The Electron Spin Resonance Spectrum of the Biphenyl Radical Cation

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The e.s.r. spectrum of the biphenyl radical cation, $Ph_2^{+\cdot}$, has been observed from the photolysis of benzene or biphenyl and mercury(II) trifluoroacetate in trifluoroacetic acid. The hyperfine coupling constants of $Ph_2^{+\cdot}$ and $Ph_2^{-\cdot}$ are compared with the predictions of various modifications of the Hückel–McConnell approximation, and it is concluded that this provides no evidence that these species are anything but planar. UHF/MINDO/3 calculations have been carried out on Ph_2, $Ph_2^{+\cdot}$, and $Ph_2^{-\cdot}$, and lead to dihedral angles of 6.5 and 6.8° for the radical cation and anion, respectively, with negligible energy differences between the planar and fully optimised structures.

The e.s.r. spectrum of the biphenyl radical anion, $Ph_2^{-\cdot}$, is well known,[1] but the spectrum of the corresponding radical cation, $Ph_2^{+\cdot}$, is notable for its absence from the literature. Thus biphenyl reacts with antimony pentachloride in dichloromethane to give not $Ph_2^{+\cdot}$, but the 4,4′-dichlorobiphenyl radical cation,[2] and with xenon difluoride it gives the 4,4′-difluorobiphenyl radical cation.[3] Irradiation of biphenyl in squalene with electrons from ^{90}Sr gives the ion pair $[Ph_2^{+\cdot}][Ph_2^{-\cdot}]$ which reacts to give a fluorescence spectrum with hyperfine coupling characteristic of the radical ions, but the resolution was not sufficient to distinguish the spectrum of the anion from that of the cation.[4] γ-Irradiation of a solid solution of biphenyl in F_3CCCl_3 gives $Ph_2^{+\cdot}$; the e.s.r. signals are broad, but show *a* (4 H) 6.8, *a* (2 H) 3.35 G.[5]

Much of the interest in the spectra of $Ph_2^{+\cdot}$ and $Ph_2^{-\cdot}$ lies in the fact that they provide a convenient testing ground for π molecular orbital theories, particularly insofar as they treat twisting about the C-1–C-7 pivot bond. Biphenyl itself is believed to have a dihedral angle between the two rings of *ca.* 40°,[6] but the LUMO is bonding between C-1 and C-7 (see Scheme 1) and addition of an electron to give $Ph_2^{-\cdot}$ would be expected to shorten the C-1–C-7 bond and reduce the dihedral angle. Similarly the HOMO is antibonding between C-1 and C-7 and removal of an electron to give $Ph_2^{+\cdot}$ should again strengthen the bond and flatten the molecule.

Discussion of the electronic and nuclear structure of the radical ions has involved either an interpretation of the e.s.r.[7–9] or ENDOR[10] spectra of $Ph_2^{-\cdot}$, or a semi-empirical MO[11–14] or self-consistent steric analysis[15] calculation. The estimates of the dihedral angle vary between 38 and 0°.

We report here the first observation of the e.s.r. spectrum of the biphenyl radical cation in fluid solution. The hyperfine coupling constants are examined against various modifications of the Hückel–McConnell approximation, and the structures of the neutral molecule and radical anion and cation are explored by MINDO/3 calculations.

E.s.r. Spectrum.—The spectrum which we assign to $Ph_2^{+\cdot}$ is shown in the Figure. It is observed when biphenyl or benzene in trifluoroacetic acid is photolysed with mercury(II) trifluoroacetate by Kochi's method;[16] presumably, when benzene is the reagent, the benzene radical cation is first formed, and then reacts rapidly with further benzene. The measured hyperfine coupling constants are listed in the first row of Table 1, together with the values for the corresponding anion, $Ph_2^{-\cdot}$, for comparison. The assignment of the hyperfine coupling constants is based on their correspondence with the calculated values, as discussed below. It will be noted that, in both the anion and cation, $a_4 = 2a_2$.

As biphenyl is an alternant hydrocarbon, the absolute values of the Hückel coefficients at corresponding positions in the HOMO and the LUMO are the same if the molecule is assumed to be planar (see Scheme 1). If the spin densities ρ are taken to be equal to c_i^2, the hyperfine coupling constants at corresponding positions in the cation and anion, given by the McConnell equation (1), should therefore differ only insofar as the constants Q differ in the two species.

$$a_i = Q\rho_i \qquad (1)$$

The ratios $a_2{:}a_3{:}a_4$ in $Ph_2^{+\cdot}$ (1:0.16:2.00) and in $Ph_2^{-\cdot}$ (1:0.15:2.01) are indeed the same. In the second row of the Table, values of a_i are calculated by equation (1), taking Q for the cation as -26.6 G as it is in $C_6H_6^{+\cdot}$, and Q for the anion -22.5 G, as it is in $C_6H_6^{-\cdot}$. Although these Q values appear to be too small for the biphenyl radical ions, the correlation with the observed values is sufficient to permit an assignment of the coupling constants.

Colpa and Bolton's modified equation [equation (2)] was designed to take account of the effect of 'excess charge' at each carbon atom;[17] the positive sign of K applies for cations, and the negative sign for anions.

$$a_i = Q_0\rho_i \pm K\rho_i^2 \qquad (2)$$

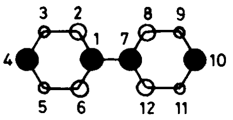
Row 3 of Table 1 gives the values of a_i calculated by equation (2), taking Q_0 as -27 G, and K as -13 G; the agreement with the experimental values is seen to be rather better.

McLachlan's modification[7] takes into account the polarisation of the spins of the π-electrons by the spin of the unpaired electron. In equation (3), π_{ir} is the atom-atom polarisability between atoms i and r, and λ is a constant.

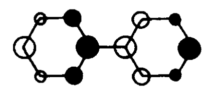
$$\rho_i = c_i^2 + \lambda \sum_{r=1}^{12} \pi_{ir} c_r^2 \qquad (3)$$

McLachlan's values of λ 1.09 and Q -24.2 G for $Ph_2^{-\cdot}$ give ρ_2 0.208, ρ_3 -0.023, and ρ_4 0.105, and the hyperfine coupling constants given in row 4 of Table 1.[7] The spin densities would be the same in the radical cation, and if the Q value is increased by the ratio of the hyperfine coupling constant (1.18) in the benzene radical cation and anion, the calculated values of a_i for $Ph_2^{+\cdot}$ which are given in row 4 of Table 1 are obtained.

The agreement of these (McLachlan) calculated values with



$$\psi_7 = 0{\cdot}351(\phi_1 + \phi_7) - 0{\cdot}299(\phi_2 + \phi_6 + \phi_8 + \phi_{12}) - 0{\cdot}140(\phi_3 + \phi_5 + \phi_9 + \phi_{11}) + 0{\cdot}398(\phi_4 - \phi_{10})$$



$$\psi_6 = 0{\cdot}351(\phi_1 - \phi_7) + 0{\cdot}299(\phi_2 + \phi_6 - \phi_8 - \phi_{12}) - 0{\cdot}140(\phi_3 + \phi_5 - \phi_9 - \phi_{11}) - 0{\cdot}398(\phi_4 - \phi_{10})$$

Scheme 1. Hückel coefficients for the HOMO and LUMO of biphenyl

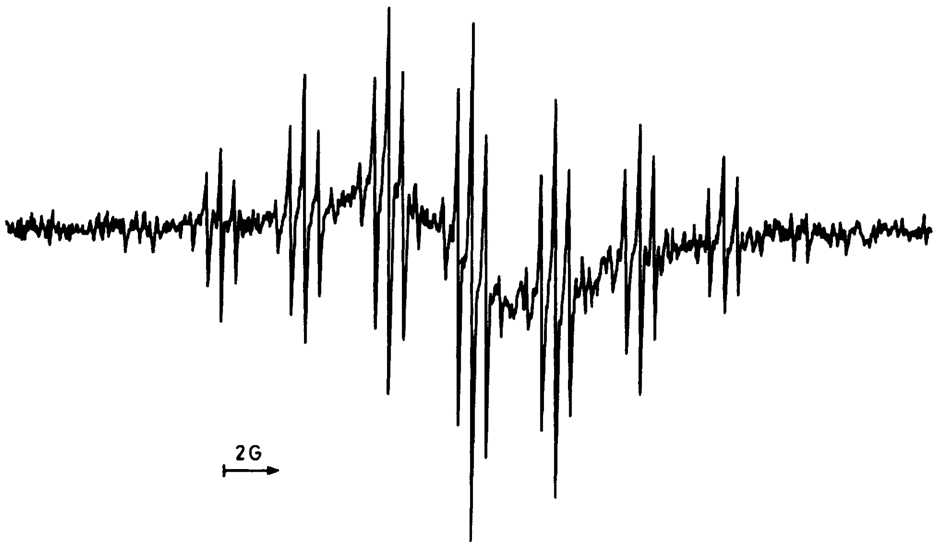


Figure. E.s.r. spectrum of the biphenyl radical cation in trifluoroacetic acid at 1 °C

Table 1. Observed and calculated e.s.r. hyperfine coupling constants (G) for $Ph_2^{+\cdot}$ and $Ph_2^{-\cdot}$

	$Ph_2^{+\cdot}$			$Ph_2^{-\cdot}$		
	a_2	a_3	a_4	a_2	a_3	a_4
1 Observed[a]	3.15	0.51	6.30	2.68	0.39	5.39
2 Calc. by equation (1)	−2.38	−0.52	−4.21	−2.01	−0.44	−3.56
3 Calc. by equation (2)	−2.51	−0.55	−4.59	−2.30	−0.53	−3.94
4 Calc. by equation (3)	−2.97	+0.65	−5.95	−2.52	+0.55	−5.04
5 Calc. by equation (3), $\beta' = 0.5\beta$	−1.86	+0.12	−5.84	−1.58	+0.10	−4.95
6 UHF/MINDO/3	−3.06	+2.21	−4.09	−3.04	+2.29	−3.79

Note $a_2 = a_6 = a_8 = a_{12}$; $a_3 = a_5 = a_9 = a_{11}$; $a_4 = a_{10}$

[a] $Ph_2^{+\cdot}$ in CF_3CO_2H solvent at 0 °C, with $CF_3CO_2^-$ or $Hg(OCOCF_3)_3^-$ as the counterion. $g = 2.0027$.

the experimental spectrum is as good as is normally obtained for a planar hydrocarbon. The fifth row of Table 1 shows the hyperfine coupling constants calculated by the McLachlan method for a twisted molecule in which the resonance integral β' for the C-1–C-7 bond is equal to 0.5β,[7] and the agreement with experiment is seen to be much less satisfactory. We conclude that within the limited accuracy of these simple treatments, there is no evidence that the biphenyl radical anion or cation is anything but planar.

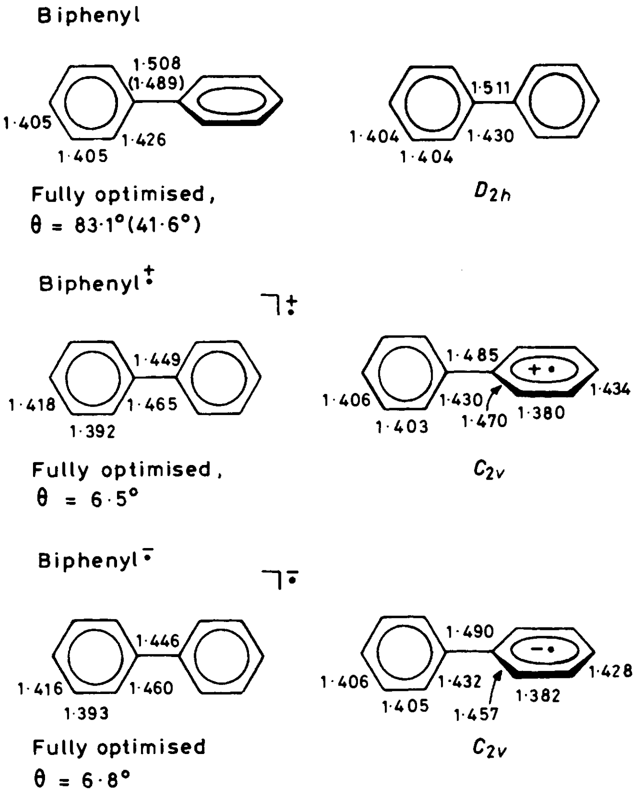
MINDO/3 Calculations.—Biphenyl and its radical cation and anion were investigated using UHF/MINDO/3 semi-empirical MO theory.[18] The neutral molecule, which has been experimentally[6,19] and theoretically[10–15,20] well investigated, serves as a calibration for the performance of MINDO/3 for this problem. The results are shown in Table 2 and in Scheme 2.

Full optimisation of biphenyl itself leads to a structure with an angle (θ_0) of 83° between the rings, compared with the experimental value of *ca.* 40°.[6] The heat of formation of this structure is practically identical with that obtained by constraining the rings to be perpendicular (see Table 2). The calculated barrier to rotation *via* the planar form is 4.3 kcal mol^{-1}, compared with experimental values[19] up to 5 kcal mol^{-1}, presumably for rotation through the perpendicular structure. The central C-1–C-7 bond length varies only slightly (from 1.508 to 1.511 Å) on going from the perpendicular to the

Table 2. MINDO/3 calculated and experimental data for biphenyl and its radical ions

	Ph_2 calc.	Ph_2 exp.	$Ph_2^{+\cdot}$ calc.	$Ph_2^{-\cdot}$ calc.
Dihedral angle θ_0 (°)	83.1	41.6[6]	6.5	6.8
Heat of formation (kcal mol^{-1})				
At θ_0	65.2	43.5[a]	241.2	60.4
Planar	69.2		241.3	60.4
Perpendicular	65.2		249.5	68.9
Rotation barrier (kcal mol^{-1})	4.3	<5[19]	8.3	8.5

[a] D. J. Colman and G. Pilcher, *Trans. Faraday Soc.*, 1966, **62**, 821.



Scheme 2. UHF/MINDO/3 calculated structures (bond lengths in Å, experimental values[6] in parentheses)

planar structure. The observed value for the planar geometry found in crystalline biphenyl is 1.496 Å[19] and for the gas phase 1.489 Å.[6] These results suggest that MINDO/3 slightly overestimates the stability of the perpendicular form as do other NDO methods,[20] although the difference between the structures is less significant than it appears because the potential energy surface is very flat and the rotation barrier small.

Both the radical cation and anion are calculated to be almost planar, with twist angles (θ_0) of 6.5 and 6.8°, respectively. Again the energy differences between the planar and fully optimised structures are very small. The calculated barriers to rotation are 8.3 and 8.5 kcal mol^{-1} for cation and anion respectively.[*] These barriers are considerably smaller than those calculated by Sullivan and Fong[14] using INDO, although our MINDO/3 optimised geometries are less twisted than those found in the earlier work.

As expected the radical ions have shorter central bonds than the neutral molecule and show quinonoid distortions of the benzene rings. The central C-1–C-7 bond lengths increase to 1.490 and 1.485 Å in the perpendicular anion and cation respectively, indicating some multiple-bond character. The hyperfine coupling constants calculated from the spin-annihilated UHF/MINDO/3 spin densities[18] are in fair agreement with the experimental values for the *ortho*-hydrogens, but are too high for the *meta* and too low for the *para* hydrogens (see row 5 of Table 1). Finally, we note that the calculated electron affinity of biphenyl is +0.21 eV, a surprisingly high value compared with that (−1.15 eV) of benzene.[23]

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[*] *X*-Ray diffraction studies show that in the crystal, the biphenyl anion in $Ph_2^{-}\cdot K^{+}(TG)_2$ (TG = tetraglyme) is planar,[21] but in $Ph_2^{-}\cdot Rb^{+}(TG)_2$ it has a dihedral angle of 9.4°.[22]

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