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^{14}N Hyperfine Structure of Triphenylaminium Radical Ions

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Unrestricted Hartree-Fock SCF LCAO MO calculations in the Pariser-Parr-Pople formalism with single annihilation were carried out on a series of *p*-substituted triphenylaminium cation radicals. The esr spectra were determined experimentally and spin densities calculated by use of the McConnell equation for the *o* and *m* hydrogens. Values of $Q^{\mathrm{N}}_{\mathrm{NN}}$ and $Q^{\mathrm{N}}_{\mathrm{CC}}$ were obtained by comparison of the "experimental" spin densities with those computed from the MO calculations. The results of several slightly different prescriptions for the spin density were compared. The degree of "twist" of the benzene rings out of the plane was also investigated.

UHF-SCF-LCAO-MO-Rechnungen wurden im Rahmen des Formalismus von Pariser-Parr-Pople für eine Reihe von *p*-substituierten Triphenylaminiumkation-Radikalen durchgeführt. Aus den gemessenen ESR-Spektren einerseits und den nach McConnell berechneten Spindichten andererseits ergeben sich jeweils die Größen $Q^{\mathrm{N}}_{\mathrm{NN}}$ und $Q^{\mathrm{N}}_{\mathrm{CC}}$, die dann miteinander verglichen werden können. Auf diese Weise lassen sich Aussagen über den Winkel, um den die Phenylringe aus der Molekülebene herausgedreht sind, gewinnen.

Des calculs en méthode de Hartree-Fock sans restrictions de spin dans le formalisme de Pariser-Parr-Pople, avec simple annihilation, ont été effectués sur une série de radicaux cations triphényl-aminium para-substitués. Les spectres r.p.e. ont été déterminés expérimentalement et les densités de spin ont été calculées pour les hydrogènes *o* et *m* utilisant l'équation de Mac Connell. Les valeurs de $Q^{\mathrm{N}}_{\mathrm{NN}}$ et $Q^{\mathrm{N}}_{\mathrm{CC}}$ ont été obtenues par comparaison entre les densités de spin «expérimentales» et celles calculées à partir des orbitales moléculaires. Les résultats de plusieurs hypothèses pour la densité de spin ont été comparé. Le degré de «torsion» des noyaux benzéniques en dehors du plan a été également étudié.

Introduction

The isotropic hyperfine splittings in the esr spectra of organic aromatic radicals have been studied frequently with an eye to comparing the data with the spin density distributions which give rise to the hyperfine splitting. Such studies have helped considerably in our understanding the mechanism behind such fine structures in esr spectra.

We report here a study on several *p*-substituted triphenylaminium cation radicals. The experimental esr spectra were obtained and unrestricted Hartree-Fock SCF LCAO MO calculations in Pariser-Parr-Pople formalism with single annihilation were carried out. The spin densities resulting from the calculations were compared with the "experimental" spin densities obtained by using the McConnell equation for A^{H} ($Q^{\mathrm{H}}_{\mathrm{CH}} = -24.0$ gauss) for ortho (*o*) and meta (*m*) hydrogens. Values of the "polarization parameters," $Q^{\mathrm{N}}_{\mathrm{NN}}$ and $Q^{\mathrm{N}}_{\mathrm{CC}}$, in the equations [1, 2]

$$A^{\mathrm{N}} = Q^{\mathrm{N}}_{\mathrm{NN}} \varrho^{\Pi}_{\mathrm{N}}$$

and

$$A^{\mathrm{N}} = Q^{\mathrm{N}}_{\mathrm{NN}} \varrho^{\Pi}_{\mathrm{N}} + Q^{\mathrm{N}}_{\mathrm{CC}} \Sigma\, \varrho^{\Pi}_{\mathrm{C}}$$

were also computed. These parameters have not been previously reported for a trivalent nitrogen bonded to three aromatic carbon atoms.[1]

Results

The esr hyperfine splitting constants and the maxima of the optical absorption spectra for triphenylaminium (TPA^+), tri-*p*-tolylaminium ($TPTA^+$), tris(*p*-chlorophenyl)aminium ($TPCPA^+$), tris(*p*-anisyl)aminium ($TPAA^+$) and tris(*p*-nitrophenyl)aminium ($TPNPA^+$) cations are given in Tables 1 and 2, respectively. The experimental spin densities at ortho and meta positions (Positions 2 and 3, see Fig. 1) are collected in Table 3. These were obtained by dividing A^H (ortho) and A^H (meta) by -24.0 gauss. (Fraenkel [2] generally used -23.7 while McLachlan [3] used -24.2 gauss for Q^H_{CH} in the simple McConnell equation.) "Experimental" spin densities obtained by dividing A^H by -27.0, a value proposed by McConnell [4], are also included.

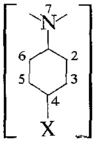

Fig. 1

In Table 4 are shown the spin densities calculated by the unrestricted Hartree-Fock SCF LCAO MO method in the Pariser-Parr-Pople formulation. The three sets of values are ϱ_{BA} (before annihilation), ϱ_A (in the Amos [5] formalism) and ϱ_{AS} (as calculated by the Amos and Snyder [6] prescription). The integrals were taken from the literature [7] or computed as recommended. In the case of $TPTA^+$, the core integrals at positions 1 and 4 (cf. Fig. 1) were varied slightly using the penetration integrals as a guide to bring the spin densities at the ortho and meta positions as close as possible to the experimental values (A^H/Q^H_{CH}, $Q^H_{CH} = -24.0$).

Calculations were also carried out for the cation $TPTA^+$ with the phenyl rings twisted 30° out of the plane, by varying β_{CN} (see Appendix) and using the Coulomb integrals for a twisted model. The calculated spin densities for the twisted model of the cation were found to be in slightly better agreement with the experimental values and these are the values collected in Table 4. The calculations for TPA^+, $TPCPA^+$, and $TPAA^+$ were carried out on the same pattern. The chlorine and oxygen core integrals and β_{C-Cl}, β_{C-O}, along with the core integrals at atom Position 4, were varied in such a way as to bring the calculated spin densities at the ortho and meta positions as close as possible to the experimental values.

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[1] In addition, it is interesting to see if such physical properties follow a Linear Free Energy Transfer equation (Hammett's σ constants). One such study was reported by Walter [10] who attempted to relate the electronic absorption spectra, the esr spectra and the Hammett constants for a series of stable *p*-substituted triphenylaminium cation radicals and diphenylpicrylhydrazyl free radicals. He concluded that the cation radicals displayed a "non-Hammett" type behavior. (However, see Tables 1 and 2 for the case of tris(*p*-nitrophenyl)aminium cation.)

Table 1. *Hyperfine Splitting Constants*

	Atom Position				
	7	2	3	4	Reference
TPA^+	9.8±0.5[a]	—	—	—	Present work
	10.16	2.28	1.22	3.32	Van Willigan [8]
TPA in conc H_2SO_4	Not paramagnetic				Present work
$TPTA^+$	9.45[b]	2.06	1.03	3.89[c]	Present work and Adams [9]
	9.5±0.2	—	—	—	Walter [10]
$TPCPA^+$	9.6±0.5[d]				Present work
	9.62	2.64	1.08	—	Present work
	9.52	1.12	0.56	[e]	Adams[e]
	9.0±0.2	—	—	—	Walter [10]
$TPAA^+$	8.97	1.22	0.61	0.61	Adams [9]
	8.90±0.2	—	—	—	Walter [10]
$TPNPA^+$	10.75±0.50[f]	—	—	—	Present work

[a] From the partially resolved (triplet) esr spectrum. Our A^N is in satisfactory agreement with that reported by Van Willigan [8].

[b] Precision better than 1% for A^N and up to 6% for A^H.

[c] From methyl protons.

[d] A triplet in concentrated H_2SO_4.

[e] R. N. Adams (private communication) reported splitting due to the chlorine nucleus as well.

[f] A triplet in concentrated H_2SO_4. This cation was noted reported by earlier workers.

Table 2. *Optical Absorption Spectra*

	Solvent	λ_{max}(mμ)	Reference
TPA^+	MeCN	640	Adams [9]
	DME	648	Present work
	EPA glass	655	Lewis and Lipkin [11]
	TPA in benzene on silica alumina	660	Dollish and Hall [12]
	H_2SO_4	685[a]	Present work
$TPTA^+$	MeCN	672	Present work
	MeCN	668	Walter [10]
	DME	675	Present work
	H_2SO_4	672	Present work
$TPCPA^+$	MeCN	690	Present work
	MeCN	685	Walter [10]
	H_2SO_4	690	Present work
$TPNPA^+$	H_2SO_4	525[b]	Present work
$TPAA^+$	MeCN	715	Walter [10]

[a] The species is most probably tetraphenylbenzidine dication produced by dimerization of the TPA^+ or reaction of TPA^+ with parent molecule and subsequent oxidation.

[b] The species should be the cation of TPNPA since TPTA and TPCPA in H_2SO_4 produce $TPTA^+$ and $TPCPA^+$, respectively. The substituents at parapositions inhibit the dimerization or coupling, the cause of unstableness of TPA^+.

Table 3. "*Experimental*" π *Electron Densities*

	Atom Position		
	o	*m*	*p*
TPTA$^+$	±0.0858	±0.0429	—
	±0.0762	±0.0382	—
TPCPA$^+$	±0.1100 (±0.0462) [9]	±0.0450 (±0.0231) [9]	—
	±0.0977 (±0.0415) [9]	±0.0400 (±0.0207) [9]	—
TPAA$^+$	— (±0.0508) [9]	— (±0.0254) [9]	—
	— (±0.0452) [9]	— (±0.0226) [9]	—
TPA$^+$	— (±0.0950) [8]	— (±0.0508) [8]	(±0.1380) [8]
	— (±0.0845) [8]	— (±0.0452) [8]	(±0.1230) [8]

For each cation, the upper entry corresponds to a value of $Q^{\mathrm{H}}_{\mathrm{CH}} = -24.0$, the lower one to $Q^{\mathrm{H}}_{\mathrm{CH}} = -27.0$ gauss. Values from the literature are given in parentheses where available.

Table 4. *Spin Densities Assuming 30° Twist*

		Atom Position					
		1	2	3	4	7	20
TPTA$^+$	ϱ_{A}	0.0071	0.0865	−0.0391	0.1100	0.3650	–
	ϱ_{AS}	0.0281	0.0689	−0.0207	0.0913	0.3544	–
	ϱ_{BA}	−0.0139	0.1041	−0.0575	0.1287	0.3756	–
TPA$^+$	ϱ_{A}	0.0098	0.0843	−0.0348	0.1034	0.3635	–
	ϱ_{AS}	0.0302	0.0687	−0.0164	0.0808	0.3531	–
	ϱ_{BA}	−0.0106	0.0999	−0.0532	0.1260	0.3739	–
TPCPA$^+$	ϱ_{A}	−0.0060	0.1046	−0.0435	0.0895	0.3606	0.0075
	ϱ_{AS}	0.0167	0.0854	−0.0235	0.0700	0.3493	0.0062
	ϱ_{BA}	−0.0287	0.1238	−0.0636	0.1090	0.3719	0.0088
(TPCPA$^+$)[a]	ϱ_{A}	−0.0061	0.0466	−0.0233	0.0519	0.2244	0.1662
	ϱ_{AS}	0.0157	0.0381	−0.0050	0.0444	0.2078	0.1381
	ϱ_{BA}	−0.0279	0.0551	−0.0415	0.0594	0.2410	0.1943
TPAA$^+$	ϱ_{A}	0.0561	0.0505	−0.0226	0.0576	0.3468	0.0477
	ϱ_{AS}	0.0674	0.0437	−0.0100	0.0465	0.3391	0.0380
	ϱ_{BA}	0.0448	0.0573	−0.0352	0.0687	0.3545	0.0574

[a] Spin densities calculated on the basis of "experimental" spin densities at *o* and *m* positions from the assignments by Adams et al. *(op. cit.)* for this cation.

Discussion

In the simplest model of hyperfine splitting for ^{14}N as discussed by Carrington and Dos Santos Veiga [1], the nuclei are assumed to interact with the electron spin density localized on the nuclei in question. This treatment leads to the relationship

$$A^{\mathrm{N}} = Q^{\mathrm{N}}_{\mathrm{NN}} \varrho^{\Pi}_{\mathrm{N}} . \tag{A}$$

Fraenkel and Karplus [2] and Henning [2] proposed that the spin densities on neighboring nuclei also contribute to the nitrogen hyperfine splitting and therefore extended the above mentioned simple McConnell type equation for A^{N}. In the present case this takes the form

$$A^{\mathrm{N}} = Q^{\mathrm{N}}_{\mathrm{NN}} \varrho^{\Pi}_{\mathrm{N}} + 3 Q^{\mathrm{N}}_{\mathrm{CC}} \varrho^{\Pi}_{\mathrm{C}} . \tag{B}$$

In order to permit comparison of the results of Eqs. A and B above describing the nitrogen hyperfine splitting of the triarylaminium cation radicals, the spin density calculations were combined with the assumed values of $Q_{\mathrm{CH}}^{\mathrm{H}}$ in the simple McConnell equation of A^{H}. Such a one-term equation for A^{H} has been widely used, since it is probably a good approximation to the correct expression, whatever it be. (However, see Amos and Snyder [6], also McDowell [13].) The value -24.0 for $Q_{\mathrm{CH}}^{\mathrm{H}}$ was adopted since we are dealing with cations which require larger (absolute) values of $Q_{\mathrm{CH}}^{\mathrm{H}}$ [14]. The Colpa and Bolton equation [15] as well as that of Giacometti, Nordio and Pavan [16] are attempts to deal with this observation. There is a possibility that $Q_{\mathrm{CH}}^{\mathrm{H}}$ should be even more negative. Therefore, the value -27.0 as proposed by McConnell [4] was also considered. The effect on the values of $Q_{\mathrm{NN}}^{\mathrm{N}}$ of Eqs. A and B, described above, of the variation of $Q_{\mathrm{CH}}^{\mathrm{H}}$ from -24.0 to -27.0 gauss was investigated as well. A^{N}, the nitrogen hyperfine splitting constant, was found to be dependent upon $\varrho_{\mathrm{N}}^{\Pi}$, the spin density on nitrogen. The latter, however, was not very sensitive to the slight variations in the spin densities at ortho and meta positions produced by varying $Q_{\mathrm{CH}}^{\mathrm{H}}$ from -24.0 to -27.0.

In investigating the co-planarity of the phenyl rings around the central nitrogen atom, β_{CN}[2] for the twisted model ($\sim 30°$) was also used and it was found that the spin densities calculated for the twisted model were in better agreement with the "experimental" spin densities when $Q_{\mathrm{CH}}^{\mathrm{H}}$ is given the value -24.0 gauss[3] than when it is given the value -27.0. Similarly, calculations were carried out on TPA^{+} where $U_{44} = 0.000$. The result of the calculations are in good agreement with the value of A^{H} reported for this cation by Van Willigan [8]. (Here $Q_{\mathrm{CH}}^{\mathrm{H}}$ was taken to be about -27.0.) ϱ_{SA}, the spin density in Snyder and Amos [6] prescriptions is too low, particularly in the meta position.[4] Likewise, ϱ_{BA} before annihilation is much too high showing too much contamination from higher spin multiplets. The calculations were performed in the same way on TPCPA^{+} and TPAA^{+}. In these cases, the core integrals at Positions 4 and 20, as well as β_{4-20} ($\beta_{\mathrm{C-Cl}}$, $\beta_{\mathrm{C-O}}$), were varied to bring the calculated spin densities close to the "experimental" ones. In these cases, it is no longer meaningful to vary β_{CN} in order to investigate the co-planarity of the phenyl rings and hence no conclusion may be drawn in this regard.

Using the one-term Equation (Eq. A), the experimental A^{N} and the calculated spin densities ϱ_{A} (from Table 4), a value of 26.30 gauss with a standard deviation of 0.51 gauss was obtained. Since Van Willigan [8] showed that the sign of A^{N} is positive and since the spin density at nitrogen center in the amine cations is positive, the sign of $Q_{\mathrm{NN}}^{\mathrm{N}}$ should be positive in accordance with the sign of $Q_{\mathrm{NN}}^{\mathrm{N}}$ reported by other workers in different systems containing nitrogen [2, 17].

The $Q_{\mathrm{NN}}^{\mathrm{N}}$ obtained by using more than one term (Eq. B) and ϱ_{A} is 26.03 with a rather large standard deviation ± 1.48 gauss. In calculating $Q_{\mathrm{NN}}^{\mathrm{N}}$, A^{N} for TPNPA^{+} was not included because of the lack of information regarding the experimental spin densities and the large number of molecular parameters involved. The values

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[2] The Coulomb integrals appropriate for the twisted model were used.

[3] The planar model required a lower $Q_{\mathrm{CH}}^{\mathrm{H}}$ value.

[4] Harriman [26] points out that in the Snyder and Amos prescription spin densities are overcompensated when the annihilation is performed.

of A^{N} and A^{H} for TPCPA$^+$ as reported by Adams were not used; a value of 9.80 was used for TPA$^+$. It was not found possible to arrive at a single value for $Q^{\mathrm{N}}_{\mathrm{CC}}$ because the spin densities at the neighboring carbon are vanishingly small and because $Q^{\mathrm{N}}_{\mathrm{CC}}$ is apparently very sensitive to the small variation in $\varrho^{\Pi}_{\mathrm{C}}$, an observation supported by Fraenkel's work [17, 18]. The vanishingly small densities on the carbon atom adjacent to the central nitrogen atom made the more-than-one-term equation effectively a one-term equation, which explains the closeness of $Q^{\mathrm{N}}_{\mathrm{NN}}$ values obtained using either equation.

The values of $Q^{\mathrm{N}}_{\mathrm{NN}}$ obtained in the present study may be compared with those reported in the literature for other systems. Barton and Fraenkel [17] used the equation of Karplus and Fraenkel [2] for A^{N} to evaluate the polarization parameters in dihydropyrazine cations. For this system one has

$$Q^{\mathrm{N}}_{\mathrm{NN}} = S^{\mathrm{N}} + 2Q^{\mathrm{N}}_{\mathrm{NC}} + Q^{\mathrm{N}}_{\mathrm{NH}}$$

and the values obtained for $Q^{\mathrm{N}}_{\mathrm{NN}}$ were 28.45 and 23.43, depending upon using the values of -23.7 and -27.2 gauss, respectively, for $Q^{\mathrm{H}}_{\mathrm{CH}}$ in the simple McConnell equation for evaluating experimental spin densities (from A^{H}). If it is assumed that $Q^{\mathrm{N}}_{\mathrm{NH}} \simeq Q^{\mathrm{N}}_{\mathrm{NC}}$, as mentioned by Barton and Fraenkel, $Q^{\mathrm{N}}_{\mathrm{NN}}$ for a system like TPA$^+$ should be close to that of dihydropyrazine system and indeed it is. Considering, however, the empiricism involved in the evaluation of the parameters obtained in the present study and the one obtained by Barton and Fraenkel, the agreement in the values of $Q^{\mathrm{N}}_{\mathrm{NN}}$ should not be overemphasized.

Bolton, Carrington and Dos Santos Veiga [19] also studied dihydropyrazine cations. With the help of HMO calculations and using one-term equations, they found $Q^{\mathrm{N}}_{\mathrm{NN}}$ to be 35–39 gauss. The values obtained by Barton and Fraenkel should be more accurate, since the only error could arise due to the use of the simple McConnell equation for A^{N}. The spin densities at other atoms were obtained by spin normalization condition.

$Q^{\mathrm{N}}_{\mathrm{NN}}$ values for the anions are different from those of cations. Henning [2] reported a value of 19.1 (± 1.7) gauss for $Q^{\mathrm{N}}_{\mathrm{NN}}$ for heterocyclic anions. If the values for S^{N} and $Q^{\mathrm{N}}_{\mathrm{NC}}$ are taken to be 11.3 and 9.8 [20], the value for $Q^{\mathrm{N}}_{\mathrm{NN}}$ in TPA$^+$ system is $\sim$40 gauss, which is much larger than the values reported here.

Experimental

Triphenylamine was obtained from Fisher Scientific Company. It was recrystallized from anhydrous ether and then from absolute ethanol and further purified by vacuum sublimation. Tri-*p*-tolylamine, tris(*p*-chlorophenyl)amine and tris(*p*-nitrophenyl)amine were synthesized by the method of Walter [22] and purified as recommended. Acetonitrile (MeCN), obtained from Fisher Scientific Company, was dried over calcium hydride and distilled twice from phosphorous penta oxide. The middle fraction was collected over calcium hydride from which the final distillation was made in vacuum (closed system). Tetraethylammonium perchlorate, from the Eastman Organic Chemical Company, was crystallized from hot water and dried in vacuum. Dimethoxyethane (DME), obtained from Fisher Scientific Company, was dried over lithium aluminum hydride and distilled from it in vacuum. Silver perchlorate (anhydrous) was obtained from G. Frederick Smith Chemical Company. It was dried at 150° C in vacuum. Never more than a gram of silver perchlorate, at a time, was handled. Resublimed iodine (Allied Chemical Company) was resublimed in vacuum.

TPTA$^+$ and TPCPA$^+$ were generated by oxidizing the amines with a mixture of $AgClO_4$ and iodine [21, 22] in DME under high vacuum conditions. TPA was also oxidized by silver perchlorate and iodine, but a special technique was required to handle TPA$^+$ which is unstable in DME. TPNPA$^+$ was generated in dissolving the amine in concentrated H_2SO_4 (saturated with nitrogen). This solution was subsequently degassed by freezing, pumping and thawing. TPTA$^+$ and TPCPA$^+$ were also prepared in concentrated H_2SO_4 in a similar manner. TPA dissolved in concentrated H_2SO_4 gave a blue solution which was not paramagnetic.

Unsuccessful attempts were made to generate TPA$^+$ electrochemically *(in vacuo)*. (TPTA$^+$ and TPCPA$^+$ were generated electrochemically, but since these species were obtained chemically not much emphasis was given to the electrochemical method.)

All the esr spectra were recorded on Japan Electron Optics Laboratory Company's esr spectrometer model JES-3BX.[5] The magnetic field was calibrated with an NMR marker and the first derivative of the spectra recorded. Optical absorption spectra were recorded on Perkin-Elmer spectrophotometer model 202. The accuracy was checked by running samples on Cary spectrophotometer model 14.

Appendix

In the unrestricted Hartree-Fock LCAO MO SCF method, the secular equation to be diagonalized is [23, 24] (for α and β spins)

$$F^A \vec{C}_i^A = \vec{C}_i^A E_i \,, \tag{1}$$

where $A = \alpha, \beta$ for the two spins and $\vec{C}_i^A$ are the LCAO coefficients. F^α, in the Pople-Pariser-Parr formalism is given as

$$F^\alpha_{\mu\mu} = U_{\mu\mu} + P^\beta_{\mu\mu}\gamma_{\mu\mu} + \sum_{\varrho \neq \mu} (P^\alpha_{\varrho\varrho} + P^\beta_{\varrho\varrho} - Z_\varrho)\gamma_{\mu\varrho} \,, \tag{2}$$

$$F^\alpha_{\mu\nu} = \beta - P^\alpha_{\mu\nu}\gamma_{\mu\nu} \,. \tag{3}$$

$\beta = 0$ for non-bonded atoms. γ_{ij} is the coulomb integral.

$$P^A_{\mu\nu} = \sum_i^P q_i \vec{C}^A_{\mu i} \vec{C}^A_{\nu i} \,, \qquad A = \alpha, \beta \,. \tag{4}$$

The unpaired spin density matrix is defined as

$$\varrho = Q^\alpha - Q^\beta \tag{5}$$

and bond charge matrix

$$Q = Q^\alpha + Q^\beta \tag{6}$$

where on orthogonal basis (i.e., $S_{\mu\nu} = \delta_{\mu\nu}$)

$$\mathbf{P}^\alpha = \mathbf{Q}^\alpha \,. \tag{7}$$

$\mathbf{P}^\alpha$ is defined in (4). The spin density in (5) is defined as $\varrho_{B \cdot A}$, i.e., spin density before annihilation, so called because the wave function is contaminated with higher spin multiplets which are not "annihilated" yet. Amos [24] proposed, on the basis of certain assumptions, that the following formula for spin density (ϱ_A) is generally sufficient in removing most of the contamination of spins.

$$\varrho_A = \mathbf{R}^\alpha - \mathbf{R}^\beta \,, \tag{8}$$

where

$$\mathbf{R} = \mathbf{P} - (\mathbf{P}^\alpha \mathbf{P}^\beta \mathbf{P}^\alpha - \tfrac{1}{2}\mathbf{P}^\alpha \mathbf{P}^\beta - \tfrac{1}{2}\mathbf{P}^\beta \mathbf{P}^\alpha)/X \,, \tag{9}$$

where

$$X = (S+1)(S+2) - (p-q)^2/4 - (p+q)/2 + \mathrm{Tr}(\mathbf{P}^\alpha \mathbf{P}^\beta) \,, \tag{10}$$

where

$$P = \mathrm{Tr} Q^A \,, \quad q = \mathrm{Tr} Q \quad \text{and} \quad S = (p-q)/2 \,. \tag{11}$$

Amos and Snyder [7] derived an expression for the spin density not incorporating any assumptions taken into account in the Amos derivation. The spin density can be equally obtained (for large molecules) as [7]

$$\varrho_{AS} = 2\varrho_A - \varrho_{BA} \,, \tag{12}$$

where ϱ_{AS} is the spin density in the Snyder-Amos prescription.

The integrals used in the calculations are given in Table 5. The Coulomb integrals for distances less than 2.80 Å were evaluated by quadratic expression [12]; for greater than 2.80 Å a charged sphere model was employed[6]. The core integrals given in the table are those corresponding to spin densities reported in Tables 3 and 4. In actual calculations, some of these integrals were varied to some extent.

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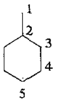
[5] The author wishes to acknowledge his indebtedness to the Japan Electron Optics Laboratory Company (Medford, Mass.) for making their esr spectrometer (model JES-3BX) available for recording the esr spectra of the samples.

[6] Z, the effective charges, are 3.25 for carbon, 3.85 for nitrogen, 4.48 for oxygen and 6.10 for chlorine. All C–C, C–O and C–N distances were taken to be 1.395 ± 0.005 Å; the C–Cl distance was taken to be 1.700 Å (for chlorobenzene). The ions are taken be planar or twisted to about 30°.

Table 5a. *Coulomb Integrals* [7]

Integral	Distance (in Å)	Value
$(11/11)_{\mathrm{CC}}$	0.00	10.53
$(11/22)_{\mathrm{CC}}$	1.39	7.30
	2.41	5.46
	2.78	4.90
$(11/11)_{\mathrm{NN}}$	0.00	12.27
$(11/22)_{\mathrm{NC}}$	1.39	7.60
	2.41	5.60
$(11/11)_{\mathrm{ClCl}}$		9.87
$(11/22)_{\mathrm{CCl}}$		6.69
$(11/33)_{\mathrm{CCl}}$		5.13
$(11/44)_{\mathrm{CCl}}$		3.95
$(11/55)_{\mathrm{CCl}}$		3.17
$(11/11)_{\mathrm{OO}}$		11.86
$(11/22)_{\mathrm{CO}}$		7.54
$(11/33)_{\mathrm{CO}}$		5.53
$(11/44)_{\mathrm{CO}}$		3.80
$(11/55)_{\mathrm{CO}}$		3.37

Integrals for distances greater than 2.80 Å are calculated by charged sphere model.

Table 5b. *Core Integrals (in eV)*

U_{77}	$= -14.340$	
U_{11}	$= -\ 0.600$	
U_{22}, U_{33}	$= \ 0.000$	
U_{44}	$= \ 0.000$	for TPA^{+}
	$= -\ 0.4000$	for TPTA^{+}
	$= -\ 1.720$	for TPAA^{+}
	$= -\ 3.650$	for TPCPA^{+}
$U_{20,20}$[a]	$= -13.460$	for TPAA^{+}
	$= -19.05$	for TPCPA^{+}
$\beta^{\circ}_{\mathrm{CN}}$ (β°_{17})	$= -\ 2.576$	
β_{CN} (β_{17})	$= -\ 2.26$	$\theta = 30°$
β_{CC} (β_{12})etc.	$= -\ 2.39$	for all
$\beta_{9,20}$[a]	$= -\ 3.00$	for TPAA^{+}
$\beta_{\mathrm{C-Cl}}$	$= -\ 2.39$	for TPCPA^{+}

[a] Position 20 is Cl in TPCPA^{+}, O in TPAA^{+}.

The computations were carried out on an IBM 7094 using the computer program originally written by Gladney [25] for hydrocarbons and modified for the present study. β_{CN} was varied as

$$\beta_{\mathrm{CN}} = \beta^{\circ}_{\mathrm{CN}} \cos\theta \qquad (\beta^{\circ}_{\mathrm{CN}} = -2.576\ \mathrm{eV}), \tag{13}$$

when the co-planarity of phenyl ring was investigated. It was found that -2.26 instead of -2.576 eV gave slightly better agreement with the experimental spin density (if $Q^{\mathrm{H}}_{\mathrm{CH}}$ is taken to be -24.0 gauss).

In the case of TPTA^{+}, an inductive model for the CH$_3$ group at atom position 4 (para position) was assumed and the effect was incorporated in the core integral U_{44} with the help of penetration integrals. By varying U_{44} and U_{11}, it was found that the calculated spin densities were only slightly sensitive to the variations in these core integrals.

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