Electron Paramagnetic Resonance Spectra of the Radical Cations of Some Benzocyclobutenes, Benzocyclopentenes and Benzocyclohexenes

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1,2,4,5-Tetrahydrobenzo[1,2:4,5]dicyclobutene, 1,2,3,5,6,7-hexahydrobenzo[1,2:4,5]dicyclopentene and 1,2,3,4,6,7,8,9-octahydrobenzo[1,2:4,5]dicyclohexene, and their dimethyl derivatives, and tetramethylbenzocyclo-butene, -pentene and -hexene have been prepared. All except the first compound have been oxidised to their corresponding radical cations, and the EPR spectra have been analysed by assigning McConnell-type *Q*-values to the substituents in the benzene ring. It is suggested that the ordering of the orbital energy levels (ψ_A above ψ_S) in 3,6-dimethylbenzo-[1,2:4,5]biscyclobutene and -pentene is a manifestation of the Mills–Nixon effect, and results from rehybridisation of the strained molecular framework.

In the radical cations of 5,10-dimethyl-1,2,3,4,6,7,8,9-octahydrobenzo[1,2:4,5]dicyclohexene and 5,6,7,8-tetramethyl-1,2,3,4-tetrahydrobenzocyclohexene the total unpaired electron density, as implied by the McConnell type of relationship, appears to be less than unity. Various possible causes of this are examined.

The rules governing EPR hyperfine coupling to hydrogen in the α- or β-position to a radical centre in arene radical ions are well established.[1]

Hyperfine coupling to hydrogen bonded to the ring results from spin polarisation of the electron pair in the C_α–C_β sigma bond, and in the simplest analysis is taken to be proportional to the unpaired electron density (ρ_{C_α}) at the carbon atom (Cα) as described in the McConnell equation [eqn. (1)].

$$a(\mathrm{H}\alpha) = \rho_{C_\alpha} Q_\alpha \qquad (1)$$

Coupling to Hβ in the group Cα–CβHβ is described by the Heller–McConnell equation [eqn. (2)]. It is similarly proportional to the unpaired electron density at Cα, but involves both a spin-polarization term (A) and a second term ($B\cos^2\theta$) which is due to hyperconjugation and which is usually dominant; θ is the dihedral angle between the axis of the 2p orbital on Cα and the Cβ–Hβ bond.

$$a(\mathrm{H}\beta) = \rho_{C_\alpha}(A + B\cos^2\theta) \qquad (2)$$

For a given alkyl group in which θ can be taken to be constant, this equation can be reduced to the form of eqn. (3).

$$a(\mathrm{H}\beta) = \rho_{C_\alpha} Q_\beta \qquad (3)$$

The unpaired electron density term ρ_{C_α} in alkyl benzenes will vary from 1/6, as it is in benzene, if the pattern of alkyl substitution breaks the degeneracy of the ψ_S and ψ_A orbitals of the benzene ring. For example the methyl groups in durene, by inductive and hyperconjugate release, raise the energy of the ψ_A orbital which has a high coefficient ($\sqrt{}1/4$) at the points of attachment, above that of the ψ_S orbital in which the relevant coefficients are only $\sqrt{}1/12$. The unpaired electron thus shows a hyperfine coupling pattern reflecting the electron distribution in the ψ_A orbital, namely *a*(4 Me) 10.70 G, *a*(2 H) 0.8 G,[2] and the ionisation energy as shown by photoelectron spectroscopy (PES) is reduced from 9.24 eV as it is in benzene to 8.05 eV.[3]

An improved (McLachlan) treatment replaces the unpaired electron densities in eqns. (1) and (2) by the spin densities.[4]

We have been interested in the potential effect of steric strain upon this simple model, and the correlation between the information on electron distribution provided by EPR spectroscopy on one hand, and PES on the other.[5] We report here the analysis in these terms of the EPR spectra of a number of benzocyclobutenes, benzocyclopentenes and benzocyclohexenes, which introduces a new manifestation of the Mills–Nixon effect,[6] *i.e.* the perturbation of an aromatic nucleus by a small fused ring.

Results

1,2,3,4,5,6,7,8,9-Nonahydrobenzotricyclopentene **3** was prepared by trimerisation of cyclopentanone, the benzocyclobutenes **9–11** by flash vacuum pyrolysis of *ortho*-methyl(chloromethyl)arenes, and the benzocyclopentenes **12–14** by Friedel Crafts annelation with β-chloropropionyl chloride, then Clemmensen reduction. Methyl groups were introduced into the aromatic ring in the benzodicyclohexene **16** by bromination, then lithiation and treatment with methyl iodide.

Radical cations were generated in liquid solution by photolysis of a solution of the substrate in trifluoroacetic acid containing mercury(II) trifluoroacetate (compounds **10** and **13**) or thallium(III) trifluoroacetate (compounds **3**, **11**, **14**, **16**, **17**). The light was obtained from a high pressure mercury arc, and was filtered through Pyrex glass. When $\mathrm{Tl(TFA)_3/TFAH}$ was used as the medium, a spectrum was often observed without the need for photolysis. The analyses of the spectra were confirmed and refined by computer simulation. Examples are given in Figs. 1–5. Despite repeated efforts using $\mathrm{Hg^{II}}$ or $\mathrm{Tl^{III}}$ in trifluoroacetic acid, or $\mathrm{AlCl_3}$ in $\mathrm{CH_2Cl_2}$, with or without photolysis, we were unable to obtain a satisfactory spectrum from the tetrahydrobenzodicyclobutene **9**.

EPR data for the compounds which we have studied, and for some related compounds from the literature, are given in Table 1. Values for the ionisation energies for compounds relevant to the discussion are included in Table 1 and in Fig. 6. We have quoted the 'best' evaluated experimental data given in ref. 3; values enclosed in parentheses imply that no auxiliary data were available to allow the accuracy to be judged, or that the heats of formation of relevant neutral species were not well established.†

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† The experimental error in PES measurements is usually accepted to be about 0.7 eV. The most useful measurements for our purpose are those[7,8] in which a series of related compounds have been studied under the same conditions by a research group.

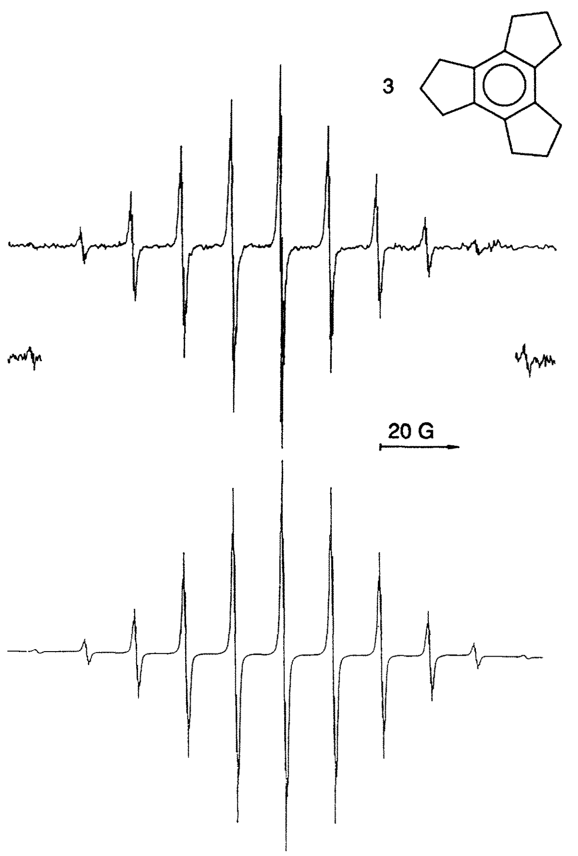

Fig. 1 EPR spectrum (top) and simulation (bottom) of the benzotricyclopentene radical cation $3^{\cdot+}$ in TFAH/Tl^{3+} at 261 K

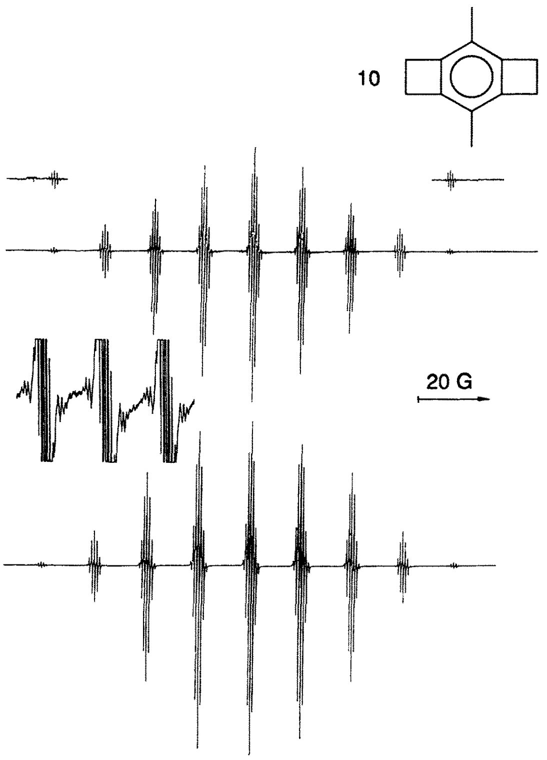

Fig. 2 EPR spectrum (top) with details (centre) of the ^{13}C satellites about the central three quintets, and simulation (bottom) of the 3,6-dimethylbenzodicyclobutene radical cation $10^{\cdot+}$ in TFAH/Hg^{2+} at 260 K

Discussion

To test the use of eqns. (1) and (3) for determining local unpaired electron densities in benzene radical cations, we have checked that the values round the ring do sum to unity, *i.e.* $\Sigma\rho_{C_\alpha} = 1$. We use the symmetrical hexasubstituted benzenes **1**–**4** to derive Q values by eqns. (1) and (3) for H (26.6 G), CH_3 (39.0 G), and the α-CH_2 groups in fused cyclopentene (68.9 G), and cyclohexene (61.4 G) rings, assuming that in each radical cation, ρ_{C_α} is 1/6. As 1,2,3,4,5,6-hexahydrobenzotricyclobutene was not available, we derive the Q value for the methylene group in the cyclobutene ring from compound **10** as described below.

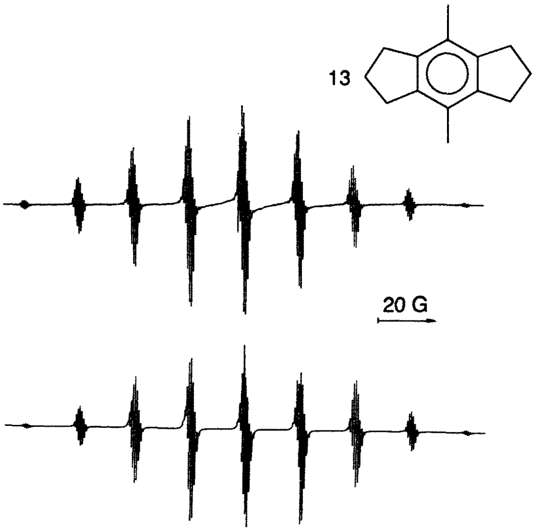

Fig. 3 EPR spectrum (top) and simulation (bottom) of the 3,6-dimethylbenzodicyclopentene radical cation $13^{\cdot+}$ in TFAH/Tl^{3+} at 260 K

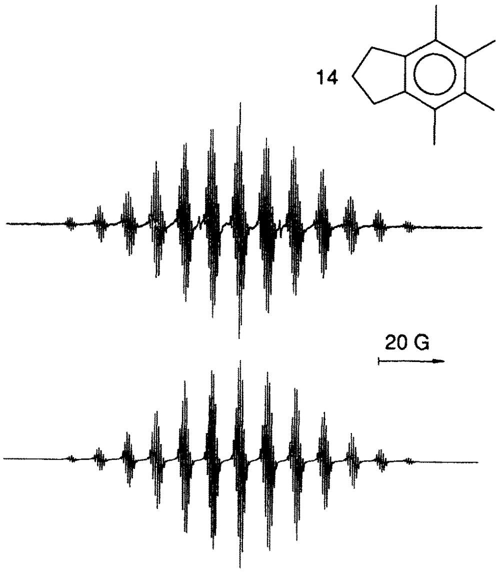

Fig. 4 EPR spectrum (top) and simulation (bottom) of the 5,6,7,8-tetramethylbenzocyclopentene radical cation $14^{\cdot+}$ in TFAH/Tl^{3+} at 261 K

With the aid of these Q values we can then reverse the argument and translate observed hyperfine coupling constants into local unpaired electron densities ρ_{C_α}. These values of ρ_{C_α} and those of $\Sigma\rho_{C_\alpha}$ are given in Table 1. As a test of the validity of this procedure we show in the Table the results for the tetra- and penta-methylbenzenes **5**–**8** using hyperfine coupling constants taken from the literature. The deviations of the calculated total unpaired electron density from unity are small, and in the case of durene **5** may result from the fact that the spin density at the ring atoms carrying hydrogen may be negative.

We then use this additivity principle to calculate from **10** the value of Q_B for the CH_2 group of a cyclobutene ring. The observed value of $a(CH_3)$, 0.68 G, corresponds, by eqn. (3), to ρ

0.0174. If the total unpaired electron density is taken to be unity, the unpaired electron density at each of the points of fusion of the cyclobutene rings must be 0.241, and the observed value of $a(CH_2)$, 13.84 G, then leads to Q_B for the cyclobutene ring as 57.3 G.

If we now use this value to calculate the total unpaired electron density in **11**, we obtain a value of 1.006. This gives us confidence that, if it is applied with caution, this way of analysing the data can be useful.*

We will consider in sequence the benzocyclobutenes, the benzocyclopentenes, and the benzocyclohexenes, in the light of these data.

Benzocyclobutenes.—The problem with the benzocyclobutenes is that of reconciling the electronic configuration of the radical cation which is indicated by the EPR spectra, with that of the SOMO which should result from the breaking of the degenerate ψ_A and ψ_S benzene orbitals by the alkyl substituents.

Comparison of the ionisation energies for the related methylated benzenes and cyclobutene-annelated benzenes (Table 1 and Fig. 6) **2** and **25**, **5** and **9**, **6** and **22**, and **18** and **19**, suggests that a pair of methyl groups repel electrons *more* strongly than does a cyclo-$(CH_2)_2$ group. On the other hand, the EPR spectra show unambiguously that the radical cations $\mathbf{10}^{\cdot +}$ and $\mathbf{11}^{\cdot +}$ have the unpaired electron situated principally in the ψ_A MO: as shown in Table 1, the unpaired electron density at the *para*-pair of methyl groups in $\mathbf{10}^{\cdot +}$ is 0.01 and in $\mathbf{11}^{\cdot +}$ it is 0.006, and at the other four positions it is correspondingly high.

These compounds can be regarded as derivatives of the orbitally degenerate hexamethylbenzene in which *ortho* pairs of methyl groups have been replaced by cyclo-$(CH_2)_2$ groups, and the orbital occupancy which is observed might be taken to imply that the methyl groups repel electrons *less* strongly than do the cyclo-$(CH_2)_2$ groups: the orbital of higher energy is that (ψ_A) in which the methyl groups lie in the nodal plane, and the cyclo-$(CH_2)_2$ groups are joined to the ring where the unpaired electron density is $\sqrt{1/4}$.

The ionisation energies which are listed in Table 1 and Fig. 6 relate to the gas phase, whereas our radical cations are heavily solvated. To check that the same sequence of ionisation energies applies in solution, we have oxidised a mixture of hexamethylbenzene **2** and 3,6-dimethyl-1,2,4,5-tetrahydrobenzodicyclobutene **10**, and of **2** and 3,4,5,6-tetramethyl-1,2-dihydrobenzocyclobutene **11** under conditions where each compound separately gives a strong spectrum of the long-lived corresponding radical cation. The radical cation which is observed from the mixture should therefore be derived from the arene with the lower ionisation energy, and indeed with both mixtures a strong spectrum of the hexamethylbenzene radical cation was observed. In a similar experiment, a mixture of 3,6-dimethyl-1,2,4,5-tetrahydrobenzodicyclobutene **10** and 3,4,5,6-tetramethyl-1,2-dihydrobenzocyclobutene **11** showed a spectrum which was less well defined, but related principally to $\mathbf{11}^{\cdot +}$. These results thus imply that an *ortho* pair of methyl groups repel electrons more strongly than does a dimethylene bridge, and support the results obtained from the gas phase studies.

We suggest that this anomaly may be another manifestation of the phenomenon associated with the names of Mills and Nixon,[6] in which the chemical and physical properties of an aromatic nucleus are perturbed when it is annelated to a small ring. Studies involving, for example, X-ray diffraction,[10,11] NMR spectroscopy,[12] and MO calculations[8,13,14] suggest that the underlying cause of the various effects is the rehybridisation of the (*ipso*) carbon atoms at the ring junctions, as first suggested by Finnegan[15] and by Streitwieser.[16] To accommodate the angle strain in the fused ring, these *ipso* carbon atoms undergo rehybridisation from sp^3 to place more p-character in the bond subtending the compressed angle, and thus more s-character in the third (aromatic *ipso–ortho*) bond.†,‡ This bond is therefore polarised, with a δ− charge on the *ipso* carbon atom and a δ+ charge on the *ortho* carbon atom (Fig. 7). This polar structure will stabilise the ψ_S MO which has a large unpaired electron density (1/3e) on each *ortho* carbon, and destabilise ψ_S which has a large electron density (1/4e) on each *ipso* carbon. This is illustrated in Fig. 8.

Benzocyclopentenes.—The EPR spectra (Table 1) show clearly that the SOMO of the benzocyclopentene radical cations $\mathbf{13}^{\cdot +}$ and $\mathbf{14}^{\cdot +}$ (and $\mathbf{12}^{\cdot +}$), like that of the corresponding benzocyclobutene radical cations, is ψ_A, but the ionisation energies in the literature for **2** and **3**,[7] **5** and **12**,[8] and **6** and **23**,[8] do not show clearly the relative electronic effects of the methyl and cyclo-$(CH_2)_3$ groups.

We have again resorted to oxidising mixtures of hexamethylbenzene **2** and 4,8-dimethyl-1,2,3,4,5,6-hexahydrobenzodicyclopentene **13**, and of **2** and 3,4,5,6-tetramethyl-2,3-dihydro-1*H*-benzocyclopentene **14** in trifluoroacetic acid with mercury(II) trifluoroacetate. Now the EPR spectra of both components could be observed initially, but the spectra of $\mathbf{13}^{\cdot +}$ and $\mathbf{14}^{\cdot +}$ decayed rapidly, and after about 5 min both solutions showed the spectra of about 90% $\mathbf{2}^{\cdot +}$ and 10% of the other component. These results are less clearcut than those obtained with the benzocyclobutenes, but they suggest that the relative electron releasing ability is *ortho*-Me_2 > cyclo-$(CH_2)_3$ > cyclo-$(CH_2)_2$.

The ordering of the energy levels thus appears again to be dominated by angle strain within the cyclopentene moiety, as illustrated for the cyclobutene analogue in Fig. 8.

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* In principle the same approach could be used for analysing the EPR spectra of the alkylbenzene radical anions, but as alkyl groups are progressively introduced it becomes more difficult to generate the radical anions, and the EPR spectra of the hexaalkylated benzenes have not been recorded. The spectra of the radical anions of toluene and of a number of dimethylbenzenes have been reported,[9] and within this very limited group of compounds, the model does appear to be satisfactory.

† The strain may also be relieved to some degree by the formation of 'bent bonds'. Boese and Bläser[10,11] have determined the structure and electron deformation densities of 1,2-dihydrobenzocyclobutene **19** and 1,2,4,5-tetrahydrobenzo[1,2:4,5]dicyclobutene **9**. They find that the latter is planar within the experimental error. The angle within the four-membered ring at the bridgehead is 93.4°, and the maximum of the electron density in the adjacent bonds in the benzene ring is offset from the vector joining the carbon nuclei. The angle within the benzene ring *ortho* to the point of fusion is 112.2°. For a total of eight benzocyclobutenes in the Cambridge Crystallographic Data Base, the average of these angles is 115.2°.

‡ A referee has suggested that evidence for rehybridisation might be obtained from the ^{13}C hyperfine couplings. The problems are, first, to measure and assign these couplings, and, second, to predict the values with confidence.

The ^{13}C satellites in the spectrum of $10^{\cdot +}$ are shown in Fig. 2. The measurement of the four different values of $a(^{13}C)$ which would be expected is rendered difficult because the relative intensities of the satellite lines suggest that two or more of the satellite quintets overlap, and under higher resolution the picture is complicated by the second-order character of the spectrum. However, it appears that one of the values of $a(^{13}C)$ is *ca.* 6.8 G.

Regarding the prediction of the ^{13}C couplings, although the hybridisation at the carbon may change, the unpaired electron remains in a 2p orbital and, on the Karplus–Fraenkel model, the increase in the contribution to the coupling which may result from spin polarization of the C–C bond with increased σ character might be offset by a reduction in the contribution from the bonds with increased π character. If any effect of rehybridisation is neglected, values of $a(^{13}C)$ at the bridgehead carbon atoms, the CH_2 carbon atoms, and the methyl-substituted carbon atoms would be predicted to be about 5.5 G, 4 G and 7 G respectively.

We do not feel justified in drawing any conclusions from these results.

Table 1 EPR spectra of radical cations

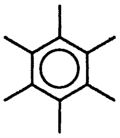
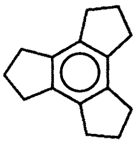
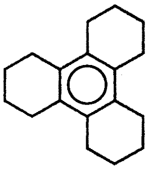
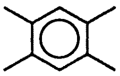
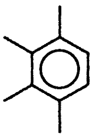
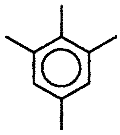
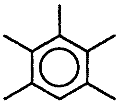
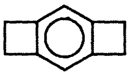
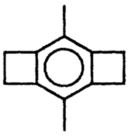
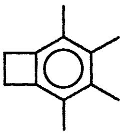
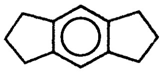
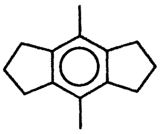
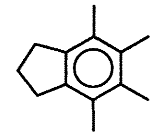
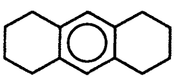
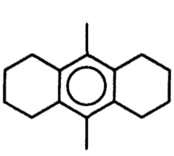
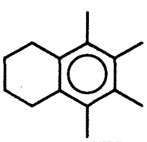
No.	Compound	E_i/eV	Condns.[a]	$a(n\ \mathrm{H})$/G	ρ_{C_α}	$\Sigma\rho_{C_\alpha}$	SOMO	Ref.
1		9.24	A	6 H 4.43	0.17	(1)	A + S	*b*
2		7.85	B	6 Me 6.5	0.17	(1)	A + S	*c*
3		(7.85)	C	6 CH_2 11.49 3 CH_2 0.34	0.17	(1)	A + S	*c*
4		(7.70)	D	6 CH_2 10.24	0.17	(1)	A + S	*d*
5		8.04	E	2 H 0.80 4 Me 10.7	0.030 0.274	1.17	A	*e*
6		8.05	E	2 Me 15.13 2 H 2.21 2 Me 2.78	0.388 0.083 0.071	0.388	S	*e*
7			E	1 Me 16.82 1 Me 14.36 2 Me 2.96 2 H 1.76	0.431 0.368 0.076 0.66	1.08	S	*e*
8			E	1 Me 0 1 H 0 2 Me 10.5 2 Me 10.05	0 0 0.258 0.258	1.03	A	*e*
9		(8.17)		—		—		*c*
10			B	2 Me 0.68 4 CH_2 13.84		(1)	A	*c*
11			C	2 Me 0.24 2 Me 10.72 2 CH_2 11.87	0.06 0.275 0.207	1.01	A	*c*
12		(7.94)	E	2 H 0 4 CH_2 19.2	0 0.279	1.11	A	*f*
13			B	2 Me 0.64 4 CH_2 18.37 2 CH_2 0.64	0.019 0.266	1.10	A	*c*

Table 1 (*continued*)

No.	Compound	E_i/eV	Condns.[a]	$a(n\ \mathrm{H})$/G	$\rho_{C\alpha}$	$\Sigma\rho_{C\alpha}$	SOMO	Ref.
14			C	2 Me 0.68 2 Me 8.86 2 CH_2 18.09 2 CH_2 0.68	0.018 0.223 0.262	1.01	A	*c*
15		(7.68)	D	2 H 0 4 CH_2 15.5	0 0.252	1.01	A	*d*
16			C	2 Me 9.27 4 CH_2 3.65	0.238 0.059	0.71	S	*c*
17			B	2 Me 9.34 2 Me 2.39 2 CH_2 3.7 2 CH_2 1.38	0.240 0.061	0.65	S	*c*

[a] Conditions: A, H_2SO_4 at 163 K; B, TFAH/Hg(TFA)$_2$ at 260–263 K; C, TFAH/Tl(TFA)$_3$ at 260–263 K; D, $CH_2Cl_2/AlCl_3$ at RT; E, TFAH/Co(OAc)$_3$ at RT. [b] M. K. Carter and G. Vincow, *J. Chem. Phys.*, 1967, **47**, 292. [c] Present work. [d] D. V. Avila, A. G. Davies and M. L. Girbal, *Tetrahedron*, 1990, **46**, 1999. [e] R. M. Dessau, S. Shih and E. I. Heiba, *J. Am. Chem. Soc.*, 1970, **92**, 412. [f] R. M. Dessau and S. Shih, *J. Chem. Phys.*, 1970, **53**, 3169.

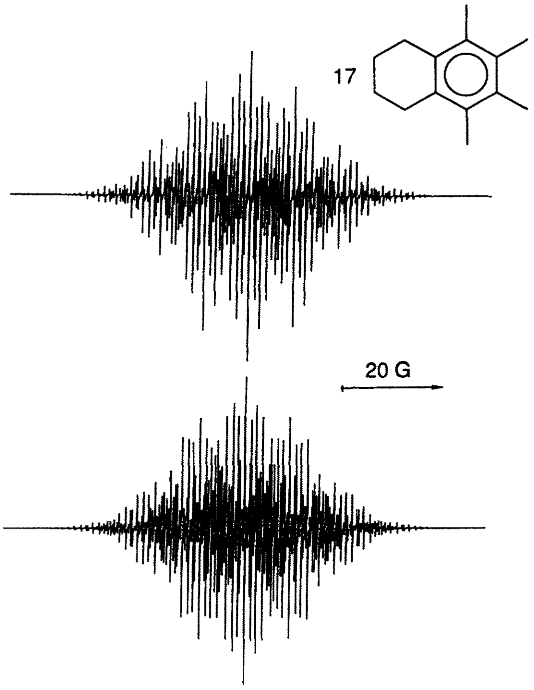


Fig. 5 EPR spectrum (top) and simulation (bottom) of the 5,6,7,8-tetramethylbenzocyclohexene radical cation **17**$^{\bullet+}$ in TFAH/Tl^{3+} at 260 K

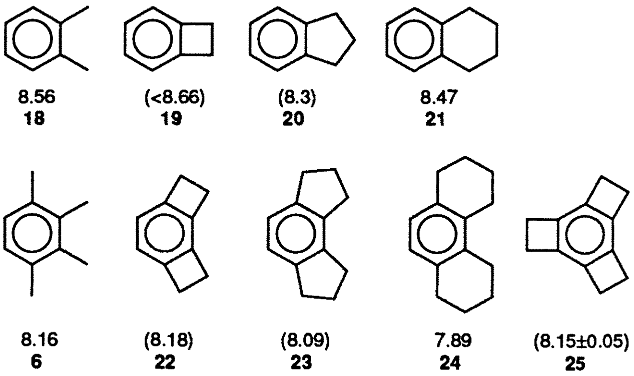


Fig. 6 Ionisation energies (eV)

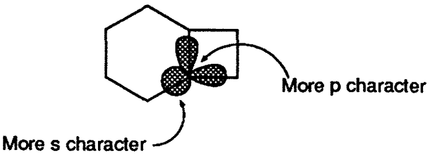


Fig. 7 The Finnegan–Streitwieser model of the Mills–Nixon effect

Benzocyclohexenes.—Angle strain within the fused cyclohexene rings should now be small, and the ordering of the energy levels might be expected to reflect simply the inductive and hyperconjugative effects of the α-methylene groups.

The EPR spectra of the radical cations of the benzocyclohexenes **16** and **17** (Fig. 5) show that, in contrast to the corresponding benzocyclobutenes **10** and **11**, and benzocyclopentenes **13** and **14**, the SOMO is ψ_S. Ionisation energies for **2** and **4**, **5** and **15**, **18** and **21**, and **6** and **24**, suggest that in the gas phase, methyl groups repel electrons less strongly than do cyclo-$(CH_2)_4$ groups, and if this sequence held in solution, the SOMO of the radical cation would be expected to be ψ_A. Unfortunately we could not find any single set of conditions under which both the methylated and the $(CH_2)_4$-annulated compounds would give strong persistent EPR spectra, so that competitive oxidations could be carried out in solution. Hexamethylbenzene **2** shows a strong EPR spectrum of the radical cation on photolysis of solutions in TFAH/Hg(TFA)$_2$, or TFAH/Tl(TFA)$_3$, or H_2SO_4, but dodecahydrobenzotricyclohexene **4** showed a spectrum only in benzene containing $AlCl_3$. When **2** and **4** in mixture were treated with TFAH/Hg(TFA)$_2$, or TFAH/Tl(TFA)$_3$ with photolysis, superimposed spectra of both **2**$^{\bullet+}$ and **4**$^{\bullet+}$ were observed. The former was rather stronger, but as the spectrum of **4**$^{\bullet+}$ alone cannot be observed under these conditions, it may be decaying more rapidly. The most the

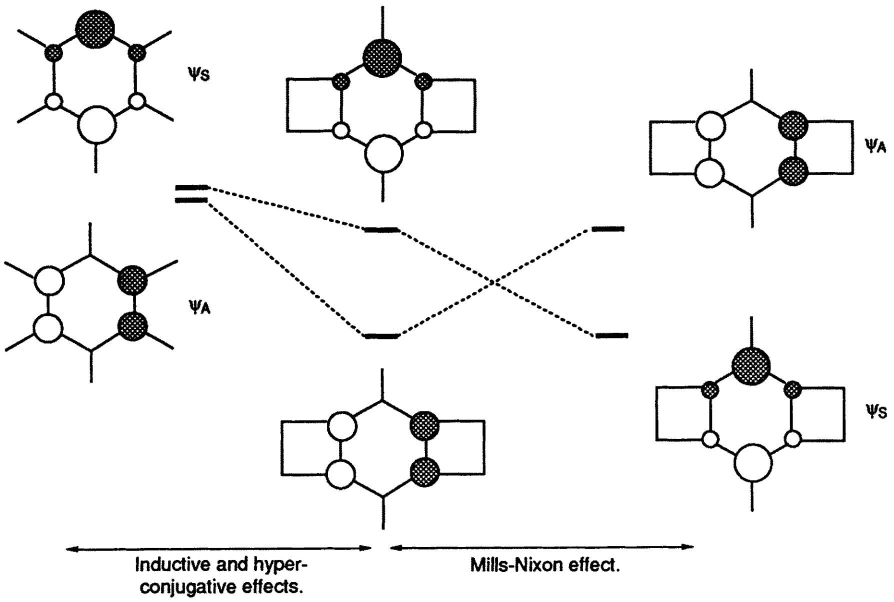


Fig. 8 MO energy levels in 3,6-dimethyl-1,2,4,5-tetrahydrobenzodicyclobutene

experiment appears to show is that the ionisation energies are rather similar under these conditions.

However there is a further, and perhaps related, problem associated with the spectra of the benzocyclohexenes **16** and **17**. 1,2,3,4,6,7,8,9-Octahydrobenzo[1,2:4,5]dicyclohexene **15** shows a total unpaired electron density $\Sigma\rho$ of 1.01, confirming the Q value for the α-CH_2 groups of the cyclohexene ring, which was derived from benzotri(cyclohexadiene), **4**, but 5,10-dimethyl-1,2,3,4,6,7,8,9-octahydrobenzo[1,2:4,5]dicyclohexene **16** and 3,4,5,6-tetramethyl-1,2,3,4-tetrahydrobenzocyclohexene **17**, alone amongst the compounds in Table 1, show very low values of $\Sigma\rho_{C_\alpha}$ of 0.71 and 0.65 respectively. We note that in both compounds the SOMO is ψ_S (but compounds **6** and **7**, which have the same SOMO, show a normal value of $\Sigma\rho$) and that in both compounds the electron deficiency occurs at all the arene ring atoms: in the ψ_S MO the unpaired electron density should be 0.333 on the C_2 axis, and 0.083 at the other positions.

The cause of this discrepancy is not clear, but we note here briefly a number of factors which might be relevant.

(1) It might be that the spectra relate not to the compounds **16** and **17** but to some impurity or some decomposition product of the first-formed radical cations. The compounds were chromatographically and analytically pure, and, apart from the low values of $\Sigma\rho$, the simulations of the spectra are consistent with the structures of the substrates.

(2) The spectra may have been wrongly analysed. This seems unlikely. The spectra have been recorded in the temperature range where inversion of the cyclohexene ring is rapid on the EPR time scale. The simulation of the spectrum of **16**$^{\bullet+}$ is very good, and that of **17**$^{\bullet+}$ is convincing though not perfect; all other simulations which we have carried out, based on alternative interpretations, are clearly incorrect.

(3) We have worked with Hückel unpaired electron densities rather than McLachlan spin densities. This is undoubtedly important, but the more sophisticated treatment usually has the effect of making large coupling constants larger and small ones smaller (perhaps changing the sign), but in **16**$^{\bullet+}$ and **17**$^{\bullet+}$ *all* the coupling constants are too small. Further, if this were the main cause, it is not clear why the effect should be limited to these two compounds.

(4) We have ignored the excess charge effect. For α-protons, this can be accommodated by the modification of the McConnell equation [eqn. (1)] which is shown in eqn. (4)[17,18] where $Q = -27$ G and $K = -12$ G.

$$a(\mathrm{H}^\alpha) = Q_\alpha\rho_{C_\alpha} + K\rho_{C_\alpha}{}^2 \qquad (4)$$

This implies only a small perturbation to the McConnell equation. If a similar equation, where Q and K have the same sign, applies to coupling to β-protons, this would not appear to be able to account for the low values of $\Sigma\rho$ in **16** and **17**, and the normal values of $\Sigma\rho$ in **6** and **7** which should have similar excess charges.

(5) The molecules may be distorted. Eqns. (1) and (3) assume sp^2 hybridisation in a planar arene. The α-methylene groups in 1,2,3,4,6,7,8,9-octahydrobenzo[1,2:4,5]dicyclohexene **15** have been shown to be displaced by 3.8° out of the plane of the arene ring,[19,20] but this compound nevertheless shows $\Sigma\rho = 1.009$. A similar and perhaps larger distortion may occur in **16** and **17**, which are more sterically congested.

(6) Interaction between the methyl groups and the cyclohexene rings might affect the $\cos^2\theta$ term in eqn. (2); we are indebted to a referee for this suggestion.

At present, none of these possible explanations seems convincing. We hope to return to the problem when the spectra of a wider range of substrates have been analysed on the same basis.

Experimental

Spectroscopy.—NMR spectra were recorded in $CDCl_3$ on a Varian XL200 or VXR-400 spectrometer, and mass spectra on a VG7070H instrument. J Values are in Hz.

EPR spectra were recorded on a Bruker ESP300 (or occasionally a Varian E109) spectrometer operating at *ca* 9.1 GHz, fitted with a 500 W high pressure mercury arc, provided with neutral (metal gauze) and glass filters. Typically, a mixture of TFAH (1 cm^3) and either $Hg(TFA)_2$ or $Tl(TFA)_3$ at *ca.* 260 K was flushed with nitrogen for 2 min. The substrate (*ca.* 10 mg) was then added in TFAH or CH_2Cl_2 and the mixture was degassed with nitrogen for a minute.

1,2,3,4,5,6,7,8,9-*Nonahydrobenzotricyclopentene* **3**.—This was prepared by the trimerisation of cyclopentanone in two steps;[21] b.p. 132 °C at 0.2 mmHg, m.p. 92–93 °C (lit.[21] b.p. 238–239 °C at 762 mmHg, m.p. 97.5–98 °C).

1,2,4,5-*Tetrahydrobenzo*[1,2:4,5]*dicyclobutene* **9**.—1,3-Dimethyl-4,6-bis(chloromethyl)benzene (1.70 g, 8.37 mmol) was distilled at 0.1 mmHg through a quartz tube at 750 °C,[22] and the pyrolysis products were condensed in a trap cooled in liquid nitrogen. The brown oil which was obtained was dissolved in pentane (50 cm^3), washed with sodium carbonate solution and dried (Na_2SO_4), then chromatographed on silica gel with pentane as the eluent. The product was recrystallised from methanol as white crystals (0.10 g; 10% yield), m.p. 101–102 °C (lit.[23] 100–101 °C); δ_H 6.76 (2 H, s, ArH), 3.09 (8 H, s, 4 CH_2).

3,6-*Dimethyl*-1,2,4,5-*tetrahydrobenzo*[1,2:4,5]*dicyclobutane* **10**.—A mixture of durene (25 g, 185 mmol), 40% aqueous formaldehyde (60 cm^3), zinc chloride (8 g), and conc. hydrochloric acid (60 cm^3) was stirred at 90 °C, with dropwise addition of hydrochloric acid to keep the concentration constant.[24] After 3 h the oily layer was separated and cooled, and then subjected to a similar treatment. This procedure was repeated twice more to give 1,4-bis(chloromethyl)-2,3,5,6-tetramethylbenzene in 26% yield, m.p. 192–194 °C (lit.[25] 193–194 °C); δ_H 4.70 (4 H, s, CH_2), 2.36 (12 H, s, CH_3). Pyrolysis of this at 700 °C and 0.05–0.1 mmHg gave **10** as white crystals (from pentane; 19%), m.p. 118–119 °C (lit.[23] 119–120 °C). δ_H 2.01 (6 H, s, 2 Me), 2.99 (8 H, s, 4 CH_2).

3,4,5,6-*Tetramethyl*-1,2-*dihydrobenzocyclobutene* **11**.—Pentamethylbenzene was chloromethylated as described above to give pentamethylbenzyl chloride as white crystals from pentane in 86% yield, m.p. 81–82 °C (lit.[25] m.p. 80–82 °C); δ_H 4.73 (2 H, s, CH_2), 2.35 (6 H, s, 2 Me), 2.23 (3 H, s, Me), 2.22 (6 H, s, 2 Me). Pyrolysis of this at 700 °C and 0.1 mmHg gave, after chromatography on silica gel (pentane eluent) compound **11** as white crystals (from methanol; 8%), m.p. 144 °C; δ_H 3.01 (4 H, s, 2 CH_2), 2.16 (6 H, s, 2 Me), 2.09 (6 H, s, 2 Me) (Found: C, 89.9; H, 10.2. $C_{12}H_{16}$ requires C, 89.94; H, 10.06%); δ_C 14.35 (Me), 15.87 (Me), 26.93 (CH_2), 128.30, 133.51 and 141.12 (Ar); *m*/*z* 160 (M^+, 100%), 159 (21.2), 147 (30.7), 146 (18.4), 145 (95.5), 130 (43.0), 117 (23.60), 115 (23.9), 105 (34.1), 91 (28.5) (Found: M^+, 160.1234. Required: *M*, 160.1252).

1,2,3,5,6,7-*Hexahydrobenzo*[1,2:4,5]*dicyclopentene* **12**.—A mixture of indane and 3-chloropropionyl chloride was treated with aluminium chloride[26] to give 5-(3-chloropropionyl)indane in 44% yield; m.p. 64 °C (lit.[26] 68–69 °C); δ_H 2.12 (2 H, quint., *J* 7.6, βCH_2), 2.95 (4 H, t, *J* 7.6, αCH_2), 3.44 (2 H, t, CH_2CO), 3.92 (2 H, t, CH_2Cl), 7.30 (1 H, d, Ar), 7.75 (1 H, d, Ar). This was treated with conc. sulfuric acid, giving *s*-hydrindacene-1-one in 43% yield, m.p. 64–65 °C (lit.[26] 69–72 °C), which was reduced with zinc amalgam and conc. hydrochloric acid to give **12** as white crystals (from ethanol) m.p. 51–52 °C (lit.[27] 52–54 °C) in 44% yield; δ_H 2.03–2.11 (4 H, quint., *J* 7.6, βCH_2), 2.84–2.87 (8 H, t, αCH_2), 7.09 (2 H, s, Ar).

4,8-*Dimethyl*-1,2,3,5,6,7-*hexahydrobenzo*[1,2:4,5]*dicyclopentene* **13**.—*p*-Xylene was subjected to Friedel Crafts acylation with 3-chloropropionyl chloride, then treated with conc. sulfuric acid to give 4,8-dimethyl-2,3-dihydrobenzocyclopentene-1-one (60%) as white crystals (from methanol), m.p. 75–76 °C (lit.[28] 76–77 °C); δ_H 2.28 (3 H, s, Me), 2.58 (3 H, s, Me), 2.64 (2 H, m, CH_2), 2.94 (2 H, m, CH_2), 7.00 (1 H, d, Ar), 7.23 (1 H, d, Ar). This was subjected to Clemmensen reduction to give 3,6-dimethyl-2,3-dihydro-1*H*-benzocyclopentene in 71% yield, b.p. 77–80 °C at 4 mmHg (lit.[29] b.p. 94–97 °C at 10 mmHg); δ_H 2.09 (2 H, quint., CH_2), 2.25 (6 H, s, Me), 2.87 (4 H, t, CH_2), 6.91 (2 H, s, Ar).

A second Friedel Crafts reaction with 3-chloropropionyl chloride followed by ring-closure gave the monoketo derivative of dimethylbenzodicyclopentene as white crystals (from methanol; 20%), m.p. 128–130 °C; δ_H 2.12 (2 H, quint., CH_2), 2.20 (3 H, s, Me), 2.54 (3 H, s, Me), 2.70 (2 H, m, CH_2), 2.80–2.90 (4 H, t, CH_2), 2.80–2.90 (2 H, m, CH_2); δ_C 14.36, 14.39, 23.74, 24.62, 30.75, 32.01, 37.44; 127.87, 131.07, 132.89, 143.05, 149.97, 153.96 (Ar); 208.26 ($C{=}O$) (Found: C, 84.25; H, 8.3. $C_{14}H_{16}O$ requires C, 83.96; 8.06%); *m*/*z* 200 (100%), 185 (11.3), 172 (29.4), 158 (28.6), 157 (51.6), 143 (30) (Found: M^+, 200.1199. Required: *M*, 200.1201).

Clemmensen reduction of this gave 4,8-dimethyl-1,2,3,5,6,7-hexahydrobenzo[1,2:4,5]dicyclopentene in 41% yield as white crystals from methanol, m.p. 108–109 °C; δ_H 2.10 (4 H, quint., CH_2), 2.17 (6 H, s, Me), 2.85 (8 H, t, CH_2); δ_C 15.97, 24.99, 31.47, 126.57 (Ar) and 140.90 (Ar); *m*/*z* 186 (53%), 185 (18), 172 (17), 171 (100), 143 (21), 128 (12.5) (Found: M^+, 186.1420. $C_{14}H_{18}$ requires: *M*, 186.1409. Found: C, 90.15; H, 9.9. Required: C, 90.25; H, 9.75%).

3,4,5,6-*Tetramethyl*-2,3-*dihydro*-1H-*benzocyclopentene* **14**.—Finely divided aluminium chloride (240 g) was added slowly with stirring to a mixture of durene (49 g, 366 mmol) and ethyl 3-chloropropionate (50 g, 366 mmol). The mixture was stirred at 145 °C for 1.5 h, then poured over ice and extracted with diethyl ether yielding 4,5,6,7-tetramethylindan-1-one as a yellow oil, b.p. 120 °C at 0.05 mmHg (lit.[30] b.p. 132 °C at 0.01 mmHg) which solidified as yellow crystals (8.5 g), m.p. 136 °C (lit. 150 °C); δ_H 2.22 (3 H, s, Me), 2.23 (3 H, s, Me), 2.25 (2 H, m, CH_2), 2.27 (3 H, s, Me), 2.32 (2 H, m, CH_2) and 2.61 (3 H, s, CH_3).

This was subjected to Clemmensen reduction, and the product was purified by chromatography on silica gel to give **14** as white crystals (from methanol), 2.37 g (31%), m.p. 96–97 °C (lit.[30] m.p. 99–100 °C); δ_H 2.89 (4 H, t, CH_2), 2.20 (12 H, s, CH_3) and 2.04 (2 H, q, CH_2); δ_C 15.96 (Me), 16.73 (Me), 24.21 (CH_2), 32.52 (CH_2), 129.34 (Ar), 132.71 (Ar) and 139.88 (Ar) (Found: C, 89.85; H, 10.4. $C_{13}H_{18}$ requires C, 89.59; H, 10.41%).

5,10-*Dimethyl*-1,2,3,4,6,7,8,9-*octahydrobenzo*[1,2:4,5]*dicyclohexene* **16**.—Octahydroanthracene was treated with bromine to give the 9,10-dibromide, m.p. 201 °C (from $CHCl_3$/EtOH) (lit.[31] 200–201 °C); δ_H 1.50–1.80 (8 H, m, βCH_2), 2.47–2.80 (8 H, m, αCH_2) (Found: M^+, 341.9689. Calc. for $C_{14}H_{16}Br_2$: *M*, 341.9615).

A solution of this dibromide (1.5 g, 4.36 mmol) in THF (50 cm^3) was treated with butyllithium (1.74 cm^3, 2.5 mol dm^{-3}) at −70 °C under nitrogen. The mixture was warmed to room temperature then treated with methyl iodide (0.62 g, 4.36 mol) in THF (10 cm^3). The mixture was then hydrolysed and extracted with diethyl ether (3 × 50 cm^3), yielding 9-*bromo*-10-*methyl*-1,2,3,4,5,6,7,8-*octahydroanthracene* (1.15 g, 72%), m.p. 152 °C (from EtOH/$CHCl_3$) (Found: C, 64.3; H, 7.0. $C_{15}H_{19}Br$ requires C, 64.52; H, 6.86%); δ_H 1.72–1.80 (8 H, m, βCH_2), 2.08 (3 H, s, Me), 2.23–2.80 (8 H, m, αCH_2) (Found: M^+, 278.0634. Required: *M*, 278.0671).

A second treatment with butyllithium and methyl iodide gave **14** (52%), m.p. 135.5 °C (from EtOH); δ_H 1.74–1.80 (8 H, m, 4 βCH_2), 2.09 (6 H, s, 2-Me), 2.64–2.70 (8 H, m, 4 αCH_2) (Found: M^+, 214.1696. $C_{16}H_{22}$ requires *M*, 214.1721).

5,6,7,8-*Tetramethyl*-1,2,3,4-*tetrahydrobenzocyclohexene* **17**.—This was prepared in 10% yield from the reaction of 1,2,3,4-tetramethylbenzene with 1,4-dichlorobutane in the presence of aluminium chloride;[32] m.p. 77–78 °C (lit.[32] 78–79 °C), δ_H 1.72–1.81 (4 H, m, 2 βCH_2), 2.17 (6 H, s, 2 Me), 2.24 (6 H, s, 2 Me) and 2.62–2.72 (4 H, m, 2 αCH_2).

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