A GRAPHICAL STUDY OF POSITIONAL ISOMERS CONTAINING BIVALENT SULPHUR

J.V.Knop[a], N.Trinajstić[a]* and T.Živković[b]

[a] *Rechenzentrum der Universität Düsseldorf,*
Haroldstrasse 28, 4000 Düsseldorf, F. R. Germany,
[b] *Institute "Rudjer Bošković", P.O.B. 1016, 41001 Zagreb, Croatia, Yugoslavia*

A graphical method is used in order to study the relative stabilities of isomeric (σ-bivalent) sulphur compounds. In all studied cases the qualitative agreement with experimental findings is obtained. Available quantum-mechanical calculations are also supporting our graphical results.

In the last few years the syntheses of various, from the preparative and theoretical point of view, interesting conjugated heterocyclic compounds containing σ-bivalent sulphur have been carried out[1-5]. Examination of the structural features of these compounds reveals that there are other molecules of various stabilities structurally closely related to them: some being very difficult to prepare whereas others are synthesized much more easily. Such sets of structurally closely related compounds are named positional isomers[6], because they formally differ only in the position of a heteroatom. The best known example of positional isomerism among the sulphur heterocyclics represents benzo[*b*]thiophene (*3*) and benzo[*c*]thiophene (*4*).

The difference in the position of a heteroatom causes dramatic changes in physical and chemical properties among the positional isomers belonging to the same set[7-9]. It has been indicated[8,9] that these differences have the origin in topology of positional isomers and hence, a number of useful predictions about their chemistry could be reached solely by inspection of topological properties without going through any sort of theoretical calculations. Examples of such an approach are described in our previous work[10-13], where an effort was made to develop a symbolism that permits chemists to think graphically instead in terms of numbers.

GRAPHICAL METHOD

The details of graphical method are outlined elsewhere[14,15]. The essence of our method is as follows: the order of relative stabilities of members of a particular

* Visiting Professor from the Rudjer Bošković Institute P.O.B. 1016, 41001 Zagreb, Croatia, Yugoslavia.

set of positional isomers can be predicted by examining the topological factors influencing the stabilities of "parent" hydrocarbons obtained by deleting heteroatoms and the adjacent bonds. Thus, we postulate that the topological factors which are responsible for the stability of "parent" hydrocarbons are also determining the stabilities of related heterocyclic molecules. Very close to this are the ideas recently expressed by Watson and Warrener[16]. Presently, there is no theoretical explanation available for this postulate. However, it can be justified by comparing predictions and experimental findings. In a way one may regard this approach as an extension of the procedure[17,18] used for predicting some properties, in the first approximation, of N-heterocyclic compounds containing $(\sigma + \sigma + \pi)$-trivalent nitrogen by considering the "parent" hydrocarbon to S-heterocycles containing $(\sigma + \sigma)$-bivalent sulphur.

Some of the topological factors which influence the stability of conjugated hydrocarbons have been analyzed previously[19]. In the cited work[19] we have studied the dependence of the total π-electron energy (E_π) on the molecular topology. The following is found: *a*) the major part of E_π comes from the number of atoms (N) and bonds (v) present in a conjugated molecule; *b*) the presence of ($4m$)- and ($4m + 2$)-membered rings (n_{4m}, n_{4m+2}) decreases and increases, respectively, the value of E_π; and *c*) the branching (σ_i) of a carbon skeleton increases E_π or decreases E_π depending whether it occurs at ($4m$)- or ($4m + 2$)-ring system respectively. *d*) The number of Kekulé structures (K) of the same parity[20] is also important in this respect, because it can be used as an indication of the relative stability of two isomers[21]. No stable conjugated molecule is possible without at least a single Kekulé structure[22]. The absence of Kekulé structures in a conjugated molecule is followed by the presence of nonbonding MO's[23] which implies energetical instability[24].

Since molecules belonging to the same set of positional isomers have equal number of atoms and bonds, and belong either to the ($4m$)- or ($4m + 2$)-class, the difference in their stability is, thus, determined by the degree of branching of the carbon skeleton and the number of Kekulé structures[25]. Hence, if we write down the π-electron energy of a particular isomer (this is, of course, valid only for its carbon skeleton part) as a function of the mentioned quantities which can be regarded as variables:

$$E_\pi(I) = f\{N, v, n_{4m} \quad (\text{or } n_{4m+2}), \quad \sigma_i, \ K\} , \tag{1}$$

then the difference in energy between the two isomers (*i.e.* the relative stability) is only a function (in the first approximation) of σ_i and K.

$$\Delta E_\pi = E_\pi(I) - E_\pi(II) = f\{\sigma_i, K\} . \tag{2}$$

Presently, we do not know the explicit formula of $E_\pi(I)$ (ref.[25]). However, our intention in the present work is to use a simple and qualitative approach instead the explicit formulae and numerical evaluation. We only point out here that although the contributions from the branching and the number of Kekulé structures of the same parity to the total E_π are small (of the order of 5%), these values are large enough to bring stabilization or destabilization to a particular conjugated molecule.
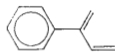
The contribution from branching to E_π has been investigated by comparing closely related isomeric hydrocarbons which have equal number of atoms, bonds, Kekulé structures and n_6

(or n_4) rings and differ only in branching, for example:
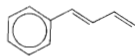
E_π (HMO) (ref.[26]) $12·93\beta$ $12·86\beta$

Discussion about the magnitude of the contribution of the number of Kekulé structures to E_π can be found in work by Gutman[27]. The importance of a number or Kekulé structures comes from the close relationship between the number of Kekulé structures (K) and det A ($A =$ adjacency matrix)[28,29]. Thus, for example, this relation for benzenoid hydrocarbons is

$$\det A = (-)^{N/2} K^2 . \qquad (3)$$

It is clearly seen from this expression how with the increase of N value the contribution of the number of Kekulé structures becomes smaller.

In the present work we simply count the branches and follow the topological rule[19]: a larger number of branches stabilizes (4m)- and destabilizes (4m + 2)-ring systems, respectively. On the other hand, the contribution of Kekulé structures of the same parity is taken into account following the suggestion of Herndon[30] to use the CSC (Corrected Structure Count)-index, because it is found in all studied cases to be in qualitative agreement with experimental indicators of stability and reactivity[30,31]. CSC-index is related[13] to the number of even (K^+, parity + 1) and odd (K^-, parity − 1) Kekulé structures[32] ($K = K^+ + K^-$):

$$\mathrm{CSC} = |K^+ - K^-| . \qquad (4)$$

Furthermore, note that it exists a relationship between the number of Kekulé structures and branching. The close examination of the various VB structures containing branches reveals the importance of the number of branches attached to the ring and the number of atoms in the particular branch. However, the branching in the side chain has smaller effect on the π-energy than ring branching. The contribution from the ring branching to E_π has been investigated by comparing number of possibilities[15]. Here we give the following example:

E_π (HMO) (ref.[26]) $10·42\beta$ $9·96\beta$

The use of our graphical method is described for isomeric thienocyclobutadienes (1) and (2), and benzothiophenes (3) and (4), respectively, in Charts I and II.

Let us consider first Chart I, where the example of the four-membered hydrocarbon ring is presented. Topological factors (c) (greater branching) and (d) (larger value of CSC-index) prefer 3,4-dimethylenecyclobutene (2a) over vinylcyclobutadiene (1a) and consequently our prediction is that thienocyclobutadiene (2) should be more stable than isomer (1). This prediction is in agree-

ment with the available experimental evidence. The preparation of 6,7-diphenyl derivative of 3-thiabicyclo-[3.2.0]heptatriene (2) has been reported[3,33]. As far as we know a compound containing the 2-thiabicyclo-[3.2.0]heptatriene moiety is not made as yet. Similarly, the synthesis of 3,4-dimethylenecyclobutene (2a) is reported[34,35] whereas the preparation of (1a) not as yet. 3,4-Dimethylenecyclobutene readily polymerizes in the presence of air, but it is stable for long periods at room temperature when stored under nitrogen[36]. Very recently it has been pointed out[37] that (2a) represents a unique planar conjugated molecule which is antiaromatic (REPE = $= -0.028\beta$) and isolable. The REPE value, for example, of vinyl cyclobutadiene is -0.15β. Therefore, the additional stabilization in (2a) should be attributed to its favourable topological properties.

Let us now consider Chart II. On this Chart the example of six-membered hydrocarbon ring is illustrated. Topological factors (c) (lesser branching) and (d) (larger value of CSC-index) prefer styrene (3a) over o-xylylene (4a). Thus, our prediction is consequently that benzo[b]thiophene (3) should be more stable than benzo[c]thiophene (4). This prediction is in agreement with experimental facts and quantum-mechanical calculations. In this way, while benzo[b]thiophene has been first prepared in the last century (1893)[38] and shows normal aromatic behaviour and stability[39,40] (DRE ≡ Dewar resonance energy and REPE ≡ resonance energy per electron values being 24·8 kcal/mol[41] and 0.044β[42], respectively), benzo[c]thiophene has been only recently made[43] (1962) and it is clearly more reactive[43–45] than isomer (3) (DRE and REPE values being 9·3 kcal/mol[41] and 0.025β[42], respectively). Similarly, styrene is well known compound where o-xylylene (1,2-benzenequinododimethide) is a very reactive species[46] which has been characterized only indirectly in the adduct from[47] and in metal complex[48]. Very recently, it has been also described the photochemical preparation of o-xylylene in rigid glass[49]. The stability of o-xylylene has been discussed by Gleicher, Newkirk, and Arnold[50] using the REPE-index of Hess and Schaad[51] and it has been shown to be a non-aromatic species (REPE = $= 0.005\beta$).

(1)   (1a)

(a) $n = 6$, $v = 6$
(b) 4m
(c) one branching
(d) CSC = 0(K⁺ = 1, K⁻ = 1)

(2)   (2a)

(a) $n = 6$, $v = 6$
(b) 4m
(c) two branchings
(d) CSC = 1(K⁺ = 1)

CHART I

RESULTS AND DISCUSSIONS

A number of isomeric polycyclic sulphur compounds have been studied using a graphical method delineated previously. These results are summarized in the Table I.

Since the results for thienocyclobutadienes and benzothiophenes are commented earlier we shall discuss the remaining sets of isomeric sulphur molecules reported in the Table I further on.

Benzothiepines: There are three possible benzo derivatives of thiepine: (5), (6), and (7). The stability prediction (5) > (7) > (6) parallels the experimental findings and theoretical calculations. Stable derivatives of benzo[b]thiepine (5) and benzo[d]-thiepine (7) are made[4,52,53] whereas neither benzo[c]thiepine (6) nor any of its derivatives are known as yet[54]. The synthesis of the valence isomer (5a) of benzo[b]-thiepine is also reported[55].

(5b)

Theoretical calculations (REPE values)[42] also indicate that benzo[b]thiepine (0·016β) and benzo[d]thiepine (0·017β) are much more stable than benzo[c]thiepine (−0·019β).

(3) ⟶ (3a)

(a) $n = 8$, $v = 8$
(b) $4m + 2$
(c) one branching
(d) $CSC = 2(K^+ = 2)$

(4) ⟶ (4a)

(a) $n = 8$, $v = 8$
(b) $4m + 2$
(c) two branchings
(d) $CSC = 1(K^+ = 1)$

CHART II

TABLE I
Summary of the Results Obtained from the Graphical Analysis of Polycyclic Sulphur Compounds

Compound	"Parent" hydrocarbon	Essential topological factors	Stability prediction[a] stability observed
(1)	(1a)	single branching CSC = 0	unstable —
(2)	(2a)	double branching CSC = 1	modestly stable; unstable under oxygen and room temp.[32,33]
(3)	(3a)	single branching CSC = 2	stable; stable[38]
(4)	(4a)	double branching CSC = 1	unstable; reactive compound[43,44]
(5)	(5a)	single branching CSC = 2	stable; stable[4,52]
(6)	(6a)	double branching CSC = 1	unstable —
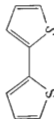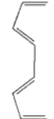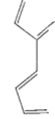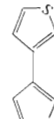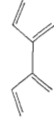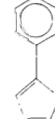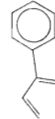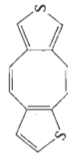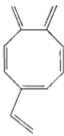
Compound	Structure	Label	Description	CSC	Stability	Ref. stability
(7)		(7a)	double branching	CSC = 2	modestly stable	stable[53]
(8)		(8a)	chain	CSC = 1	stable	stable[56]
(9)		(9a)	chain single branching	CSC = 1	stable	stable[57,58]
(10)		(10a)	chain double branching	CSC = 1	stable	stable[56]
(11)		(11a)	single branching	CSC = 2	stable	stable[63]
(12)		(12a)	ring and chain single branching	CSC = 2	stable	stable[64,65]
(13)		(13a)	double branching	CSC = 0	unstable	—

TABLE I
(Continued)

Compound	"Parent" hydrocarbon	Essential topological factors	Stability prediction[a] / stability observed
(14)	(14a)	triple branching $CSC = 1$	modestly stable —
(15)	(15a)	double branching $CSC = 0$	unstable —
(16)	(16a)	quadruple branching $CSC = 1$	stable —
(17)	(17a)	double branching $CSC = 0$	unstable —
(18)	(18a)	triple branching $CSC = 1$	modesty stable —
(19)	(19a)	double branching $CSC = 0$	unstable —
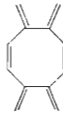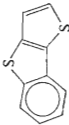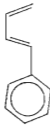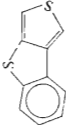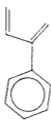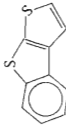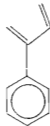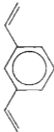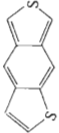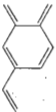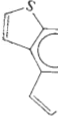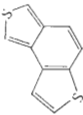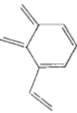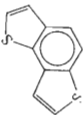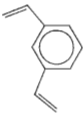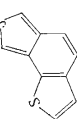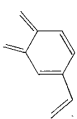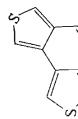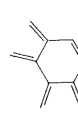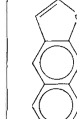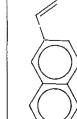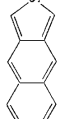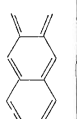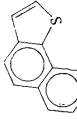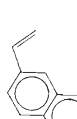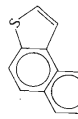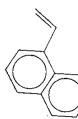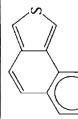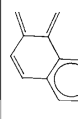
(20)	(20a)	quadruple branching CSC = 1	stable	—
(21)	(21a)	single branching CSC = 1	unstable	—
(22)	(22a)	double branching CSC = 2	stable	stable white crystalline solid [71,72]
(23)	(23a)	single branching CSC = 2	stable	stable [5]
(24)	(24a)	ring and chain single branching CSC = 2	stable	—
(25)	(25a)	ring and chain single branching CSC = 2	stable	—
(26)	(26a)	double branching CSC = 2	stable	—

TABLE I
(Continued)

Compound		"Parent" hydrocarbon		Essential topological factors	Stability prediction[a] / stability observed
	(27)		(27a)	triple branching CSC = 1	unstable / —
	(28)		(28a)	double branching CSC = 2	stable / —
	(29)		(29a)	double branching CSC = 2	stable / stable[75,76]
	(30)		(30a)	triple branching CSC = 1	unstable / —
	(31)		(31a)	double branching CSC = 2	stable / stable[77,78]
	(32)		(32a)	double branching CSC = 2	stable / stable[79]

	(33)		(33a)	triple branching CSC = 1	unstable —
	(34)		(34a)	quadruple branching CSC = 1	unstable white solid sensitive to oxygen[80]
	(35)		(35a)	single branching CSC = 1	stable stable[83,84]
	(36)		(36a)	double branching CSC = 1	unstable reactive compound
	(37)		(37a)	single branching CSC = 3	stable stable[85]
	(38)		(38a)	single branching CSC = 3	stable stable[86]
	(39)		(39a)	double branching CSC = 2	modestly stable modestly stable[2,44]

Bithiophenes: Bithiophenes $(8)-(10)$ represent an interesting group of hetero-aromatic molecules formed by two thiophene rings being linked together by an essentially single bond ($\sim 1\cdot 47$ Å). Bithiophenes are all predicted to be stable molecules, and indeed all three isomeric bithiophenes have been synthesized[56−58]. The stability prediction of bithiophenes is also supported by SCF MO π-calculations[41]: DRE values being for 2,2'-bithiophene (8) 12·7 kcal/mol, 2,3'-bithiophene (9) 12·1 kcal/mol, and 3,3'-bithiophene (10) 11·0 kcal/mol, respectively. Although the energetical stability of all three isomeric bithiophenes is nearly the same (the small differences in stability parallel the chain branching correctly: 2,2'-bithiophene (no branching, 12·7 kcal/mol) > 2,3'-bithiophene (one branching, 12·1 kcal/mol) > 3,3'-bithiophene (two branchings, 11·0 kcal/mol)) the order of the kinetic stability should be as follows: 3,3'- > 2,3'- > 2,2'-isomer.

On the other hand, bithiophenes show a marked blue shift in the UV spectra of 2,3'- and 3,3'-isomers ($\sim 0\cdot 7$ eV) when compared with the 2,2'-isomer. This effect can be also anticipated by following our simple graphical approach. The progressive branching in the "polyenic system" causes an increase in the first transition energy because the chain branching is followed by the increase of the energy gap between the occupied and empty molecular orbitals[59]. Compare, for example, the HOMO–LUMO energy gap in hexatriene (no branching, $0\cdot 89\beta$) and 2-vinylbutadiene (one branching, $1\cdot 04\beta$). The direct evidence in this sense is offered by the very strong blue shift (~ 1 eV) observed in the UV spectra[60,61] going on from 1,3,5,7-octatetraene $(8a)$, 2-vinylhexatriene $(9a)$ to 2,3-divinylbutadiene $(10a)$. Wynberg, Sinnige, and Creemers[62] have recently rationalized empirically UV spectra of bithiophenes and alike compounds with similar argument.

Phenylthiophenes: Isomeric phenylthiophenes (11) and (12) are also formed by linking two ring systems (benzene and thiophene) together by an essentially single bond ($\sim 1\cdot 47$ Å). These molecules are predicted to be stable. Phenylthiophenes were prepared in the last century[63−65] and are very stable molecules indeed. DRE values could be estimated using an expression:

$$\mathrm{DRE}\,(A-B) \simeq \mathrm{DRE}\,(A) + \mathrm{DRE}\,(B), \qquad (5)$$

because it was found earlier[66,67] that if an aromatic component A is linked together with an aromatic component B by an essentially single bond, the DRE value of the parent compound A−B can be estimated rather accurately from the DRE values of components A and B. Since the DRE values of benzene and thiophene are known

---

[a] Term *stability* is used in everyday laboratory sense, *i.e. stable* denotes isolable compounds with well defined properties, *modestly stable* denotes compounds stable in solution or when isolated they have a limited life time, and *unstable* denotes reactive and short lived species.

(20·0 kcal/mol and 6·5 kcal/mol, respectively)[41,68], the DRE value of phenylthiophenes (∼26·5 kcal/mol) indicate that these compounds are expected to be energetically stable as it is the case.

In the UV spectrum of 3-phenylthiophene[46] (12) a blue shift (∼0·4 eV) is observed when compared with the UV spectrum of 2-phenylthiophene (11). The same graphical reasoning for this observation can be used as for the isomeric bithiophenes.

Bithienylenes: There are four isomeric bithienylenes possible (13)−(16). The stability prediction is (16) > (14) > (13) ≃ (15). There are no experimental data available to check this prediction. For the stability of these compounds it is, of course, also important to consider the strain in the four-membered moiety, which is not included in our study. Wynberg and co-workers[69] attempted to prepare (16) but without success. Wynberg attributed these difficulties to the presence of a highly strained four-membered ring system.

The ring strain of the four-membered ring has been approximately estimated using the modified Dauben's formula[70]

$$\text{strain energy} = \tfrac{1}{2} A \, (\Delta\alpha)^2 \, , \qquad (6)$$

where $\Delta\alpha$ is the strain angle at the atom i and A is a constant $(0·024 \text{ kcal/deg}^2)$ obtained considering the experimental energies of monocyclic olefins and paraffins. The strain angle in the polycyclic conjugated hydrocarbons represents the angle distortion from 120°. Only the carbon skeleton of a molecule is considered. The strain in the four-membered ring system is thus found to be about 43 kcal/mol.

Therefore, the strain argument should be used in considering all polycyclic sulphur compounds, where the four-membered ring appears. The strain argument is not altering our qualitative predictions except that it is giving insight where the additional destabilization in the considered systems comes from.

Cyclooctadithiophenes: Among the four isomeric cyclooctadithiophenes only the tetraphenyl derivative of (20)[3] was prepared. The stability prediction is as follows (20) > (18) > (17) ≃ (19). Quantum-mechanical calculations were not performed on these molecules as yet and in general presently only very little is known about the chemistry of cyclooctadithiophenes. We hope that these very simple and qualitative studies may stimulate further research on this class of sulphur molecules in both experimental and theoretical ways.

Thianorbiphenylenes: There are two possible isomeric thianorbiphenylenes (21) and (22). The stability prediction is (22) > (21). This result nicely parallels the experimental facts. 2-Thianorbiphenylene (22) has been recently synthesized[71,72] whereas 1-thianorbiphenylene (21) is still an unknown compound. Of course, it is also important to consider the strain within the four-membered ring system and this is, probably, the reason why (22) eluded synthesis for some time. Similarly, the derivatives

of (22a) are known[73], e.g. (22b)[74]. Neither (21a) nor its derivatives are presently known.
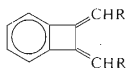
(22b)

Thienobenzothiophenes: The fusion of benzene ring to the 2,3 bond of 1,4-thiophthene, 1,5-thiophthene, and 1,6-thiophthene produces three isomeric thienobenzothiophenes (23)−(25). The stability prediction is (23) ≃ (24) ≃ (25). Thieno[3,2-b][1]benzothiophene was recently prepared[5]. Otherwise very little is known about the chemistry of thienobenzothiophenes. It turns out from our considerations, since all three isomers (23)−(25) differ very little in their topologies (only in the side chain branching, which is bringing only a very little destabilization to the system), that the syntheses of (24) and (25) could be carried out following similar methods to those in the preparation of (23).

Thiophene analogs of anthracene: The fusion of two thiophene rings to the 1,2 and 4,5 bonds of a benzene ring leads to three possible thiophene analogs of anthra-
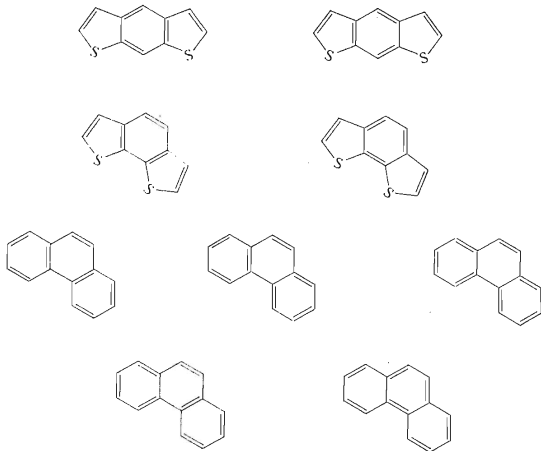
CHART III

cene (26)—(28). The stability prediction is as follows: (26) ≃ (28) > (27). The chemical and physical properties of these compounds are scarcely investigated. Thus far no synthesis of any of them has been reported. From our considerations it turns out that at least (26) and (28) can be prepared. The reason, perhaps, why these molecules are in general less stable than, for example, the thiophene analogs of phenanthrene is that it is impossible to have simultaneously two thiophene units a in single Kekulé structure of them (Chart III), besides having a smaller number of Kekulé structures of the same parity. This is important if we consider thiophene rings as invariant subunits which most of the time preserve the stability of thiophene ring with sextet of π-electrons.

Benzodithiophenes: The fusion of two thiophene rings to adjacent positions (at the 1,2 and 3,4 bonds) of a benzene ring can rise to six possible isomeric benzodithiophenes (29)—(34). The stability prediction is (29) ≃ (31) ≃ (32) > (30) ≃ (33) > > (34). Our prediction parallels the experimental findings because the following isomers: benzo[1,2-b : 4,3-b']dithiophene (29), benzo[2,1-b : 3,4-b']dithiophene (32) have been synthesized[75-79]. These are stable compounds. Neither benzo[1,2-b : 3,4'-c'] dithiophene (30) and benzo[2,1-b : 3,4-c']dithiophene (33) nor any of their derivatives are at present known. Note, that benzo[1,2-c : 3,4-c']dithiophene (34) was prepared[80], but it is sensitive to an exposure to air.

Angular benzodithiophenes are in fact the thiophene analogs of phenanthrene and are to a certain extent less stable than the parent hydrocarbon. From the VB point of view this is understandable[20,27] because phenanthrene has more Kekulé structures of the same parity (5) than any of benzodithiophenes (2) (Chart III).

The spectral characteristics of (29), (31), and (32) have been studied recently[81] and this is so far the only quantum-mechanical calculation carried out for these compounds.

Napthothiophenes: This class of sulphur cyclic compounds is well known and many derivatives of some of them have been prepared generally as potential dyestuffs[82]. There are five isomeric naphthothiophenes possible (35)—(39). The stability prediction is as follows: (35) ≃ (37) ≃ (38) > (39) > (36). Experimental evidence support this prediction. Thus, naphtho[2,3-b]thiophene (35), naphtho[3,4-b]thiophene (37), naphtho[1,2-b]thiophene (38) are prepared[83-86] without difficulties and are stable aromatic compounds. Naphtho[1,2-c]thiophene (39) was only recently prepared[2,44] and it is a modestly stable molecule. On the other hand, naphtho[2,3-c]thiophene (36) which is also recently synthesized[1] is a rather reactive compound. Previously, only the UV spectral characteristics of these compounds have been studied by theoretical methods[87,88].

CONCLUSIONS

A simple and qualitative graphical method presented here has correctly distinguished between the delocalized and quinonoid structures, the former being more stable in the case of $(4m + 2)$-rings whereas the latter in the case of $(4m)$-ring systems. The graphical method has correctly predicted the more stable isomer in all studied cases and thus the validity of the method at the qualitative level is indicated. This method can be used straightforwardly and quickly. The "simplicity" of the method is the most attractive feature of it. Hence, we point out in advocating our approach that many useful results for chemistry can be obtained from the very simple and qualitative methods and that it is not always necessary to employ sophisticated mathematical theories currently used in chemistry. A good example to illustrate this point are the Dewar — Evans Rules[89].

REFERENCES

1. MacDowell D. W. H., Jeffries A. T., Meyers M. B.: J. Org. Chem. *36*, 1416 (1971).
2. Cava M. P., Pollack N. M., Mamer O. A.: J. Org. Chem. *36*, 3032 (1971).
3. Garratt P. J., Vollhardt K. P. C.: J. Am. Chem. Soc. *94*, 1022 (1972).
4. Hoffmann H., Meyer B., Hoffmann P.: Angew. Chem. *84*, 477 (1972).
5. Jacquignon P., Croisy A., Ricci A., Balucani D.: J. Chem. Soc. Perkin I, *1973*, 734.
6. Trinajstić N.: Record Chem. Progr. *32*, 85 (1971).
7. Warrener R. N.: J. Am. Chem. Soc. *93*, 2346 (1971).
8. Klasinc L., Trinajstić N.: Tetrahedron *27*, 4045 (1971).
9. Klasinc L., Pop E., Trinajstić N., Knop J. V.: Tetrahedron *28*, 3465 (1972).
10. Cvetković D., Gutman I., Trinajstić N.: Croat. Chem. Acta *44*, 365 (1972).
11. Gutman I., Trinajstić N.: Croat. Chem. Acta *45*, 423 (1973); Naturwissenschaften *60*, 475 (1973).
12. Gutman I., Trinajstić N., Živković T.: Tetrahedron *29*, 3449 (1973).
13. Cvetković D., Gutman I., Trinajstić N.: J. Chem. Phys., in press.
14. Knop J. V., Trinajstić N., Gutman I., Klasinc L.: Naturwissenschaften *60*, 475 (1973).
15. Knop J. V., Trinajstić N., Živković Z.: Unpublished results..
16. Watson P. L., Warrener R. N.: Australian J. Chem. *26*, 1725 (1973).
17. Dewar M. J. S.: *The Molecular Orbital Theory of Organic Chemistry.* McGraw-Hill, New York 1969.
18. Coulson. C. A., Longuet-Higgins H. C.: Proc. Roy Soc. (London) A *193*, 447 (1948).
19. Gutman I., Trinajstić N.: Chem. Phys. Letters *17*, 535 (1972).
20. Cvetković D., Gutman I., Trinajstić N., Živković T.: Unpublished results.
21. Wheland G. W.: *The Theory of Resonance and Its Application to Organic Chemistry.* Wiley, New York 1953.
22. Clar E., Kemp W., Stewart D. G.: Tetrahedron *3*, 325 (1958).
23. Longuet-Higgins H. C.: J. Chem. Phys. *18*, 265 (1950).
24. Fukui K.: Topics Curr. Chem. *15*, 1 (1970).
25. Gutman I., Trinajstić N.: Unpublished results.

26. Coulson C. A., Streitwieser jr, A.: *Dictionary of π-Electron Calculations*. Pergamon Press, Oxford 1965.
27. Gutman I.: Chem. Phys. Letters *24*, 283 (1974).
28. Graovac A., Gutman I., Trinajstić N., Živković T.: Theoret. Chim. Acta *26*, 67 (1972).
29. Gutman I., Trinajstić N.: Topics Curr. Chem. *42*, 49 (1973).
30. Herndon W. C.: Tetrahedron *29*, 3 (1973).
31. Herndon W. C.: J. Am. Chem. Soc. *95*, 2404 (1973).
32. Dewar M. J. S., Longuet-Higgins H. C.: Proc. Roy. Soc. (London) A *214*, 482 (1952).
33. Longworth S. W., McOmie J. F. W.: J. Chem. Soc. Chem. Comm. *1972*, 623.
34. Blomquist A. T., Maitlis P. M.: Proc. Chem. Soc. *1961*, 339.
35. Hopf H., Lenich F. T.: Chem. Ber. *106*, 3461 (1973).
36. Hunstman W. D., Wristers H. J.: J. Am. Chem. Soc. *89*, 342 (1967).
37. Hess B. A., Schaad L. J.: Australian J. Chem. *25*, 2231 (1972).
38. Gatterman A., Lockhart A. E.: Ber. *26*, 2808 (1893).
39. Fukushima D. K. in the book: *Heterocyclic Chemistry*, Vol. 3, (R. C. Elderfield, Ed.), p. 145. Wiley, New York 1951.
40. Iddon B., Scrowston R. M.: Advan. Heterocycl. Chem. *11*, 177 (1970).
41. Dewar M. J. S., Trinajstić N.: J. Am. Chem. Soc. *92*, 1453 (1970).
42. Hess B. A., Schaad L. J.: J. Am. Chem. Soc. *95*, 3907 (1973).
43. Mayer R., Kleinert H., Richter S., Gewald K.: Angew. Chem. *74*, 118 (1962); J. Prakt. Chem. *20*, 244 (1963).
44. Cava M. P., Pollack N. M.: J. Am. Chem. Soc. *88*, 4112 (1966).
45. Iddon B.: Advan. Heterocycl. Chem. *14*, 331 (1972).
46. Elpern B., Nachod F. C.: J. Am. Chem. Soc. *72*, 3379 (1958).
47. Cava M. P., Deanna A. A.: J. Am. Chem. Soc. *81*, 4266 (1959).
48. Roth W. R., Meier J. D.: Tetrahedron Lett. *1967*, 2053.
49. Flynn C. R., Michl J.: J. Am. Chem. Soc. *95*, 5802 (1973).
50. Gleicher G. J., Newkirk D. D., Arnold J. C.: J. Am. Chem. Soc. *95*, 2526 (1973).
51. Hess B. A., Schaad L. J.: J. Am. Chem. Soc. *93*, 305 (1971).
52. Reinhoudt D. N., Kouwenhoven C. G.: J. Chem. Soc. Chem. Commun. *1972*, 1232.
53. Traynelis V. J.: Heterocycl. Compounds *26*, 714 (1972).
54. Traynelis V. J.: Heterocycl. Compounds *26*, 709 (1972).
55. Murata I., Tatsuoka T., Sugihara Y.: Tetrahedron Letters *1973*, 4261.
56. Auwers K., Bredt T. V.: Ber. *27*, 1741 (1894).
57. Teste J., Lozach N.: Bull. Soc. Chim. France *1954*, 492.
58. Wynberg H., Logothetis A., VerPloeg D.: J. Am. Chem. Soc. *79*, 1972 (1957).
59. Wynberg H., Bantjes A.: J. Org. Chem. *24*, 1421 (1959).
60. Woods G. F., Schwartzman L. H.: J. Am. Chem. Soc. *71* 1396 (1949).
61. Skatebøl L., Charlton J. L., de Mayo P.: Tetrahedron Letters *1966*. 2257.
62. Wynberg H., Sinnige H. J. M., Creemers H. M. J. C.: J. Org. Chem. *36*, 1011 (1971).
63. Kues A., Paal C.: Ber. *19*, 3142 (1886).
64. Mohlau B., Berger D.: Ber. *26*, 2001 (1893); Ber. *30*, 37 (1897).
65. Bomberger E.: Ber. *30*, 367, 369 (1897).
66. Dewar M. J. S., Harget A. J.: Proc. Roy. Soc (London) A *315*, 443 (1971).
67. Bodor N., Farkas M., Trinajstić N.: Croat. Chem. Acta *43*, 107 (1971).
68. Dewar M. J. S., de Llano C.: J. Am. Chem. Soc. *91*, 789 (1969).
69. Wynberg H.: Accounts Chem. Res. *4*, 65 (1971).
70. Hess B. A., Schaad L. J.: J. Am. Chem. Soc. *94*, 3068 (1972).
71. Garratt P. J., Vollhardt K. P. C.: Chem. Comm. *1970*, 109.

72. Garratt P. J., Vollhardt K. P. C.: J. Am. Chem. Soc. *94*, 7087 (1972).
73. Heaney H.: Ann. Reports Chem. Soc. *68*, 543 (1971).
74. Blomquist A. T., Hruby V. J.: J. Am. Chem. Soc. *89*, 4969 (1967).
75. Rao D. S., Rilak B. D.: J. Sci. Ind. Res. (India) *16*, 65 (1957).
76. Loader C. A., Timmons C. J.: J. Chem. Soc. C *1967*, 1677.
77. Rao D. S., Tilak B. D.: J. Sci. Ind. Res. (India) *13B*, 289 (1954).
78. Kellog R. M., Groen M. B., Wynberg H.: J. Org. Chem. *32*, 3093 (1967).
79. Rao D. S., Tilak B. D.: J. Sci. Ind. Res. (India) *17B*, 260 (1958).
80. Mac Dowell D. W. H., Maxwell M. H.: J. Org. Chem. *35*, 799 (1970).
81. Klasinc L., Knop J. V.: Z. Naturforsch. *26b*, 1235 (1971).
82. Hartough H. D., Meisel S. L.: *Compounds with Condensed Thiophene Rings*, p. 284. Interscience, New York 1954.
83. Wilputte R., Mastin R.: Bull. Soc. Chim. Belges *65*, 874 (1956).
84. Carruthers W., Crowder J. R.: J. Chem. Soc. *1957*, 1932.
85. Szmuszkovicz J., Modest E. J.: J. Am. Chem. Soc. *72*, 571 (1950).
86. Mayer F.: Liebigs Ann. Chem. *488*, 259 (1931).
87. Zahradník R.: Advan. Heterocyc. Chem. *5*, 1 (1965).
88. Trinajstić N., Hinchliffe A.: Z. Physik. Chem. (Frankfurt) *59*, 271 (1968).
89. Dewar M. J. S.: Angew. Chem. Intern. Edit. *10*, 761 (1971).