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The diphenyl-amino radical dimer

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E.S.R. measurements on the photodissociation-products of tetraphenyl-hydrazine in rigid solution at 77°K indicate that the principal product of this dissociation is the dimer of the diphenyl amino radical. This assignment is confirmed by a measurement of a half-field signal and computer simulation of the E.S.R. spectra in rigid solution. A long wavelength charge-transfer band arises through the interaction of the two diphenyl amino radicals. An SCMO calculation is presented, which gives a theoretical background to the latter assignment.

1. Introduction

Already in 1911 Wieland [1] established that the tetra-aryl hydrazines in solution dissociate partially into the corresponding diaryl nitrogen radicals:

$$AR_2N - NAr_2 \rightleftharpoons 2Ar_2N \cdot$$

Later many investigators studied these dissociation products by optical and magnetic resonance experiments. Lewis and Lipkin [2] achieved the dissociation by exposing a dilute solution of tetraphenylhydrazine (T.P.H.) at 77°K to u.v. light and, also from other experiments, concluded that the principal product of the dissociation is the diphenylamino radical (D.P.A.). They attributed the green colour of the rigid solution to an absorption of the radical at about 7300 Å. However, they noticed the green colour of the rigid solution at low temperature to be more dependent on the rigidity of the solution than on the temperature.

In 1964 Garafano and Santangelo [3] re-investigated the photo-dissociation by means of E.S.R. and concluded the principal product of the dissociation to be D.P.A. indeed, with an isotropic nitrogen hyperfine splitting of 40 gauss. In the footsteps of Wieland [1], however, others tried to obtain the radical in solution. Hoskins [4] heated a dilute solution of T.P.H. in toluene and found a five-line spectrum which he attributed to the T.P.H. radical. Das *et al.* [5] after heating a solution of T.P.H. in xylene and Pannell [6] after a reaction between diphenyl-amine and di-tert.butylperoxide, obtained E.S.R. spectra they assigned to D.P.A. with isotropic hyperfine splittings for the nitrogen of about 9 gauss. A year later [7, 8], however, it became clear that these spectra should have been attributed to the diphenylnitroxide radical $((C_6H_5)_2NO\cdot)$. After heating a dilute solution of T.P.H. in anisole Franzen [9] reported an absorption band at 4600 Å which he ascribed to D.P.A. From optical measurements as a function of temperature he calculated the heat of dissociation of T.P.H. to be 23·5 kcal/mol. Recently Neugebauer and Fischer [8] reported E.S.R. and u.v. spectra of the dissociation products of a few derivatives of tetraphenylhydrazine, but they could not find any indication for the dissociation in solution of T.P.H. itself.

There thus appears to be considerable disagreement in the literature about the colour and the E.S.R. spectrum of D.P.A., all previous assignments of the E.S.R. spectra at room temperature having been shown to be erroneous. At low temperatures a hyperfine coupling constant of 40 gauss was reported [3]. This, however, appears to be unusually high; for an electron in a π system one would expect something in the order of 10 gauss [8, 10].

It thus appeared worthwhile to re-investigate this problem. We found that the E.S.R. spectra of irradiated T.P.H. in rigid glasses should be interpreted on the basis of a dipolar coupling between two radicals. Therefore, we conclude that photo-dissociation leads to a radical dimer. From SCMO calculations we derive that the green colour is due to a charge-transfer transition between the constituting components of the dimer. In the following we will first present the results and the interpretation of the E.S.R. spectra and their computer simulation. Then the electronic spectra and their interpretation on the basis of an SCMO calculation are given. These calculations also yield the hyperfine coupling constants of the radical and the dipolar splitting parameter D observed for the radical dimer.

2. E.S.R. MEASUREMENTS

Figure 1 gives a typical E.S.R. spectrum of irradiated T.P.H. at 77°K in a rigid glass (EPA). The spectrum was obtained on an E–3 Varian spectrometer with appropriate low temperature equipment. The solution was irradiated at 77°K with light from an SP–500 Philips high-pressure mercury arc, filtered so as to pass light of $\lambda > 2700$ Å only. This spectrum can be interpreted on the basis of a randomly oriented set of triplets with 'axial' symmetry. The inset shows the half-field signal found. A very slight amount of free radical signal at $g = 2$ is
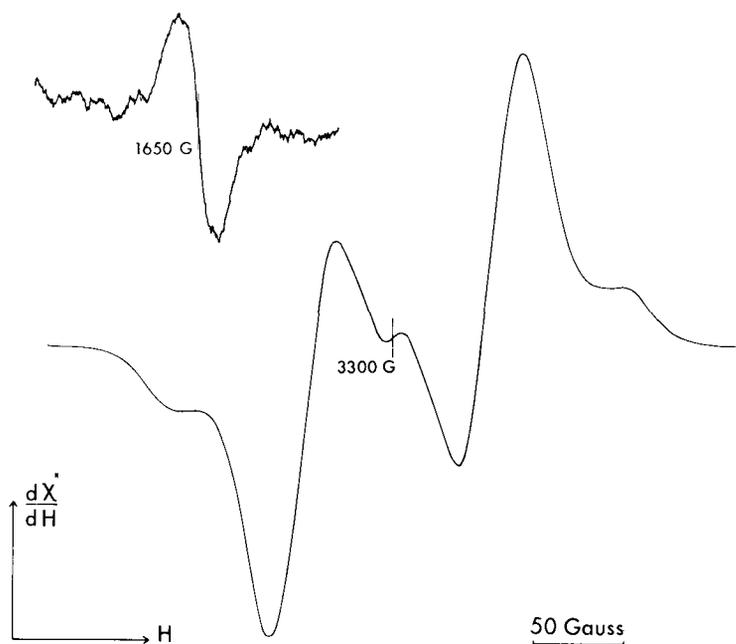

Figure 1.   E.S.R. spectrum of the di-phenyl-amino radical dimer in a rigid EPA glass at 77°K.   Inset shows half-field signal.

observed. Under some conditions this signal can be quite appreciable and this has probably led previous workers [3] to interpret the spectrum to be due to a nitrogen hyperfine splitting. The saturation behaviour of the radical and the triplet spectrum is quite different. Also, the intensity of the middle line depends on the nature of the solvent and the time of irradiation.

The spectrum can be analysed in the following manner: Assuming for simplicity an isotropic g value, the spin Hamiltonian for the system is

$$\mathcal{H} = g\beta[S \cdot H + D(S_z{}^2 - \tfrac{1}{3}S^2) + E(S_x{}^2 - S_y{}^2)],$$

where the symbols have the usual significance [11]. To interpret the spectra we will assume $E = 0$ at this point. The Hamiltonian then reduces to

$$\mathcal{H} = g\beta[S \cdot H + D(S_z{}^2 - \tfrac{1}{3}S^2)].$$

Using a $|m_s\rangle$ basis where $m_s = 0,\ \pm 1$ the first-order energy levels of $\mathcal{H}$ are calculated to be:

$$E(m_s = +1) = g\beta H + \tfrac{1}{6}g\beta D(3\cos^2\theta - 1),$$

$$E(m_s = 0) = -\tfrac{1}{3}g_0\beta D(3\cos^2\theta - 1),$$

$$E(m_s = -1) = -g\beta H + \tfrac{1}{6}g\beta D(3\cos^2\theta - 1) \quad (D \text{ in gauss}),$$

θ defines the angle between the magnetic field and the vector connecting the two dipoles. When $E = 0$, considerations of symmetry lead to an identification of the N–N direction with this vector. The forbidden $\Delta m_s = +2$ transition yields an absorption at $H = (h\nu/2g\beta)$ (half-field signal). Applying the selection rules $\Delta m_s = \pm 1$, the allowed transitions are in first order predicted at magnetic field values $H = (h\nu/g\beta) \pm \tfrac{1}{2}D$ $(3\cos^2\theta - 1)$. This means that for those dimers with their N–N direction parallel to the direction of the magnetic field $(\theta = 0)$ absorption occurs at $H = (h\nu/g\beta) \pm D$, for dimers with their N–N vector in a plane perpendicular to the direction of the magnetic field absorption occurs at fields $H = (h\nu/g\beta) \pm \tfrac{1}{2}D$. There are many more dimers with their N–N vector in this plane than with this vector along the magnetic field. Therefore, the high intensity peaks in the spectrum have a separation D, while the low intensity peaks have a separation $2D$. Thus, from our spectra we can immediately derive an estimate for D of 125 gauss. A more accurate determination of D can be obtained by a computer simulation of the spectra. A computer programme for this simulation was written and the results of this simulation are shown in figure 2. The programme treats the general case of dipolar splitting including g anisotropy. First, the resonance fields are solved from a third degree polynomial in H^2, then wave functions and transition probabilities are computed for two-spin systems in varying orientations with respect to the direction of the oscillating magnetic field, finally the so-called stick spectrum is broadened by a gaussian derivative with a constant linewidth. The best fit of the theoretical and the experimental spectra as shown in figure 2 was obtained for values of $D = 132 \pm 1\cdot5$ gauss and a linewidth $\Delta H = 37\cdot5$ gauss (peak to peak). It appears that simulations of this type are thus necessary to obtain accurate values for the dipolar parameters in these randomized cases. The computer simulation also provides a check on the assumption of 'axial' symmetry $(E = 0)$. Spectra could be simulated with various values for E. The maximum value of E, which could be tolerated to still

give agreement with the experimental spectrum was $E = \pm 6$ gauss. The slight mismatch on the high field side of the spectrum may be due to a slightly anisotropic g value. The linewidth is appropriate for a hyperfine broadening by the nitrogen and the protons of the radicals.
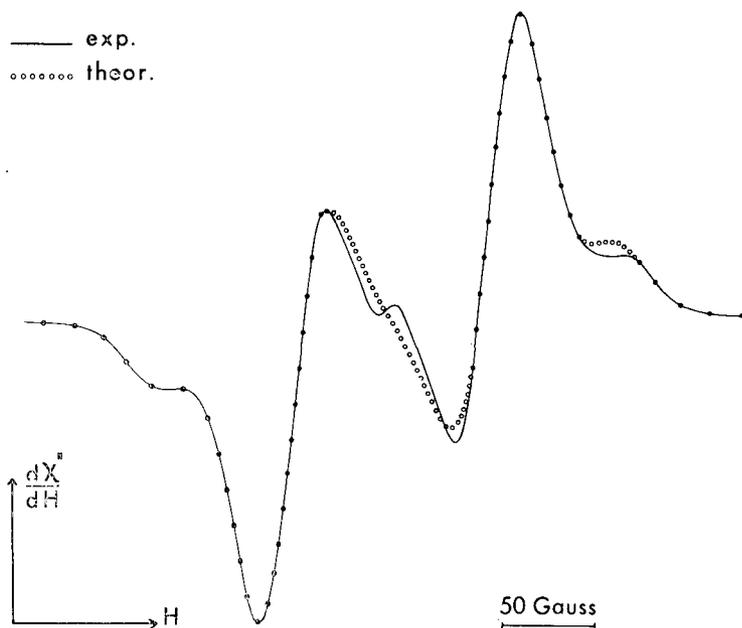

Figure 2. Comparison of experimental and computer simulated E.S.R. spectra of randomly oriented D.P.A. dimers.

In agreement with the assignment of the spectra to the TPH radical dimer are the following observations. Heating of irradiated samples to about 90°K completely destroyed the dimer spectrum, its place at first being taken by a spectrum typical for a solid solution of one or more radicals. Subsequent heating to about 120°K yields a three-line spectrum, with hyperfine splittings of 9·5 gauss. At room temperature, this spectrum develops into that typical of the diphenyl-nitroxide radical. Apparently upon heating, the dimers dissociate partially into isolated diphenylamino radicals, which react with oxygen to give the nitroxide radical. It should be noted that in this process the green colour of the radical dimer disappears.

Dipolar split spectra of this general nature can also be obtained by irradiating a powder of TPH at low temperatures. Figure 3 gives such a spectrum. Now, there are two splittings $D = 125$ and $D = 240$ gauss, respectively, and a considerable amount of free radical signal at $g = 2$. The relative intensities of these dipolar spectra vary with the particle size of the powder. Fine powders yield high intensity 'inner' spectra, large mesh powders yield high intensity 'outer' spectra. It appears logical to assume that the 'inner' spectrum, arising from the dimers with the largest intermolecular separation, derives from pairs of molecules situated at the surface of the crystal. In single crystals we found similar but more complex dipolar spectra. The analysis of these spectra will be continued after the crystal structure of T.P.H. has been solved.
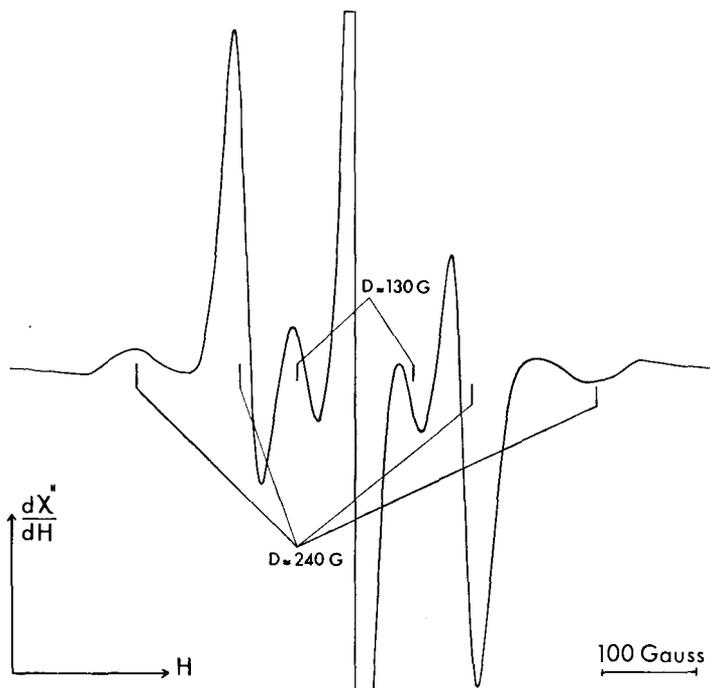
Figure 3. E.S.R. spectrum of u.v. irradiated tetra-phenyl-hydrazine powder at 77°K.

3. THE ELECTRONIC ABSORPTION SPECTRA

Figure 4 gives the visible and u.v. absorption spectra of T.P.H. and photo dissociated T.P.H. at liquid nitrogen temperature, the latter being coincident with the appearance of an E.S.R. spectrum as shown in figure 1. The most remarkable absorptions are those at 3200 and 7700 Å. Previous workers [3] assigned these to excitations of isolated radicals to low lying singlet states, arising through configurational interaction as pointed out by Longuet-Higgins and Pople [12]. However, since the D.P.A.-radical is not an odd alternating hydrocarbon radical, but contains a nitrogen nucleus, the above interpretation appears to be incorrect. Since there is no qualitative way to explain this absorption spectrum we were forced to make some calculations. From the E.S.R. measurements it is known that the absorption spectrum results from a radical-dimer, but it is unknown how much interaction these radicals have. Therefore we will first try to explain the absorption spectrum as arising solely from the monomer D.P.A.-radical.

An SCMO and an SCMO–CI calculation† were performed for the D.P.A. radical, in the P.P.P.-approximation scheme [13], assuming sp hybridization at the nitrogen nucleus. The approximations used in this computation were the following:

(1) The *repulsion integrals* $\langle pq \,|\, G \,|\, pq \rangle$ were evaluated by using Parr's uniformly charged sphere method [13].

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† We are indebted to Mr. W. Th. A. M. van der Lugt of the Theoretical Chemistry Department of the University of Leyden for performing the C–I part of the calculation.
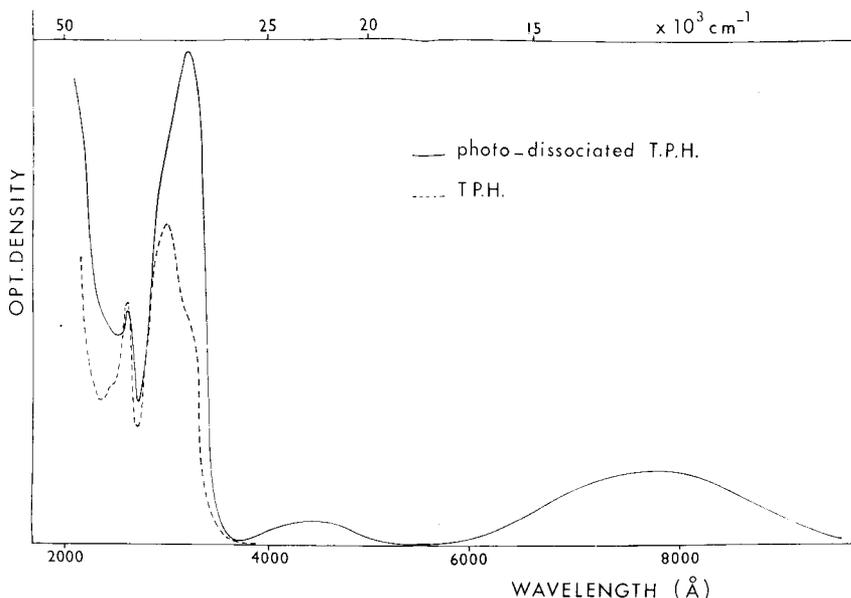
Figure 4.   Electronic absorption spectra of T.P.H. and u.v. irradiated T.P.H. at 77°K.

(2) The *ionization potential* $I_c{}^{\pi}$ was taken from tables in Landölt–Bernstein [14], while $I_N{}^{\pi}$ was varied over a region near the experimental value.   The actual values used were $I_N{}^{\pi} = 12 \cdot 11$ ev and $I_c{}^{\pi} = 11 \cdot 16$ ev.

(3) The *resonance integrals* H_{pq} for neighbouring ring carbon atoms have been given the convential value $-2 \cdot 40$ ev and H_{cN} has been varied so as to give best results.   The ' best ' value found was $-2 \cdot 76$ ev, which is consistent with our assumption that the C–N bond is shorter than the C–C bond in the D.P.A. radical. With these parameters the results given in table 1 emerge.   As is obvious from these results the 7700 Å absorption cannot, under any choice of parameters, be assigned to the D.P.A. radical.   However, if we identify the absorptions at $2 \cdot 85$, $3 \cdot 90$ and $4 \cdot 75$ ev with the theoretical values of $2 \cdot 67$, $4 \cdot 11$ and $4 \cdot 13$, $4 \cdot 47$ ev, respectively, reasonable agreement is obtained for the excitation energies as well as for the oscillator strengths.   This assignment would agree very well with the results of Franzen [9], who found a temperature dependent absorption near 4600 Å on heating a solution of T.P.H. in anisole.   This absorption would be due to partial dissociation of T.P.H. into the diphenyl aminoradical.

SCMO	SCMO–CI	Experiment
		$1 \cdot 6 \ (0 \cdot 16)$
$3 \cdot 01 \ (0 \cdot 91, y)$	$2 \cdot 67 \ (0 \cdot 17, y)$	$2 \cdot 85 \ (0 \cdot 05)$
$3 \cdot 65 \ (0 \cdot 12, x)$	$4 \cdot 11 \ (0 \cdot 87, y)$ ⎫	$3 \cdot 90 \ (1 \cdot 00)$
$4 \cdot 20 \ (0 \cdot 88, y)$	$4 \cdot 13 \ (0 \cdot 13, x)$ ⎭	
$4 \cdot 70 \ (0 \cdot 19, x)$	$4 \cdot 47 \ (0 \cdot 32, y)$	$4 \cdot 75(?) \ (0 \cdot 08)$

Table 1.   Excitation energies (ev), oscillator strengths and polarizations
of the D.P.A. radical.

Thus, it appears reasonable to assign the absorption near 7700 Å to an electronic transition of the radical dimer. The dominant interaction in this dimer will be a charge transfer interaction between the configurations D.P.A.$^{+}$/D.P.A.$^{-}$ and D.P.A.$^{-}$/D.P.A.$^{+}$ and the ground state. The half-filled orbitals of the monomer radicals will readily accommodate an extra electron, and therefore these configurations will be fairly close in energy to the ground state, thus giving a sizeable charge transfer interaction. This qualitative conclusion can be supported by a slightly modified SCMO calculation. For such a calculation it is necessary to assume a configuration of the radical dimer. In the T.P.H. molecule a configuration of minimal repulsion, with the planes each containing the two nitrogens and the axes of the phenyl rings at right angles to each other might be favoured, particularly at low temperatures. Then, the photo-dissociation probably proceeds as depicted in figure 5. Thus, for the radical dimer a D_{2d} configuration was chosen, which is also consistent with the E.S.R. result of $E \approx 0$ gauss.
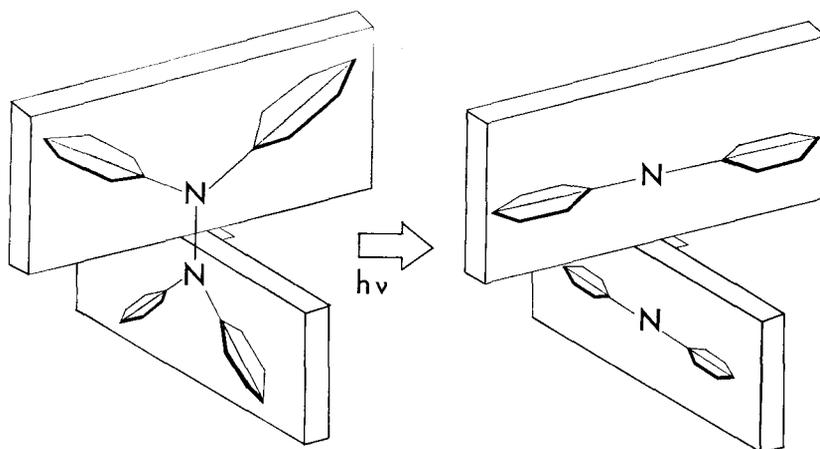

Figure 5. Configurations of T.P.H. and the D.P.A. radical dimer.

To perform the SCMO calculation two 13×13 Hückel matrices were joined into a 26×26 matrix. To admit some interaction between the two systems some resonance should be admitted between the two cores. The resonance integrals were calculated from $\beta = \beta_0 \exp(-kr)$, where $\beta_0 = -2517$ ev for C, $\beta_0 = -2337$ ev for N, while $k = 5 \cdot 007$ Å^{-1} in both cases [20].

Since atoms of different cores cannot be called neighbours this procedure would be inconsistent with the normal P.P.P. scheme. Therefore, resonance was also admitted between non-neighbouring atoms in the respective cores, using the same exponential expression.

Through this resonance and the electron repulsion, the two cores now 'feel' each other, which leads to a transition moment along the line connecting the two ions, which can be interpreted as a 'charge-transfer' transition of the radical dimer [15]. The results of this calculation for a distance of 4 Å between the two radicals are shown in table 2.

The more outstanding result of this calculation is the appearance of an extra absorption at $1 \cdot 44$ ev, which, through its polarization can be characterized as a charge-transfer absorption. It agrees very well with the broad absorption found at $1 \cdot 60$ ev in the radical dimer containing glass. It is not surprising that the

SCMO	Experiment
1·44 (0·61, *z*)	1·61 (0·16)
3·19 (1·08, *x*, *y*)	2·85 (0·05)
4·17 (1·00, *x*, *y*)	3·90 (1·00)
4·38 (0·09, *x*, *y*)	4·75(?) (0·08)

Table 2. Excitation-energies (ev), oscillator strengths and polarizations
of the D.P.A. radical-dimer.

SCMO calculation yields this charge-transfer band since it is formally equivalent to a first-order configuration interaction [16] and thus includes the ground state interactions with the configurations D.P.A.$^+$/D.P.A.$^-$ and D.P.A.$^-$/D.P.A.$^+$ as required for charge transfer. This interaction does not appear to strongly affect the positions of the monomer D.P.A. absorptions, in agreement with experiment. So far, only singlet states have been considered. Of course, our magnetic measurements must derive from a triplet state. In our calculations, doubly excited configurations and therefore correlation energies are not taken into account. The energy separations between the singlet and triplet manifolds depend on the exchange and the correlation energy. Because of the large separation between the two cores the exchange energy is very small, and therefore correlation effects will largely determine the singlet-triplet separation, which is therefore very unreliable from this calculation. This should not be so for the spin density distribution in the lowest triplet state, particularly since each spin will be situated on its own core.
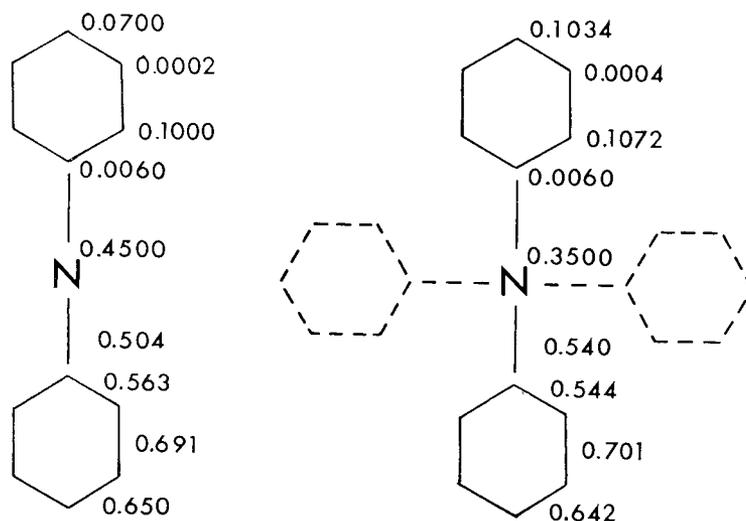

Figure 6. Comparison of the bond orders and spin densities of the D.P.A. monomer with those of the D.P.A. dimer (including electron–electron repulsion).

Figure 6 compares the spin density distribution and the bond orders of the dimer in the lowest triplet state with those of the monomer. The mutual polarization of the cores, due to the electron repulsion, is clearly evident.

With the aid of the following equations:

$$D = \tfrac{3}{4}g^2\beta^2 \sum_{p \neq q} \frac{r_{pq}^2 - 3z_{pq}^2}{r_{pq}^5} [C_{pi}^2 C_{qk}^2 - C_{pi}C_{pk}C_{qi}C_{qk}],$$

$$E = \tfrac{3}{4}g^2\beta^2 \sum_{p \neq q} \frac{y_{pq}^2 - x_{pq}^2}{r_{pq}^5} [C_{pi}^2 C_{qk}^2 - C_{pi}C_{pk}C_{qi}C_{qk}],$$

where r_{pq} is the distance between atom p and q and C_{pi}, C_{qk}, etc. are the coefficients of the atoms found in the orbitals with one unpaired electron of the dimer, we calculate with the coefficients of the thirteenth and fourteenth orbital of the dimer for a distance of 4 Å between the radicals $D = 138$ gauss very close to the experimental value of $D = 132 \cdot 5$ gauss found in a solid solution at low temperatures. As required by symmetry $E = 0$. When, however, the distance is calculated assuming the two D.P.A. radicals approaching each other with unchanged electronic distribution, a distance of $4 \cdot 8$ Å is found. Finally the distance between the two radicals can also be found using the formula $D = \tfrac{3}{2}g\beta h r^{-3}$. Then, to match D the average distance between the unpaired electrons must be $5 \cdot 9$ Å. Therefore, this formula, as used by van Willigen and Weissman [17] gives only a very rough indication of the distance between the radicals. Table 3 collects these results. When we compare the values of the distances between the rings derived from D via the dimer and monomer calculation, it can be concluded that through re-arrangement of the electronic distribution the radicals approach each other more closely than would be expected on a simple two monomer calculation.
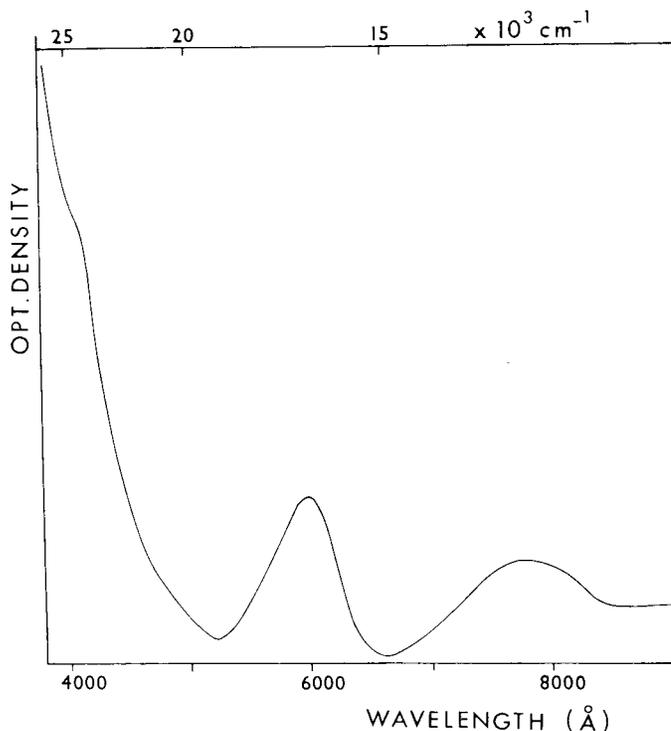

Figure 7.   The electronic absorption spectrum of u.v. irradiated crystalline
T.P.H. at 77°K.

Method	Distance in Å
Dimer calculations	4·0
Monomer calculations	4·8
$D = \frac{3}{2}g\beta h r^{-3}$	5·9

Table 3.   Distance between the radicals for a dipolar interaction of
$D = 132 \cdot 5$ gauss.

As was pointed out in the previous section, in a powder two dipolar splittings are observed.   Figure 7 gives the electronic spectrum of an array of single crystals of irradiated T.P.H.   Now two charge transfer absorptions appear, in agreement with what one would expect for two different radical pairs.   We are presently engaged in determining polarization directions and the correlation of these electronic spectra with single crystal E.S.R. results.
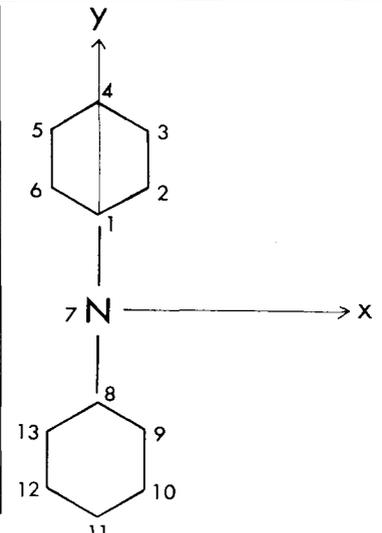
Atom	Spin densities	Proton or nitrogen hyperfine coupling constants in gauss	
1	6×10^{-3}	—	
2	10^{-1}	2·7	
3	2×10^{-4}	5×10^{-3}	
4	7×10^{-2}	1.9	
7	$4 \cdot 5 \times 10^{-1}$	9.0	

Table 4.   Spin densities and hyperfine coupling constants for the D.P.A. radical from SCMO calculations.

Finally table 4 gives the spin densities and the hyperfine coupling constants in the D.P.A. radical monomer resulting from the SCMO calculation.   The relations of McConnell [18] $a_H = Q_H \cdot \rho_H$ and from Henning and de Waard [19]

$$a_N = Q_1^N \rho_N + Q_2^N \sum_i \rho_i$$

were used to connect spin densities with the hyperfine coupling constants; the values $Q_H = 27$ gauss, $Q_1^N = 20$ gauss and $Q_2^N = 7 \cdot 5$ gauss were used.   The hyperfine coupling constants for the D.P.A. radical monomer are not known but the nitrogen splitting of 9 gauss is in good agreement with the value of $8 \cdot 74$ gauss obtained for the closely related di-paratoluyl-amino radical [8].

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