

## On the oxidation of dibenzo[*fg,ij*]pentaphene and dinaphtho[2,1,8,7-*defg*:2',1',8',7'-*ijkl*]pentaphene dianions

IVAN GUTMAN

Faculty of Science, University of Kragujevac, P.O. Box 60, YU-34000 Kragujevac, Yugoslavia

(Received 6 April 1999)

The dianion of dibenzo[*fg,ij*]pentaphene has recently been synthesized and shown to react with oxygen, forming the 15,16-dioxo derivative in nearly quantitative yield. Oxidation of the dianion of dinaphtho[2,1,8,7-*defg*:2',1',8',7'-*ijkl*]pentaphene under similar conditions does not result in any dioxo product. It is shown that these findings are a consequence of the different modes of cyclic conjugation in the two dianions. Cyclic conjugation in the mentioned two dianions, as well as in a number of other structurally related benzenoid dianions is assessed by means of a quantum-chemical method, developed earlier by the author.

*Key words:* dianions, benzenoid hydrocarbons, cyclic conjugation.

Continuing their studies<sup>1-5</sup> of the dianions of benzenoid hydrocarbons, Rabinovitz *et al.* have recently reported<sup>6</sup> the synthesis of the dianion **1**<sup>2-</sup> of dibenzo[*fg,ij*]pentaphene (**1**, see Fig. 1) and its reaction with oxygen (O<sub>2</sub>) or air. Oxidation of benzenoid dianions by oxygen or air usually results in the formation of the parent hydrocarbon.<sup>2,3</sup> However, in the case of **1**<sup>2-</sup>, the product is 15,16-dioxo-dibenzo[*fg,ij*]pentaphene (**2**), which is obtained in almost quantitative yield. Under similar experimental conditions, the oxidation of the dianion of the structurally closely related benzenoid hydrocarbon dinaphtho[2,1,8,7-*defg*:2',1',8',7'-*ijkl*]pentaphene (**3**) does not yield any dioxo-product.<sup>6,7</sup>

Rabinovitz *et al.*<sup>6</sup> have related these unusual findings to the differences in the charge density distribution in **1**<sup>2-</sup> and **3**<sup>2-</sup>, which, in turn, can be assessed from the chemical shifts in the respective <sup>13</sup>C-NMR spectra.<sup>1-6</sup> However, by this the problem is not resolved: one would need an explanation of why the charge density distributions in **1**<sup>2-</sup> and **3**<sup>2-</sup> are different, what causes this difference and, in particular, why the electron density in **1**<sup>2-</sup> is maximal in the close-lying (and therefore from the point of view of electrostatic repulsion inconvenient) position 15 and 16.

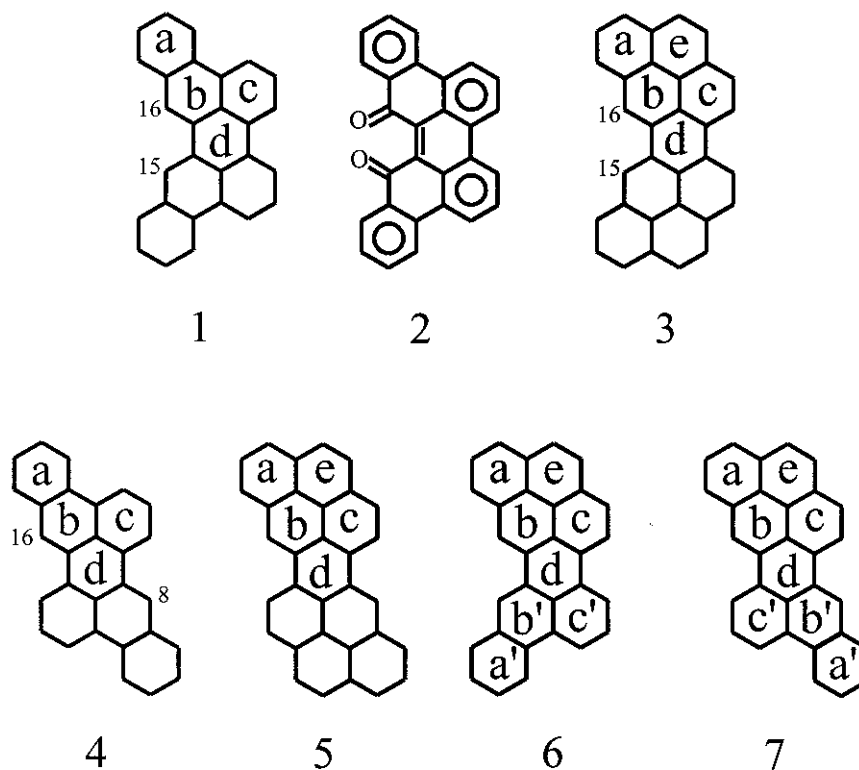


Fig. 1. The benzenoid molecules considered in this work and the labeling of their (symmetry non-equivalent) hexagons; mutually analogous hexagons in different benzenoids are denoted by the same symbol.

The aim of this work is to offer an explanation of the above outlined facts.

#### THE METHOD

Some time ago a quantum-chemical theory was elaborated,<sup>8-11</sup> by means of which the contribution of individual cycles to the total  $\pi$ -electron energy of a polycyclic conjugated molecule can be calculated. These energy effects measure the intensity of cyclic conjugation in the respective cycles. The theory found numerous chemical applications; for a review see,<sup>11</sup> for the most recent works in this area see<sup>12-14</sup> and the references quoted therein.

The theory of cyclic conjugation was for a long time applied only to non-charged conjugated hydrocarbons. Recently, however, the calculation method was modified so as to be applicable to dianions.<sup>14</sup> Then it could be demonstrated that the charge density distribution (or more precisely: the  $\pi$ -electron charge density

distribution) in benzenoid dianions is primarily determined by the mode and intensity of the  $\pi$ -electron conjugation along various cycles contained in the molecule, especially along the 6-membered cycles. These considerations are now extended to the dianions of dibenzo[*fg,ij*]pentaphene and dinaphtho[2,1,8,7-*defg*:2',1',8',7'-*ijkl*]pentaphene and show that the conclusions drawn from our theory of cyclic conjugation are in perfect agreement with their experimentally established<sup>6</sup> behavior, and can be used for the explanation thereof. In addition, the cyclic conjugation in a few other, structurally related, benzenoid dianions is analyzed.

The details of the method employed have been outlined elsewhere.<sup>8-11,14</sup> Let  $G$  be the molecular graph, representing the  $\pi$ -electron network of the conjugated molecule considered.<sup>15</sup> Then in the case of neutral hydrocarbons, the energy effect of the cycle  $Z$  contained in  $G$  is expressed as

$$ef_0(G,Z) = \frac{2}{\pi} \int_0^\infty \left| \frac{\phi(G,ix)}{\phi(G,ix) + 2\phi(G-Z,ix)} \right| dx \quad (1)$$

whereas in the case of dianions, this energy effect is given by

$$ef_{-2}(G,Z) = ef_0(G,Z) + 2(\lambda_{\text{LUMO}} - \lambda_{\text{LUMO}}^R) \quad (2)$$

In the above formulas  $\phi(H,x)$  denotes the characteristic polynomial of the graph  $H$  (where  $H = G$  or  $H = G - Z$ ), whereas  $\lambda_{\text{LUMO}}$  and  $\lambda_{\text{LUMO}}^R$  are the solutions of the equations  $\phi(G,x) = 0$  and  $\phi(G,x) + 2\phi(G-Z,x) = 0$ , respectively, pertaining to the highest unoccupied molecular orbital (LUMO) energy level. Further,  $i = \sqrt{-1}$ .

The quantities  $ef_0(G,Z)$  and  $ef_{-2}(G,Z)$ , as defined *via* Eqs. (1) and (2), are expressed in the units of the HMO carbon-carbon resonance integral  $\beta$ . Consequently, positive *ef*-values imply thermodynamic stabilization. The greater a (positive) *ef*-value is, the more intense is the cyclic conjugation in the corresponding cycle.

#### CYCLIC CONJUGATION IN DIBENZO[*fg,ij*]PENTAPHENE AND DINAPHTHO[2,1,8,7-*defg*:2',1',8',7'-*ijkl*]PENTAPHENE AND THEIR DIANIONS

The benzenoid system **1** can be viewed as a pair of phenanthrene fragments joined by means of two essentially single bonds.<sup>16</sup> (These latter bonds form the cycle  $d$ , see Fig. 1). Analogously, **3** should be regarded as a system formed by two pyrene fragments joined through the cycle  $d$ . One may consider **1** and **3** as the *cis*-isomers, in which case the benzenoid species **4** and **5** would be the *trans*-isomers, see Fig. 1. The "mixed" *cis*- and *trans*-isomers **6** and **7**, respectively, depicted in Fig. 1 have also been examined.

The *ef*-values of the 6- and 10-membered cycles of the benzenoid hydrocarbons considered and of their dianions are given in Table I. In this section attention will be focused only on the systems **1**, **1**<sup>2-</sup>, **3** and **3**<sup>2-</sup>.

TABLE I. Energy effects, calculated according to Eqs. (1) and (2), of symmetry non-equivalent 6- and 10-membered cycles of the benzenoid hydrocarbons (b. h.), shown in Fig. 1;  $n$  – non-charged molecule,  $d$  – dianion

| cycle   |     | b. h.   | b. h.   | b. h.  | b. h.  | b. h.  | b. h.  |
|---------|-----|---------|---------|--------|--------|--------|--------|
|         |     | 1       | 4       | 3      | 5      | 6      | 7      |
| $a$     | $n$ | 0.1547  | 0.1547  | 0.1019 | 0.1019 | 0.1024 | 0.1025 |
|         | $d$ | 0.1169  | 0.1170  | 0.0776 | 0.0773 | 0.0696 | 0.0698 |
| $b$     | $n$ | 0.0482  | 0.0483  | 0.0480 | 0.0472 | 0.0478 | 0.0480 |
|         | $d$ | 0.0411  | 0.0424  | 0.0561 | 0.0531 | 0.0605 | 0.0616 |
| $c$     | $n$ | 0.1435  | 0.1431  | 0.0922 | 0.0935 | 0.0943 | 0.0940 |
|         | $d$ | 0.0849  | 0.0794  | 0.0570 | 0.0616 | 0.0526 | 0.0510 |
| $d$     | $n$ | 0.0197  | 0.0197  | 0.0231 | 0.0231 | 0.0213 | 0.0213 |
|         | $d$ | 0.0283  | 0.0284  | 0.0359 | 0.0362 | 0.0320 | 0.0319 |
| $e$     | $n$ | –       | –       | 0.0564 | 0.0563 | 0.0559 | 0.0559 |
|         | $d$ | –       | –       | 0.0774 | 0.0773 | 0.0853 | 0.0852 |
| $a'$    | $n$ | –       | –       | –      | –      | 0.1542 | 0.1542 |
|         | $d$ | –       | –       | –      | –      | 0.1302 | 0.1298 |
| $b'$    | $n$ | –       | –       | –      | –      | 0.0482 | 0.0475 |
|         | $d$ | –       | –       | –      | –      | 0.0437 | 0.0408 |
| $c'$    | $n$ | –       | –       | –      | –      | 0.1407 | 0.1427 |
|         | $d$ | –       | –       | –      | –      | 0.0917 | 0.1033 |
| $a+b$   | $n$ | 0.0254  | 0.0255  | 0.0183 | 0.0179 | 0.0183 | 0.0183 |
|         | $d$ | 0.0141  | 0.0160  | 0.0155 | 0.0136 | 0.0143 | 0.0151 |
| $a+e$   | $n$ | –       | –       | 0.0195 | 0.0195 | 0.0195 | 0.0195 |
|         | $d$ | –       | –       | 0.0192 | 0.0187 | 0.0188 | 0.0191 |
| $b+c$   | $n$ | 0.0226  | 0.0226  | 0.0154 | 0.0154 | 0.0158 | 0.0158 |
|         | $d$ | -0.0033 | -0.0033 | 0.0055 | 0.0055 | 0.0041 | 0.0041 |
| $b+d$   | $n$ | 0.0019  | 0.0019  | 0.0028 | 0.0028 | 0.0024 | 0.0024 |
|         | $d$ | 0.0044  | 0.0044  | 0.0060 | 0.0061 | 0.0052 | 0.0052 |
| $b+e$   | $n$ | –       | –       | 0.0058 | 0.0056 | 0.0057 | 0.0057 |
|         | $d$ | –       | –       | 0.0146 | 0.0134 | 0.0186 | 0.0190 |
| $c+d$   | $n$ | 0.0046  | 0.0046  | 0.0036 | 0.0036 | 0.0031 | 0.0031 |
|         | $d$ | 0.0164  | 0.0164  | 0.0082 | 0.0084 | 0.0072 | 0.0072 |
| $c+e$   | $n$ | –       | –       | 0.0179 | 0.0183 | 0.0183 | 0.0183 |
|         | $d$ | –       | –       | 0.0135 | 0.0157 | 0.0151 | 0.0142 |
| $a'+b'$ | $n$ | –       | –       | –      | –      | 0.0254 | 0.0250 |
|         | $d$ | –       | –       | –      | –      | 0.0192 | 0.0158 |
| $b'+c'$ | $n$ | –       | –       | –      | –      | 0.0221 | 0.0220 |
|         | $d$ | –       | –       | –      | –      | 0.0042 | 0.0043 |
| $b'+d$  | $n$ | –       | –       | –      | –      | 0.0022 | 0.0022 |
|         | $d$ | –       | –       | –      | –      | 0.0050 | 0.0049 |
| $c'+d'$ | $n$ | –       | –       | –      | –      | 0.0053 | 0.0053 |
|         | $d$ | –       | –       | –      | –      | 0.0174 | 0.0172 |

Cyclic conjugation in the non-charged benzenoid hydrocarbons **1** and **3** is well represented by the (unique) Clar aromatic sextet formulas<sup>16,17</sup> **1a** and **3a**, see Fig. 2. Recall that the circles in the Clar formulas indicate sextets of  $\pi$ -electrons, that are expected to be mainly localized in the respective hexagon.

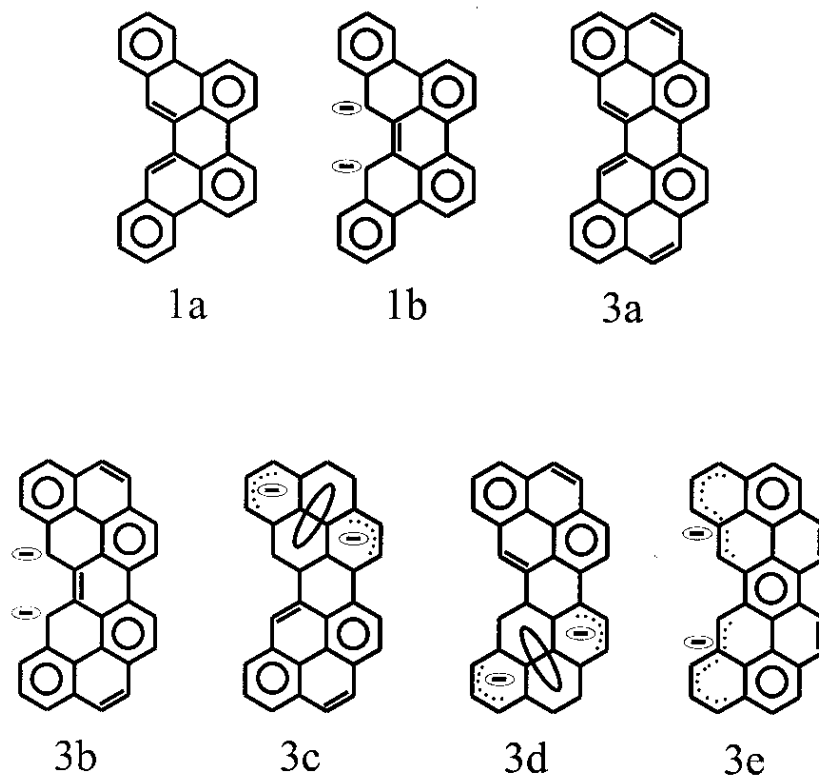


Fig. 2. Clar-type structural formulas of **1**, **3** and their dianions.

It has been demonstrated<sup>11,18,19</sup> that in benzenoid molecules with a unique Clar formula, the energy effects of the 6-membered cycles, as calculated by means of Eq. (1), are in good (although not perfect) agreement with the Clar picture: "full" hexagons (*i.e.*, hexagons in which the circles in the Clar formula are drawn) have large *ef*-values, whereas the "empty" hexagons have significantly smaller, yet positive, *ef*-values. In the case of **1** and **3** (as well as **4–7**) the "full" hexagons are those labeled by *a* and *c*, whereas the hexagons *b*, *d* and *e* are "empty". The data in Table I corroborate this earlier established regularity.

In the case of **1**<sup>2-</sup>, all energy effects are somewhat diminished relative to **1** (a feature characteristic for benzenoid dianions<sup>14</sup>), but otherwise the same pattern is maintained: the "full" hexagons have large and the "empty" hexagons small *ef*-values. Thus one may expect that a Clar-type formula, in which the hexagons, *a* and *c*

are "full" will represent the dominant modes of cyclic conjugation in  $1^{2-}$ . Then, however, the two negative charges must be in positions 15 and 16, as shown by formula **1b**, depicted in Fig. 2. [Formula **1b** explains also why  $ef_{-2}(1,d)$  is greater than  $ef_0(1,d)$ : in **1b** the hexagon  $d$  possesses a pair of  $\pi$ -electrons and participates in a weak phenanthrene-type conjugation mode; in **1a** this hexagon is devoid of any cyclic conjugation.]

The above reasoning, based on the consideration of cyclic conjugation, explains why the negative charge in  $1^{2-}$  is to a great extent localized in the (otherwise unexpected) positions 15 and 16 and why reaction with oxygen occurs just at these two carbon atoms.

The charge-localization in  $1^{2-}$  was confirmed by both NMR measurements and AM1-type semiempirical calculations.<sup>6</sup>

The case of  $3^{2-}$  is different. Because **1** and **3** have very similar cyclic conjugation modes (*cf.* formulas **1a** and **3a**), one could be inclined to expect that the same holds also for  $1^{2-}$  and  $3^{2-}$ , namely that cyclic conjugation in  $3^{2-}$  is well represented by the Clar-type formula **3b**, Fig. 2. The results of our energy-effect calculations, based on Eq. (2) and shown in Table I, indicate the opposite.

Consider first cyclic conjugation in a simpler benzenoid system – pyrene (**8**) and its dianion, see Fig. 3. The respective energy effects are:

$$\begin{array}{ll} ef_0(\mathbf{8}, r) = 0.1063 & ef_{-2}(\mathbf{8}, r) = 0.0389 \\ ef_0(\mathbf{8}, s) = 0.0528 & ef_{-2}(\mathbf{8}, s) = 0.1154 \\ ef_0(\mathbf{8}, r+s) = 0.0198 & ef_{-2}(\mathbf{8}, r+s) = 0.0198 \\ ef_0(\mathbf{8}, s+s') = 0.0056 & ef_{-2}(\mathbf{8}, s+s') = 0.0522 \end{array}$$

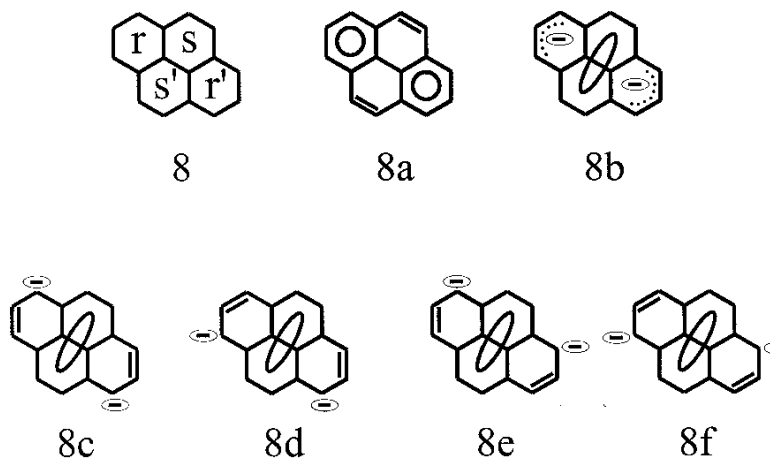


Fig. 3. Concerning cyclic conjugation in pyrene and its dianion; for details see text.

The *ef*-values pertaining to the non-charged pyrene are in full agreement with the Clar formula **8a**. On the other hand, in the case of the pyrene dianion, cyclic conjugation in the hexagons *r* and *r'* has significantly decreased, whereas in the hexagons *s* and *s'* has significantly increased. This is best seen by the almost ten-fold increase of the *ef*-value of the 10-membered cycle *s* + *s'*. All this clearly indicates that cyclic conjugation in **8**<sup>2-</sup> should be represented by the formula **8b**, which is just a concise way of depicting the quartet of Clar-type formulas **8c–8f**, see Fig. 3. Anyway, the negative charge in **8**<sup>2-</sup> is mainly located in the hexagons *r* and *r'*.

Returning now to **3**<sup>2-</sup> one can easily recognize that its cyclic conjugation modes resemble those of the pyrene dianion: *ef*<sub>-2</sub>(**3**,*b*) and *ef*<sub>-2</sub>(**3**,*e*) are greater than *ef*<sub>0</sub>(**3**,*b*) and *ef*<sub>0</sub>(**3**,*e*), respectively, and are nearly equal to *ef*<sub>-2</sub>(**3**,*a*) and *ef*<sub>-2</sub>(**3**,*c*). Further, *ef*<sub>-2</sub>(**3**,*b*+*e*) is significantly greater than *ef*<sub>0</sub>(**3**,*b* + *e*). This all points towards cyclic conjugation represented by formulas **3c** and **3d**.

The fact that *ef*<sub>-2</sub>(**3**,*d*) is much greater than *ef*<sub>0</sub>(**3**,*b*) implies that also a third mode of cyclic conjugation must be taken into account, namely the one represented by formula **3e**. This conjugation mode is responsible for *ef*<sub>-2</sub>(**3**,*e*) being greater than *ef*<sub>-2</sub>(**3**,*b*), exceeding even the value of *ef*<sub>-2</sub>(**3**,*a*).

In summary cyclic conjugation in **3**<sup>2-</sup> follows a complicated pattern, the dominant modes of which are represented by formulas **3b–3e**, Fig. 2. As a consequence, only a fraction of the negative charge is localized in positions 15 and 16, the rest being distributed over the entire molecule. Consequently, no carbon atoms in **3**<sup>2-</sup> are particularly reactive with regard to oxygen.

The lack of non-uniformity in the charge density distribution in **3**<sup>2-</sup> has been confirmed by AM1 calculations.<sup>6</sup>

#### ON CYCLIC CONJUGATION IN RELATED BENZENOID DIANIONS

From the data given in Table I one may infer about the characteristics of cyclic conjugation in the dianions of the benzenoid hydrocarbons **4–7**. Cyclic conjugation in **4**<sup>2-</sup>–**7**<sup>2-</sup> is closely analogous to what has been discussed above (especially in the case of **5**<sup>2-</sup> and **3**<sup>2-</sup>), and will not be analyzed any further.

The *ef*-values of **4**<sup>2-</sup> indicate that also in this dianion intensive cyclic conjugation takes place in the hexagons *a* and *c*. This, however, implies that the negative charge must be localized in positions 8 and 16. Thus, it can be predicted that the dianion of dibenzo[*fg,qr*]pentacene (**4**) will react with oxygen forming as the dominant product 8,16-dioxo-dibenzo[*fg,qr*]pentacene.

*Acknowledgement.* A significant part of the research communicated in this paper has been done during air raid alarms, but not in a shelter. The author thanks Prophet Obadiah for pointing out that:

*For soon the day of the Lord will come on all the nations:  
you shall be treated as you have treated others,  
and your deeds will recoil on your own head.*

## ИЗВОД

О ОКСИДАЦИЈИ ДИАНЈОНА ДИБЕНЗО[*fg,ij*]ПЕНТАФЕНА И ДИНАФТО[2,1,8,7*defg*:2',1',8',7'-*ijkl*]ПЕНТАФЕНА

ИВАН ГУТМАН

*Природно-математички факултет у Крагујевцу*

Дианјон дибензо[*fg,ij*]пентафена је недавно синтетисан и нађено је да реагује са кисеоником, градећи у скоро квантитативном приносу 15,16-диоксо дериват. Оксидација дианјона динафто[2,1,8,7-*defg*:2',1',8',7'-*ijkl*]пентафена под сличним условима не даје никакве диоксо продукте. Показујемо да су наведени резултати последица разлике у цикличној коњугацији у овим дианјонима. Циклична коњугација у поменутом два дианјона, као и у још неким структурно сродним бензеноидним дианјонима, процењена је помоћу једне кванто-хемијске методе, раније развијене од стране аутора.

(Примљено 6. априла 1999)

## REFERENCES

1. A. Minsky, M. Rabinovitz, *J. Am. Chem.* **106** (1984) 6755
2. Y. Cohen, A. Y. Meyer, M. Rabinovitz, *J. Am. Chem. Soc.* **108** (1986) 7039
3. M. Rabinovitz, *Topics Curr. Chem.* **146** (1988) 99
4. L. Zelikovich, R. E. Hoffman, A. Ayalon, M. Rabinovitz, *J. Chem. Soc., Perkin Trans. 2* (1992) 1758
5. M. Rabinovitz, A. Ayalon, *Pyre Appl. Chem.* **65** (1993) 111
6. R. Benshafrut, R. E. Hoffman, M. Rabinovitz, K. Mullen, *J. Org. Chem.* **64** (1999) 644
7. In this work the compounds are named and their atoms numbered according to the IUPAC rules (L. C. Sander, S. A. Wise, *Polycyclic Aromatic Hydrocarbon Structure Index*, National Institute of Standards and Technology, Washington, 1997); this is different to that used by Benshafrut *et al.*<sup>6</sup>
8. I. Gutman, S. Bosanac, *Tetrahedron* **33** (1977) 1809
9. I. Gutman, O. E. Polansky, *Theor. Chim. Acta* **60** (1981) 203
10. I. Gutman, *Theor. Chim. Acta* **77** (1984) 43
11. I. Gutman, *Bull. Acad. Serbe Sci. Arts (Cl. Math. Natur.)* **106** (1993) 37
12. I. Gutman, V. Ivanov-Petrović, *J. Mol. Struct. (Theochem)* **389** (1997) 227
13. I. Gutman, V. Ivanov-Petrović *Bull. Chem. Technol. Maced.* **16** (1997) 91
14. I. Gutman, *J. Mol. Struct. (Theochem)* **428** (1998) 227
15. I. Gutman, O. E. Polansky, *Mathematical Concepts in Organic Chemistry*, Springer-Verlag, Berlin 1986
16. I. Gutman, S. J. Cyvin, *Introduction to the Theory of Benzenoid Hydrocarbons*, Springer-Verlag, Berlin 1980
17. E. Clar, *The Aromatic Sextet*, Wiley, London 1972
18. I. Gutman, *Rep. Mol. Theory* **1** (1990) 115
19. I. Gutman, I. Agranat, *Polyc. Arom. Comp.* **2** (1991) 63.