

Geometrical structures and magnetic properties of trinaphtho[*abc,ghi,mno*][18]annulene and its congeners[†]

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Pariser–Parr–Pople-type SCF MO and semiempirical magnetic-susceptibility calculations show that trinaphtho[*abc,ghi,mno*]- and two kinds of triazuleno[*abc,ghi,mno*][18]annulenes have large diamagnetic susceptibilities and aromatic-islands structures in which three naphthalenes or three azulenes are linked by three olefinic bridges, whereas tripentaleno[*abc,ghi,mno*]- and triheptaleno[*abc,ghi,mno*][18]annulenes have small diamagnetic susceptibilities and polyolefine structures where bond alternations are distributed all over their molecular planes.

Keywords: bond alternation, magnetic susceptibility, [18]Annulene

As early as 1992, Meier *et al.* succeeded in preparing trinaphtho[*abc,ghi,mno*][18]annulene (**1**) (Fig. 1).¹ This molecule has a disk-like structure² in which three naphthalene molecules are condensed to [18]annulene. On the basis of the analysis of the NMR spectrum of **1**, Meier *et al.* have pointed out that in **1**, three naphthalene moieties are connected by three (*E*)-form olefinic bridges, and that the central 18-membered ring of **1** does not have a macrocyclic diamagnetic ring current.¹ Its nonalternant congeners **2**, **3**, **4**, and **5** (Fig. 1) are of interest as well. In **2** and **3**, pentalene and heptalene molecules are, respectively, condensed to [18]annulene whereas in **4** and **5**, three azulene molecules are condensed to [18]annulene. In this paper, we assume **1–5** to be planar and examine their geometrical structures with respect to C–C bond lengths by using the symmetry rule^{3,4} and the Pariser–Parr–Pople (PPP)-type SCF MO method with the variable bond length technique.⁴ Further, the magnetic susceptibilities of **1–5** have been calculated by the Yamaguchi–Nakajima procedure.⁵ Although the geometrical structure and magnetic properties of **1** have previously been examined,⁶ for the sake of comparison we give the calculated results for **1** in the present paper.

We first examined the stability of the most symmetrical structures of these molecules by using the symmetrical rule for predicting bond distortions of conjugated hydrocarbons, proposed by Nakajima and coworkers: if the energy gap between the ground and the lowest unsymmetrical excited singlet state of a molecule is smaller than a critical value, about 1.2 eV, the molecule should be distorted into a less symmetrical structure.^{4a,b} In **1–5**, such excited singlet states are of *E'* symmetry. The energy difference between the ground and the lowest *E'* singlet state is calculated to be 3.72 for **1**, 2.43 for **2**, 2.23 for **3**, 1.93 for **4**, and 2.02 eV for **5**. These values are much larger than the critical value and hence indicate no bond distortions in **1–5**.

Figure 1 shows the optimised C–C bond lengths of **1–5**. The values are given in Å unit.

As shown in Fig. 1, **1** has three naphthalene moieties connected by three olefinic bridges. This structure is predicted by Meier *et al.* on the basis of NMR spectrum of **1**.¹ Our calculation supports the prediction of Meier and coworkers.

The geometrical features of **2** and **3** are quite different from that of **1**. Molecules **2** and **3** have polyolefine structures, in which bond alternations are distributed in the whole molecules. Fig. 1 shows that **2** includes three fulvene-like parts and **3** three heptalene-like parts.

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[†] This is a Short Paper, there is therefore no corresponding material in *J. Chem. Research (M)*.

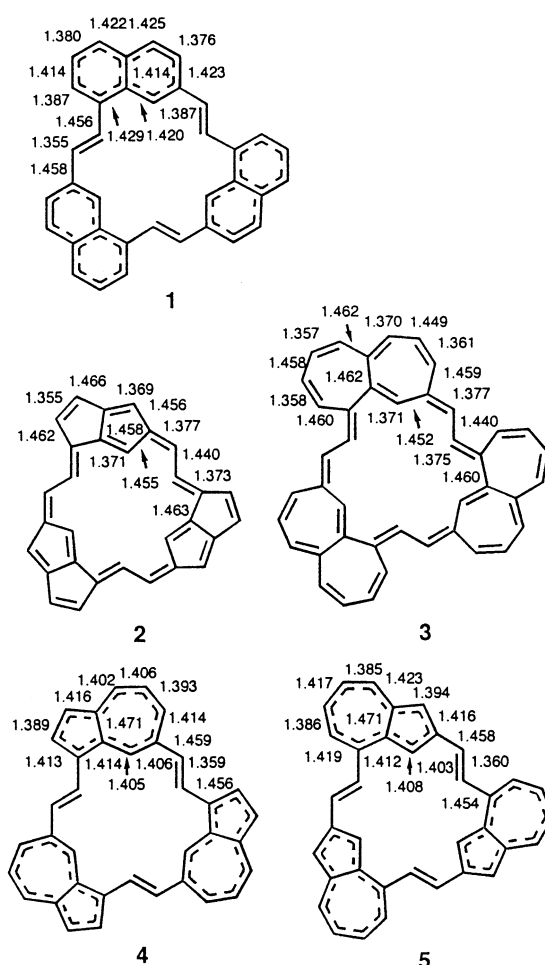


Fig. 1 Calculated C–C bond lengths (Å) of **1–5**.

In contrast, **4** and **5** have aromatic-island structures¹ in which three azulene molecules are linked by three olefinic bridges. This structural feature is similar to **1**.

We next calculated the magnetic susceptibilities of **1–5** by the Yamaguchi–Nakajima procedure, which is useful for examining the magnetic susceptibilities of planar conjugated hydrocarbons.⁵ In **4** and **5**, the geometrical structure obtained with this procedure had the bond alternation on the azulene moieties, being different from the geometries calculated with the PPP-type SCF MO method and the variable bond length technique (Fig. 1). The optimized bond lengths shown in Fig. 1

Table 1 Calculated magnetic susceptibilities

Molecule	$\Delta K/\Delta K_b$
1	5.78
2	0.36
3	0.83
4	8.55
5	7.90
[18]annulene	13.68
Naphthalene	1.86
Fulvene	0.13
Heptafulvene	0.17
Azulene	2.20

were, therefore, used to calculate the magnetic susceptibilities of **4** and **5**. The calculated results (ΔK), given in the unit of the magnetic susceptibility of benzene (ΔK_b), are summarised in Table 1. For comparison, the values of [18]annulene, naphthalene, fulvene, heptafulvene, and azulene are also provided.

Table 1 shows that the calculated magnetic susceptibility of **1** is about three times as large as that of naphthalene. From the viewpoint of magnetic susceptibility, **1** can be considered to be composed of three naphthalene molecules: that is, **1** does not have a macrocyclic diamagnetic ring current because the magnetic susceptibility of **1** is calculated to be much smaller than that of [18]annulene (Table 1), which exhibits a macrocyclic diamagnetic ring current. The calculated result for the magnetic property of **1** is in good agreement with that for the geometrical structure of **1** (Fig. 1) and also with the prediction of Meier and coworkers.¹

The calculated value of **2** is about three times larger than that of fulvene. On the other hand, **3** is found to have about five times as large a magnitude as that of heptafulvene. It is most likely that the ring parts other than the heptafulvene moieties contribute to the magnetic character of **3**. The results for **2** and **3** indicate that these molecules have polyolefinic character, losing macrocyclic ring currents.

In contrast to **2** and **3**, **4** and **5** are similar to **1** in their magnetic properties. The calculated magnetic susceptibilities of **4** and **5** are, respectively, 3.9 and 3.6 times as large as that of azulene. This suggests that in these molecules, the azulene-like parts as well as the other ring parts such as the 18-membered ring contribute to the magnetic susceptibility.

In conclusion, we have theoretically examined the geometrical structures with respect to the C–C bonds of **1–5** and their magnetic susceptibilities. It can be said from the results obtained that **1**, **4**, and **5** should be aromatic hydrocarbons, while **2** and **3** should be nonaromatic hydrocarbons.

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