2$
63			ring and chain single branching ASC = 2	stable —	$(2R_1 + S_1 + SS_2 + SS_3)/2$
64			ring and chain single branching ASC = 2	stable —	$(2R_1 + 2S_1 + S_2)/2$
65			double branching ASC = 2	stable —	$(2R_1 + 2S_1 + 2S_2)/2$
66			triple branching ASC = 1	unstable —	$S_1 + S_2 + SS_3$
67			double branching ASC = 2	stable —	$(2R_1 + 2S_1 + 2S_2)/2$
68			double branching ASC = 2	stable stable[k,l]	$(2R_1 + 2S_1 + 2S_2 + SS_3)/2$
69			triple branching ASC = 1	unstable —	$2S_1 + S_2$
70			double branching ASC = 2	stable stable[m,n]	$(2R_1 + 2S_1 + 2S_2 + SS_3)/2$

TABLE 4 (*continued*)

No.	Compound	"parent" hydrocarbon	Essential topo-logical factors	Stability predicted* Stability observed	RE (conjugated circuits)
71			double branching ASC = 2	stable stable[o]	$(2R_1 + 2S_1 + 2S_2 + SS_3)/2$
72			triple branching ASC = 1	unstable —	$2S_1 + S_2$
73			quadruple branching ASC = 1	unstable white solid, sen-sitive to oxygen[p,r]	$2S_1 + SS_3$
74			single branching ASC = 1	stable stable[v,s,t]	$(4R_1 + 2R_2 + S_1 + S_2 + S_3)/3$
75			double branching ASC = 1	unstable reactive compound[u]	$S_1 + S_2 + S_3$
76			single branching ASC = 3	stable stable[v,w]	$(4R_1 + 2R_2 + 2S_1 + S_2 + S_3)/3$

77			single branching ASC = 3	$\frac{\text{stable}}{\text{stable}^{z,aa}}$	$(4R_1 + 2R_2 + 2S_1 + S_2 + S_3)/3$
78			double branching ASC = 2	$\frac{\text{modestly stable}}{\text{modestly stable}^{bb,cc}}$	$(2R_1 + S_1 + S_2 + S_3)/2$

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* The term *stability* is used in the everyday laboratory sense, i.e. *stable* denotes isolable compounds with well-defined properties, *modestly stable* denotes compounds stable in solution or when isolated with a limited life-time, and *unstable* denotes reactive and short-lived species.

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[aa] Y. Tominaga, M. L. Tedjamulia, R. N. Castle, and M. L. Lee, *J. Heterocycl. Chem.*, *20*, 487 (1983).
[bb] M. P. Cava, N. M. Pollack, and O. A. Mamer, *J. Org. Chem.*, **36**, 3032 (1971).
[cc] M. P. Cava and N. M. Pollack, *J. Am. Chem. Soc.*, **88**, 4112 (1966).

POLYCYCLIC SYSTEMS CONTAINING DIVALENT SULFUR

As can be already observed in Table 4, with an increase in the number of fused rings both parent and sulfur contribution increase. In order to obtain the expressions for molecular RE we have to analyze all Kekulé valence structures. In Figure 3 we show molecular structures for compounds investigated containing a single divalent sulfur

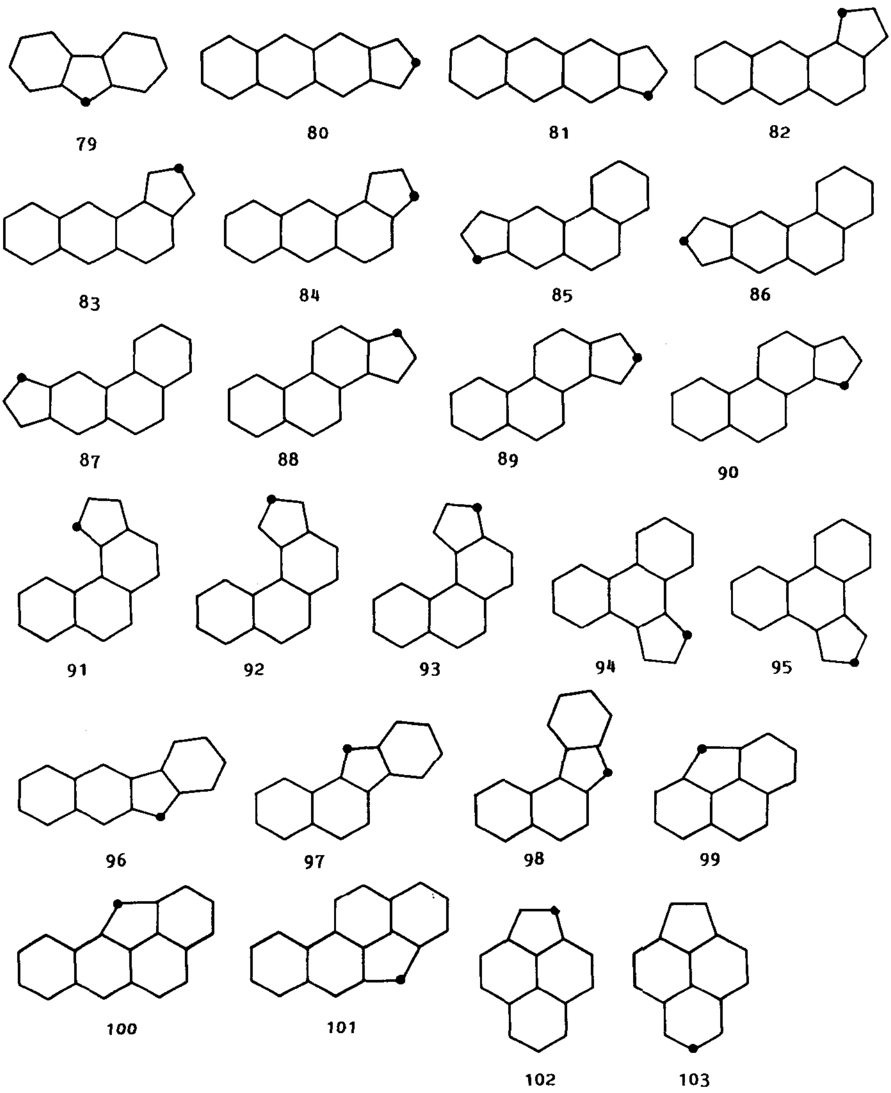

FIGURE 3 Diagrams of polycyclic conjugated molecules containing a single sulfur atom.

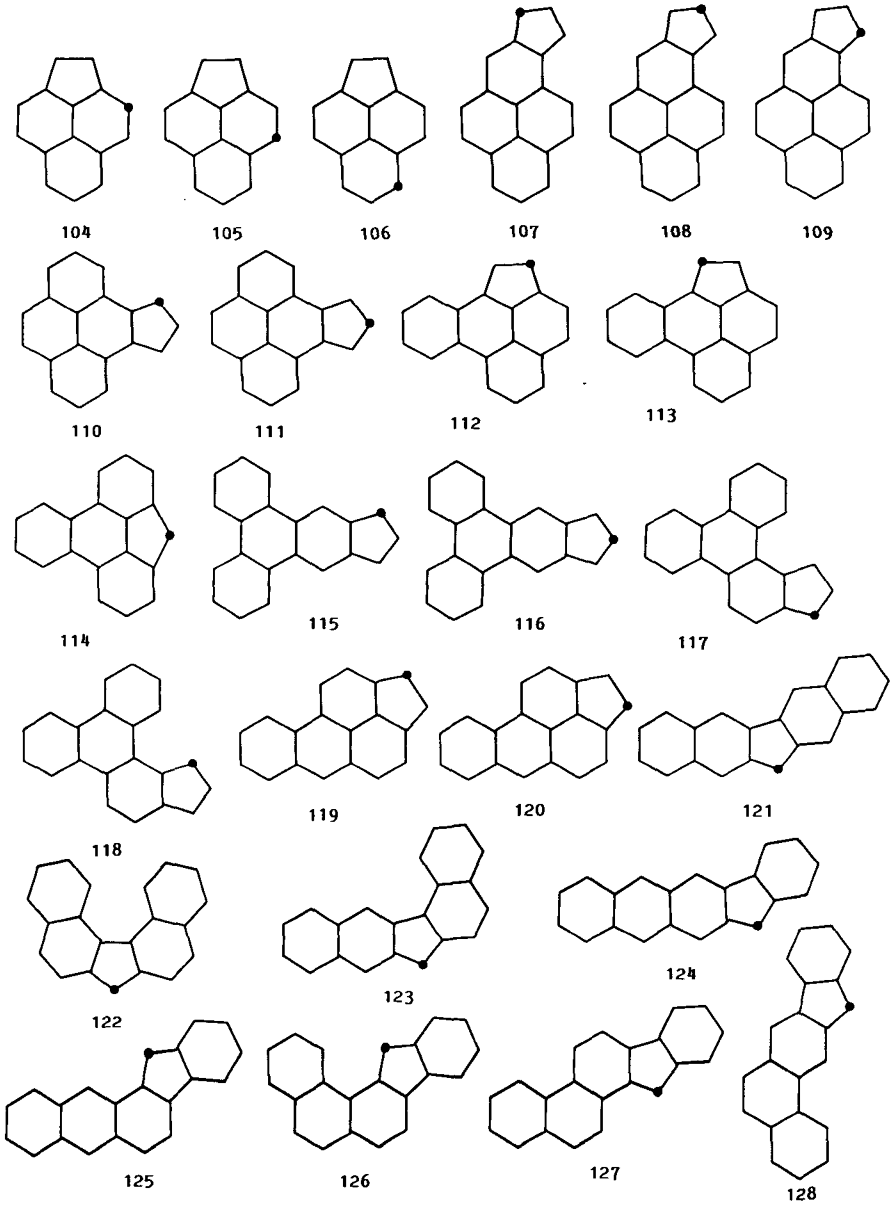

FIGURE 3 (*continued*)

atom and in Figure 4 we show molecular structures for polycyclic systems containing two divalent sulfur atoms. Many of the compounds investigated have been experimentally prepared and studied, primarily by R. N. Castle and by L. H. Klemm, although other sources have also been used (for exact references see Table 5 and

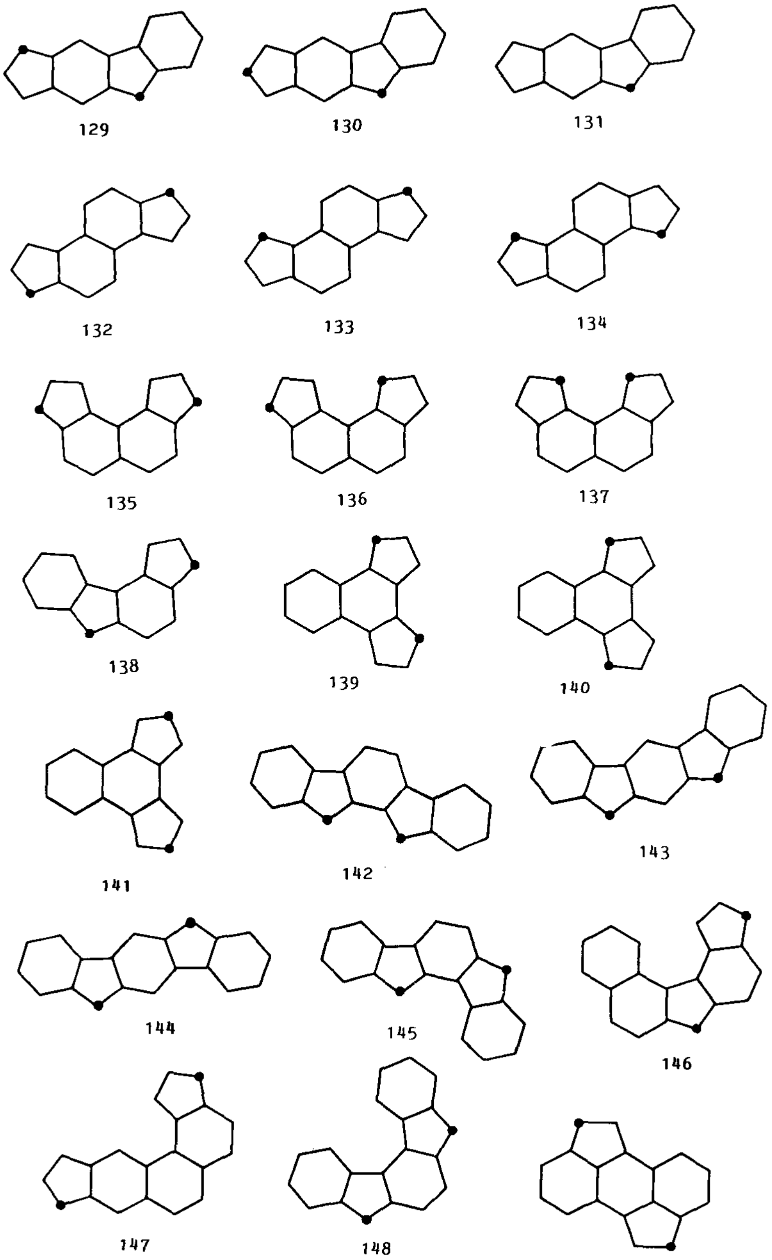

FIGURE 4 Diagrams of polycyclic conjugated molecules containing two non-adjacent divalent sulfur atoms.

TABLE 5

Resonance Energy Expressions for Polycyclic Compounds Containing a Divalent Sulfur Atom (Diagrams 79–128 in Figure 3).

	Compound	RE(parent)		RE(Sulfur-part)	Ref.
79	Dibenzothiophene	2RE(Ben)	+	$(S_1 + 2S_2 + S_3)/4$	a
80	Anthra[2,3-c]thiophene			$(S_1 + S_2 + S_3 + S_4)$	b
81	Anthra[2,3-b]thiophene	RE(Ant)	+	$(S_1 + S_2 + S_3 + S_4)$	c
82	Anthra[1,2-b]thiophene	RE(Ant)	+	$(3S_1 + S_2 + S_3 + S_4)/4$	c,d
83	Anthra[2,3-c]thiophene	RE(Nap)	+	$(3S_1 + S_2 + S_3 + S_4)/3$	
84	Anthra[2,1-b]thiophene	same as (*82*)			c,d
85	Phenanthro[2,3-b]thiophene	RE(Phe)	+	$(2S_1 + 3S_2 + S_3 + S_4)/5$	e,f
86	Phenanthro[2,3-c]thiophene	RE(Ben)	+	$(2S_1 + 2S_2 + S_3 + S_4)/2$	
87	Phenanthro[3,2-b]thiophene	same as (*85*)			e,f
88	Phenanthro[2,1-b]thiophene	RE(Phe)	+	$(3S_1 + 2S_2 + S_3 + S_4)/5$	f,g–i
89	Phenanthro[1,2-c]thiophene	same as (*83*)			j
90	Phenanthro[1,2-b]thiophene	same as (*88*)			f,af
91	Phenanthro[4,3-b]thiophene	same as (*88*)			f
92	Phenanthro[4,3-c]thiophene	same as (*83*)			
93	Phenanthro[3,4-b]thophene	same as (*88*)			f
94	Phenanthro[9,10-b]thiophene	RE(Phe)	+	$(4S_1 + S_2 + 2S_3 + S_4)/5$	f,k
95	Phenanthro[9,10-c]thiophene	2RE(Ben)	+	$(4S_1 + S_2 + 2S_3 + S_4)/4$	b,l–s
96	Benzo[b]naphtho[2,3-d]thiophene	RE(Ben)+RE(Nap)	+	$(S_1 + 2S_2 + 2S_3 + S_4)/6$	c,t,v,vv
97	Benzo[b]naphtho[2,1-d]thiophene	RE(Ben)+RE(Nap)	+	$(2S_1 + 3S_2 + 2S_3 + S_4)/6$	c,v,w,z,az,eee,azz
98	Benzo[b]naphtho[1,2-d]thiophene	same as (*97*)			c,z,aa–cc,ccc

TABLE 5 (*continued*)

	Compound	RE(parent)		RE(Sulfur-part)	Ref.
99	Phenanthro[4,5-bcd]thiophene	RE(Phe)	+	$(S_1 + 2S_2 + 2S_3)/5$	dd,ee,eee
100	Benzo[2,3]phenanthro[4,5-bcd]thiophene	RE(B-Ant)	+	$(2S_1 + 3S_2 + 3S_3 + 2S_4)/7$	u,au
101	Chryseno[4,5-bcd]thiophene	RE(Chr)	+	$(S_1 + 2S_2 + 3S_3 + 2S_4)/8$	u
102	Phenaleno[1,9-bc]thiophene	RE(Nap)	+	$(2S_1 + 2S_2 + 3S_3)/3$	c
103				$3S_3$	
104		same as (*103*)			
105		same as (*103*)			
106		same as (*103*)			
107	Pyreno[2,1-b]thiophene	RE(Pyr)	+	$(3S_1 + 2S_2 + 2S_3 + 3S_4)/6$	ff
108	Pyreno[2,1-c]thiophene			$S_1 + S_2 + S_3$	
109	Pyreno[1,2-b]thiophene	same as (*107*)			ff,gg
110	Pyreno[4,5-b]thiophene	RE(Pyr)	+	$(5S_1 + S_2 + 2S_3 + 2S_4)/6$	ff
111	Pyreno[4,5-c]thiophene	RE(Phe)	+	$(5S_1 + S_2 + 2S_3 + 2S_4)/5$	
112	Benzo[1,2]phenaleno[4,3-bc]thiophene	RE(Ben)+RE(Nap)	+	$(2S_1 + 2S_2 +5S_3 + S_4)/6$	ah
113	Benzo[1,2]phenaleno[3,4-bc]thiophene	RE(Phe)	+	$(3S_1 + 5S_3 + 2S_4)/5$	ah
114	Triphenylo[4,5-bcd]thiophene	RE(Tri)	+	$(2S_1 + 4S_2 + 3S_3 + S_4)/9$	hh,eee
115	Triphenyleno[2,3-b]thiophene	RE(Tri)	+	$(4S_1 + 4S_2 + S_3 + 2S_4 + S_5)/9$	ii
116	Triphenyleno[2,3-c]thiophene	2RE(Ben)	+	$(4S_1 + 2S_3 + S_4 + S_5)/4$	
117	Triphenyleno[2,1-b]thiophene	RE(Tri)	+	$(5S_1 + 4S_2 + S_3 + 2S_4 + S_5)/9$	iii
118	Triphenyleno[1,2-b]thiophene	same as (*117*)			iii
119	Benzo[4,5]phenaleno[1,9-bc]thiophene	RE(Phe)	+	$(3S_1 + 3S_2 + 3S_3 + 3S_4)/5$	jj,jjj
120	Benzo[4,5]phenaleno[9,1-bc]thiophene	RE(Ant)	+	$(3S_1 + 3S_2 + 3S_3 + 3S_4)/4$	jjj
121	Dinaphtho[2,3-b:2′,3′-d]thiophene	2RE(Nap)	+	$(S_1 + 2S_2 + 3S_3 + 2S_4 + S_5)/9$	kk,kkk

122	Dinaphtho[2,1-b:1′,2′-d]thiophene	2RE(Nap)	+	$(4S_1 + 4S_2 + 4S_3 + 2S_4 + S_5)/9$	ll,mm,kkk
123	Dinaphtho[2,1-b:2′,3′-d]thiophene	2RE(Nap)	+	$(2S_1 + 3S_2 + 4S_3 + 2S_4 + S_5)/9$	kk,kkk
124	Anthra[2,3-b]benzo[d]thiophene	RE(Ben)+RE(Ant)	+	$(S_1 + 2S_2 + 2S_3 + 2S_4 + S_5)/8$	nn,oo,ooo
125	Anthra[1,2-b]benzo[d]thiophene	RE(Ben)+RE(Ant)	+	$(3S_1 + 4S_2 + 2S_3 + 2S_4 + S_5)/8$	oo–ss,ooo,uuu
126	Benzo[b]phenanthro[3,4-d]throphene	RE(Ben)+RE(Phe)	+	$(3S_1 + 5S_2 + 3S_3 + S_4 + S_5)/10$	z,tt,uuu
127	Benzo[b]phenanthro[2,1-d]thiophene	same as (*126*)			z,ss–uu,uuu
128	Benzo[b]phenanthro[2,3-d]thiophene	RE(Ben)+RE(Phe)	+	$(2S_1 + 4S_2 + 3S_3 + 2S_4 + S_5)/10$	z,tt,vv,zz

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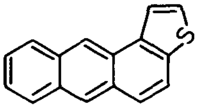
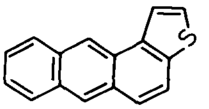
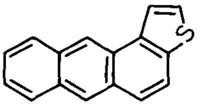
Table 6). Let us illustrate a few of these more complex compounds. In the case of anthra[2,1-b]thiophene (*84*):



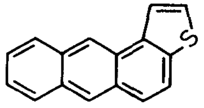
S_1



S_1



S_1



$S_2 + S_3 + S_4$

we immediately see that the presence of the sulfur in no way interferes with the conjugation in the parent fragment—anthracene. Hence instead of enumerating all conjugated circuits we can simplify the work by focusing attention on the sulfur atom and count conjugated circuits involving the sulfur alone. Under each of the four possible Kekulé valence structures of anthra[2,1-b]thiophene we have indicated the type and the size of the conjugated circuits involving sulfur. For the whole molecule we can now simply write:

$$\text{RE (anthra[2,1-b]thiophene)} = \text{RE (anthracene)} + (3S_1 + S_2 + S_3 + S_4)/4$$

where RE (anthracene) can be found in previous studies of conjugation and aromaticity in conjugated hydrocarbons, namely[2]:

$$\text{RE (anthracene)} = (6R_1 + 4R_2 + 2R_3)/4$$

The above example is particularly simple because the sulfur participates in an external ring. But in the case of benzo[b]naphtho[d]thiophene (*96* in Figure 3) the sulfur is located in an internal ring which makes somewhat less apparent that again we can simply *add* the RE of disjoint hydrocarbon parts, to which the contribution for sulfur participation has to be added.

Hence in the above case we would have:

$$\text{RE (benzo[b]naphtho[2,3-d]thiopnene)} = \text{RE (benzene)} + \text{RE (naphthalene)} + \text{RE (sulfur-containing conjugated circuits)}$$

That this is correct can be seen by inspecting Figure 5 where all Kekulé structures of benzo[b]naphto[2,3-d]thiophene are shown and where one sees that (upon dividing by 6, the total number of Kekulé structures) we obtain the indicated form for the RE.

Because inclusion of a divalent sulfur atom does not alter the contribution of the parent hydrocarbon fragment in Table 5 and Table 6 we have listed the RE of numerous polycyclic sulfur compounds by showing explicitly only the contributions of

TABLE 6

Resonance Energy Expressions for Polycyclic Compounds Containing Two Non-Adjacent Divalent Sulfur-Atoms (Diagrams 129–149).

	Compound	RE(parent)	RE(Sulfur-part)	Ref.
129	[1]Benzothieno[5,6-b][1]benzothiophene	2RE(Ben)	+ $(3S_1 + 4S_2 + S_3)/4$	a,b
130	[1]Benzothieno[6,5-b][1]benzothiophene	same as (*129*)		c
131	[2]Benzothieno[5,6-b][1]benzothiophene	RE(Ben)	+ $(2S_1 + 2S_2 + SS_3 + SS_4)/2$	d
132	Naphtho[2,1-b:6,5-b′]dithiophene	RE(Nap)	+ $(4S_1 + 2S_2 + 2S_3)/3$	e,f
133	Naphtho[1,2-b:6,5-b′]dithiophene	same as (*132*)		e
134	Naphtho[1,2-b:5,6-b′]dithiophene	same as (*132*)		e,g
135	Naphtho[2,1-b:7,8-b′]dithiophene	same as (*132*)		h
136	Naphtho[1,2-b:7,8-b′]dithiophene	same as (*132*)		e
137	Naphtho[1,2-b:8,7-b′]dithiophene	same as (*132*)		i
138	[1]Benzothieno[5,4-b][1]benzothiophene	2RE(Ben)	+ $(3S_1 + 4S_2 + S_3 + SS_3 + SS_4)/4$	j
139	Naphtho[1,2-b:3,4-b′]dithiophene	RE(Nap)	+ $(4S_1 + 2S_2 + 2S_3 + SS_4)/3$	g
140	Naphtho[1,2-b:4,3-b′]dithiophene	same as (*139*)		g
141	Naphtho[1,2-c:3,4-c′]dithiophene	RE(Ben)	+ $(4S_1 + SS_3 + SS_4)/2$	k
142	Benzo[2,1-b:3,4-b′]bis[1]benzothiophene	3RE(Ben)	+ $(4S_1 + 8S_2 + 4S_3 + SS_4 + 2SS_4 + SS_5)/8$	l,m,o
143	Benzo[1,2-b:5,4-b′]bis[1]benzothiophene	3RE(Ben)	+ $(4S_1 + 8S_2 + 4S_3)/8$	o,b,e,p,r
144	Benzo[1,2-b:4,5-b′]bis[1]benzothiophene	same as (*143*)		a–c,l,r

145	Benzo[1,2-b:3,4-b′]bis[1]benzothiophene	same as (*142*)		m,r–t
146	Naphtho[1,2-b]benzo[1,2-b:4,3-b′]dithiophene	RE(Ben)+RE(Nap)	$+ (5S_1 + 6S_2 + 2S_3 + 2SS_3 + SS_4 + SS_5)/6$	j
147	Phenanthro[3,4-b:6,5-b′]dithiophene	RE(Phe)	$+ (6S_1 + 4S_2\ 2S_3 + SS_5)/5$	u
148	Benzo[1,2-b:4,3-b′]bis[1]benzothiophene	same as (*142*)		c,u,w
149	Anthra[1,9-bc:5,10-b′c′]dithiophene	2RE(Ben)	$+ S_1 + S_2$	x

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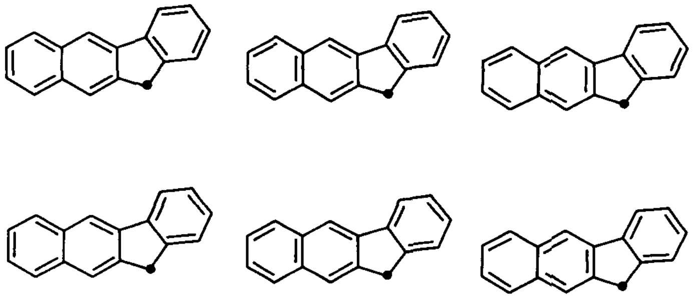


FIGURE 5 Kekulé structures for benzo[b]naphtho[2,3-b]thiophene.

sulfur-containing conjugated circuits. The hydrocarbon part is presented in abbreviated form as RE(Ben), RE(Nap) for the resonance energies of benzene and naphthalene, respectively. In Table 7 we give explicit expressions for all such contributions appearing in Table 5 and Table 6 for compounds containing one and two sulfur atoms, respectively.

A close look at Table 5 reveals a number of instances where positional isomers have the same RE. The critical factor which determines whether positional isomers would have the same or different RE is the mode of fusion of the ring containing sulfur. If

TABLE 7

Resonance Energy Expressions and Numerical Values for Benzenoid Hydrocarbons Whose Conjugated Circuits Appear as Parts of Conjugated Circuit Counts for Polycyclic Conjugated Compounds Containing Bivalent Sulfur

Compound	Resonance energy expression	eV
Benzene	RE(Ben) = $(2R_1/2)$	0.869
Naphthalene	RE(Nap) = $(4R_1 + 2R_2)/3$	1.323
Anthracene	RE(Ant) = $(6R_1 + 4R_2 + 2R_3)/4$	1.600
Phenanthrene	RE(Phe) = $(10R_1 + 4R_2 + 2R_3)/5$[a]	1.975[a]
	[= $(10R_1 + 4R_4 + R_3)/5$][b]	(1.955)[b]
Chrysene	RE(Chr) = $(20R_1 + 10R_2 + 4R_3 + 2R_4)/8$[a]	2.540[a]
	[= $(20R_1 + 10R_2 + 2R_3)/8$][b]	(2.505)[b]
Benzanthracene	RE(B-ant) = $(16R_1 + 8R_2 + 4R_3 + 2R_4)/7$[a]	2.336[a]
	[= $(16R_1 + 8R_2 + 4R_3)/7$][b]	(2.330)[b]
Pyrene	RE(Pyr) = $(12R_1 + 8R_2 + 6R_3)/6$[a]	2.166[a]
	[= $(12R_1 + 8R_2 + 4R_3)/6$][b]	(2.133)[b]
Triphenylene	RE(Tri) = $(26R_1 + 6R_2 + 6R_3 + 2R_4)/9$[a]	2.750[a]
	[= $(26R_1 + 6R_2 + 3R_3 + R_4)/9$][b]	(2.723)[b]

[a] These expressions and values were revised by taking into account all conjugated circuits, while in Ref. 2 linearly dependent conjugated circuits were neglected. Disjoint conjugated circuits in both cases are not considered.

[b] Expressions and values for resonance energy containing only linearly independent conjugated circuits.[2]

the ring is so fused that it in two isomers is attached to CC bonds which in the parent structure have the same Pauling bond order, and fusion does not alter the bond type of the fusion, the resulting positional isomers (which differ in the site of the sulfur atom within the so fused ring) will have the same RE. In Figure 6 we have collected all such cases from Table 5 adding additional compounds that have the same RE as some

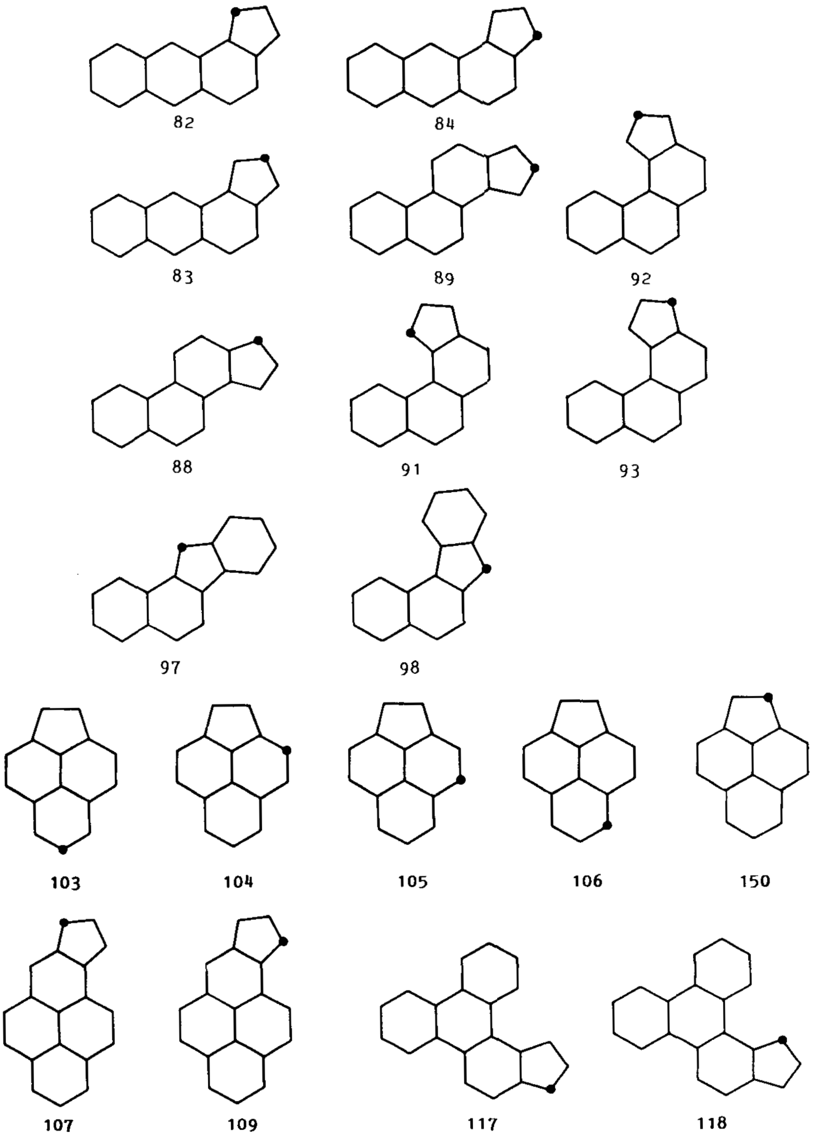


FIGURE 6 Examples of polycyclic conjugated compounds containing a single divalent sulfur atom which possess the same resonance energy expressions.

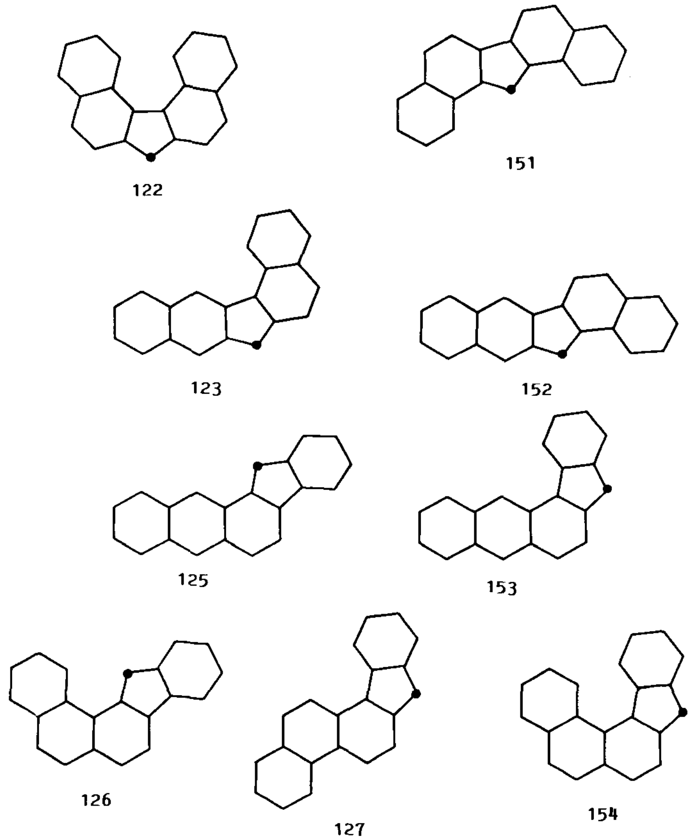


FIGURE 6 (*continued*)

of those listed in the Table 5, while in Figure 7 we present positional isomers to compounds of Table 6 (having two sulfur atoms) having the same RE as the compounds listed in Table 6.

Observe also that all compounds in Table 5 and Table 6 have only 4n+2 conjugated circuits (both in their parent portion and in their sulfur-containing circuits), hence the compounds can be viewed as heteroaromatics. We assume that all S_n and SS_n conjugated circuits make some (though possibly minor) stabilizing contribution.

DISCUSSION

Even though we have not considered the numerical parametrization for the graph theoretical quantities S_n and S_{nn} (as well as T_n and T_{nn} which appear in the compounds of Table 4 in particular) the approach is fundamentally quantitative. Our hesitation on rushing to assign some numerical values to S_n and S_{nn} quantities, that would then

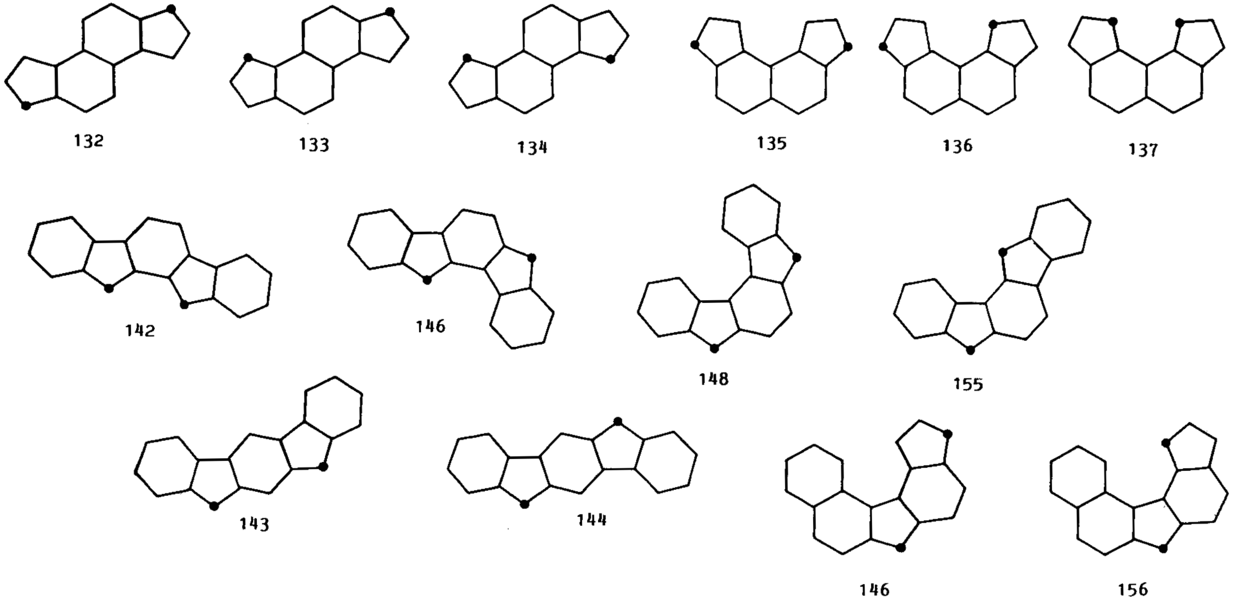
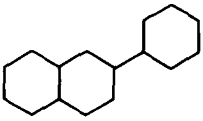


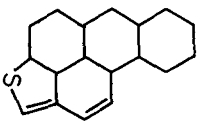
FIGURE 7 Examples of polycyclic conjugated compounds containing two nonadjacent divalent sulfur atoms which possess the same resonance energy expressions.

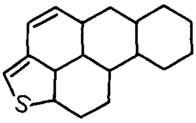
numerically predict molecular RE, is due to the lack of reliable computations, but as soon as quantum chemists can deliver some such reliable results one would be in the position to make useful estimates, even rather accurate derivations, for the needed parameters. Briefly, graph theory delivers the *frame* for comparison of *selected* results for various molecules, but does not produce numerical results of its own. They follow from other *sources*, be they experimental or theoretical. The situation is somewhat analogous to the use of group theory in chemistry, which provides us with, for instance, selection rules for various transitions, but does not tell much about the relative intensities of the transition, for which one has to look for other sources, experimental or theoretical. We have also emphasized *selected* properties, here molecular resonance energies. If a property is not of a topological and combinatorial origin, clearly graph theory will not be able to provide the answer, but if it is, like many thermochemical and a number of physical properties, then graph theory can not only give an answer, but also provide an insight in the origin of minor (isomeric, for instance) differences. Our Table 4 to Table 6 illustrate the situation with respect to the molecular RE of divalent sulfur conjugated cyclic and polycyclic compounds. A look at Table 5 immediately illustrates the difference between *96* and *97*, for example. Both benzo[b]napthothiophenes have the same parent contributions, hence would not be differentiated if only parent fragments are considered, because the excision of the sulfur leads in both cases to the identical subgraph:



However, they differ substantially in the participation of the sulfur. In the case of *97* we have a greater number of conjugated circuits, and for each size (S_1, S_2, S_3, S_4) *97* either dominates or at least has an equal number of circuits. This allows one immediately to deduce that *97* should be significantly (even if not considerably, in view of the possibilities that the S_n contributions may be relatively of minor magnitude compared to the corresponding quantities involving only carbon atoms) more stable. There are many such situations that allow valid conclusions on the relative stability. For example, the three dinaphthothiophenes: *122*, *123*, and *121* are to be ordered as shown, with *122* being the most stable (i.e., having the largest RE). A similar comparison of triphenylenethiophenes allows immediately to deduce that *117* dominates *115*, but both of these cannot be compared to *114* without some additional considerations. The problem arises with the fact that the latter, even though having fewer S_1 and S_2 conjugated circuits, has a larger number of S_3 conjugated circuits. We have in this case to invoke the assumption (very plausible and certainly valid for conjugated circuits involving carbon atoms only—hence expected valid also here) that S_1 dominates S_3, which then suggests that *114* has the least RE of the three compounds.

Besides the already mentioned comparison of isomers that have the same parent contributions we can make meaningful and quantitative comparisons between compounds having the same sulfur contribution and different parent components. Take, for example, the two benzo[4,5]phenalenothiophenes *119* and *120*:





Their REs are, respectively:

$$\text{RE (Phe)} + (3S_1 + 3S_2 + 3S_3 + 3S_4)/5$$

and

$$\text{RE (Ant)} + (3S_1 + 3S_2 + 3S_3 + 3S_4)/4$$

The sulfur part differs by a *factor* only, hence by making a simple manipulation to make the two sulfur parts the same we obtain:

$$4 \text{ RE } (119) - 5 \text{ RE } (120) = 4 \text{ RE (Phe)} - 5 \text{ RE (Ant)}$$

But the right-hand side can be viewed as known, the RE of phenanthrene and anthracene are well established, hence we can use the values for these, respectively[2] 1.955 eV and 1.600 eV. Thus we find for the difference 4 RE (*119*) − 5 RE (*120*) to be practically zero (i.e., −0.02 eV), which tells us that the two REs are with great accuracy numerically in the ratio 5/4. The above is an illustration of a case in which sulfur conjugation does not perturb the dominant role of the parent structures, which can account for the difference in relative stabilities of the two positional isomers, even though they are associated with *different* parent compounds. This situation is not always occurring as we see from a comparison of the benzo[1,2]phenalenothiophenes *112* and *113* in which the sulfur contributions differ and do not allow the simple algebra which would cancel their contributions.

In the case of compounds containing two sulfur atoms (Table 6) it is worth observing that here we have compounds that only require one sulfur atom parameter S_n while others require both S_n and SS_n. The former class is thus only formally involving two sulfurs, but in fact, as far as resonance stabilization is concerned, there is no evidence of sulfur-sulfur interactions. In view of the fact that one may expect S_n to make larger positive contributions than SS_n (the former already represents a "weakening" of normal carbon conjugated circuits, while the latter introduces two such "interuptions" within the same conjugated circuit) we see that the former are to be expected to have some additional resonance stabilization with respect to the latter, other contributions being equal. (Compounds having SS_n contributions have also contributions involving a single sulfur in conjugation!).

Finally, as is particularly evident from the compounds of Table 4 we see that numerous compounds containing divalent sulfur have a single Kekulé valence structure (e.g., all compounds in Fig. 2). Nevertheless, these single-Kekulé structure compounds yield RE, as is already the case with thiophene:

Hence, the RE here is to be viewed strictly as a departure of the molecular energy from a bond additive model, not as a result of some "resonating" mechanism, as one customarily associates with the two Kekulé structure of benzene. The distinction is not only semantic. It shows that in heterocyclic compounds there may be different terms making contributions, some to be identified as usual resonance of alternative Kekulé valence structures, others due to the presence of conjugated circuits, regardless of the number of valence structures. It is, however, possible that there is some parallelism between the presence of a single conjugated circuit, such as in thiophene, and the possibilities of having additional valence structures based on the assumption of some role being played by tetravalent sulfur structures, ionic structures, and "excited structures", all of which have been neglected. Thus, a single conjugated circuit involving a divalent sulfur atom may compensate for "higher" terms that our model (and other models of similar complexity) neglect. Be that as it may, we can consider the effective role of sulfur-containing conjugated circuits towards resonance energy and only when refinement of experimental data requires further improvements, e.g., important variations among properties of isomers predicted here to have essentially the same characteristics, such additional contributions may have to be analyzed. No data warrant such extensions at this time.

MISCELLANEOUS COMPOUNDS

In Table 8 we give results for some known compounds, and numerous other not yet known (see Fig. 8). Table 8 can be viewed as a theoretical screening of hypothetical structures. It allows experimental chemists to examine possible by-products or intermediates when contemplating novel synthetic steps. We see from a few illustrations that divalent sulfur compounds offer a vast versatility of compounds that differ in their conjugation content. The compounds have been included primarily on the basis of having significantly different contributions, not for the potential challenge in their synthesis or possible use. In contrast to heterocyclic systems containing nitrogen, which can be incorporated in any site of the molecular frame, divalent sulfur necessarily has to be located at the molecular periphery. This is the reason why its addition does not change the conjugation content of the parent structure. Being at the periphery the sulfur atom can be a probe for the importance of peripheral conjugation, which has been exaggerated by Platt's peripheral model[49], and which can be tested by comparison between molecules of similar periphery, e.g.: one being a conjugated hydrocarbon, the other containing divalent sulfur, or by comparison of positional isomers with sulfur atoms in different sites. The example of

TABLE 8

Resonance Energy Expressions for Miscellaneous Polycyclic Conjugated Compounds Containing One, Two, or Three Divalent Sulfur Atoms (Diagrams 157–242 in Figure 8).

Compound	RE(parent)	RE(Sulfur-part)	Ref.
157	RE(Nap)	$+ (3S_1)/3$	a
158	same as (*157*)		b
159	RE(Phe)+RE(Ben)	$+ (2S_1 + 4S_2 + 3S_3 + 2S_4 + S_5)/10$	c
160	RE(Chr)	$+ (5S_1 + 3S_2 + 2S_3 + S_4 + S_5)/8$	
161	RE(Phe)	$+ (5S_1 + 3S_2 + 2S_3 + S_4 + S_5)/5$	
162	same as (*160*)		d
163	RE(B-ant)	$+ (5S_1 + 2S_2 + 2S_3 + S_4 + S_5)/7$	d
164	RE(Ant)	$+ (5S_1 + 2S_2 + 2S_3 + S_4 + S_5)/5$	
165	same as (*163*)		
166	RE(Tri)+RE(Ben)	$+ (5S_1 + 9S_2 + 5S_3 + 3S_4 + 3S_5 + S_6)/18$	d
167	same as (*166*)		d
168	RE(B-tri)+RE(Ben)	$+ (9S_1 + 14S_2 + 9S_3 + 5S_4 + S_6 + S_7)/28$	d
169	same as(*168*)		d
170	RE(B-tri)+RE(Ben)	$+ (5S_1 + 9S_2 + 10S_3 + 5S_4 + 3S_5 + 3S_6 + S_7)/28$	d
171	RE(Chr)+RE(Ben)	$+ (5S_1 + 8S_2 + 5S_3 + 3S_4 + 2S_5 + S_6)/16$	e
172	RE(B-phe)+RE(Ben)	$+ (5S_1 + 8S_2 + 5S_3 + 3S_4 + 2S_5 + S_6)/16$	e
173	same as (*172*)		e
174	same as (*172*)		e
175	same as (*172*)		e
176	same as (*171*)		e

TABLE 8 (*continued*)

Compound	RE(parent)	RE(Sulfur-part)	Ref.
177	same as (*171*)		
178	RE(Chr)+RE(Ben)	+ $(3S_1 + 6S_2 + 5S_3 + 3S_4 + 2S_5 + S_6)/16$	e
179	RE(B-ant)+RE(Ben)	+ $(5S_1 + 7S_2 + 4S_3 + 3S_4 + 2S_5 + S_6)/14$	e
180	RE(Nap)+2RE(Ben)	+ $(5S_1 + 8S_2 + 7S_3 + 2S_4 + SS_3 + 2SS_4 + 2SS_5 + SS_6)12$	
181	same as (*180*)		
182	RE(Nap)+2RE(Ben)	+ $(7S_1 + 12S_2 + 7S_3 + 2S_4 + 2SS_3 + 3SS_4 + SS_5 + SS_6)/12$	
183	same as (*182*)		
184	same as (*182*)		
185	same as (*182*)		
186	same as (*182*)		
187	same as (*182*)		
188	same as (*182*)		
189	3RE(Ben)	+ $(12S_1 + 24S_2 + 12S_3 + SSS_4 + 3SSS_5 + 3SSS_6 + SSS_7)16$	f
190	same as (*189*)		
191	RE(Ace-ant)	+ $(3S_1 + S_2 + S_3 + S_4)/4$	g
192	2RE(Ben)	+ $(4S_1 + 8S_2)/4$	
193	same as (*192*)		
194		$3S_1 + SSS_3$	h
195	RE(Ben)	+ $3S_1$	g,i
196	same as(*195*)		
197		$3S_1 + S_2$	
198		$3S_1 + 2S_2$	

199	2RE(Ben)	+ $(4S_1 + T_2 + 2T_3 + T_4)/4$	
200	3RE(Ben)	+ $(T_2 + 3T_3 + 3T_4 + T_5)/8$	j
201		$S_1 + TT_3$	
202	same as (*201*)		
203		TT_4	
204	same as (*201*)		
205	RE(Nap)	+ $(4S_1 + 2S_2 + 2S_3 + SS_4)/3$	
206	same as (*201*)		
207	same as (*205*)		k
208	same as (*205*)		k
209	RE(Ben)	+ $(4S_1 + SS_3 + SS_4)/2$	l
210	same as (*201*)		
211	RE(Ben)	+ $(4S_1 + 2S_2)/4$	
212	same as (*201*)		
213		$T_2 + 2TT_3 + TTT_4$	
214		$2T_3$	m
215		TT_3	m
216	same as (*213*)		
217		$3S_1 + T_2$	
218		$3S_1 + TT_3$	
219	same as (*218*)		
220		$3S_1 + TTT_4$	
221	same as (*218*)		
222	same as (*220*)		
223		$3S_1$ $TTTT_5$	

TABLE 8 (*continued*)

Compound	RE(parent)	RE(Sulfur-part)	Ref.
224	same as (*218*)		
225	same as (*220*)		
226	same as (*218*)		
227	same as (*217*)		
228	same as (*218*)		

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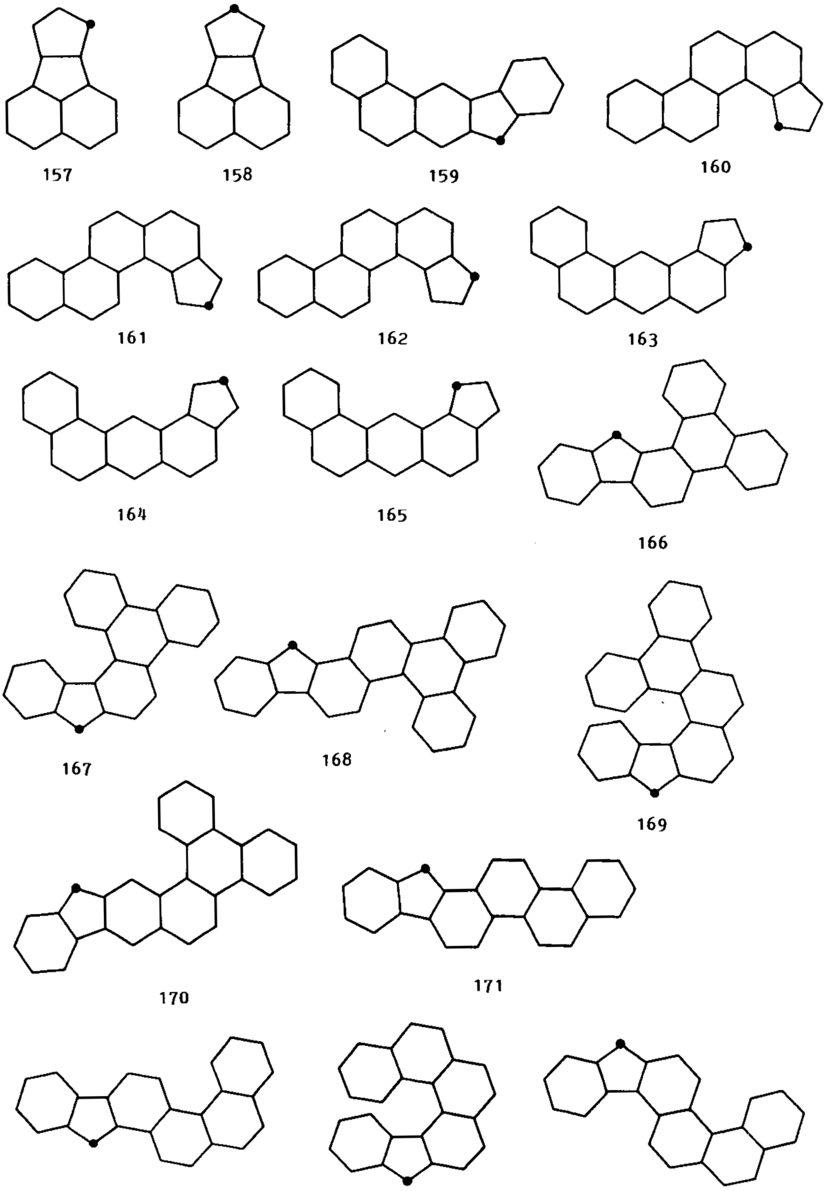
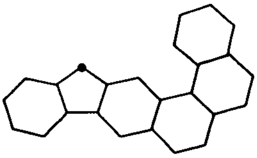


FIGURE 8 Miscellaneous polycyclic conjugated compounds containing one, two, or three bivalent sulfur atoms.



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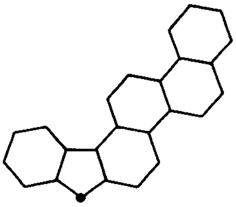

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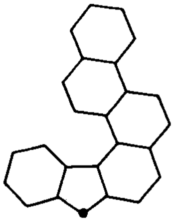

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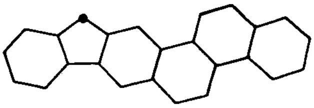

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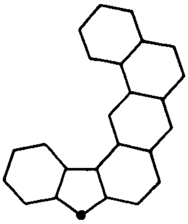

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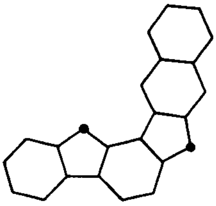

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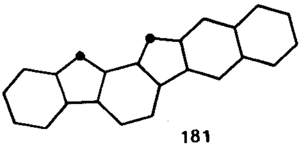

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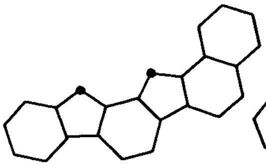

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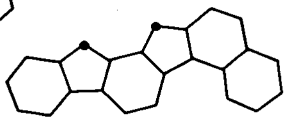

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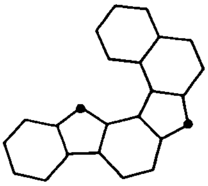

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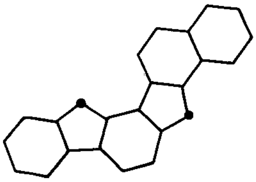

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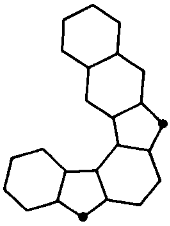

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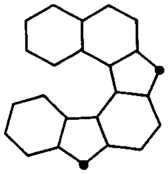

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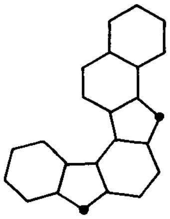

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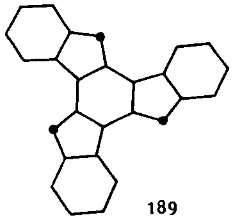

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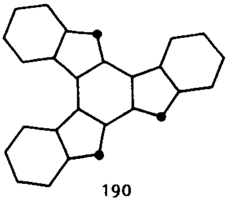

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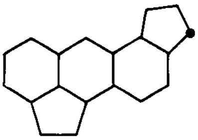

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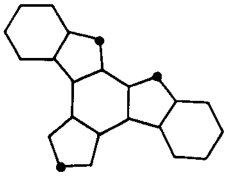

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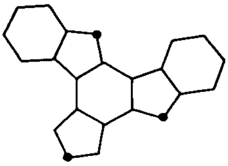

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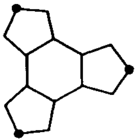

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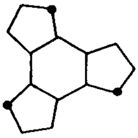

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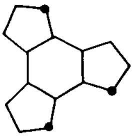

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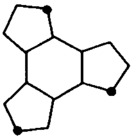

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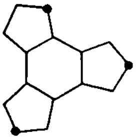

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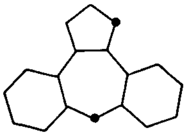

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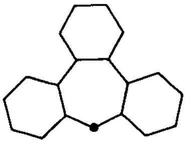

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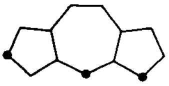

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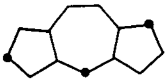

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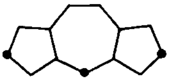

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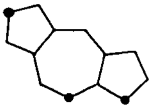

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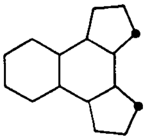

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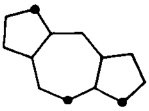

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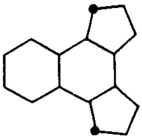

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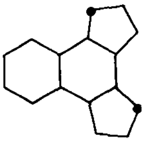

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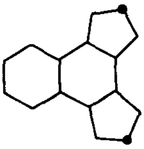

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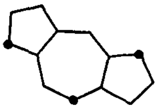

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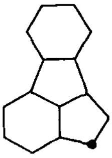

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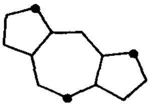

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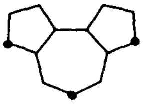

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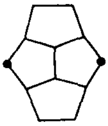

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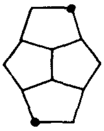

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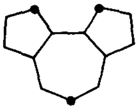

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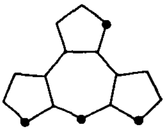

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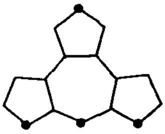

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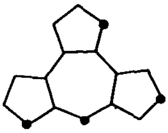
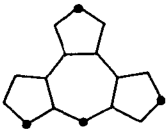
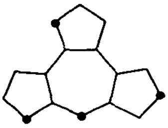


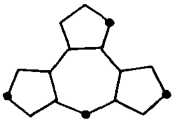
219



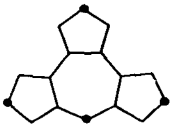
220



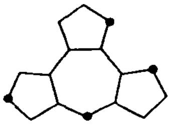
221



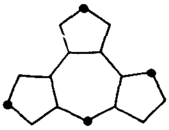
222



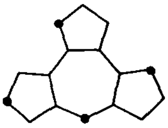
223



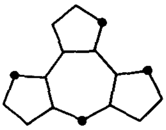
224



225



226



227

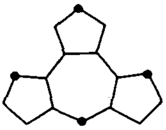


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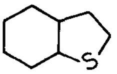
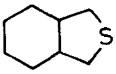
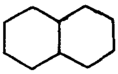
FIGURE 8 (*continued*)

benzo[b]thiophene, benzo[c]thiophene, and iso-π-electronic naphthalene:







illustrates that periphery is not a critical component. If it were, the two benzothiophenes should not differ markedly, (they have for our needs equivalent periphery). But they do differ, whether one makes the comparison within the Hückel MO approach of Hess and Schaad[25], the graphical approach of Knop, Trinajstić, and Živković[27], or the present graph theoretical approach based on the enumeration of conjugated circuits. This suggests that the peripheral model, popular, like HMO, for too long, is not likely to be of use even for qualitative discussions of heterocyclic systems, and ought to be replaced by the conjugated circuit model, which is capable of qualitative and quantitative predictions in the chemistry of conjugated systems, including in particular divalent sulfur compounds.

Acknowledgement Part of this work was carried out whilst one of us (NT) visited the Department of Chemistry, Wright State University, Dayton, Ohio. NT is grateful to his host Professor Vladimir Katović for support, hospitality, and many discussions on the (thermodynamic and kinetic) stability of conjugated molecules.

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