Pyracyclene: Neutral, Dication, and Dianion

By DONALD H. LO and M. A. WHITEHEAD*
(*Quantum Chemistry Laboratory, McGill University, Montreal 2, Canada*)

THE theoretical discussion of whether, or not, pyracyclene (I) is a 'pentalenoid' system[1] has been stimulated by the recent synthesis of this hydrocarbon by Trost and Bright.[2] They used controlled bromination of pyracene to give a 1,2,5,6-tetrabromopyracene, which was debrominated with iodide ion to give pyracyclene in solution. Two possible structures are proposed for this molecule, (I) a naphthalene core (NN) with two vinyl bridges (*f*) and (II) a cyclododecahexene with an internal cross-linked ethylenic unit (E).

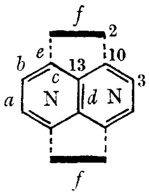
Trost and Bright compared the n.m.r. chemical shifts of the outer protons of [16]annulene and [24]annulene[3] (τ 4·6 and 5·27), which possess a $4n$-type paramagnetic ring current,[4] with that of pyracyclene (τ at C-3, 3·48), which is shifted upfield from its dihydropyracyclene precursor (τ_3 2·35). They concluded that the peripheral structure (II) is a better representation of pyracyclene, because it would have a $4n$ peripheral paramagnetic ring current to cause the upfield shift in τ.

The LCAO-MO-SCF-PPP ($\pi + \sigma$) method,[5] was applied to pyracyclene, as the neutral molecule, dication, and dianion. The results are shown in Tables 1 and 2.

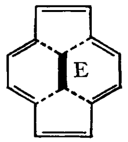
The calculated geometries for these three species correspond to their most stable planar conformations.[5] The bond lengths estimated for neutral pyracyclene resemble (I) whose (NN)-core bond lengths are almost identical to those of a free naphthalene molecule[5] (Table 2), while the dication has uniform peripheral bond lengths about 1·41 Å, which resemble those of structure (II), and the dianion has a 'fulvalene-dianion-like' core (FF), cross-linked by two external ethylenic bonds, (III).

The total π-electron densities support these structures. The (NN)-core in the neutral molecule (I) has 9·946 π-electrons; the peripheral twelve carbon unit in the dication (II) has 10·066 π-electrons; and the fulvene unit (F) in the dianion (III) has 5·761 π-electrons. The results agree with the conclusion, previously drawn in the 8-membered fused-ring compounds,[6] that any composite ring unit that can accommodate approximately $(4n + 2)$ π-electrons, will stabilize the molecule in which it occurs.

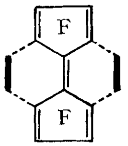
The chemical properties of neutral pyracyclene are consistent with the calculated properties of (I), since hydrogenation of pyracyclene[2] takes place in quantitative yield, only at the 1,2- and 5,6-positions to give pyracene, in agreement with the



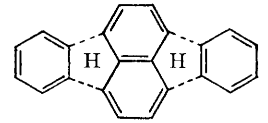
(I)



(II)



(III)



(IV)

—— 1·40 ± 0·02Å ▬ 1·35 ± 0·02Å
---- 1·46 ± 0·02Å

TABLE 1

Energies (in ev)

State	π-bond energy[a]	σ-bond energy[b]	Stabilization energy per C–C bond (SECC)[c]
Neutral	20·676	62·938	0·3103
Dication	18·860	63·654	0·3451
Dianion	21·167	63·516	0·4727

[a] π-bond energy $E_{\pi b} = -[E_\pi - \sum_i q_i W_{pi} - n_l \gamma_{ii}]$ where E_π is the total π-electronice nergy plus the effective nuclear interaction energy of the carbon sigma core[7] (J. A. Pople, *Trans. Faraday Soc.*, 1963, **49**, 1375), q_i is the self-consistent π-electron density, W_{pi} is the trigonally hybridized carbon valence-state ionization potential, γ_{ii} is the one-centre electronic repulsion energy and n_l is the number of lone pair π-electrons in an A.O.; n_l is 1 for an anion, 2 for a dianion, etc.

[b] σ-bond energy $E_{\sigma b}$ is the sum of all individual C–C bond energies, each of which is a function of its specific bond length R_{ij}. The bond lengths are calculated by direct maximization of $E_{\pi b}$ and $E_{\sigma b}$ with respect to each R_{ij}.

[c] $$\text{SECC} = \frac{(E_{\pi b} + E_{\sigma b})\text{ theory} - (E_{\pi b} + E_{\sigma b})\text{ valence bond reference structure}}{\text{Total number of C–C bonds}}.$$

presence of two isolated vinyl bridges (*f*) predicted for (I). The presence of a long-life dibromo-intermediate in the debromination reaction of 1,2,5,6-tetrabromopyracene to form pyracyclene, strongly suggests that pyracyclene is not much more stable than pyracene, its saturated vinyl analogue.

TABLE 2

Bond lengths (Å)

State	*a*	*b*	*c*	*d*	*e*	*f*
Reference structure*	1·419	1·382	1·426	1·420	1·505	1·334
Neutral	1·417	1·389	1·430	1·418	1·466	1·349
Dication	1·412	1·411	1·466	1·364	1·413	1·423
Dianion	1·373	1·443	1·423	1·431	1·420	1·403

* Pyracyclene is taken as a free naphthalene molecule, with bonds (*a*) to (*d*) possessing the free naphthalene bond lengths,[5] bonded by four pure single bonds (*e*) to two pure double bonds (*f*).

The stabilization energy per C–C bond (SECC) values for naphthalene (0·3355),[5] acenaphthylene (0·3222), and pyracylene (0·3105 ev), support these chemical properties since the higher the SECC the more stable the molecule.[5] Furthermore the higher SECC for the pyracyclene dianion (0·4727) and for the pyracyclene dication (0·3451 ev) suggest that pyracyclene can be easily reduced but less easily oxidized, and that it can possibly occur as the ion, rather than as the neutral molecule, in suitable solutions.

Does a $4n$ paramagnetic ring current exist in pyracyclene with the geometry of (I)? A hypothetical model of pyracyclene with the geometry of a free naphthalene molecule, linked by four pure single bonds (*e*) (1·505 Å)[5] to two pure double bonds (*f*) (1·334 Å),[5] would represent a structure with disrupted conjugation in the peripheral bonds. Now, bonds (*a*, *b*, *e*, *f*) of the predicted neutral molecule (I) have intermediate bond lengths between the above reference structure with disrupted conjugation, and the dication with full conjugation. Therefore, a paramagnetic ring current, possibly decreased due to bond length alterations,[4] may still exist in pyracyclene.

The deshielding or shielding effect of ring currents on ring protons was developed for neutral $(4n + 2)$ or $4n$ monocyclopolyenes, but will apply to charged species containing these numbers of π-electrons. Consequently the dication of pyracyclene will have a diamagnetic ring current and could not give the reported[2] chemical shifts.

3,4-*peri*-Phenylenefluoranthene (IV) is related to pyracyclene (I) by the fusion of two benzo-groups to the bonds (*f*) in (I). Structure (IV) has a higher SECC value than that of benzene or naphthalene. This indicates that the 5-membered ring in this compound is capable of establishing an additional stabilization between the composite benzenoidal units, and that the rings (H) in (IV) might act as "electron holes", similar to those in Clar's hydrocarbons.[5] In addition to (IV) the following compounds have been calculated: floranthene, 1,2-benzofluoranthene, 3,4-benzofluoranthene, 10,11-benzofluoranthene, and 11,12-benzofluoranthene. Bond energies, stabilization energies, and bond lengths can be obtained from the authors.

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[5] D. H. Lo and M. A. Whitehead, *Canad. J. Chem.*, in the press.
[6] D. H. Lo and M. A. Whitehead, to be published.