Phenanthrene Dianion is not Planar

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Ab initio calculations show that phenanthrene dianion deviates from planarity.

Physical organic chemistry has produced a lot of arguments in favour of the flexibility of the skeleton of the phenanthrene dianion, 1^{2-}. Circumstantial evidence for the non-planarity of dianions derived from phenanthrene substituted at the 'bay' position has been published.[1,2] It has also been demonstrated that 1^{2-} is a highly paratropic species and is hence regarded as a so-called antiaromatic molecule.[3,4] It was suggested that in order to minimize paratropicity the molecular skeleton may undergo a deformation so that the efficiency of the π-conjugation is reduced and antiaromaticity is less pronounced.[5] At the same time semiempirical calculations predict that 1^{2-} is planar, and only a sophisticated treatment including the counter-ion enabled the non-planarity of $1^{2-}/2\ Li^+$ to be achieved computationally.[2,6]

We find that *ab initio* calculations in minimal basis set (STO-3G) as well as semiempirical methods (MINDO/3, MNDO, AM1) describe the ground state of 1^{2-} as a planar structure. However, when the basis set for *ab initio* calculations was extended to STO 3-21G and further to STO 4-31G, the planar structure of 1^{2-} proved to be not a minimum, but a transition state ($\nu_{im} = -53\ cm^{-1}$ on HF/3-21G level) between two non-planar minima with a dihedral angle C(4)–C(4a)–C(5a)–C(5) = 15.8° (HF/3-21G)–16.8° (HF/4-31G).†

Calculated geometrical structures and charges (C or C + H) are shown in Fig. 1 for the minimum and planar transition state of 1^{2-} as well as for neutral phenanthrene (1) and its dication (1^{2+}).

These data show that the structures of 1^{2-} in the ground and the transition states do not differ significantly, with the only obvious exception of the $H^4 \cdots H^5$ non-bonding distance, which enlarges from *ca.* 2.0 in structure **b** to *ca.* 2.1 Å in structure **a**. H–H Repulsion is definitely not the main factor that leads to non-planarity as in neutral phenanthrene, which is planar, the same H···H distance is also *ca.* 2.0 Å (Fig. 1), nevertheless H–H repulsion can be a contributor to the deviation from planarity of 1^{2-}. There is a delicate balance between σ and π contributions that determines the planarity or non-planarity of **1** and its charged derivatives. At the same time both phenanthrene ions, *i.e.* the dianion 1^{2-} and dication 1^{2+} exhibit a significant distortion of C–C bonds relative to the neutral phenanthrene (**1**) (*cf.* **a**, **c** and **d** of Fig. 1); not all these differences could be derived directly from the structure of Hückel MO Ψ_7 and Ψ_8 (Fig. 2), especially the least obvious pattern of dication and dianion molecules *i.e.* their 'biallyl' structure of C^1–C^2–C^3 and C^6–C^7–C^8 regions.

The energy difference between the minimum and the transition state for 1^{2-} was estimated using more sophisticated single-point calculations (further extension of the basis set or inclusion of Møller–Plesset second-order correlation energy), and the results seem to converge to the value of 0.7–0.9 kcal mol^{-1} in favour of a non-planar structure, which did survive as a global minimum for 1^{2-} even after inclusion of zero-point energy (ZPE) corrections (see Table 1).‡

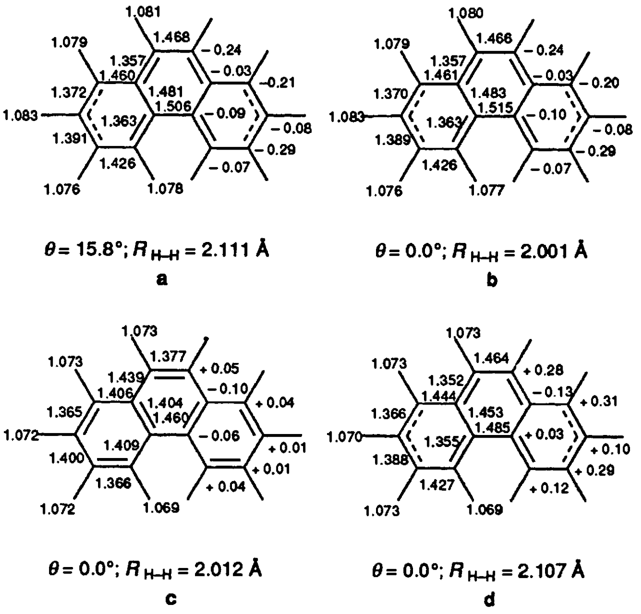

Fig. 1 Calculated (HF/3-21G) internuclear distances (Å) and atomic (C) or group (CH) charges (esu) for: **a**, phenanthrene dianion non-planar minimum; **b**, phenanthrene dianion planar transition state; **c**, neutral phenanthrene; **d**, phenanthrene dication. For all structures: θ = dihedral angles C^4–C^{4a}–C^{5a}–C^5; *R* = distance between H^4 and H^5.

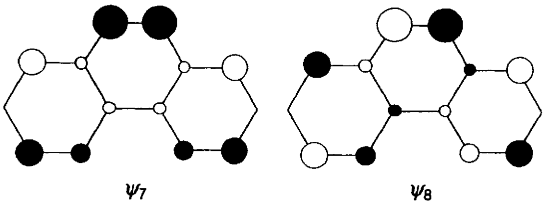

Fig. 2 Hückel MO Ψ_7 and Ψ_8 for phenanthrene

The energy profile of 1^{2-} as shown in Fig. 3 is extremely flat even in comparison with neutral phenanthrene (**1**) and its dication, 1^{2+}. The last two molecules on the same calculation level possess a planar ground state, but also possess flat energy profiles with respect to the bay torsion angle C^4–C^{4a}–C^{5a}–C^5 (Fig. 3).

These results may clarify some discrepancies concerning 1^{2-}, in particular the deviation of the corresponding point from the general relationship between experimentally observed paratropic shifts and calculated HOMO–LUMO gaps for condensed benzenoid polycyclic dianions,[8] since all these

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† All the computations were performed with the GAUSSIAN-90 series of programs[7] on IBM/RS6000 (model 550) workstations of Ben-Gurion University and the Hebrew University.

‡ 1 cal = 4.184 J.

Table 1 Energy differences between minimum and transition state of 1^{2-}

Method of calculation	ΔE/kcal mol^{-1}
HF/3-21G//HF/3-21G	0.29
HF/3-21G//HF/3-21G[a]	0.20
MP2=FC/3-21G//HF/3-21G	0.91
HF/4-31G/HF/4-31G	0.40
HF/6-31G//HF/4-31G	0.46
HF/6-31G*//HF/4-31G	0.55
HF/6-31G**//HF/4-31G	0.56
HF/6-311G*//HF/4-31G	0.69
HF/6-311G**//HF/4-31G	0.68

[a] With ZPE corrections.

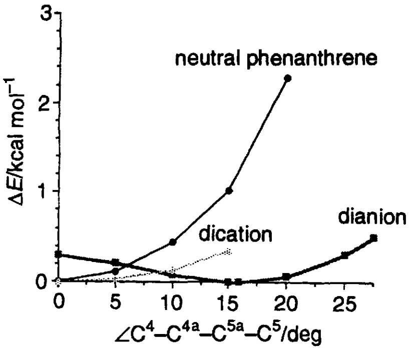

Fig. 3 Electron energy *vs.* bay torsion angle in neutral phenanthrene and its dianion and dication. All data from HF/3-21G calculations with fixed named dihedral angle and optimization of all other degrees of freedom.

calculations did refer to planar structures, which are correct for all compounds but not for 1^{2-}.

It should also be noted that the isoelectronic analogues of 1^{2-}, *e.g.* the dihydrodiazaphenanthrene derivatives, also should be non-planar, or, at least, very flat with respect to the bay dihedral angle. Really, *ab initio* calculations at the HF/3-21G level reveal this conclusion. At the same time it seems worthwhile to note, that these stable uncharged analogues of phenanthrene dianion (1^{2-}) due to their non-planarity and/or flexibility might offer guidelines for designing new complexation agents.

Phenanthrenes substituted at the 4,5-positions (bay region) have a helical structure due to steric hindrance. The anions derived from such distorted phenanthrenes show a reduced degree of paratropicity which is in line with the degree of the deviation from planarity of the parent neutral systems.

In conclusion, it should be emphasized, that non-planarity is an intrinsic property of the phenanthrene dianion and its analogues. This property however may originate from the system's driving force to reduce antiaromaticity.

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