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ON THE PLANARITY OF TETRACYCLO $[5.5.1.0^{4,13}0^{10,13}]$ TRIDECAHEXAENE

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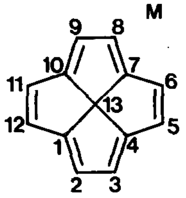
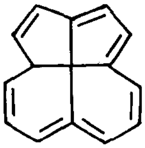
Summary. MINDO/3 calculations indicate that tetracyclo $[5.5.1.0^{4,13}0^{10,13}]$ *tridecahexaene* (**1a**) *is nonplanar* (D_2 *symmetry) in its ground state with pronounced bond alternance.*

Recently it was proposed that a central tetracoordinate carbon atom enclosed by a [12] annulene (**1**) should have a planar shape [1]. It was argued that the energetically unfavourable HOMO (a_{2u}) at the planar central atom is stabilized by interaction with the LUMO of a 12 π system [2].

To test this proposal we have carried out MINDO/3 calculations [3] on **1a**, the corresponding dianion **1b** and dication **1c** and the analogous [14]annulenes **2** and **3** by minimizing the total energy with respect to all geometrical parameters.



1a M = 0
1b M = -2
1c M = +2



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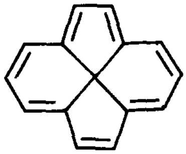

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The total energy of **1a**, **1b** and **1c** under various geometrical constraints was studied in detail. For the neutral species **1a** it was found that the structure of lowest energy belongs to point group D_2. The angles and bond lengths of **1a** together with the structural parameters of the ionic counterparts **1b** and **1c** are collected in Figure 1. From Table 1 it is seen that the two structures with a planar central atom are much higher in energy; the energy difference between D_2 and D_{2h} is 49.09 kcal/mol, the D_{4h} triplet conformation is separated by 59.61 kcal/mol from the structure of lowest energy. This result is anticipated if one compares the energy calculated for the structural deformation $T_d \rightarrow D_{4h}$ of methane (80-100 kcal/mol) [2] [5] [6] [7] with resonance energies calculated for annulenes [8]. Inspection of Figure 1 shows a marked bond alternation of the peripheral ring in the D_{2h} and D_2 structure of **1a**.

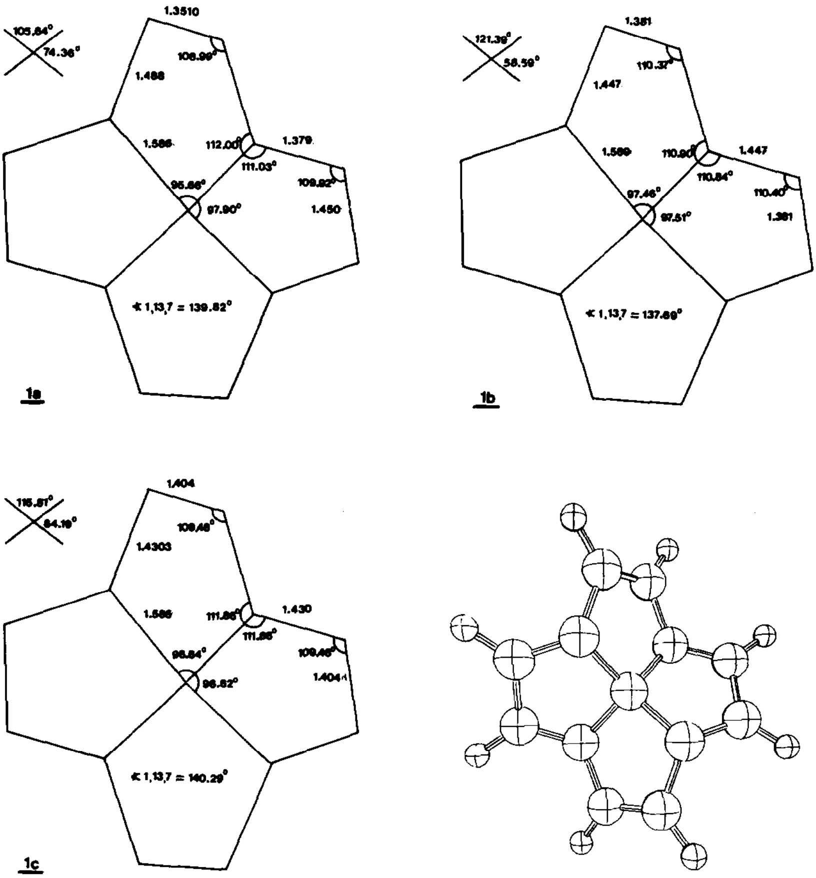
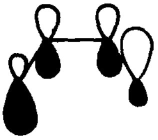


Figure 1. Bond lengths and bond angles of 1a, 1b and 1c together with perspective view of 1a

In Table 2 we have listed the calculated net charges of the carbon atoms. While in both planar forms D_{2h} and D_{4h} there is a strong negative charge at the central atom, there is no charge separation between the central unit and the surrounding moiety in the structure of lowest energy, D_2.

To study geometrical preferences as a function of the occupation numbers of the frontier orbitals and to simulate the effect of electron-donating and electron-withdrawing substituents at the molecular periphery, we also performed calculations on the charged species 1b and 1c. Once again the D_2 structure emerges as the one of lowest energy; in 1b D_{4h} and D_2 are separated by 46.93 kcal/mol, while the energy difference in case of the dication 1c amounts to 44.40 kcal/mol. A comparison between the structures 1a, 1b and 1c shows that the bond localization is less marked in the two charged systems; both planar structures 1b and 1c belong to the point group D_{4h}. Inspection of Table 2 leads to the surprisingly result, that the central atom carries more negative charge in the cationic compound 1c than in 1b.

A common aspect of the three systems **1a**, **1b** and **1c** is the remarkable tendency to avoid a planar conformation of the central carbon atom and distribute the strain energy over all carbon centers. This leads to highly directed "π-orbitals" at C_1, C_4, C_7 and C_{10} as shown below. The sum of all carbon-carbon angles at these centers reaches a value of 348.22^0 in **1a** and 345.17^0/349.95^{0}in **1b**/**1c** respectively. This sum is in between the value of 328.41^0 for sp^3 hybridization and 360^0 for sp^2 hybridization.



The tendency to maintain a tetrahedral carbon atom at the center in **2** and **3** is more pronounced than in **1** due to the greater flexibility of the systems. Once again our calculations predict a strong bond localization for both structures leading to a pair of unequivalent five- and six-membered rings around the nonplanar central atom.

This study indicates that the various synthetic attempts [1] [9] towards a compound like **1** to **3** with a planar tetracoordinated central atom will lead at most to energetically unfavourable olefinic ring systems.

Table 1

Heats of formation (ΔH_f in kcal/mol) of **1a**, **1b** and **1c**

System	Point Group	Spin Multiplicity	ΔH_f(kcal/mol)
1a	D_{4h}	Triplet	262.08
	D_{2h}	Singlet	251.57
	D_2	Singlet	202.48
1b	D_{4h}	Singlet	314.16
	D_2	Singlet	267.23
1c	D_{4h}	Singlet	654.06
	D_2	Singlet	609.65

Table 2

Net charges in **1a**, **1b** and **1c**

System	Point Group	Carbon-Center	Net Charge
1a	D_{4h}	1	.082
		2	-.037
		13	-.169
1a	D_{2h}	1	.145
		2	-.076
		5	-.036
		13	-.295
1a	D_2	1	.011
		2	-.016
		5	-.010
		13	.017
1b	D_{4h}	1	-.011
		2	-.143
		13	-.100
1b	D_2	1	-.134
		2	-.088
		5	-.088
		13	.142
1c	D_{4h}	1	.246
		2	.055
		13	-.393
1c	D_2	1	.125
		2	.087
		5	.087
		13	-.102

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