The EPR Spectrum of the Dibenzo[*b*,*h*]biphenylene Radical Anion and Cation: the Pairing Principle and the Mills–Nixon Effect

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The EPR/ENDOR spectra of the radical ions of dibenzo[*b*,*h*]biphenylene provide an exception to the rule (the pairing principle) that these spectra should be similar in the radical cation and anion of planar alternant hydrocarbons. It is suggested that this breakdown of the pairing principle can be understood in terms of the Finnegan–Streitwieser model of the Mills–Nixon effect, which, by inducing charge separation and changes in bond lengths, can exchange the ordering of the energy levels of adjacent orbitals.

The pairing theorem states that in an alternant Hückel π-system, each bonding Hückel molecular orbital of energy $\alpha + x\beta$ has a corresponding antibonding MO of energy $\alpha - x\beta$ with the same absolute values of the LCAO coefficients.[1,2] As EPR hyperfine coupling constants are related to electron densities (or more precisely, spin densities), by the McConnell equation [eqn. (1)] the spectrum of a radical cation, with single

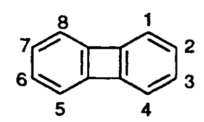
$$a_{\mathrm{H}_{\alpha j}} = Qc_j^2 \qquad (1)$$

occupancy of the HOMO, should differ from that of the radical anion, with single occupancy of the LUMO, only insofar as the McConnell constant Q for the cation is different (larger) from that for the anion.[3,4] An early example of this was provided by biphenylene (**1**, Table 1);[5] the assignment of the coupling constants has since been confirmed by methyl substitution.[6,7]

Our attention was drawn to Gerson's observation[8] that in benzo[*b*]biphenylene (**2**), with the coupling constants for the radical ions shown in Table 2, the pairing principle appears to be breaking down, and that, although the spectrum of the radical anion of dibenzo[*b*,*h*]biphenylene, **3** (binaphthylene) was known,[8] that of the radical cation $\mathbf{3}^{\bullet+}$ had never been observed.[7,8]

We have recorded the EPR spectrum of $\mathbf{3}^{\bullet+}$. This severely contravenes the pairing principle, and we offer an interpretation of this breakdown of the theorem with compounds **2** and **3** on the basis of the Mills–Nixon effect.[9,10]

Table 1 Hyperfine coupling constants (G)[a] for $\mathbf{1}^{\bullet-}$ and $\mathbf{1}^{\bullet+}$

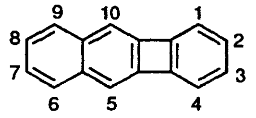


1

	$\mathbf{1}^{\bullet-}$	$\mathbf{1}^{\bullet+}$
a(4H-1,4,5,8)	0.19	0.21
a(H-2,3,6,7)	2.78	3.58

[a] 1 G = 0.1 mT.

Table 2 Hyperfine coupling constants[a] (G) for $\mathbf{2}^{\bullet-}$ and $\mathbf{2}^{\bullet+}$



2

	$\mathbf{2}^{\bullet-b}$	$\mathbf{2}^{\bullet+c}$
a(2H-1,4)	1.19 (1.10)	0.09 (0.085)
a(2H-2,3)	2.42 (2.47)	3.19 (3.256)
a(2H-5,10)	1.22 (1.41)	0.58 (0.68)
a(2H-6,9)	0.54 (0.47)	0.09 (0.085)
a(2H-7,8)	1.62 (1.52)	1.92 (1.83)

[a] Literature values[7] are given in parentheses. [b] Assignments based on MO calculations. [c] Assignments uncertain.

Results

Benzo[*b*]biphenylene **2** was reduced to the radical anion with potassium in THF in the presence of benzo-18-crown-6, and gave a spectrum of $\mathbf{2}^{\bullet-}$ (Table 2), similar to that reported previously.[7] Similarly $\mathbf{2}^{\bullet+}$ was prepared by treating **2** in trifluoroacetic acid (TFAH) with $\mathrm{Tl(TFA)_3}$ and showed a spectrum with hyperfine coupling constants close to the literature values.[7]

Dibenzo[*b*,*h*]biphenylene, **3**, was reduced with potassium metal in THF, and gave the radical anion with the spectrum shown in Fig. 1, with hyperfine coupling constants (Table 3) similar to those reported in ref. 7. The assignment of the largest coupling constant to positions 1, 6, 7 and 12 has been established by methylation,[7] and the two smaller values are assigned on the basis of the McLachlan calculation.

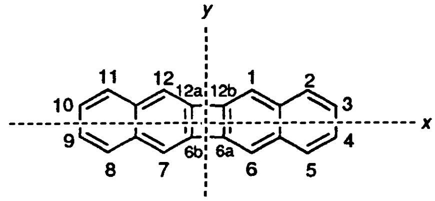
The radical $\mathbf{3}^{\bullet+}$ was prepared by treating **3** in TFAH with $\mathrm{Hg(TFA)_2}$, or $\mathrm{Tl(TFA)_3}$, or DDQ; all three methods give a similar spectrum, as shown in Fig. 2, with *a*(4 H) 1.73 G and *a* (4 H) 0.61 G, *g* 2.0026. The ENDOR spectrum (Fig. 3) confirms these two major splittings, and discloses a further small coupling, which, from the width of the signal at ν_{H} (modulation 31 kHz) is determined to be < 0.04 G.

Discussion

The overall span of the spectrum of $\mathbf{3}^{\bullet-}$ is 26.8 G, and that of $\mathbf{3}^{\bullet+}$ is 9.36 G, whereas radical cations usually have larger Q values than the corresponding radical anions (*cf.* $\mathbf{1}^{\bullet-}$ and $\mathbf{1}^{\bullet+}$), and the radical cation would be expected to show the spectrum with the wider span. Further, there is no apparent correlation between the spectra of $\mathbf{3}^{\bullet-}$ and $\mathbf{3}^{\bullet+}$.

We suggest that this breakdown of the pairing principle, obviously in **3**, and rather less obviously in **2**, can be understood in terms of the Finnegan–Streitwieser model of the Mills–Nixon

Table 3 Experimental and calculated hyperfine coupling constants of $\mathbf{3}^{\cdot+}$ and $\mathbf{3}^{\cdot-}$



3

Species	Method	1,6,7,12	2,5,8,11	3,4,9,10
$\mathbf{3}^{\cdot-}$	Experiment	4.23[a]	1.57[a]	0.90[a]
$\mathbf{3}^{\cdot-}$	HMO[b]	2.93 (−4.0)	1.98 (−2.0)	0.85 (−0.6)
$\mathbf{3}^{\cdot-}$	INDO[c]	−4.89	−1.81	+0.27
$\mathbf{3}^{\cdot+}$	Experiment	0.61	<0.04	1.73
$\mathbf{3}^{\cdot+}$	HMO[b]	2.93 (−4.0)	1.98 (−2.0)	0.85 (−0.6)
$\mathbf{3}^{\cdot+}$	HMO[d]	1.05 (−0.7)	0.18 (+0.3)	1.21 (−1.4)
$\mathbf{3}^{\cdot+}$	INDO[e]	+0.17	+0.41	−0.93
$\mathbf{3}^{\cdot+}$	INDO[e]	−33.97	−1.31	+0.35

[a] Literature values[7] 4.31, 1.62, 0.93 G. [b] HMO-McLachlan (λ = 1.2) values in parentheses. [c] Geometry based on 3-21G (D_{2h}) optimisation of $\mathbf{3}^{\cdot-}$. [d] Parameters adjusted to bond lengths and charge polarisations predicted by 3-21G calculations of $\mathbf{3}^{\cdot+}$: $k_{6a,6b,12a,12b} = -0.2$, $h_a = 0.8$, $h_b = 0.85$, $h_c = 1.2$, $h_d = 0.9$. HMO-McLachlan (λ = 1.2) values in parentheses. [e] Geometry based on 3-21G (D_{2h}) optimisation of $\mathbf{3}^{\cdot+}$.

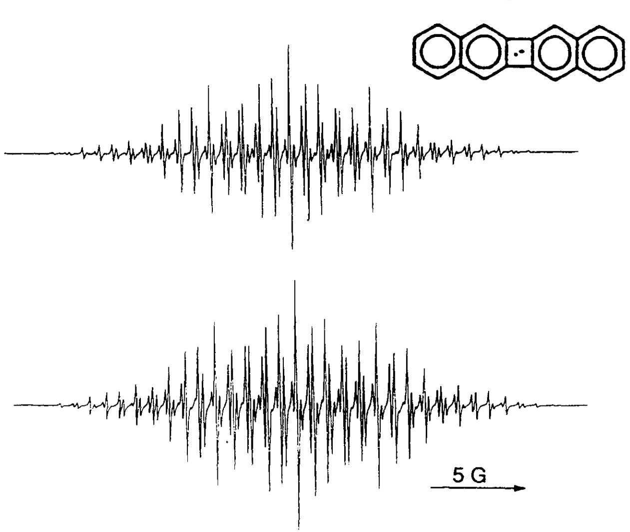


Fig. 1 EPR Spectrum (top) and simulation (bottom) of the dibenzo[*b*,*h*]biphenylene radical anion, $\mathbf{3}^{\cdot-}$ K^+, in THF at 243 K

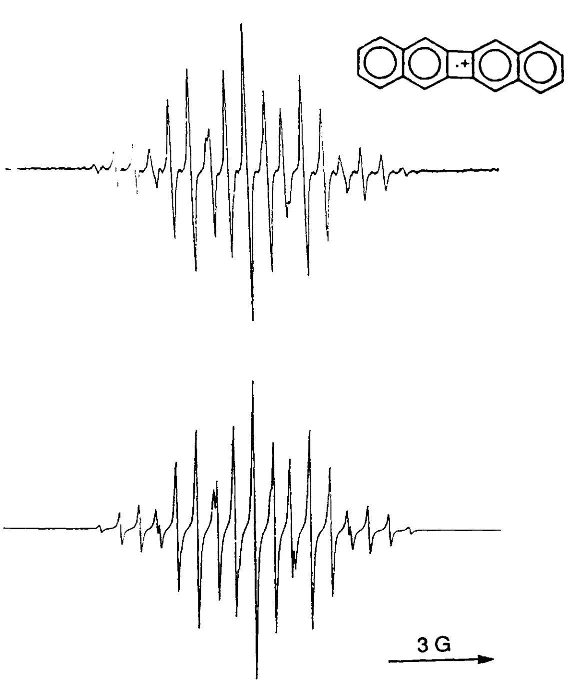


Fig. 2 EPR Spectrum (top) and simulation (bottom) of the dibenzo[*b*,*h*]biphenylene radical cation, $\mathbf{3}^{\cdot+}$, in TFAH–Tl(TFA)$_3$ at 260 K

effect,[9,10] which we have recently invoked to explain the ordering of the energy levels in the molecular orbitals of benzocyclobutenes.[11]

The two highest bonding and two lowest antibonding MOs of dibenzo[*b*,*h*]biphenylene are shown in Scheme 1, using Gerson's labelling.[7] The subscripts S and A imply that the wave function is symmetric or antisymmetric respectively about the mirror planes *xz* (first letter) and *yz* (second letter). HMO Calculations show that the HOMO and the HOMO − 1, and (as required by the pairing principle) the LUMO and LUMO + 1 of **3** are almost degenerate ($\Delta E = 0.0039\beta$).[6,7]

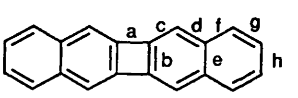
On the Finnegan–Streitwieser model of the Mills–Nixon effect the hydridisation of the carbon atoms in the central 'cyclobutadiene' unit will change to relieve the angle strain, putting more p-character into the σ-bonds of the four-membered ring and hence more s-character into the adjacent bonds in the aromatic ring [Scheme 2(*a*)]. This will result in the development of charges, and the changes in bond lengths which are indicated in Scheme 2(b).

The Hückel HOMO ψ_{AA} is stabilised by this rehybridisation because it has a high electron density at positions 1, 6, 7 and 12 to which the positive charge is polarised, and because the bonds stretch where the MO is locally antibonding, and contract where it is locally bonding. The HOMO − 1, ψ_{SA}, will be destabilised because it has a high electron density at positions 6a, 6b, 12a and 12b, which are negatively charged, and the changes in bond length may also make a small net contribution. As the initial separation between ψ_{AA} and ψ_{SA} is small, this Mills–Nixon effect causes ψ_{SA} to become the HOMO, and ψ_{AA} to drop into the HOMO − 1 position as illustrated in Scheme 1.

By similar arguments, the LUMO ψ_{SS} and the LUMO + 1 ψ_{AS}, will diverge, ψ_{SS} remaining as the LUMO.

As the phenomena underlying the Mills–Nixon effect cannot be derived from an HMO calculation, but have to be introduced as given perturbations, we have performed preliminary *ab initio* calculations on $\mathbf{3}^{\cdot+}$, **3** and $\mathbf{3}^{\cdot-}$, using the 3-21 G basis set, the symmetry being restricted to D_{2h} for each of the redox stages. Maksic has carried out *ab initio* calculations with STO-3G, 3-21G and 6-31G basis sets on biphenylene.[12] Both

Table 4 Bond lengths (Å) for dibenzo[*b*,*h*]biphenylene according to *ab initio* calculations (3-21G basis set, symmetry restricted to D_{2h})



3

Redox stage	*a*	*b*	*c*	*d*	*e*	*f*	*g*	*h*
$\mathbf{3}^{\cdot+}$	1.469	1.458	1.355	1.414	1.453	1.422	1.352	1.426
3	1.509	1.447	1.335	1.446	1.416	1.408	1.365	1.403
$\mathbf{3}^{\cdot-}$	1.487	1.440	1.358	1.457	1.436	1.393	1.386	1.381

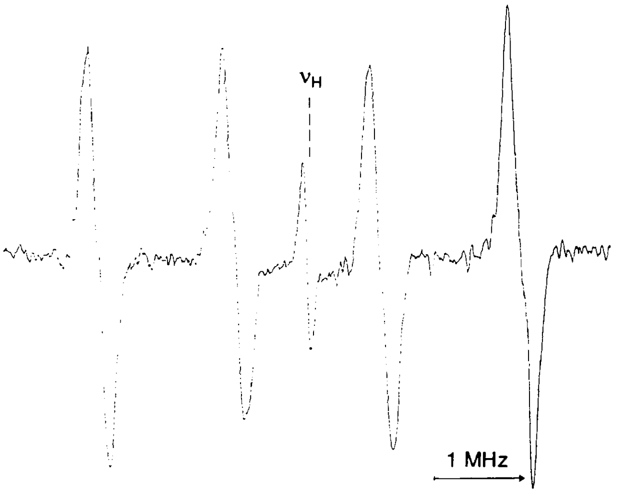
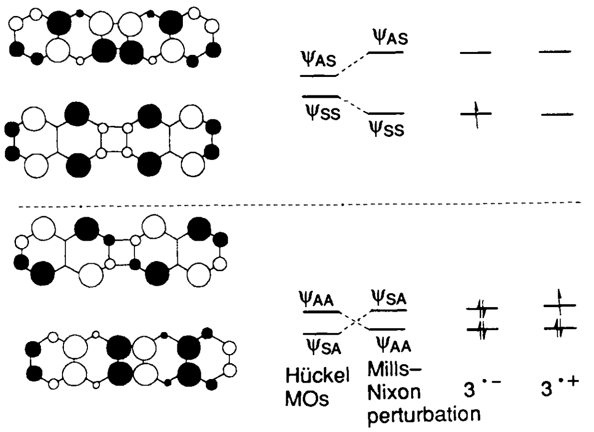
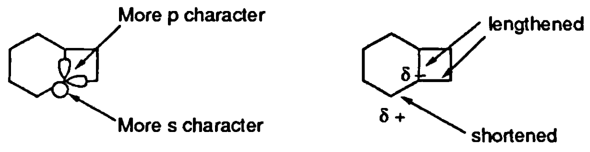


Fig. 3 ENDOR spectrum of the dibenzo[*b*,*h*]biphenylene radical cation, $\mathbf{3}^{\cdot+}$, in THF at 283 K



Scheme 1



Scheme 2

the 3-21G and 6-31G levels of refinement gave good agreement with the bond lengths as determined by X-ray diffraction, with average deviations of 0.013 Å and 0.007 Å, respectively. In particular, they reproduced correctly the changes in bond lengths at the bridgeheads as set out in Scheme 2(*b*). Similarly 3-21G optimised geometries of several cyclobutabenzenes reveal a good agreement with X-ray data.[13]

Our calculated bond lengths for $\mathbf{3}^{\cdot+}$, **3** and $\mathbf{3}^{\cdot-}$ are given in Table 4. It will be seen that the extension of the bonds *a* and *b*, and the compression of the bonds *c*, [Scheme 2(*b*)] is correctly predicted by the calculations.

These geometries were then used for the calculation of the spin densities for the radical ions $\mathbf{3}^{\cdot+}$ and $\mathbf{3}^{\cdot-}$ by the INDO method. For $\mathbf{3}^{\cdot+}$, the calculation gives a SOMO of type ψ_{SA}, as predicted by our argument above, and yields the coupling constants *a*(4H-1,6,7,12) 0.17 G, *a*(4H-2,5,8,11) 0.41 G, and *a*(4H-3,4,9,10) 0.93 G. We therefore tentatively assign the observed coupling constants as shown in Table 4.

For $\mathbf{3}^{\cdot-}$, the INDO calculation gives ψ_{SS} as the SOMO with the coupling constants *a*(4H-1,6,7,12) 4.89 G, *a*(4H-2,5,8,11) 1.81 G and *a*(4H-3,4,9,10) 0.27 G, to be compared with our observed values of 4.23, 1.57 and 0.90 G.

These attributes can be incorporated in the HMO model. The introduction of perturbation parameters in positions 1, 6, 7 and 12 where the positive charge is induced by the Mills–Nixon effect ($h = 0.2$) and for the lengthened and shortened bonds (see Table 3, footnote *d*) leads to the switch of the two highest occupied orbitals, ψ_{SA} (b_{2g}) becoming the singly occupied orbital.

These calculations must be treated with caution however, because the near degeneracy of ψ_{SA} and ψ_{AA} makes the results very sensitive to the input geometry. For example, if the bond lengths shown in Table 4 for $\mathbf{3}^{\cdot-}$ are used for calculating the spin population in $\mathbf{3}^{\cdot+}$, it places ψ_{AA} above ψ_{SA} (Table 3). It is noteworthy that the *ab initio* calculation for the structure of the radical anion $\mathbf{3}^{\cdot-}$ does not indicate such marked bond localisation and polarisation (see above) and therefore the above HMO parameters are not relevant for $\mathbf{3}^{\cdot-}$. This finding is in line with earlier reports that the release of strain is an important factor for the stabilising of radical cations[14] whereas radical anions are best stabilised by effective delocalisation. The Mills–Nixon perturbation and thus the divergence of the LUMO ψ_{SS} and the LUMO +1, ψ_{AS}, should therefore be less marked.

The electronic[15] and the photoelectronic[16] spectra of dibenzo[*b*,*h*]biphenylene are reported in the literature, and were interpreted with the aid of CNDO/S CI calculations, modelling the geometry on that of biphenylene and naphthalene, and assuming D_{2h} symmetry. These calculations gave the same ordering of energy levels as we obtain (ψ_{SA} above ψ_{AA}), but again the choice of geometry may be crucial to the outcome of the calculation.

The forms of the frontier Hückel orbitals for benzo[*b*]biphenylene, **2** are illustrated in ref. 6. If a similar reasoning is carried out on this system, it is concluded that the HOMO and HOMO −1 will diverge and the LUMO and LUMO +1 will probably converge, and again this may lead to a deviation from the pairing theorem.

In biphenylene itself (**1**), similar perturbations in the energies of the orbitals will occur. The HOMO −1 and the HOMO should diverge, but the effect of the changes in charge and of bond length on the LUMO and LUMO +1 will be opposed, and the net effect will be rather unpredictable but small. The separation between the HOMO and HOMO −1 and between the LUMO and LUMO +1 is too large (0.434β) for the electronic configuration of $\mathbf{1}^{\cdot+}$ or $\mathbf{1}^{\cdot-}$ to be affected, and the pairing principle holds.

We conclude that the EPR and ENDOR spectra establish that dibenzo[*b*,*h*]biphenylene (**3**) disobeys the pairing principle, $\mathbf{3}^{\cdot+}$ being derived from ψ_{SA}, and $\mathbf{3}^{\cdot-}$ from ψ_{SS}. We believe that this is due to angle strain, and this is supported by MO calculations. As far as we are aware, this is the first evidence for an unsubstituted planar alternant hydrocarbon which does not obey the pairing principle.

In 1975,[7] Gerson was able to obtain the spectrum of the 1,6,7,12-tetramethyldibenzo[*b*,*h*]biphenylene radical anion $\mathbf{4}^{\cdot-}$ (and thereby to confirm the assignment of the largest proton coupling constants in $\mathbf{3}^{\cdot-}$ to the 1,6,7 and 12 positions, supporting the ψ_{SS} as SOMO), but he was unable to obtain the spectrum of the radical cation $\mathbf{4}^{\cdot+}$. It would be interesting to try again to obtain this spectrum, by using the better techniques which are now available. As in ψ_{SA}, the methylated position would not be that where the spin-density is greatest, and the identification of the SOMO should be unambiguous.

Experimental

Benzo[*b*]biphenylene (**2**) was prepared as described in ref. 17.

Dibenzo[b,h]*biphenylene* **3**.—Potassium *tert*-butoxide (0.50 g) was added in one portion to a stirred solution of 1,2-bis(bromomethyl)benzene and 1,2-dibromo-1,2-dihydrocyclobuta[*b*]naphthalene[18] (190 mg) in THF (10 cm^3). When the vigorously exothermic reaction had subsided, the mixture was poured onto water and the pale buff residue was filtered off and dried. This residue was washed with dichloromethane (3 × 50 cm^3) leaving the highly insoluble dibenzo[*b*,*h*]biphenylene (63 mg) (Found: C, 95.1; H, 4.9. $C_{20}H_{12}$ requires C, 95.2, H, 4.76%); δ($CDCl_3$) 7.60 (m, 4 H, 2,5,8,11-H), 7.35 (m, 4 H, 3,4,9,10-H), 7.28 (s, 4 H, 1,6,7,12-H).

EPR spectra were recorded on a Bruker ESP 300 or Varian E9 spectrometer, and ENDOR spectra on a Bruker ESP 300 spectrometer system. Trifluoroacetic acid was condensed into the EPR tube under high vacuum or added by teat pipette, and degassed. $Tl(TFA)_3$, $Hg(TFA)_2$ and DDQ were used as purchased.

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