The E.S.R. Spectra and Spin Distributions of Benzobarrelene Radical Cations

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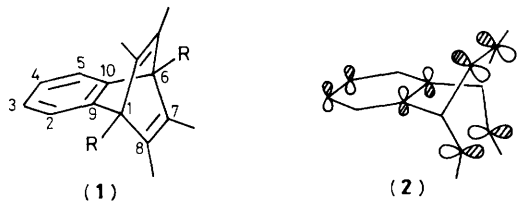
The e.s.r. spectra of two benzobarrelene radical cations have been observed and interpreted.

The question of the interaction of conjugated and non-conjugated double bonds has attracted a great deal of experimental and theoretical attention. The energies of the resultant molecular orbitals can be probed by photoelectron spectroscopy,[1,2] and the nature of these orbitals is best determined by e.s.r. spectroscopy of the molecular radical cations,[3] whose singly occupied molecular orbital (SOMO) corresponds to the highest occupied molecular orbital (HOMO) of the parent molecule.

Hoffmann, Heilbronner, and Gleiter[4] discussed the interactions between non-conjugated double bonds in terms of two extreme situations; molecules such as planar cyclohexa-1,4-diene, in which hyperconjugation dominates, and those such as non-planar norbornadiene or barrelene, in which the π-systems communicate by through-space interactions. The cyclohexa-1,4-diene[5] and norbornadiene[6] radical cations have been observed in frozen Freon matrices, but no data have been available on these radicals in fluid solution, or on any barrelene radical cation.

We have previously reported the observation of the e.s.r. spectra of conjugated buta-1,3-diene, cyclobutadiene, and cyclopenta-1,3-diene radical cations in fluid solution.[3] We now report the observation of benzobarrelene radical cations in solution, and discuss their structures with the aid of molecular orbital (M.O.) calculations.

The hexamethylbenzobarrelene (**1a**) was photolysed (Pyrex-filtered u.v. light) at −78 °C in degassed dichloromethane containing aluminium chloride, giving rise to the spectrum shown in Figure 1. The tetramethylbenzobarrelene (**1b**) showed a similar spectrum, together with some lines from a second unidentified radical. Each spectrum showed hyperfine coupling to four equivalent methyl groups and two other equivalent protons. As the spectra of (**1a**$^{\bullet+}$) and (**1b**$^{\bullet+}$) are essentially the same, the bridgehead methyl groups or



(1)

a; R = Me

b; R = H

(2)

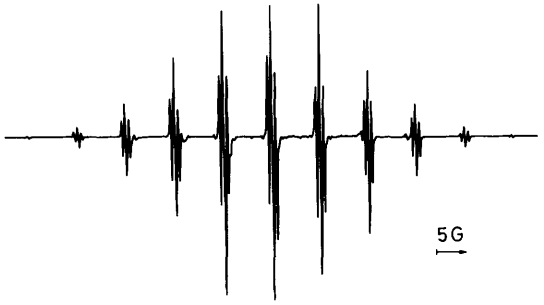


Figure 1. E.s.r. spectrum of the radical cation (**1a**$^{\bullet+}$) in CH_2Cl_2 at −78 °C.

Table 1. E.s.r. spectra of benzobarrelene radical cations in dichloromethane.

	T/°C	*a*(4Me)/G	*a*(2H-3,-4)/G	*g*
(**1a**$^{\bullet+}$)	−99	8.56	0.63	2.0022
	0	8.38	0.75	
(**1b**$^{\bullet+}$)	−100	8.58	0.68	2.0022
	−64	8.53	0.65	

hydrogen atoms are presumably not involved in coupling, and this is supported by an INDO calculation[7] (using the UHF/MNDO-optimised geometry[8]) for (**1a**$^{\bullet+}$), which gives *a*(7-,8-,11-,12-Me) 10.36, *a*(3-,4-H) −0.43, *a*(1-,6-Me) 0.06, *a*(2-,5-H) 0.06 G.† The hyperfine coupling constants and their assignments, are given in Table 1.

Three aspects of these spectra deserve comment, namely (i) the density of the unpaired spin in the phenyl ring, (ii) the equivalence of the coupling from all four of the olefinic methyl groups, and (iii) the absence of detectable coupling from the bridgehead substituents.

If the benzene radical cation[9] and hexamethylbenzene radical cation[10] are used as models to estimate the spin density at the aromatic and olefinic carbon atoms respectively, and it is assumed that the two fused aromatic carbon atoms carry the same amount of spin as those at the opposite side of the benzene ring, we obtain an estimate of 22.1% spin on each of the four olefinic carbon atoms, and 9.6% in the benzene ring.

† 1 G = 10^{-4} T

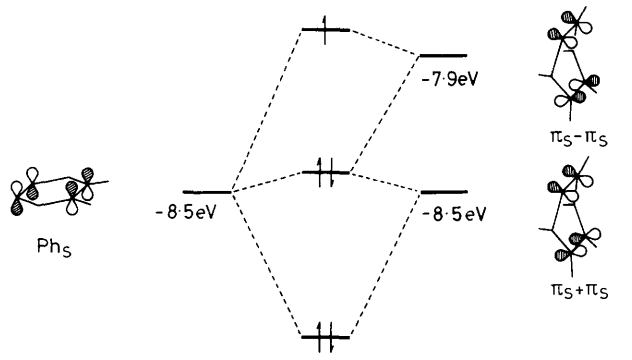


Figure 2. Orbital-interaction diagram for the tetramethylbenzobarrelene radical cations (**1**$^{\bullet+}$). The energy levels are approximate, and are in eV.

This gives a total spin of 98%, and suggests that the formally sp^2 olefinic carbons are planar or very nearly so.

The radical cations (**1**$^{\bullet+}$) are therefore essentially cyclohexa-1,4-diene radical cations, with little spin delocalisation into the aromatic ring. The enforced boat conformation of the cyclohexadiene leads to the very small or zero coupling constants found for the bridgehead substituents, in contrast to the planar cyclohexa-1,4-diene radical cation[5] which shows *a*[4H(olefinic)] 4.0; *a*[4H(methylenic)] 67.1 G. This absence of coupling at the bridgehead positions was also found for norbornadiene.[6]

The orbital-interaction analysis given by Haselbach *et al.*[2] for benzobarrelene itself must be modified for the methylated benzobarrelenes (**1**). The energy levels of the diene ($\pi_s + \pi_s$) and ($\pi_s - \pi_s$) orbitals are raised by *ca.* 1.2 eV by the methyl groups so that the ($\pi_s + \pi_s$) orbital is much closer in energy to the aromatic Ph_s orbital than is the ($\pi_s - \pi_s$) orbital (see Figure 2). This latter orbital therefore plays little part in the through-space interaction between diene and aromatic ring so that the resulting SOMO in the radical cation is concentrated on the olefinic carbons as illustrated in (**2**).

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