Electron Resonance Study of Schlenk's Hydrocarbon

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Three paramagnetic species may be formed when the dichloride precursor of Schlenk's hydrocarbon is treated with zinc. We have measured and analysed their electron resonance spectra in both fluid and solid solution. Theoretical calculations of the zero-field splitting for various conformations of Schlenk's hydrocarbon suggest that this is indeed the species responsible for the solid-state spectrum. A marked deviation from planarity of the triplet state is indicated by the calculations. The two other radicals yield high-resolution electron resonance spectra in fluid solution. One of the radicals is identified as *m*-(diphenylmethyl)triphenylmethyl, formed from the triplet state by hydrogen-atom abstraction from the solvent. The third species is also a *meta*-substituted triphenylmethyl radical, although we are unable to identify the substituent.

The spin hamiltonian required to interpret the solution electron resonance spectrum of a biradical is equation (1)

$$\mathscr{H} = g\beta H(S_z^{(1)} + S_z^{(2)}) + \sum_{i=1}^{n} a^{(i)}(I_z^{(1,i)}S_z^{(1)} + I_z^{(2,i)}S_z^{(2)}) + JS^{(1)} \cdot S^{(2)} \quad (1)$$

provided the biridical is symmetric.[1] The first term in $\mathscr{H}$ is the Zeeman coupling of the two electron spins to the magnetic field while the last term is the coupling of the electron spins to each other. The summation in the spin hamiltonian represents the coupling of a particular electron to the n nuclei in its half of the

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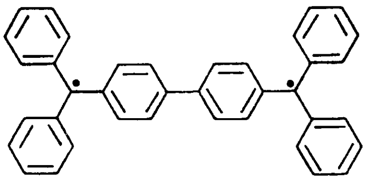
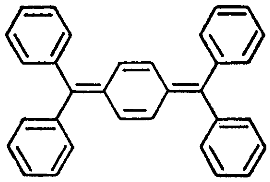
[1] D. C. Reitz and S. I. Weissman, *J. Chem. Phys.*, 1960, **33**, 700.

biradical. The validity of the hamiltonian has been amply demonstrated by its use in interpreting the electron resonance spectra of many stable nitroxide biradicals.[2,3] Originally, however, the hamiltonian was developed in order to understand the spectra of conjugated biradicals[1] such as Tschitschibabin's hydrocarbon (I). Solutions of (I) certainly give high-resolution electron resonance spectra, but it was only after years of controversy that the species responsible for the spectrum was finally identified as a substituted *p*-biphenylyldiphenylmethyl radical.[4,5] The ground state of Tschitschibabin's hydrocarbon is a singlet, although the thermally populated triplet (I) has been observed in the solid state.[6] Similarly, the ground state of (II) is a singlet, although solutions in toluene do exhibit a high-resolution electron resonance spectrum which has been attributed to a *para*-substituted triphenylmethyl radical.[7] The multiplicity of the ground state of a particular compound is determined by two factors. One is the energy gap between the two molecular orbitals containing the unpaired electrons in the triplet state and the other is the magnitude of the triplet–singlet separation, J.

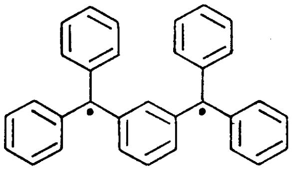


(I)



(II)

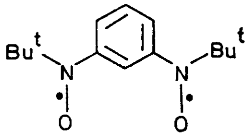
The structure of both these compounds (I) and (II) can be formulated as either a singlet or a triplet state; experimentally the ground state is found to be a singlet. Similar results are now known for a wide range of compounds which includes binitrones,[8] isatogens,[9] and bianthrone.[10] The analogy may be taken further, for all these compounds give solution electron resonance spectra. These are thought to be of monoradicals formed through hydrogen-atom abstraction, from the solvent, by the thermally populated triplet state.[8] The radical from (II) appears to be anomalous and is apparently not formed in this way.[7]



(III)

We have studied Schlenk's hydrocarbon[11] (III) in order to cast more light on the structure and reactions of conjugated biradicals. Schlenk's hydrocarbon was chosen because it is impossible to write a conventional singlet state structure for this species. By analogy with *NN'*-di-t-butyl-*m*-phenylenebinitroxide[12] (IV) which has a triplet ground state, in contrast to the singlet ground states of its *ortho*- and *para*-isomers, we expect (III) to possess a triplet ground state. In both cases the appropriate molecular orbitals are degenerate and so the multiplicity of the ground state is determined by the absolute magnitude of J.

A poorly resolved electron resonance spectrum has been reported for solutions of (III) although not analysed.[1] The radical had been enriched at the methyl carbons with carbon-13 and from the determination of the carbon-13 hyperfine splitting the triplet–singlet separation J was determined to be zero.[1] This result is in marked contrast to a theoretical estimate of 6 × 10^5 MHz obtained by McConnell[13] for structurally related compounds. We now report the measurement and analysis of the electron resonance spectrum of (III) in both fluid and solid solutions.



(IV)

EXPERIMENTAL

The dichloride precursor to Schlenk's hydrocarbon (III) was prepared by following the original synthesis described by Schlenk and Brauns.[11] The hydrocarbon was obtained by treating the dichloride, dissolved in toluene, with powdered zinc. The reaction was performed in an electron resonance quartz sample tube which was sealed after the sample had been degassed. A radical was formed im-

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[2] R. Briere, R. M. Dupeyre, H. Lemaire, A. Rassat, and P. Rey, *Bull. Soc. chim. France*, 1965, 3290.

[3] S. H. Glarum and J. H. Marshall, *J. Chem. Phys.*, 1967, **47**, 1374.

[4] H.-D. Brauer, H. Stieger, J. S. Hyde, L. D. Kispert, and G. R. Luckhurst, *Mol. Phys.*, 1969, **17**, 457.

[5] W. J. van der Hart and L. J. Oosterhoff, *Mol. Phys.*, 1970, **18**, 281.

[6] H.-D. Brauer, H. Steiger, and H. Hartmann, *Z. phys. Chem.*, 1969, **63**, 50.

[7] P. Cavalieri d'Oro, A. Mangini, G. F. Pedulli, P. Spagnolo, and M. Tiecco, *Mol. Phys.*, 1970, **18**, 861.

[8] A. R. Forrester, R. H. Thomson, and G. R. Luckhurst, *J. Chem. Soc.* (*B*), 1968, 1311.

[9] L. Lunazzi, G. Maccagnani, A. Mangini, and G. F. Pedulli, *J. Chem. Soc.* (*B*), 1967, 1072.

[10] I. Agranat, M. Rabinovitz, H. R. Falle, G. R. Luckhurst, and J. N. Ockwell, *J. Chem. Soc.* (*B*), 1970, 294.

[11] W. Schlenk and M. Brauns, *Ber.*, 1915, **48**, 661.

[12] A. Calder, A. R. Forrester, P. G. James, and G. R. Luckhurst, *J. Amer. Chem. Soc.*, 1969, **91**, 3724.

[13] H. M. McConnell, *J. Chem. Phys.*, 1960, **33**, 115.

mediately and its solution electron resonance spectrum, measured at room temperature with a Varian E-3 spectrometer, is shown in Figure 1. After several days the appearance of the spectrum changed; the new spectrum is given in Figure 2. In contrast, solutions of Schlenk's hydrocarbon in carbon tetrachloride give only the initial spectrum illustrated in Figure 1. A freshly prepared solution in toluene was frozen at 173 K and the electron resonance spectrum shown in Figure 3 was obtained.

Analysis.—The intense line in the centre of the solid-state spectrum (*cf*. Figure 3) may be associated with a doublet state radical. The less intense peaks are attributed to a triplet state species.[14] The analysis of the spectrum is straightforward and the zero-field splitting parameters D and E are found to be 192 and 17 MHz. The relationship [14] between D and E and the line positions is given in Figure 3.

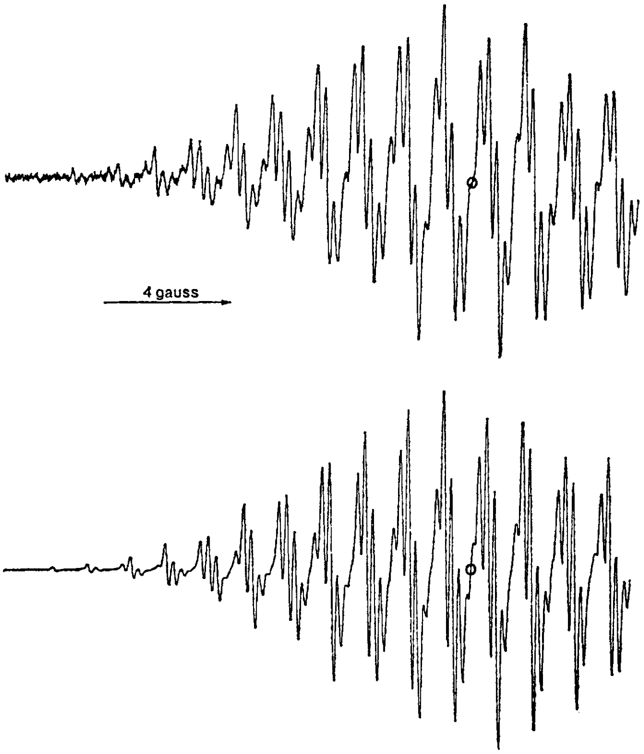

FIGURE 1 The solution electron resonance spectrum of radical (V). Only one half the spectrum is shown; the centre is marked by a circle. The upper spectrum is experimental and the lower is a simulation based on the coupling constants given in the Table

We now return to the solution spectra. The triplet state cannot be responsible for the high-resolution solution spectra since its linewidth should be about 1 gauss [15] and experimentally the linewidth in both spectra is only one tenth of this value. The species yielding the solution spectra must therefore be monoradicals or biradicals with a small zero-field splitting. By analogy with the previous analyses of the high-resolution spectra of solutions of compounds [4,7] (I) and (II) we expect the species to be *meta*-substituted triphenylmethyl radicals with structure (V).

The spectrum of the first radical is readily analysed in terms of coupling to all the triphenylmethyl protons but no coupling to the *meta*-substituent. The proton coupling constants, which are given in the Table, were obtained by comparing computer-simulated spectra with the experimental spectrum. The theoretical spectra were calculated with a Varian 620/i computer on-line to the E-3 spectrometer on which the simulated spectra were

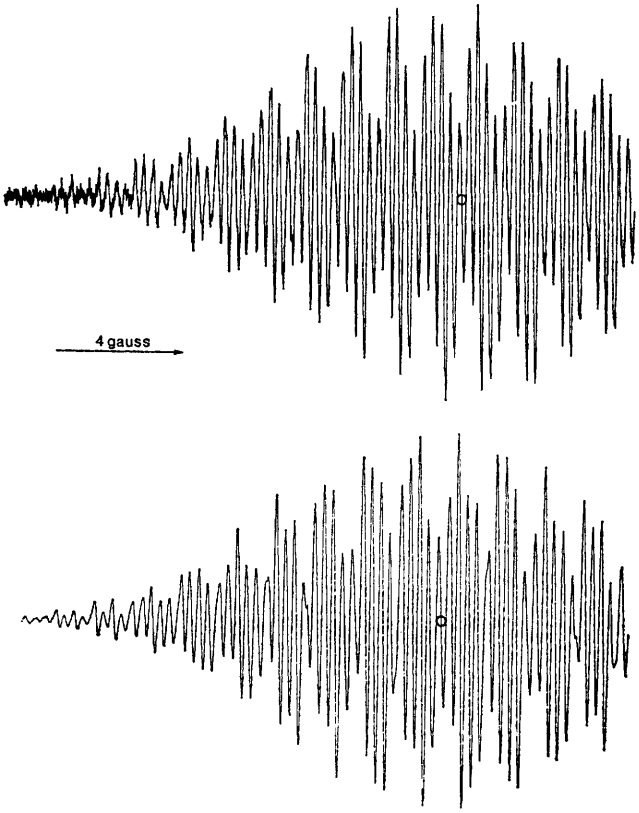

FIGURE 2 The solution electron resonance spectrum of (V; X = H). The upper spectrum is experimental, while the lower spectrum is a reconstruction based on the coupling constants in the Table, together with an additional doublet splitting of 1·485 MHz

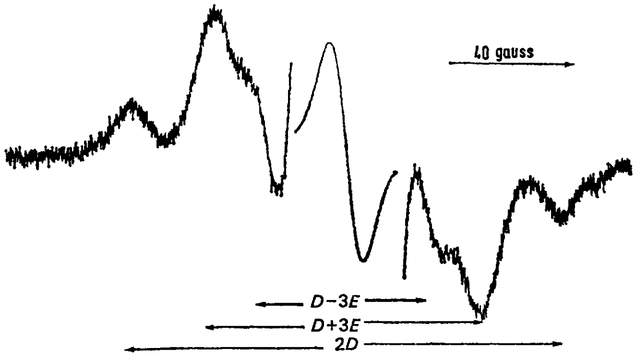

FIGURE 3 The electron resonance spectrum of a frozen solution of Schlenk's hydrocarbon (III) in toluene at 173 K

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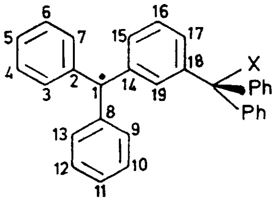
[14] E. Wasserman, L. C. Snyder, and W. A. Yager, *J. Chem. Phys.*, 1964, **41**, 1763.

[15] A. Carrington and G. R. Luckhurst, *Mol. Phys.*, 1964, **8**, 125.

recorded. The programme for spectrum simulation was supplied by Varian Associates, although we have modified the output routine. The theoretical spectrum, corresponding to the coupling constants in the Table, is in complete agreement with experiment (*cf.* Figure 1).



(V)

The analysis of the spectrum in Figure 2 is not so straightforward because the first radical does not decay completely. Consequently, the second spectrum is contaminated by lines from the first. However, the line positions can be completely accounted for if X is taken to be hydrogen with a coupling constant of 1·485 MHz. If all other couplings are given the values in the Table, then the theoretical spectrum in Figure 2 is obtained. The agreement with experiment is good, but not perfect because the intensities of the experimental lines are distorted by the presence of traces of the first radical.

The proton coupling constants for (V)

Coupling constant/ MHz	Number of protons	Assignment
7·80	2	5, 11
7·66	1	17
7·22	1	15 or 19
7·15	4	3, 7, 9, 13
7·07	1	19 or 15
3·180	5	4, 6, 10, 12, 16

DISCUSSION

The Species in Solution.—The coupling constants given in the Table are remarkably close to those found for triphenylmethyl.[16] This strengthens our identification of the first species formed as a *meta*-substituted triphenylmethyl radical. A tentative assignment of the coupling constants based on a comparison of the results for triphenylmethyl is given in the Table. We are unable to identify the substituent from the electron resonance spectrum, because its nuclei do not interact with the unpaired electron. The close similarity of the coupling constants for triphenylmethyl and radical (V) together with the marked differences between the coupling constants for triphenylmethyl and *p*-biphenylyldiphenylmethyl,[16] where the substituent is conjugated, suggests that in (V) the *meta*-substituent is aliphatic. The most plausible group is a substituted diphenylmethyl and the problem now is to identify X. Clearly, if the dechlorination were incomplete X could be a chlorine atom. However, the excess of zinc employed in the reaction, together with the ability to regenerate the radical thermally argues against this possibility. We prefer therefore to think of the radical as a polymeric species, although we are unable to offer further evidence for this identification. The structure of the polymer could be analogous to that envisaged by Waring and Sloan [17] for the paramagnetic species present in solutions of Tschitschibabin's hydrocarbon (I), although there is now some doubt about this structure.[4]

The second species, formed following the decay of the first radical, is almost certainly the *m*-(diphenylmethyl)-triphenylmethyl radical (V; X = H). If the group containing the proton was freely rotating the splitting would approximate to that for a *meta*-proton, 3·180 MHz. The low value of the observed splitting (1·485 MHz) indicates hindered rotation in accord with the presence of the two phenyl groups.[18] By analogy with the results for binitrones,[8] isatogens,[9] and bianthrone [10] we expect the second radical to be formed by hydrogen-atom extraction from the solvent, toluene, by the triplet state (III). The inability to generate the radical in carbon tetrachloride solutions supports this hypothesis. The corresponding radical was not detected for the *para*-isomer (II) of Schlenk's hydrocarbon.[7] Presumably the triplet-state intermediate is never formed to any appreciable extent because the singlet–triplet separation is so large.

The Triplet State.—Ulusoy *et al.*[19] failed to detect the half-field transition associated with the triplet state of (III). This failure could result from two factors. The first is the extreme reaction conditions used in the synthesis of (III) which may have led to its destruction. Secondly, the intensity of the half-field transition will be greatly reduced in comparison with the $\Delta m = 1$ spectrum because of the small zero-field splitting. Indeed, we were unable to detect the half-field line.

The most obvious assignment of the triplet-state spectrum observed in the solid state is to Schlenk's hydrocarbon (III) itself. In an attempt to confirm this identification we have calculated the zero-field splitting parameters for (III). The zero-field splitting tensor **D** for a hydrocarbon triplet state is [20] (2) provided

$$\mathbf{D} = \tfrac{1}{2}g^2\beta^2\langle\psi(1,2)|\mathbf{D}_{\mathrm{op}}|\psi(1,2)\rangle \qquad (2)$$

spin–orbit coupling is ignored. $\mathbf{D}_{\mathrm{op}}$ is the dipole–dipole operator and has components (3) and (4), *etc.*, where r_{12} is the separation between electrons 1 and 2. The wavefunction ψ (1,2) is related to the molecular

$$D_{zz} = \frac{r_{12}^2 - 3Z_{12}^2}{r_{12}^5} \qquad (3)$$

$$D_{xz} = \frac{-3X_{12}Z_{12}}{r_{13}^5} \qquad (4)$$

orbitals γ_i and γ_j containing the unpaired electrons by

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[16] A. H. Maki, R. D. Allendoerfer, J. C. Danner, and R. T. Keys, *J. Amer. Chem. Soc.*, 1968, **90**, 4225.

[17] R. K. Waring, jun., and G. J. Sloan, *J. Chem. Phys.*, 1964, **40**, 772.

[18] A. Carrington and P. F. Todd, *Mol. Phys.*, 1964, **8**, 299.

[19] E. Ulusoy, H. Hartmann, and J. Heidberg, *Z. Naturforsch.*, 1969, **24b**, 249.

[20] M. Gouterman, *J. Chem. Phys.*, 1959, **30**, 1369.

equation (6). A molecule such as (III) can adopt many

$$\psi(1,2) = \frac{1}{\sqrt{2}}\{\gamma_i(1)\gamma_j(2) - \gamma_j(1)\gamma_i(2)\} \qquad (6)$$

conformations and in order to reduce the numerical analysis we have made a number of simplifying assumptions when calculating **D**. All three-centre and higher integrals are neglected and so **D** can be written as[21] (7) where C_{iq} is the coefficient of the $2p_z$ atomic

$$\mathbf{D} = \tfrac{1}{2}g^2\beta^2 \sum_{p<q} [C_{ip}C_{jq} - C_{iq}C_{jp}]^2\langle pp|qq\rangle \qquad (7)$$

orbital on atom q in the ith molecular orbital. In our calculations the C_{iq} are taken to be Hückel coefficients. The two-centre integrals $\langle pp|qq\rangle$ are given by (8)

$$\langle pp|qq\rangle = \langle \chi_p(1)\chi_p(1)|\mathbf{D}_{op}|\chi_q(2)\chi_q(2)\rangle \qquad (8)$$

where χ_p is a $2p_z$ atomic orbital on carbon atom p. The $2p_z$ orbitals are conveniently represented as two half-charges located above and below the plane containing the carbon atom.[21] Although this approximation may seem crude it has been shown to be quite good if the half-charges are separated by 1·4 Å.[21] The approximation is expected to be especially valid in our calculations because the small zero-field splitting implies large electron–electron separations.[12] The tensor is evaluated in some convenient molecular axis system, x, y, z and then diagonalized. It is important not to confuse the axes x, y, z commonly used to denote the tensor components, with the laboratory frame. The zero-field splitting parameter D is three-halves the largest principal component and E is one half the difference of the remaining two components.

Initially (III) was assumed to be planar. For the Hückel molecular orbital calculation all coulomb integrals were set equal to α and all resonance integrals equal to β. Evaluation of the two-centre integrals is simply a geometrical problem; for this all ring carbon–carbon bond lengths were taken as 1·39 Å and the bond-lengths between rings as 1·50 Å. The theoretical zero-field splitting parameters for the planar conformation are $D = 410$ MHz and $E = 108$ MHz. They are clearly in poor agreement with the experimental values of 192 and 17 MHz.

The conformation of (III) is almost certainly non-planar and so we have calculated D and E for a variety of geometries. Initially the non-planar conformations were generated by rotating each phenyl ring through an angle ϕ. The resonance integrals for the bonds involved in the rotation were then written as $\beta \cos \phi$. The variation of D and E with the deviation from planarity is shown in Figure 4. There is clearly no value of ϕ which predicts a sufficiently small value of D. In fact, even at best the theoretical value is twice the experimental D. Similarly, except for very large values of ϕ, the theoretical value of E is always too large.

We were therefore forced to consider geometries which preserved the two-fold symmetry of the molecule, but did not retain the equality of all angles. In fact, the angles ϕ_2 were set at zero and the zero-field splitting was calculated as a function of ϕ_1; the angles are defined as in (VI). As expected, the smallest value of D was obtained when ϕ_1 was 90°, in other words, when the central ring is orthogonal to the other four. In this conformation $D = 238$ MHz and $E = 11$ MHz. The agreement with experiment is fair, although the theoretical D is still slightly large.

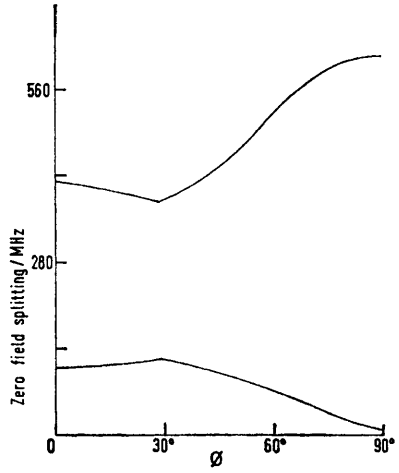
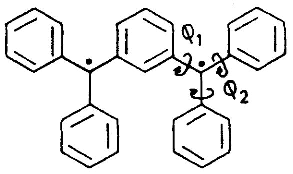


FIGURE 4 The zeo-field splitting parameters D and E calculated for structure (III) as a function of the deviation from planarity

At first sight the conformation predicted by the calculations appears unreasonable for the deviation from planarity is much larger than in triphenylmethyl.[16] This unreasonableness need not imply that the triplet state species does not have structure (III). Several factors influence the conformation of an aromatic compound such as (III); on the one hand steric forces favour non-planarity, whereas electron delocalisation will stabilise a planar structure. A third factor, electron correlation, must be considered for a triplet state. Electron correlation tends to increase the electron–electron separation and may therefore favour a non-planar conformation. It is difficult to gauge the relative importance of these three factors. However, three other ground-state triplets also exhibit marked deviations from planarity;[12,22] this indicates the importance of electron correlation and so supports our assignment.



(VI)

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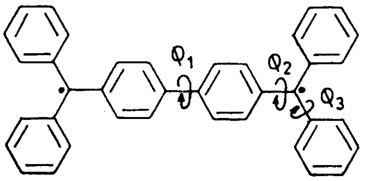
[21] A. Pullman and E. Kochanski, *Internat. J. Quantum Chem.*, 1967, **1**, 251.

[22] E. F. Ullman and D. G. B. Boocock, *Chem. Comm.*, 1969, 1161.

The molecular orbitals containing the unpaired electrons will possess considerable σ-character in the orthogonal conformation.[23,24] Accordingly, the agreement between the theory, based solely on π-molecular orbitals, and experiment is not expected to be perfect.

We have attempted to test the assumptions in the theory by calculating the zero-field splitting for Tschitschibabin's hydrocarbon (I). The predicted parameters for the planar conformation are $D = 312$ MHz and $E = 35$ MHz, whereas experimentally $D = 404$ MHz and $E = 14$ MHz.[6] In contrast to the calculations for Schlenk's hydrocarbon the theoretical D is smaller than experiment. If the non-planar structure is assumed to retain its two-fold symmetry axes, then the deviation from planarity can be defined by the three angles ϕ_1, ϕ_2, ϕ_3 as shown in (VII). Originally ϕ_1 was given the value of 30° and ϕ_2 and ϕ_3 were set equal and varied from 0 to 90°. The values of D and E obtained in these calculations are plotted as a function of ϕ_2 in Figure 5. The agreement with experiment is still poor even for the largest value of D, which corresponds to the conformation with ϕ_2 and ϕ_3 equal to zero.



(VII)

Finally, we set ϕ_1 equal to 25° and ϕ_2 to 20° when calculating the zero-field splitting as a function of ϕ_3. When this angle is 50°, $D = 401$ MHz and $E = 28$ MHz in excellent agreement with experiment. This geometry is entirely reasonable for Tschitschibabin's hydrocarbon (I) and tends to support both the calculations and the identification of this species.[6] The only problem now is the relatively small departure from planarity shown by (I) when compared with (III). We offer the following explanation. The triplet state of Tschitschibabin's hydrocarbon is the excited state which is thermally populated. The diamagnetic ground state should be essentially planar because the electron correlation effects, apparently so important in the triplet state, are absent. This planarity is then retained, even on thermal excitation to the triplet state, because the solid matrix surrounding the molecule prevents any distortion.

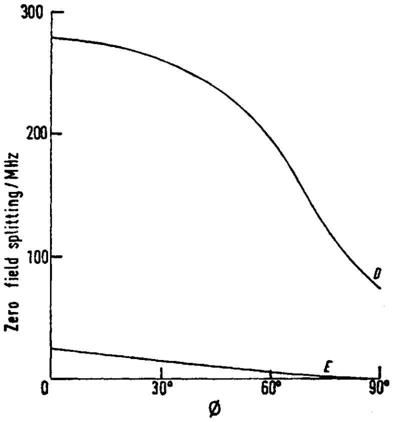


FIGURE 5 The conformational dependence of D and E for Tschitschibabin's hydrocarbon (I)

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[23] J. A. Pople and D. L. Beveridge, *J. Chem. Phys.*, 1968, **49**, 4725.

[24] A. Calder, A. R. Forrester, J. W. Emsley, G. R. Luckhurst, and R. A. Storey, *Mol. Phys.*, 1970, **18**, 481.