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

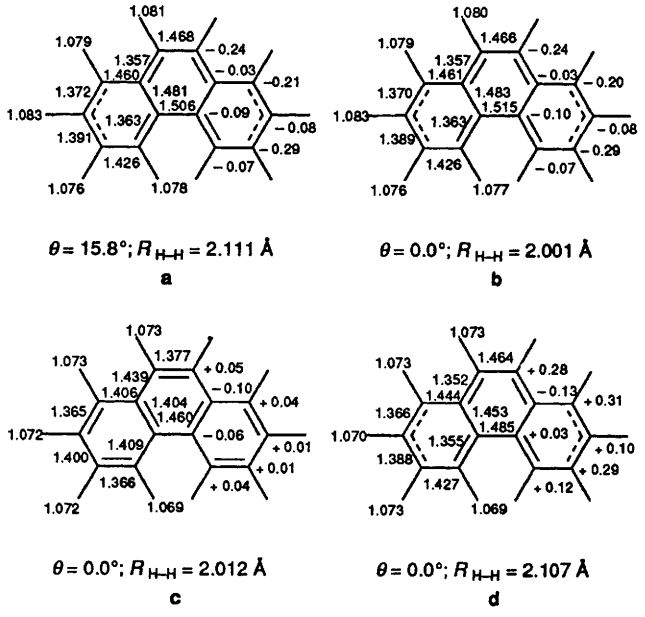

Fig. 1 Calculated (HF/3-21G) internuclear distances (Å) and atomic (C) or group (CH) charges (esu) for: **a**, phenanthrene dianion non-planar minimum; **b**, phenanthrene dianion planar transition state; **c**, neutral phenanthrene; **d**, phenanthrene dication. For all structures: θ = dihedral angles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

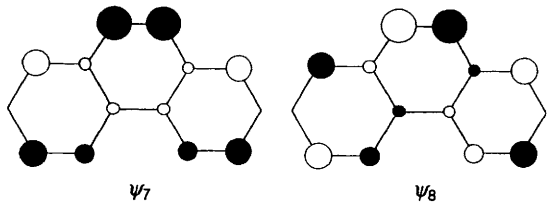

Fig. 2 Hückel MO Ψ_7 and Ψ_8 for phenanthrene

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).‡

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

† 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.

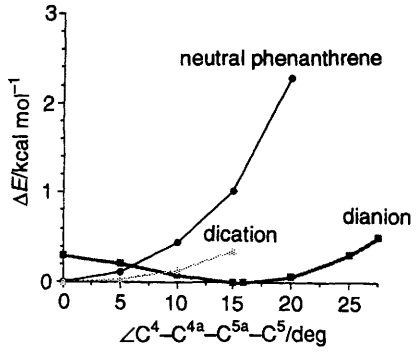

Fig. 3 Electron energy *vs.* bay torsion angle in neutral phenanthrene and its dianion and dication. All data from HF/3-21G calculations with fixed named dihedral angle and optimization of all other degrees of freedom.

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.

Acknowledgements

The authors are indebted to Professor S. Shaik (Hebrew University) for fruitful discussions. Grants from the Ministry of Absorbtion (A. I.) and the US–Israel Binational Science Foundation (A. A. and M. R.) are gratefully acknowledged.

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Paper 4/02072C
Received 5*th April* 1994
Accepted 18*th April* 1994