EPR Spectroscopic Evidence for the Mills–Nixon Effect

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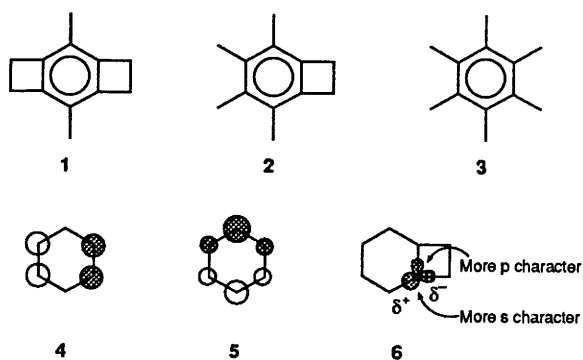*Chemistry Department, University College London, 20 Gordon Street, London WC1H 0AJ, UK*

The electron paramagnetic resonance spectra of 3,6-dimethyl-1,2,4,5-tetrahydrobenzobiscyclobutene and 3,4,5,6-tetramethyl-1,2-dihydrobenzocyclobutene show that the ψ_A MO lies above the ψ_S MO, although the reverse order would be expected from the relative electron releasing power of the substituents; this is rationalised in terms of rehybridisation of the arene carbon atoms imposed by ring strain.

The Mills–Nixon[1] effect relates to the modulation of the chemical and physical properties of an aromatic nucleus when it is fused to a small ring. Involving as it does the two fundamental concepts of steric strain and of aromaticity, it continues to excite attention more than 60 years after it was first described;[2] recent work has involved, in particular, NMR spectroscopy[3] and *ab initio* MO calculations.[4] We report here what we believe to be a new manifestation of the effect in the EPR spectra of some benzocyclobutenes.

When a solution of 3,6-dimethyl-1,2,4,5-tetrahydrobenzo-[1,2:4,5]biscyclobutene (1) in trifluoroacetic acid containing mercury(II) trifluoroacetate is irradiated with UV light, a strong EPR spectrum of the radical cation is observed. This can be simulated with the hyperfine coupling constants $a(2\text{Me})$ 0.68 G, $a(4\text{CH}_2)$ 13.84 G; clearly the unpaired electron occupies the ψ_A orbital 4 in which the methyl groups lie on the nodal plane. The radical cation of 3,4,5,6-tetramethyl-1,2-dihydrobenzocyclobutene (2), generated under the same conditions, has the same configuration, with $a(2\text{Me})$ 0.24 G, $a(2\text{Me})$ 10.72 G, $a(2\text{CH}_2)$ 11.87 G.

These benzocyclobutenes can be regarded as derivatives of the orbitally degenerate hexamethylbenzene (3) in which *ortho* pairs of methyl groups have been replaced by a CH_2CH_2 bridge, and the occupancy of the ψ_A SOMO, in which the bridging groups are concentrated at the centres of high (1/4e) unpaired electron density, and the methyl groups lie in the nodal plane, would normally be taken to imply that the CH_2CH_2 bridges repel electrons *more* strongly than do an *ortho* pair of methyl groups.

Fig. 1 Vertical ionisation energies (eV)

Fig. 2 MO Energy levels of 3,6-dimethyl-1,2,4,5-tetrahydrobenzobiscyclobutene

This however is contrary to the evidence of photoelectron spectroscopy. Vertical ionisation energies[5–7] are given in Fig. 1, and imply that a CH_2CH_2 bridge repels electrons *less* strongly than do an *ortho* pair of methyl groups, so that the SOMO in 1 and 2 should be ψ_S (5).

These PES spectra, however, relate to molecules in the gas phase, whereas the EPR spectra relate to ions in solution. We have therefore oxidised a mixture of 1 and 3, where each alone shows a strong persistent spectrum of the corresponding radical
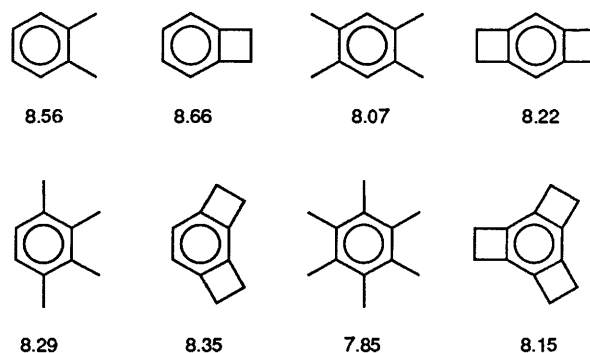
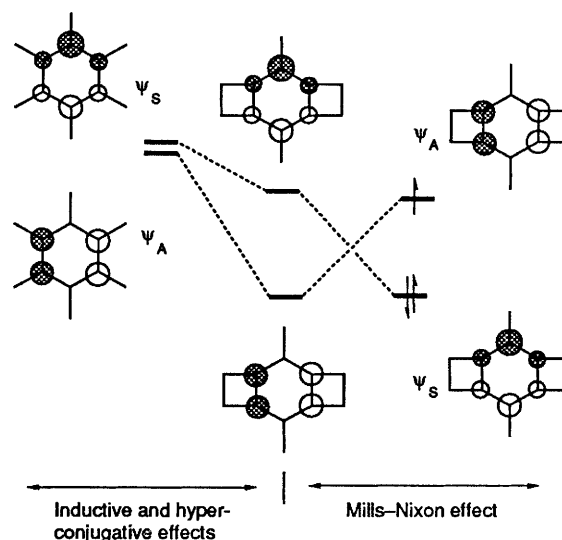cation. The mixture showed a strong spectrum of the radical cations of only the annulated arene, confirming that, also in solution, this has the lower ionisation energy.

We suggest that this apparent contradiction can be resolved if the Mills–Nixon effect is considered. Finnegan[8] and Streitwieser's[9] model of the effect, which is supported by recent MO calculations,[4] assumes that, to relieve angle strain in the small ring, the aromatic (*ipso*) carbon atoms at the points of fusion rehybridise away from sp² to place more p-character in the bonds subtending the strained angle, and hence more s character in the bond to the *ortho* position as illustrated in 6. This *ipso–ortho* bond will therefore be polarised with a partial negative charge on the *ipso* carbon atom and a positive charge on the *ortho* carbon atom as shown in 6. This will stabilise

preferentially the ψ_S MO which has a high coefficient ($\sqrt{1/3}$) on the *ortho* carbon atoms, and destabilise the ψ_A MO which has a high coefficient ($\sqrt{1/4}$) on the *ipso* positions, leaving ψ_A as the SOMO. This interplay of the electronic (inductive and hyperconjugative) and stereoelectronic (Mills–Nixon) effects is illustrated in Fig. 2

References

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