Journal of Molecular Structure (Theochem), 181 (1988) 111–140
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

ON THE AROMATIC STABILITIES OF THIOPHENE ANALOGUES OF HELICENES

MILAN RANDIĆ

Department of Mathematics and Computer Science, Drake University, Des Moines, Iowa 50311 and Ames Laboratory-DOE, Iowa State University, Ames, IA 50011 (U.S.A.)*

BENJAMIN M. GIMARC

Department of Chemistry, The University of South Carolina, Columbia, SC 29208 (U.S.A.)

SONJA NIKOLIĆ and NENAD TRINAJSTIĆ

The Rugjer Bošković Institute, P.O.B. 1016, 41001 Zagreb, Croatia (Yugoslavia)

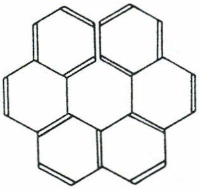
(Received 4 February 1988)

ABSTRACT

The conjugated circuits model is used to predict the relative aromatic stabilities of a variety of thia-helicenes, i.e., thiophene analogues of helicenes. All studied thia-helicenes are predicted to be aromatic structures. The parent helicenes are always found to be more aromatic than the corresponding daughter thia-helicenes. The theoretical predictions are supported by modest experimental evidence.

INTRODUCTION

Helicenes are angularly (*ortho*-) annelated benzenoid hydrocarbons which possess the symmetry of helix [1,2]. The first reported helicene was [6] helicene, hexahelicene (**1**) [3]. The complete series of [*N*]helicenes (*N*=the number of rings in the helicene) through [14]helicene has been synthesized [3–9].



1

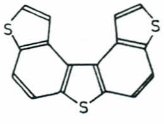
---

*Ames Laboratory is operated by Iowa State University for the U.S. Government-Department of Energy under the contract No. W-7405-ENG-82. This work was supported in part by the Office of the Director.

0166-1280/88/$03.50

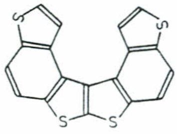
The name heterohelicenes has been applied to a class of helicenic structures formed from the *ortho*-fused benzenoids and five- or six-membered heterocyclic rings [1]. Thiophene analogues of [*N*]helicenes or thia-helicenes represent a subclass of heterohelicenes. They are the most studied heterohelicenes [1,2].

Several types of thia-helicenes are possible. Much work has been done on the series composed of alternating thiophene and benzene rings with thiophenes as the terminal rings [1,2]. As an example of a thiophene analogue of [5]-helicene, thia[5]helicene (**2**) [10] is shown below.



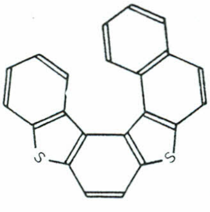
2

All members with up to 15 rings of this series are known [10,11]. In addition to the series of alternating thia-helicenes, a number of less regular fusions of benzene and thiophene rings have been prepared such as the thia[6]helicene **3** [12].

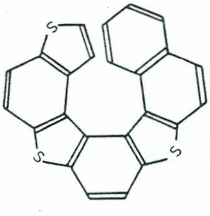


3

Another subclass of thia-helicenes contain beside the benzene moiety other benzenoids such as naphthalene and phenanthrene as building blocks. Already the first reported pair of thia-helicenes [13], thia[6]helicene(**4**) and thia[7]helicene(**5**) contain benzene and naphthalene as the hydrocarbon subunits.



4



5

There are several additional types of thia-helicenes, which will be considered later.

In the present work we will report on the application of a simple resonance-theoretic model, namely the conjugated circuits model [14,15] to thia-helicenes. Such an application will allow us to predict the relative aromatic stabilities of thia-helicenes. The aromatic stability of a conjugated system is its intrinsic stability against decomposition. The resonance energy (RE) is a convenient parameter that gives a measure of this intrinsic stability. RE is defined as the part of the molecular binding energy giving a deviation from the simple bond additivity. This extra stability present in some polycyclic conjugated systems is associated with the aromatic character of the compound, and one speaks of aromatic stability of polycyclic (heterocyclic) conjugated systems.

There are two fundamentally different approaches to molecular resonance energy and aromaticity: (a) use of quantum chemical computational methods that will produce numerical values for REs and (b) use of graph–theoretical and combinatorial methods that will give algebraic expressions for REs. The former will yield the values for RE of conjugated systems of interest, the latter only trends of RE. Nevertheless even without a knowledge of precise individual magnitudes of REs, the graph–theoretical approach based on the concept of conjugated circuits offers a theoretical model belonging to the latter approaches which is capable of answering many questions on molecular structure and aromaticity with considerable reliability [14–16].

The conjugated circuits model has already been rather successfully applied to a variety of polycyclic conjugated hydrocarbons [14,17–23], their ions [24,25], excited states of benzenoid hydrocarbons [26], Möbius systems [27], heterocyclic conjugated systems [28–31], and buckminsterfullerene and related carbon cages [32–35].

The structure of the article is as follows. First the conjugated circuits model and its extension to conjugated compounds containing divalent sulphur will be briefly presented. The next two sections will be devoted to the enumeration of Kekulé structures and conjugated circuits for thia-helicenes. The last section contains results (RE expressions and numerical values) and discussion on aromatic stabilities of thia-helicenes.

THE CONJUGATED CIRCUITS MODEL

The conjugated circuits model is a simple resonance-theoretic model which was introduced for studying conjugation and aromaticity in polycyclic conjugated molecules [14]. This model was motivated from an empirical point of view [14,17,18] elaborating Clar's ideas [36,37]. This model may also be reached from a more quantum chemical view [38–40] developing some of Pauling's resonance-theoretic ideas [41–45].

The conjugated circuit model is a graph–theoretical model which is based on Kekulé valence structures. Graph–theoretical analysis of Kekulé structures revealed that each Kekulé structure may be partitioned into several conjugated circuits. Conjugated circuit has been defined as a circuit within Kekulé valence structure in which there is a regular alternation of formal carbon–carbon single and double bonds. Thus, the conjugated circuits are necessarily of even length.

The circuit decomposition of individual Kekulé structures leads to $4n+2$ and/or $4n$ (n=integer) linearly independent, linearly dependent and disconnected circuits. The total number of all conjugated circuits within a single Kekulé valence structure is equal to $K-1$ [46], where K is the number of Kekulé structures for a conjugated molecule. Linearly independent circuits are those that cannot be represented by a superposition of conjugated circuits of smaller size. The $(4n+2)$ circuits are denoted by R_n, whilst the $4n$ circuits by Q_n.

The total π-electron resonance energy for a conjugated molecule M, within the conjugated circuits model, may be expressed in terms of R_n and/or Q_n quantities

$$\mathrm{RE(M)}=\frac{1}{K}\sum_n (a_n R_n + b_n Q_n) \qquad (1)$$

where K is the number of Kekulé structures for a molecule, R_n and Q_n are, respectively, the parametric values for the conjugated circuits of size $4n+2$ and $4n$ containing only carbon atoms, whilst a_n and b_n represent, respectively, the number of R_n and Q_n circuits for a given value of n. Only linear independent and linear dependent circuits are considered. The R_n quantities contribute towards the aromatic stability of a molecule. The Q_n quantities, on the other hand, have a negative effect on the aromatic stability of a molecule.

It is found that a larger molecule has, as a rule, a larger RE, because the deviations from bond additivities accumulate [47]. To eliminate the size effect, we consider RE per π-electron, RE/e, which is given as

$$\mathrm{RE}/e=\mathrm{RE}/N \qquad (2)$$

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

We have truncated the set of conjugated circuits at those of size fourteen ($n=3$) [16]. In considering only the smallest three conjugated circuits of types R_n and Q_n, we have followed the empirical findings that only the smallest circuits make appreciable contributions to the RE [38–40]. In principle, one could include higher terms, but the data needed for establishing the parameters are very scarce, especially for heterocyclic molecules. This then limits the extent of parametrization to the dominant conjugated circuits.

The numerical values of the R_n (n=1,2,3) parameters are obtained [14] from the parametrization procedure based on the SCF π-MO REs of Dewar and Llano [47]. The R_n (n=1,2,3) parameters are $R_1=0.869$ eV*, $R_2=0.247$ eV; $R_3=0.100$ eV.

The numerical values of the Q_n (n=1,2,3) parameters are obtained from the

---

*1 eV = 1.60219×10^{-19} J.

SCF π-MO RE of cyclobutadiene [48] and by utilizing the approximation [14,40,49]

$$Q_n = \frac{R_n}{R_1} Q_1 \tag{3}$$

The Q_n $(n=1,2,3)$ parameters are $Q_1 = -0.781$ eV; $Q_2 = -0.222$ eV; $Q_3 = -0.090$ eV.

There are two combinatorial problems connected with the application of the conjugated circuits model. The first is the enumeration and generation of Kekulé valence structures and the second is the enumeration of conjugated circuits. We will discuss both these problems in the following sections.

As an illustration of the conjugated circuits approach to conjugated hydrocarbons we consider phenanthrene. In Fig. 1 we give the Kekulé structures of phenanthrene and their circuit decomposition. The RE of phenanthrene is given by

$$\begin{aligned} \mathrm{RE(phenanthrene)} &= (10R_1 + 4R_2 + 2R_3)/5 \\ &= 2R_1 + 0.8R_2 + 0.4R_3 \\ &= 1.976 \text{ eV} \end{aligned} \tag{4}$$

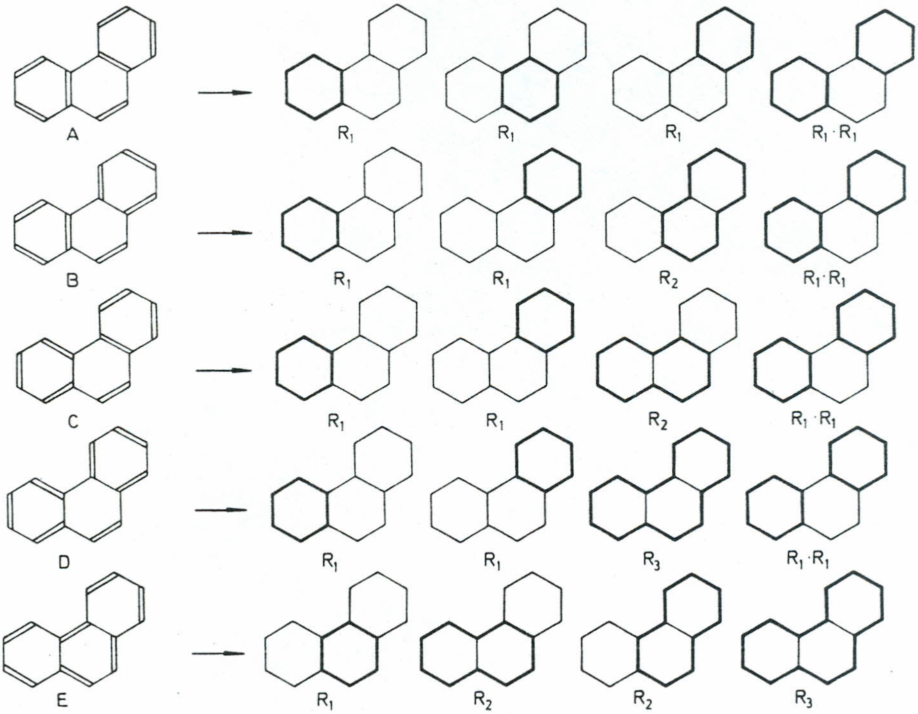


Fig. 1. Kekulé structures of phenanthrene and their circuit decomposition.

or $RE/e = 0.141$ eV. (5)

EXTENSION OF THE MODEL TO SYSTEMS CONTAINING DIVALENT SULPHUR

A divalent sulphur partly "interrupts" conjugation, because it only partly contributes its π-electrons to the pool of π-electrons delocalized overall the σ skeleton of the heterocycle. Since we consider only heterocycles containing divalent sulphur, the bonds adjacent to sulphur, i.e., the carbon–sulphur bonds, are formally single bonds. We can therefore imagine sulphur with its two π-electrons as formally equivalent to an isolated double bond "contracted" to a single atomic site. Actually we can always formally derive a heterocycle containing divalent sulphur from a conjugated hydrocarbon by replacing –HC=CH– with $-\ddot{S}-$ (Fig. 2).

In this way we can derive all thia-helicenes purely formally from helicenes. For example, thia-helicenes **2** and **3** may be derived from [5]helicene and [6]helicene, respectively, in the manner shown in Fig. 3.

On comparing polycyclic conjugated hydrocarbons and the corresponding heterocycles containing divalent sulphur, we observe a change in the number of Kekulé structures between the parent hydrocarbon and the daughter molecules. The parent hydrocarbon always possesses more Kekulé structures than the corresponding thia-derivative. For example, K(phenanthrene) = 5 and K(dibenzothiophene) = 4, K([5]helicene) and K(**2**) = 4, K([6]helicene) = 21 and K(**3**) = 4, etc.

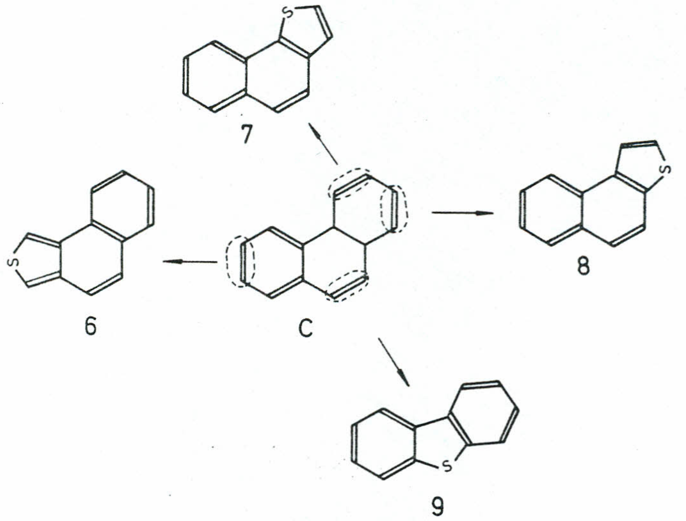
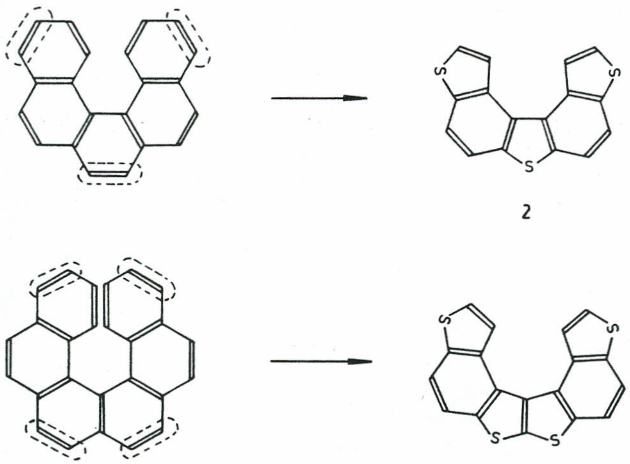


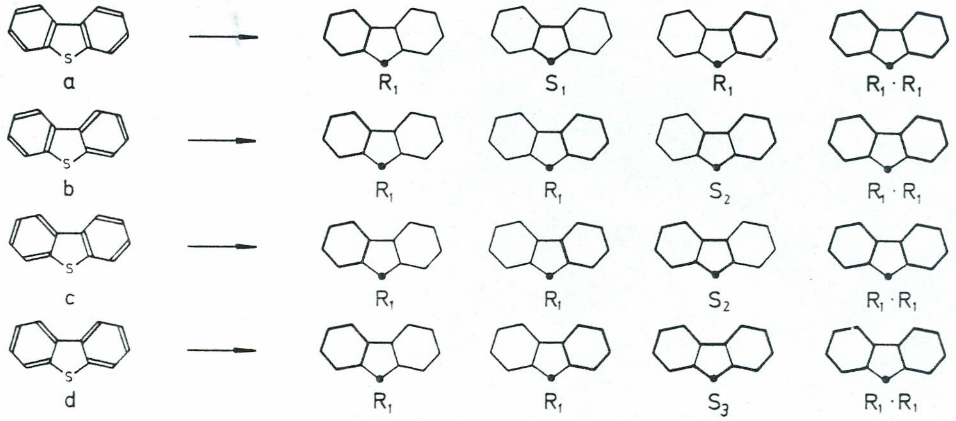
Fig. 2. Formal generation of the thia-phenanthrenes from phenanthrene by intrusion of the divalent sulphur instead of the ethylenic fragment into the desired position.



2

3

Fig. 3. Formal generation of thia-helicenes **2** and **3** from [5]helicene and [6]helicene.



TOTAL CIRCUIT DECOMPOSITION: $8R_1 + S_1 + 2S_2 + S_3 + 4R_1 \cdot R_1$

Fig. 4. The circuit decomposition of Kekulé structures of dibenzothiophene. The black dot denotes the position of the sulphur atom.

In order to illustrate the conjugated circuits of S-containing polycycles, we will consider dibenzothiophene. Dibenzothiophene may be viewed as formally derived from phenanthrene by replacing a CC double bond by an S atom (Fig. 2). The circuit decomposition of dibenzothiophene is given in Fig. 4. The $(4n+2)$ circuits containing carbon atoms and a sulphur atom are denoted by S_n.

The total number of all conjugated circuits (i.e., linearly independent, linearly dependent and disjoint circuits) for a given Kekulé structure of a thiahelicene is also equal to $K-1$, where K is the total number of Kekulé structures of the parent helicene. For example, [5]helicene possesses 13 Kekulé structures. Therefore, each Kekulé structure of the corresponding thia-helicene **2** must be decomposable into 12 conjugated circuits. This is shown for one Kekulé structure of thia[5]helicene(**2**) in Fig. 5. Note that the symbol $(SS)_3$ in Fig. 5 stands for $(4n+2)$ conjugated circuit with $n=3$ and two divalent sulphur atoms.

The resonance energies of thia-helicenes can be calculated from the following expression [31]

$$RE=\frac{1}{K}\sum_n (a_n R_n + c_n S_n) \tag{6}$$

where S_n is the parametric value for the $4n+2$ conjugated circuits containing the sulphur atom, c_n represents the number of S_n and the rest of symbols have their previous meaning.

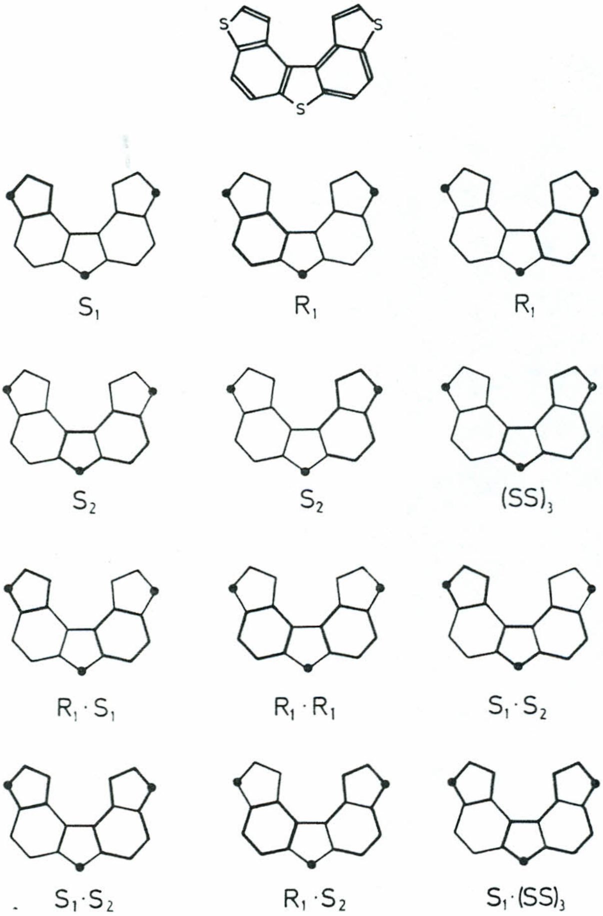


Fig. 5. All conjugated circuits in one Kekulé structure of **2**. Black dots denote the positions of the sulphur atom.

The numerical values for S_n ($n=1,2,3$) parameters are obtained from the SCF π-MO RE of thiophene [50] and by applying the approximation [28,31,49]

$$S_n = \frac{R_n}{R_1} S_1 \tag{7}$$

The S_n parameters are $S_1=0.282$ eV; $S_2=0.080$ eV; $S_3=0.030$ eV. As an example we calculated the RE of dibenzothiophene

$$\begin{aligned} \mathrm{RE(dibenzothiophene)} &= (8R_1+S_1+2S_2+S_3)/4 \\ &= 1.856 \text{ eV} \end{aligned} \tag{8}$$

or

$$\mathrm{RE}/e = 0.133 \text{ eV} \tag{9}$$

Dibenzothiophene is predicted to be aromatic, though less aromatic than the parent hydrocarbon phenanthrene. This is in agreement with other theoretical studies [51] and experimental facts [52,53].

THE KEKULÉ STRUCTURE COUNTS

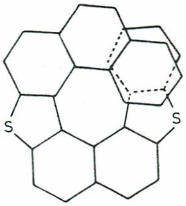
A simple formula may be used for the Kekulé structure counts K for the thiophene analogues of [N]helicenes

$$K = \prod_i K_i \tag{10}$$

where K_i are the Kekulé counts for the benzenoid fragments in the molecule.

Thia-helicenes containing benzenoid fragments

Thia[8]helicene **10** is an example of this class of thia-helicenes.

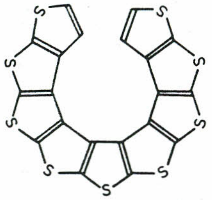


10

Thia-helicene **10** consists of two thiophene moieties ($K=1$) and three benzenoid fragments: benzene ($K=2$), naphthalene ($K=3$) and phenanthrene ($K=5$). Therefore, the Kekulé structure count for **10** is given by the product: $K=2\cdot1\cdot3\cdot1\cdot5=30$.

Thia-helicenes consisting of only thiophene rings

An example of such a thia-helicene is structure **11**.



11

Thia-helicenes such as **11** possess necessarily only one Kekulé structure as shown above.

Regular thia-helicenes

We refer to thia-helicenes composed of alternating thiophene and benzene rings as regular thia[N]helicenes. The Kekulé structure count for this class of thia-helicenes is given by

$$K=2^{B} \tag{11}$$

where B is the number of benzene rings in the regular thia-helicene.

Regular thia-helicenes can be classified as: (a) regular thia-helicenes which have the same number of benzene (B) and thiophene (T) rings and (b) regular thia-helicenes which have the different number of benzene and thiophene rings. Consequently the end-rings are either benzene and thiophene (a) or both end-rings are either benzenes (b_1) or thiophenes (b_2). The corresponding three classes possess the following molecular formulae: (a) $C_{3N+2}H_{N+2}S_{\frac{1}{2}N}$, ($b_1$) $C_{3N+3}H_{N+5}S_{\frac{1}{2}(N-1)}$ and (b_2) $C_{3N+1}H_{N+3}S_{\frac{1}{2}(N+1)}$, where N=the number of rings in thia-helicene.

THE CONJUGATED CIRCUITS COUNT

In most cases thia-helicenes must be treated individually. The conjugated circuits count depends on the number of benzenoid and thiophene rings, the number of Kekulé structures and the end-rings of a thia-helicene. However, some regularities do appear in the counts of the conjugated circuits for regular thia[N]helicenes. If we consider the regular thia[N]helicenes consisting of benzene and thiophene fragments, then the expressions for counting R_1, S_1, S_2 and S_3 circuits are available. The count of the R_1 circuits is related to the Kekulé structure count (K) and the number of benzene fragments (B) in the regular thia-helicene

$$\text{Count of the } R_1 \text{ circuits} = KB \tag{12}$$

The count of the S_n ($n=1,2,3$) circuits is related to the Kekulé counts and the number of thiophene rings in the regular thia[N]helicene. The enumeration of the S_1 circuits depends on the type of the regular thia[N]helicene. The counting formulae for the S_1 circuits are given by

(i) a-type regular thia[N]helicenes

Count of the S_1 circuits $=\frac{1}{4}K(T+1)$ (13)

(ii) b_1-type regular thia[N]helicenes

Count of the S_1 circuits $=\frac{1}{4}KT$ (14)

(iii) b_2-type regular thia[N]helicenes

Count of the S_1 circuits $=\frac{1}{4}K(T+2)$ (15)

The number of the S_2 circuits is given by

Count of the S_2 circuits $=\frac{1}{2}KT$. (16)

Finally, the counting formulae for the S_3 circuits depend also on the type of the regular thia[N]helicene

(i) a-type regular thia[N]helicenes

Count of the S_3 circuits $=\frac{1}{4}K(T-1)$ (17)

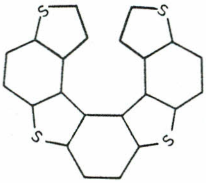
(ii) b_1-type regular thia[N]helicenes

Count of the S_3 circuits $=\frac{1}{4}KT$ (18)

(iii) b_2-type regular thia[N]helicenes

Count of the S_3 circuits $=\frac{1}{4}K(T-2)$ (19)

As an example we will give the conjugated circuits count for the regular b_2-type thia[7]helicene **12**.



12

The circuits count for **12** can be obtained by means of expressions (8), (11), (12) and (15) collected together below

$$KBR_1+\tfrac{1}{4}K(T+2)S_1+\tfrac{1}{2}KTS_2+\tfrac{1}{4}K(T-2)S_3 \quad (20)$$

and by introducing $K=8$, $B=3$ and $T=4$

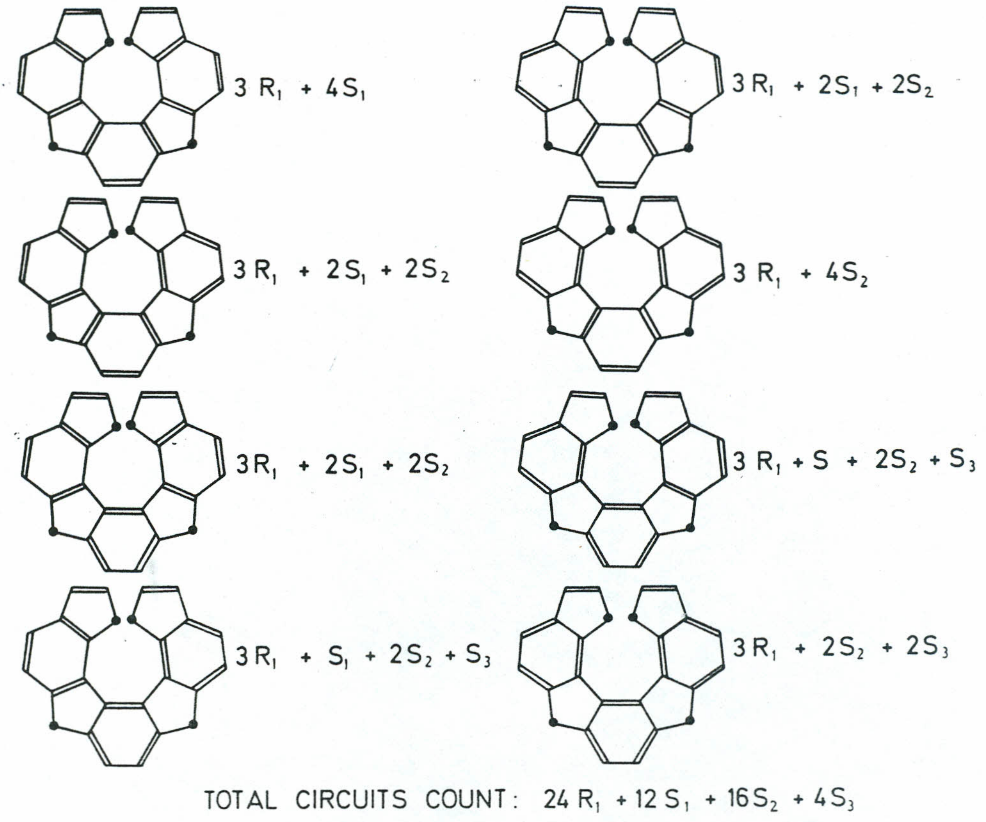


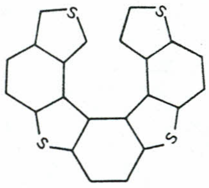
Fig. 6. The conjugated circuits count for the regular thia[6]helicene **12**. The black dots denote the positions of the sulphur atoms.

$$24R_1+12S_1+16S_2+4S_3 \tag{21}$$

This result is checked by the direct construction of Kekulé structures of **12** and the enumeration of conjugated circuits by hand. This is shown in Fig. 6. Both sets of results match as expected.

In the enumeration disjoint conjugated circuits and circuits containing two or more sulphur atoms are neglected because their contributions are negligible [14,31].

In Fig. 7 we give the conjugated circuits count for another thia[7]helicene (**13**) which is a positional isomer of **12**.



13

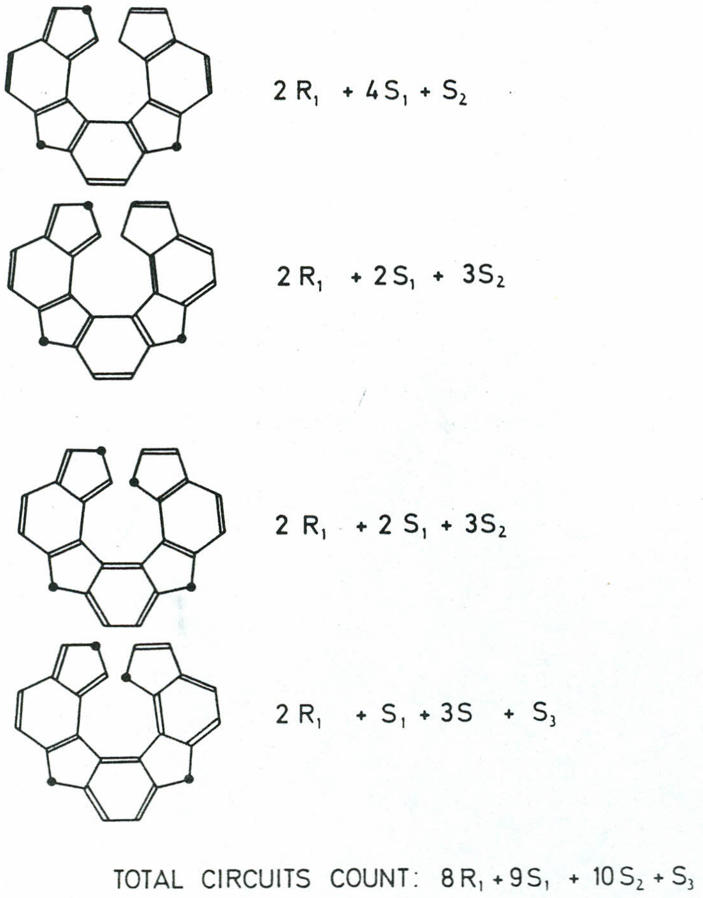


Fig. 7. The conjugated circuits count for the thia[7]helicene **13**. The black dots denote the positions of the sulphur atoms.

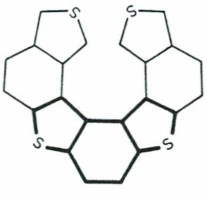
Positional isomers **12** and **13** differ only in the position of one sulphur. This change of the position of one sulphur atom also causes the change in the number of Kekulé structures and consequently in the number of conjugated circuits. The conjugated circuits count for such structures is equal to the count of conjugated circuits for a thia[$N-2$]helicene, i.e., a thia-helicene without the benzo[c]thiophene fragment, plus $2^K(S_1+S_2)$, where K is the Kekulé count for the thia[N]helicene.

We see that the circuits count for **13** is, according to the above given by the expression

$$\text{Circuits count for } \mathbf{13} = \text{Circuits count for } \mathbf{2} + 4(S_1+S_2)$$

$$= 8R_1 + 9S_1 + 10S_2 + S_3 \tag{22}$$

The two benzo[c]thiophene fragments could be attached to both ends of a regular b_2-type thia-helicene producing another positional isomer of **12**: thia[7]helicene **14**.



14

The conjugated circuits count for this type of structures is identical to the circuits count for a thia[$N-4$]helicene, i.e., a thia-helicene without two benzo[*c*]thiophene fragments plus $2^K(S_1+S_2)$. Therefore, the conjugated circuits count for **14** is then reduced to the circuits count for the thia[3]helicene **14a** (the structure **14a** is embedded in **14** and denoted by thicker lines) plus $4(S_1+S_2)$

Circuits count for **14** = Circuits count for **14a** $+4(S_1+S_2)$

$$=2R_1+6S_1+6S_2 \tag{23}$$

The circuits count for **14a** is $2(R_1+S_1+S_2)$.

If we compare the RE expression for these three positional isomers

$$\mathrm{RE}(\mathbf{12})=(24R_1+12S_1+16S_2+4S_3)/8$$

$$=3R_1+1.5S_1+2S_2+0.5S_3 \tag{24}$$

$$\mathrm{RE}(\mathbf{13})=(8R_1+9S_1+10S_2+S_3)/4$$

$$=2R_1+2.25S_1+2.5S_2+0.25S_3 \tag{25}$$

$$\mathrm{RE}(\mathbf{14})=(2R_1+6S_1+6S_2)/2$$

$$=R_1+3S_1+3S_2 \tag{26}$$

We can immediately predict their stability order (**12** > **13** > **14**) if we express S_1, S_2 and S_3 in terms of R_1 ($S_1=0.325R_1$, $S_2=0.092R_1$, $S_3=0.037R_1$). Thia[7]helicenes **13** and **14** are destabilized by the presence of the benzo[*c*]thiophene fragments causing a decrease in the number of Kekulé structures for the thia-helicene and consequently the loss of R_1 contributions to the RE arising from the conjugation within the individual benzene rings.

RESULTS AND DISCUSSION

Diagrams of regular thia[*N*]helicenes having the same (even-membered regular thia[*N*]helicenes) or different (odd-membered regular thia[*N*]heli-

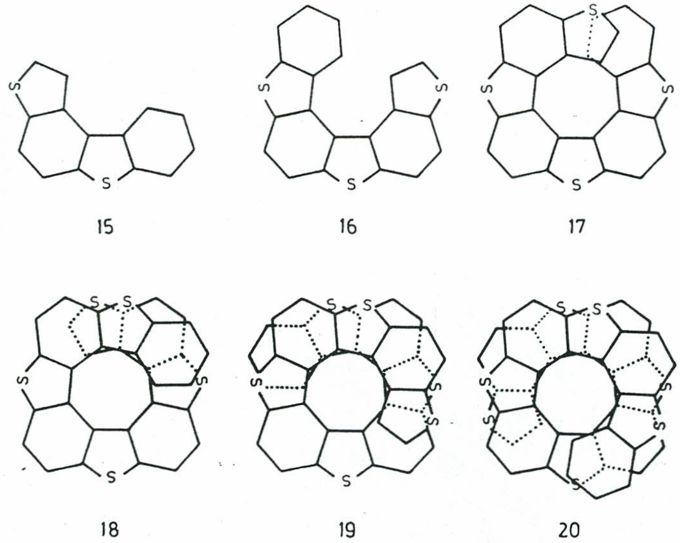


Fig. 8. Diagrams of even-membered (a-type) regular thia[N]helicenes $C_{3N+2}H_{N+2}S_{\frac{1}{2}N}$.

cenes) number of benzene and thiophene rings are given, respectively, in Fig. 8 (the a-type thia-helicenes), Fig. 9 (the b_1-type thia-helicenes) and Fig. 10 (the b_2-type thia-helicenes).

The resonance energy expressions for these thia-helicenes are derived from the following master formulae

(i) a-type regular thia[N]helicenes

$$\mathrm{RE}=[K\cdot B\cdot R_1+\tfrac{1}{4}K(T+1)S_1+\tfrac{1}{2}K\cdot T\cdot S_2+\tfrac{1}{4}K(T-1)S_3]/K \qquad (27)$$

(ii) b_1-type regular thia[N]helicenes

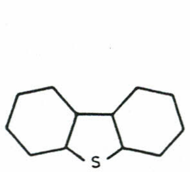
$$\mathrm{RE}=(K\cdot B\cdot R_1+\tfrac{1}{4}K\cdot T\cdot S_1+\tfrac{1}{2}K\cdot T\cdot S_2+\tfrac{1}{4}K\cdot T\cdot S_3)/K \qquad (28)$$

(iii) b_2-type regular thia[N]helicenes

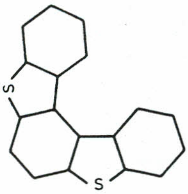
$$\mathrm{RE}=[K\cdot B\cdot R_1+\tfrac{1}{4}K(T+2)S_1+\tfrac{1}{2}K\cdot T\cdot S_2+\tfrac{1}{4}K(T-2)S_3]/K \qquad (29)$$

The explicit RE expressions and the numerical values of the REs for the above three types of regular thia[N]helicenes are reported in Tables 1–3.

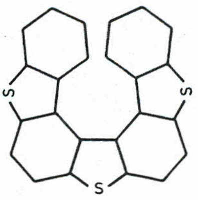
All regular thia[N]helicenes have high values of the RE and thus it appears that all of them should possess a considerable aromatic character. One would then expect a number of these compounds to be known. It is therefore surprising that only a few regular thia[N]helicenes are prepared and most of these are those of the b_2-type [1,2,10]. If we consider as a theoretical index of aromaticity RE/e, then we observe that this quantity rather slowly diminishes with the size increase in the a-type and b_1-type regular thia[N]helicenes. The



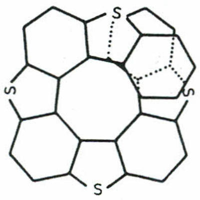
21



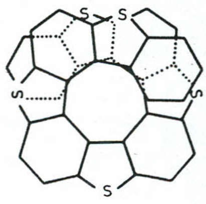
22



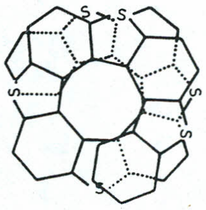
23



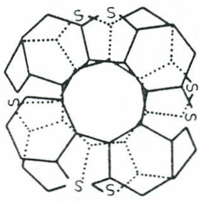
24



25



26



27

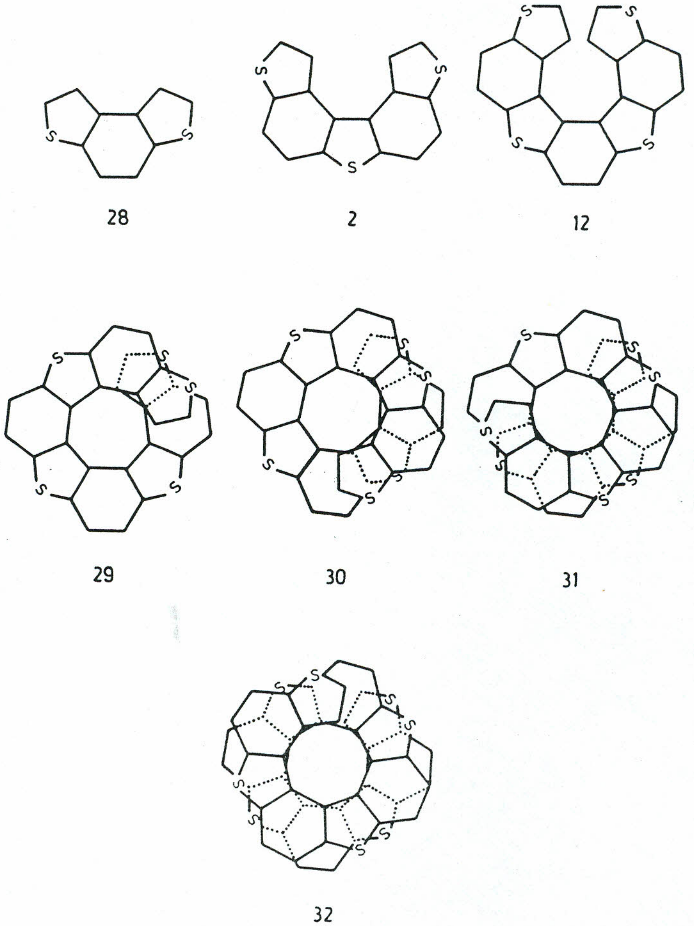
Fig. 9. Diagrams of odd-membered (b-type) regular thia[N]helicenes $C_{3N+3}H_{N+5}S_{\frac{1}{2}(N-1)}$.

opposite is true in the case of the b_2-type regular thia[N]helicenes: the RE/e values increase with the size.

Since all the studied thia[N]helicenes are regular structures, the members of each class differ amongst themselves for well-defined structural fragments; the RE difference between the successive members of the class is constant (ΔRE$=1.137R_1$ or 0.988 eV). Thus, if we know the value of the RE for the first member in the class, we can immediately derive the RE values for the other members by means of the formulae

$$\mathrm{RE}(N+1)=\mathrm{RE}(N)+0.988\ \mathrm{eV} \tag{30}$$

The difference in the REs between the related members in two classes of regular thia[N]helicenes having odd number of rings (class $C_{3N+3}H_{N+5}S_{\frac{1}{2}(N-1)}$ and class $C_{3N+1}H_{N+3}S_{\frac{1}{2}(N+1)}$) is also constant ($\Delta$RE$=0.719R_1$ or 0.624 eV).


28 2 12

29 30 31

32

Fig. 10. Diagrams of odd-membered (b_2-type) regular thia[N]helicenes $C_{3N+1}H_{N+3}S_{\frac{1}{2}(N+1)}$.

Thus, if we know the RE of a given member of class $C_{3N+3}H_{N+5}S_{\frac{1}{2}(N-1)}$, we immediately know the RE of the related member of class $C_{3N+1}H_{N+3}S_{\frac{1}{2}(N+1)}$, because of the relationship

$$\mathrm{RE}(C_{3N+3}H_{N+5}S_{\frac{1}{2}(N-1)}) = \mathrm{RE}(C_{3N+1}H_{N+3}S_{\frac{1}{2}(N+1)}) + 0.624 \text{ eV} \tag{31}$$

The parent [N]helicenes are always more stable than the corresponding daughter thia[N]helicenes. The resonance energies of [N]helicenes are reported in Table 4. Formulae for counting the Kekulé structures, conjugated circuits and resonance energies of helicenes are given elsewhere [22,54,55].

There is a nearly constant increase of ΔRE = 0.59 eV between the two members of the series, which indicates that the higher [N]helicenes should be increasingly stabilized. Therefore, the RE of the [$N+1$]helicene may be obtained

TABLE 1

Resonance energies of even-membered (a-type) regular thia[N]helicenes $C_{3N+2}H_{N+2}S_{\frac{1}{2}N}$

Molecule[a]	K[b]	Resonance energy		RE/e (eV)	Reference to preparative work
		Expression[c]	Numerical value (eV)		
15	4	$1/4(8R_1+3S_1+4S_2+S_3)=2.346R_1$	2.038	0.113	
16	8	$1/8(24R_1+8S_1+12S_2+4S_3)=3.483R_1$	3.026	0.116	[76,77]
17	16	$1/16(64R_1+20S_1+32S_2+12S_3)=4.619R_1$	4.014	0.118	
18	32	$1/32(160R_1+48S_1+80S_2+32S_3)=5.756R_1$	5.002	0.119	
19	64	$1/64(384R_1+112S_1+192S_2+80S_3)=6.893R_1$	5.990	0.120	
20	128	$1/128(896R_1+256S_1+448S_2+192S_3)=8.030R_1$	6.978	0.120	

[a] Labels correspond to structures in Fig. 8. [b] K=the number of Kekulé structures. [c] $S_1=0.326R_1$, $S_2=0.092R_1$, $S_3=0.037R_1$.

TABLE 2

Resonance energies of odd-membered (b_1-type) regular thia[N]helicenes with end-rings benzenes $C_{3N+3}H_{N+5}S_{\frac{1}{2}(N-1)}$

Molecule[a]	K[b]	Resonance energy		RE/e (eV)	Reference to preparative work
		Expression[c]	Numerical value (eV)		
21	4	$1/4(8R_1+S_1+2S_2+S_3)=2.137R_1$	1.857	0.133	[78,79]
22	8	$1/8(24R_1+4S_1+8S_2+4S_3)=3.274R_1$	2.845	0.129	
23	16	$1/16(64R_1+12S_1+24S_2+12S_3)=4.410R_1$	3.873	0.128	
24	32	$1/32(160R_1+32S_1+64S_2+32S_3)=5.547R_1$	4.820	0.127	
25	64	$1/64(384R_1+80S_1+160S_2+80S_3)=6.684R_1$	5.808	0.1263	
26	128	$1/128(896R_1+192S_1+384S_2+192S_3)=7.821R_1$	6.796	0.1259	
27	256	$1/256(2048R_1+448S_1+896S_2+448S_3)=8.957R_1$	7.784	0.1255	

[a] Labels correspond to structures in Fig. 9. [b] K=the number of Kekulé structures. [c] $S_1=0.326R_1$, $S_2=0.092R_1$, $S_3=0.037R_1$.

from the RE of the [N]helicene by

$$\mathrm{RE}([N+1]\mathrm{helicene})=\mathrm{RE}([N]\mathrm{helicene})+0.59\ \mathrm{eV} \qquad (32)$$

The comparison of the relative aromatic stabilities between the helicenes and the corresponding thia-helicenes, given by the difference in their RE values, indicate the increase in the stability of higher helicenes.

TABLE 3

Resonance energies of odd-membered regular (b_2-type) thia[*N*]helicenes with end-ring thiophenes $C_{3N+1}H_{N+3}S_{\frac{1}{2}(N+1)}$

Molecule[a]	K[b]	Resonance energy		RE/*e* (eV)	Reference to preparative work
		Expression[c]	Numerical value (eV)		
28	2	$1/2(2R_1+2S_1+2S_2)=1.418R_1$	1.232	0.088	[76,80]
2	4	$1/4(8R_1+5S_1+6S_2+S_3)=2.555R_1$	2.220	0.101	[81]
12	8	$1/8(24R_1+12S_1+16S_2+4S_3)=3.692R_1$	3.208	0.107	[77,81,82]
29	16	$1/16(64R_1+28S_1+40S_2+12S_3)=4.828R_1$	4.196	0.110	[82]
30	32	$1/32(160R_1+64S_1+96S_2+32S_3)=5.965R_1$	5.184	0.113	[82]
31	64	$1/64(384R_1+144S_1+224S_2+80S_3)=7.102R_1$	6.171	0.114	[82]
32	128	$1/128(896R_1+320S_1+512S_2+192S_3)=8.239R_1$	7.159	0.1155	[82]

[a] Numbers correspond to structures in Fig. 10. [b] K = the number of Kekulé structures. [c] $S_1=0.236R_1$, $S_2=0.092R_1$, $S_3=0.037R_1$.

TABLE 4

Resonance energies of [*N*]helicenes

[*N*]helicene	K[a]	Resonance energy expression[b]	RE (eV)	RE/*e* (eV)	Reference to preparative work
[3][c]	5	$(10R_1+4R_2+2R_3)/5$	1.976	0.1411	[83]
[4][d]	8	$(20R_1+10R_2+4R_3)/8$	2.531	0.1406	[84]
[5][e]	13	$(40R_1+20R_2+10R_3)/13$	3.131	0.1423	[85]
[6]	21	$(76R_1+40R_2+20R_3)/21$	3.711	0.1427	[86]
[7]	34	$(142R_1+76R_2+40R_3)/34$	4.299	0.1433	[87]
[8]	55	$(260R_1+142R_2+76R_3)/55$	4.884	0.1436	[88]
[9]	89	$(470R_1+260R_2+142R_3)/89$	5.470	0.1439	[89]
[10]	144	$(840R_1+470R_2+260R_3)/144$	6.056	0.1442	[90]
[11]	233	$(1488R_1+840R_2+470R_3)/233$	6.642	0.1444	[91]
[12]	377	$(2616R_1+1488R_2+840R_3)/377$	7.228	0.1446	[91]
[13]	610	$(4570R_1+2616R_2+1488R_3)/610$	7.814	0.1447	[92]
[14]	987	$(7940R_1+4570R_2+2616R_3)/987$	8.399	0.1448	[91]
[15]	1597	$(13730R_1+7940R_2+4570R_3)/1597$	8.985	0.1449	Unknown

[a] K = the number of Kekulé structures. [b] The RE expressions are taken from M. Randić, B. M. Gimarc and N. Trinajstić, Croat. Chem. Acta, 59 (1986) 345, and M. Randić, B. M. Gimarc, S. Nikolić and N. Trinajstić, Gazz. Chim. Ital., in press. [c] Phenanthrene. [d] 3,4-Benzo-phenanthrene. [e] 3,4,5,6-Dibenzo-phenanthrene.

(a) N=even

[N]helicene vs. thia[N]helicene $C_{3N+2}H_{N+2}S_{\frac{1}{2}N}$	ΔRE(eV)
[4]	0.493
[6]	0.685
[8]	0.870
[10]	1.054
[12]	1.238
[14]	1.421

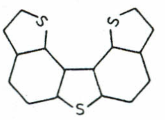
(b) N=odd

[N]helicene vs. thia[N]helicene $C_{3N+3}H_{N+5}S_{\frac{1}{2}(N-1)}$	ΔRE(eV)
[3]	0.119
[5]	0.286
[7]	0.426
[9]	0.650
[11]	0.834
[13]	1.018
[15]	1.201

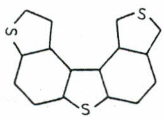
[N]helicene vs. thia[N]helicene $C_{3N+1}H_{N+3}S_{\frac{1}{2}(N+1)}$	ΔRE(eV)
[3]	0.744
[5]	0.911
[7]	1.091
[9]	1.274
[11]	1.458
[13]	1.643
[15]	1.826

This also reveals that class b_1 is the closest in aromatic stability to helicenes, whilst class b_2 is very different from the hydrocarbon helicenes. This is related to the fact that thiophene is less aromatic than benzene [36,37,47,48,50,51,56–59]. Therefore, whenever we replace a benzene ring with a thiophene ring, we produce a less stable structure.

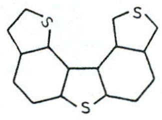
Let us also mention that there are possible three positional isomers of each regular a-type thia[N]helicene and six of each regular b_2-type thia[N]helicene. For, example, thia-helicene **2** has five positional isomers



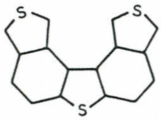
33



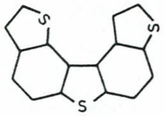
34



35

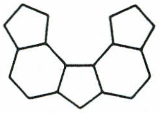


36



37

If we consider the underlying structure



and select various sites on the terminal rings to populate with sulphur atoms, we find that some symmetry non-equivalent sites give rise to the same count of Kekulé structures and consequently the same count of conjugated circuits. Let us consider a pair of such sites on the structure above

We refer to sites labelled by α and β as a pair of isoconjugated positions. If sites α and β are populated by S, the corresponding positional isomers have identical number of Kekulé valence structures, the counts of conjugated circuits and resonance energies. Thus in the above set of positional isomers the following are isoconjugated structures: **2, 33, 37** and **34, 35**.

The resonance energies for the positional isomers **2** and **33–37** are as follows

$$\mathrm{RE}(\mathbf{2}) = \mathrm{RE}(\mathbf{33}) = \mathrm{RE}(\mathbf{37}) = (24R_1 + 12S_1 + 16S_2 + 4S_3)/4 = 2.220\ \mathrm{eV} \tag{33}$$

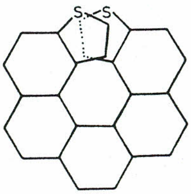
$$\mathrm{RE}(\mathbf{34}) = \mathrm{RE}(\mathbf{35}) = (2R_1 + 4S_1 + 4S_2)/2 = 1.593\ \mathrm{eV} \tag{34}$$

$$\mathrm{RE}(\mathbf{36}) = 3S_1 + 2S_2 = 1.006\ \mathrm{eV} \tag{35}$$

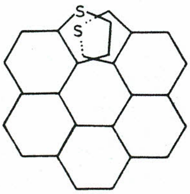
According to their REs we can order this set of thia-helicenes in the following way:

$$\mathbf{2} = \mathbf{33} = \mathbf{37} > \mathbf{34} = \mathbf{35} > \mathbf{36} \tag{36}$$

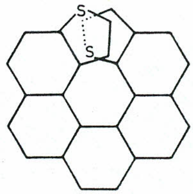
Thia-helicenes **34** and **35** contain one benzo[*c*]thiophene unit, whilst **36** contains two. Benzo[*c*]thiophene is considerably less aromatic than benzo[*b*]thiophene [29,31,50,51,56–59] and thus, it is bringing destabilization to thia-helicenes. Therefore, benzo[*c*]thiophene structural units are responsible for the lower stabilities of **34, 35** and **36** in comparison with isomers **2, 33** and **37**. This finding is of general validity. Whenever the benzo[*c*]thiophene (or related quinoid-type structures) appears as a substructural unit, the thia-helicene containing it is always less stable than its positional isomer free of it. As a consequence we can always order the positional isomers of a given thia-helicene system by inspecting only their structures. To illustrate this point further we give the positional isomers of thia-helicene **38** and their stability order.



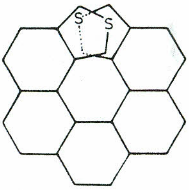
38



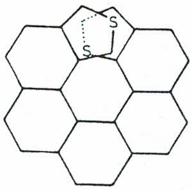
39



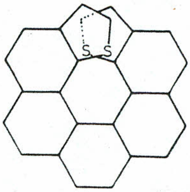
40



41



42



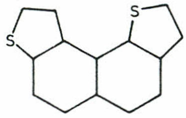
43

$$\mathbf{38}=\mathbf{40}=\mathbf{43}>\mathbf{39}=\mathbf{42}>\mathbf{41} \qquad (37)$$

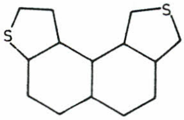
This order follows the count of the R_1 circuits which bring the greatest contribution to the RE of molecule.

Positional isomer $C_{26}H_{14}S_2$	Count of the R_1 circuits normalized by the Kekulé count
38	$40R_1/13=3.076R_1$
40	$40R_1/13=3.076R_1$
43	$40R_1/13=3.076R_1$
39	$20R_1/8\ \ =2.500R_1$
42	$20R_1/8\ \ =2.500R_1$
41	$10R_1/5\ \ =2R_1$

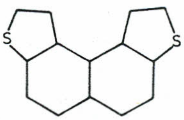
There is practically no experimental work available on either of the two sets of positional isomers (**2, 33–36** and **38–43**) considered above. Amongst these only one thia-helicene is known, i.e. **2** [10]. However, some limited experimental evidence exists for other families of positional isomers of thia-helicenes. For example, out of the following six positional isomers of thia[4]helicene **44**, the three most stable have been synthesized.



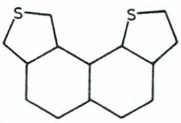
44



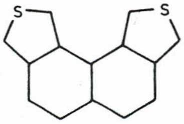
45



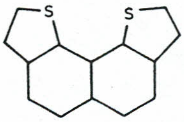
46



47



48



49

The predicted stability order is

$$\mathbf{44}=\mathbf{46}=\mathbf{49}>\mathbf{45}=\mathbf{48}>\mathbf{47} \tag{38}$$

Isomers **44, 46** and **49** are known [60–62], whilst the other, less stable ones, as yet are unknown.

In Fig. 11 we give diagrams of thia[N]helicenes consisting exclusively of thiophene rings. Since this class of thia[N]helicenes represents highly regular structures, the formula for computing their resonance energies is rather simple

$$\mathrm{RE}=NS_1=0.282N \tag{39}$$

Therefore, the above class of thia-helicenes also contains aromatic systems, though less stable than the regular thia[N]helicenes or parent [N]helicenes. It is somewhat surprising that no attempt to prepare a compound in this family of aromatic thia-helicenes has been reported to our knowledge except for the first two members [60,63] thiophene and thieno[2,3-*b*]thiophene.

We conclude with a report on some known and unknown miscellaneous thia-helicenes (Fig. 12). Resonance energies of thia-helicenes in Fig. 12 are reported in Table 5. All molecules in Fig. 12 are predicted to be aromatic. Their degrees of aromaticity are related to the presence of the benzenoid hydrocarbon parts. Thus, the most aromatic are predicted to be **10** and **74**. It is surprising that neither of these two molecules has been prepared.

A good example to illustrate how important the benzenoid hydrocarbon part for the aromaticity of thia-helicenes is the comparison between the three isomeric thia[5]helicenes **63, 75** and **76**

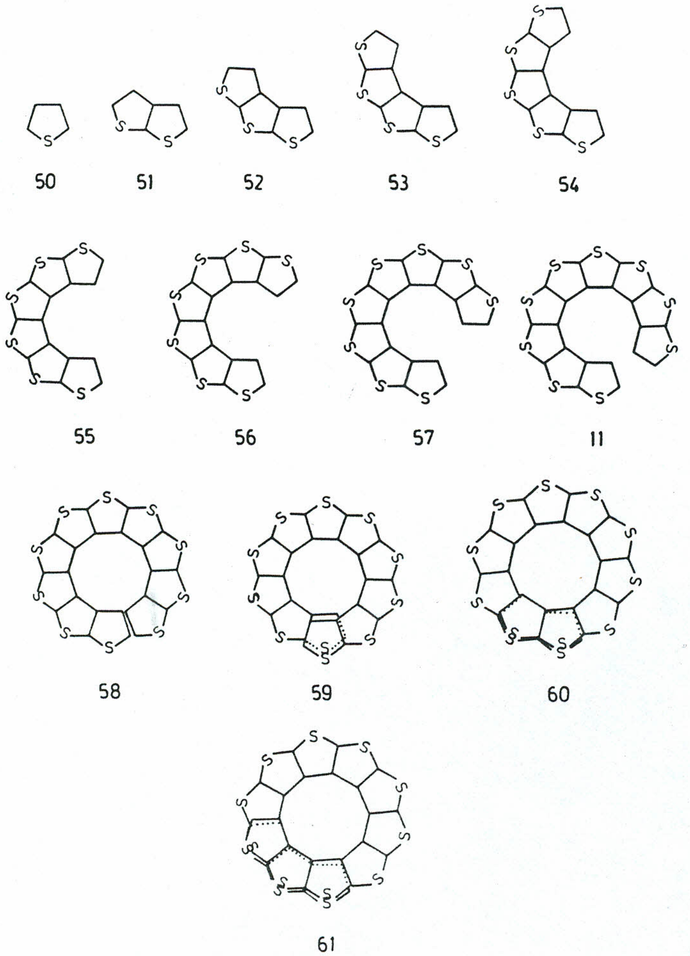
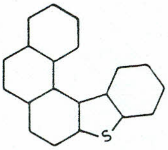


Fig. 11. Thia-helicenes consisting of thiophene rings only.



75

$$\mathrm{RE}(\mathbf{75}) = (30R_1 + 8R_2 + 4R_3 + 3S_1 + 5S_2 + 3S_3)/10$$

$$= 3.428\ R_1 = 2.979\ \mathrm{eV} \qquad (40)$$

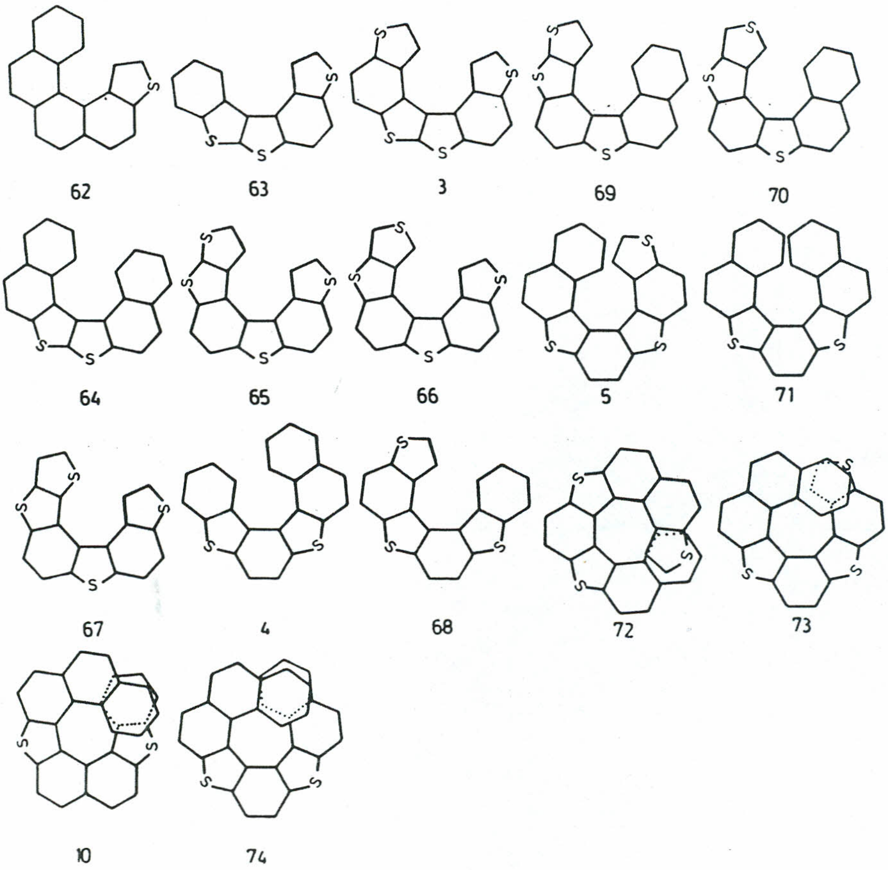
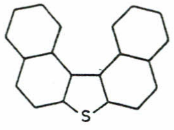


Fig. 12. Diagrams of some miscellaneous thia-helicenes.



76

$$\mathrm{RE}(\mathbf{76}) = (24R_1 + 12R_2 + 4S_1 + 4S_2 + 5S_3)/9$$

$$= 3.241R_1 = 2.816\ \mathrm{eV} \qquad (41)$$

The most stable is predicted to be the structure containing a benzene fragment in accordance with empirical observation by Armit and Robinson [64], Fries [65,66], Clar [36,37], and others [67,68] that structures possessing the greatest number of benzene and benzene-like rings (e.g., terminal rings in phenanthrene) [69] are the most stable. The count of benzene and benzene-like rings is given in terms of the R_1 circuits. The stability order **75** > **76** > **63**

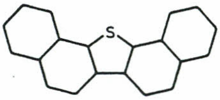
TABLE 5

Resonance energies of miscellaneous thia-helicenes

Molecule[a]	K[b]	Resonance energy		RE/e (eV)	Reference to preparative work
		Expression[c]	Numerical value (eV)		
62	8	$(20R_1+10R_2+4R_3+5S_1+3S_2+2S_3)/8=3.160R_1$	2.476	0.125	[93]
63	4	$(8R_1+6S_1+6S_2)/4=2.627R_1$	2.283	0.104	
3	4	$(8R_1+8S_1+8S_2)/4=2.836R_1$	2.464	0.095	[94]
64	9	$(24R_1+12R_2+11S_1+7S_2+7S_3)/9=3.544R_1$	3.080	0.118	
65	4	$(8R_1+9S_1+6S_2+S_3)/4=2.881R_1$	2.503	0.096	
66	4	$(8R_1+7S_1+4S_2+S_3)/4=2.672R_1$	2.322	0.089	
67	4	$(8R_1+9S_1+6S_2+S_3)/4=2.881R_1$	2.503	0.096	
4	12	$(40R_1+8R_2+7S_1+12S_2+7S_3)/12=3.826R_1$	3.325	0.128	[77,95]
68	8	$(24R_1+8S_1+12S_2+4S_3)/8=3.483R_1$	3.026	0.116	
69	6	$(14R_1+4R_2+11S_1+6S_2+S_3)/6=3.219R_1$	2.797	0.108	[77]
70	6	$(14R_1+4R_2+8S_1+3S_2+S_3)/6=3.010R_1$	2.615	0.101	
5	12	$(40R_1+8R_2+13S_1+18S_2+7S_3)/12=4.035R_1$	3.507	0.117	[76,80,95]
71	18	$(66R_1+24R_2+12S_1+17S_2+12S_3)/18=4.374R_1$	3.801	0.127	[76,80]
72	18	$(66R_1+24R_2+24S_1+23S_2+18S_3)/18=4.635R_1$	4.027	0.118	
73	20	$(80R_1+16R_2+8R_3+18S_1+30S_2+12S_3)/20=4.737R_1$	4.108	0.121	
74	30	$(130R_1+44R_2+12R_3+19S_1+30S_2+19S_3)/30=5.107R_1$	4.438	0.131	
10	30	$(130R_1+44R_2+12R_3+24S_1+25S_2+19S_3)/30=5.157R_1$	4.481	0.132	

[a] Labels correspond to structures in Fig. 12. [b] K = the number of Kekulé structures. [c] $R_2=0.284R_1$, $R_3=0.115R_1$, $S_1=0.326R_1$, $S_2=0.092R_1$, $S_3=0.037R_1$.

follows these observations. The normalized count of the R_1 circuits is $30R_1/10=3.0R_1$, $24R_1/9=2.67R_1$ and $20R_1/8=2.5R_1$. The normalization factor is the Kekulé count for the structure. Molecules **63** and **75** have been prepared and exhibit aromatic properties [70,71]. The isoconjugated structure (**77**) of **76** has also been prepared [72] and is stable.



77

CONCLUDING REMARKS

The conjugated circuits model is used to study aromaticity in thia-helicenes. The conjugated circuits model is based on intuitive chemical ideas such as Clar's aromatic sextets [36,37,73] and it can be related to resonance-theoretic arguments [74].

The conjugated circuits model is applicable to all kinds of polycyclic conjugated structures and in association with the conjugated chains concept [75] to all conjugated systems: (poly)cyclic, acyclic and (poly)cyclic with *exo*-cyclic linear and branched unsaturated fragments.

The conjugated circuits model, which is a simple structural model, ignores the question of stereochemistry and the role of non-bonded repulsions in 3D conjugated molecules. These features are essential structural components in helical systems as [*N*]helicenes and thia[*N*]helicenes. Since many helicenes and thia-helicenes have been synthesized, the stabilization which comes from the aromaticity of these components apparently must considerably exceed the destabilization produced by steric crowding in the higher members of the [*N*]helicene family and the thia[*N*]helicene family. If we wish to include the steric contributions to the REs, then they must be obtained by theoretical methods which are suited for such calculations.

REFERENCES

1 H. Wynberg, Acc. Chem. Res., 4 (1971) 65.

2 R.H. Martin, Angew. Chem., 86 (1974) 727.

3 M. S. Newman and D. Lednicer, J. Am. Chem. Soc., 78 (1956) 4765.

4 M. Flammang-Barbieux, J. Nasielski and R. H. Martin, Tetrahedron Lett., (1967) 743.

5 R. H. Martin, M. Flammang-Barbieux, J. P. Cosyn and M. Gelbcke, Tetrahedron Lett., (1968) 3507.

6 H. Kagan, A. Moradpour, G. Balavoine, J. F. Nicaud, R. H. Martin and J. P. Cosyn, Tetrahedron Lett., (1971) 2479.

7 A. Moradpour, H. Kagan, M. Baes, G. Morreu and R. H. Martin, Tetrahedron, 31 (1975) 2139.

8 R. H. Martin and M. Baes, Tetrahedron, 31 (1975) 2135.
9 R. H. Martin, G. Morreu and J. J. Schurter, Tetrahedron Lett., (1975) 3683.
10 P. G. Lehman and H. Wynberg, Aust. J. Chem., 27 (1974) 315.
11 K. Yamada, S. Ogaskiwa, H. Tanaka, H. Nagakawa and H. Kawazura, Chem. Lett., (1981) 343.
12 J. H. Dopper, D. Oudman and H. Wynberg, J. Org. Chem., 40 (1975) 3398.
13 H. Wynberg and M. Groen, J. Am. Chem. Soc., 90 (1968) 5339.
14 M. Randić, Chem. Phys. Lett., 38 (1976) 68.
15 N. Trinajstić, Chemical Graph Theory, CRC, Boca Raton, FL, 1983, Vol. II, Ch. 3.
16 M. Randić and N. Trinajstić, J. Am. Chem. Soc., 109 (1987) 6923.
17 M. Randić, J. Am. Chem. Soc., 99 (1977) 444.
18 M. Randić, Tetrahedron, 33 (1977) 1905.
19 A. Graovac, I. Gutman, M. Randić and N. Trinajstić, Coll. Czech. Chem. Commun., 43 (1978) 415.
20 M. Randić, Int. J. Quantum Chem., 17 (1980) 549.
21 M. Randić and N. Trinajstić, J. Am. Chem. Soc., 106 (1984) 4428.
22 M. Randić, B. M. Gimarc and N. Trinajstić, Croat. Chem. Acta, 59 (1986) 345.
23 M. Randić, V. Solomon, S. C. Grossman, D. J. Klein and N. Trinajstić, Int. J. Quantum Chem., 32 (1987) 35.
24 M. Randić, J. Phys. Chem., 86 (1982) 3970.
25 M. Randić and F. Nettleton, Int. J. Quantum Chem. Symp., 20 (1986) 203.
26 M. Randić, D. Plavšić and N. Trinajstić, J. Mol. Struct. (Theochem), in press.
27 M. Randić and H. E. Zimmerman, Int. J. Quantum Chem. Symp., 20 (1986) 185.
28 M. Randić, N. Trinajstić, J. V. Knop and Ž. Jeričević, J. Am. Chem. Soc., 107 (1985) 849.
29 M. Randić and N. Trinajstić, Sulfur Reports, 6 (1986) 379.
30 S. Nikolić, N. Trinajstić and A. Jurić, Heterocycles, 26 (1987) 2025.
31 M. Randić, S. Nikolić and N. Trinajstić, Coll. Czech. Chem. Commun., in press.
32 D. J. Klein, T. G. Schmalz, G. E. Hite and W. A. Seitz, J. Am. Chem. Soc., 108 (1986) 1301.
33 T. G. Schmalz, W. A. Seitz, D. J. Klein and G. E. Hite, Chem. Phys. Lett., 130 (1986) 203.
34 D. J. Klein, W. A. Seitz and T.G. Schmalz, Nature (Lond.), 323 (1986) 703.
35 M. Randić, S. Nikolić and N. Trinajstić, Croat. Chem. Acta, 60 (1987) 595.
36 E. Clar, Chimia, 18 (1964) 375.
37 E. Clar, The Aromatic Sextet, Wiley, New York, 1972.
38 W. C. Herndon, J. Am. Chem. Soc., 95 (1973) 2404.
39 W. C. Herndon and M. L. Ellzey, Jr., J. Am. Chem. Soc., 96 (1974) 6631.
40 W. C. Herndon, Isr. J. Chem., 20 (1980) 270.
41 L. Pauling, Proc. Natl. Acad. Sci. U.S.A., 18 (1932) 293.
42 L. Pauling and G. W. Wheland, J. Chem. Phys., 1 (1933) 362.
43 L. Pauling and J. Sherman, J. Chem. Phys., 1 (1933) 606.
44 L. Pauling, The Nature of the Chemical Bond, 2nd edn., Cornell University Press, Ithaca, 1948.
45 L. Pauling, Acta Crystallogr. Sect. B, 36 (1980) 1898.
46 I. Gutman and M. Randić, Chem. Phys., 41 (1979) 265.
47 B. A. Hess, Jr. and L. J. Schaad, J. Am. Chem. Soc., 93 (1971) 305.
48 M. J. S. Dewar and C. de Llano, J. Am. Chem. Soc., 91 (1969) 789.
49 M. Randić, S. Nikolić and N. Trinajstić, in: R. B. King and D. H. Rouvray (Eds.), Applications of Graph Theory and Topology to Chemistry, Elsevier, Amsterdam, 1987, p. 429.
50 M. J. S. Dewar and N. Trinajstić, J. Am. Chem. Soc., 92 (1970) 1453.
51 B. A. Hess, Jr. and L. J. Schaad, J. Am. Chem. Soc., 93 (1971) 2413.
52 D. K. Fukushima, in: R. C. Elderfield (Ed.), Heterocyclic Compounds, Wiley, New York, 1951, p. 164.

53 M. L. Tedjamulia, Y. Tominaga, R. N. Castle and M. L. Lee, J. Heterocycl. Chem., 20 (1983) 1485.
54 M. Randić, S. Nikolić and N. Trinajstić, Croat. Chem. Acta, in press.
55 M. Randić, B. M. Gimarc, S. Nikolić and N. Trinajstić, Gazz. Chim. Ital., in press.
56 B. Iddon, Adv. Heterocycl. Chem., 14 (1972) 331.
57 I. Gutman, M. Milun and N. Trinajstić, J. Am. Chem. Soc., 97 (1977) 1692.
58 L. H. Klemm, Adv. Heterocycl. Chem., 32 (1982) 127.
59 S. Gronowitz (Ed.), Thiophene and Its Derivatives, Part I-III, Wiley, New York, 1985-1986.
60 V. V. Ghaisas, K. Rabindran and B. D. Tilak, Proc. Indian Acad. Sci., 37A (1953) 114.
61 H. D. Harthough and S. L. Meisel, in: A. Weissberger (Ed.), Compounds with Condensed Thiophene Rings, Wiley, New York, 1954, Chs. 6, 7.
62 D. Muller, J.-F. Muller and D. Cagniant, J. Chem. Res. (S), (1977) 328.
63 H. D. Hartough, Thiophene and Its Derivatives, Wiley, New York, 1952.
64 J. W. Armit and R. Robinson, J. Chem. Soc., 127 (1925) 1604.
65 K. Fries, Justus Liebigs Ann. Chem., 454 (1927) 121.
66 K. Fries, R. Walter and K. Schilling, Justus Liebigs Ann. Chem., 516 (1935) 248.
67 F. Sondheimer, Chimia, 28 (1974) 163.
68 J. R. Dias, Handbook of Polycyclic Hydrocarbons, Part A: Benzenoid Hydrocarbons, Elsevier, Amsterdam, 1987.
69 M. Randić, S. Nikolić and N. Trinajstić, Gazz. Chim. Ital., 117 (1987) 69.
70 J. H. Dopper and H. Wynberg, J. Org. Chem., 40 (1975) 1957.
71 A. S. Zektzer, J. G. Stuart, G. E. Martin and R. N. Castle, J. Heterocycl. Chem., 23 (1986) 1587.
72 M. L. Tedjamulia, Y. Tominaga, R. N. Castle and M. L. Lee, J. Heterocycl. Chem., 20 (1983) 1143.
73 E. Clar, Polycyclic Hydrocarbons, Pergamon, Oxford, 1964.
74 L. J. Schaad and B. A. Hess, Jr., Pure Appl. Chem., 54 (1982) 1097.
75 M. Randić and N. Trinajstić, in R. C. Lacher (Ed.), MATH/CHEM/COMP 1987 - An International Course and Conference on the Interfaces between Mathematics, Chemistry and Computer Science, Elsevier, Amsterdam, 1988, p. 109.
76 M. B. Groen, H. Schadenberg and H. Wynberg, J. Org. Chem., 36 (1971) 2797.
77 J. H. Dopper, D. Oudman and H. Wynberg, J. Am. Chem. Soc., 95 (1973) 3692.
78 D. K. Fukushima, in R. L. Elderfield (Ed.), Heterocyclic Chemistry, Wiley, New York, 1951, p. 164.
79 M. L. Tedjamulia, Y. Tominaga, R. N. Castle and M. L. Lee, J. Heterocycl. Chem., 20 (1983) 1485.
80 P. G. Lehman and H. Wynberg, Rec. Trav. Chim. Pays-Bas, 90 (1971) 1113.
81 P. G. Lehman and H. Wynberg, Aust. J. Chem., 27 (1974) 315.
82 K.-i. Yamada, S. Ogashiwa, H. Tanaka, H. Nagajawa and H. Kawazura, Chem. Lett., (1981) 343.
83 C. Glaser, Chem. Ber., 58 (1872) 982.
84 C. L. Hewett, J. Chem. Soc., (1936) 596.
85 R. Weitzenböck and A. Klinger, Monatsch. Chem., 39 (1918) 315.
86 M. S. Newman and D. Lednicer, J. Am. Chem. Soc., 78 (1956) 4765.
87 M. Flammang-Barbieux, J. Nasielski and R. H. Martin, Tetrahedron Lett., (1967) 743.
88 R. H. Martin, M. Flammang-Barbieux, J. P. Cosyn and M. Gelbcke, Tetrahedron Lett., (1968) 3507.
89 H. Kagan, A. Moradpour, G. Balavoine, J. F. Nicaud, R. H. Martin and J. P. Cosyn, Tetrahedron Lett., (1971) 2479.
90 A. Moradpour, H. Kagan, M. Boes, G. Morreu and R. H. Martin, Tetrahedron, 31 (1975) 2139.

91 R. H. Martin and M. Baes, Tetrahedron, 31 (1975) 2135.
92 R. H. Martin, G. Morreu and J. J. Schurter, Tetrahedron Lett., (1975) 3683.
93 J. H. Dopper and H. Wynberg, J. Org. Chem., 40 (1975) 1957.
94 J. H. Dopper, D. Oudman and H. Wynberg, J. Org. Chem., 40 (1975) 3398.
95 H. Wynberg and M. B. Groen, J. Am. Chem. Soc., 90 (1968) 5339.