ENDOR Studies on Low-Symmetry Triphenylmethyl with *ortho*- or *para*-Methoxy Substituents

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ENDOR observations were carried out for several triphenylmethyl derivatives with *ortho*- or *para*-methoxy substituents. The alteration of the spin-density distribution caused by steric hindrance, in particular, due to the low symmetrical substitution, was investigated. Using a revised MO parameter proposed by Kulkarni, McLachlan MO calculations were carried out and the twisting angles of the hindered phenyl groups are estimated.

Triphenylmethyl is one of the typical neutral radicals on which a number of ESR studies have been made. In the case of methoxy derivatives, however, the observed ESR hyperfine structures are often complicated by overlapping due to the small methoxy proton splitting, and, sometimes, by modulation of hindered rotation of the substituents.

To the authors' knowledge, the derivatives which have already been studied are chiefly those of higher molecular symmetry such as 4,4′,4″-trimethoxytriphenylmethyl[1] and 2,2′,2″,6,6′,6″-hexamethoxytriphenylmethyl.[2] In the present work, ENDOR studies of several methoxy derivatives of triphenylmethyl with low-symmetrical substitution, as shown in Fig. 1, are reported.

Perturbation of the spin density due to steric hindrance was measured in detail, and the conformation of the hindered phenyls was investigated in terms of McLachlan MO calculations including a correction for the Coulomb integral of the central methyl carbon due to Kulkarni.

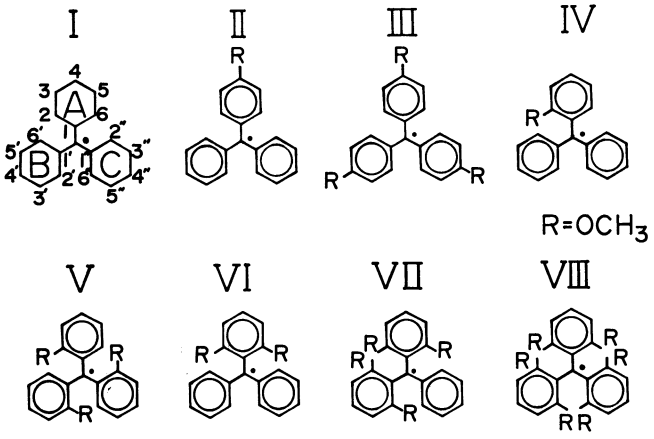

Fig. 1.

Experimental

Triphenylmethanols I, II, III, IV, and V, were synthesized by the Gomberg method,[3] and VI, VII, and VIII were prepared by reactions of 2,6-dimethoxyphenyllithium with benzophenone, ethyl benzoate and ethyl carbonate, respectively. The crude materials produced were purified by recrystallization in a hexane–benzene mixture; [I] mp 165 °C, [II] mp 61 °C, Found: C, 83.21; H, 6.34%. Calcd: C, 82.73; H, 6.25%. [III] Mp 85 °C, Found: C, 75.48; H, 6.31%. Calcd: C, 75.41; H, 6.33%. [IV] Mp 132 °C. Found: C, 83.92; H, 6.19%. Calcd: C, 82.73; H, 6.25%. [V] Mp 188 °C, Found: C, 75.64; H, 6.33%. Calcd: C, 75.41; H, 6.33%. [VI] Mp 137 °C, Found: C, 78.75; H, 6.11%. Calcd: C, 78.73; H, 6.29%. [VII] Mp 107 °C, Found: C, 72.53; H, 6.35%. Calcd: C, 72.61, H, 6.36%. [VIII] Mp 166 °C, Found: C, 67.91; H, 6.44%. Calcd: C, 68.17, H, 6.41%. Radicals VII and VIII were prepared by reduction of the corresponding carbonium ions, which are easily produced by dissolving the alcohols in 10% aqueous sulfuric acid.[2] Radicals I, II, III, IV, V, and VI were obtained by the Gomberg procedure applied to the corresponding chlorides, which were synthesized by treating the alcohols with thionyl chloride in dichloromethane.[4] ENDOR measurements were carried out in a toluene solution of the free radicals according to the procedure described previously.[5]

Results and Discussion

ENDOR Spectrum and the Hyperfine Splittings. A typical example of the ENDOR spectrum observed for 2-methoxytriphenylmethyl [IV] is shown in Fig. 2. Eight sets of the ENDOR signals seen in the figure (a—h) can be assigned with reference to the ENDOR spectrum of the parent triphenylmethyl as follows: signals (d), (g), and (h) are ascribed to the meta-, ortho- and para-ring protons of non-substituted phenyls (B, C) and (a), (b, c), (e), and (f) to the methoxyl protons and the meta-, ortho- and para-ring protons

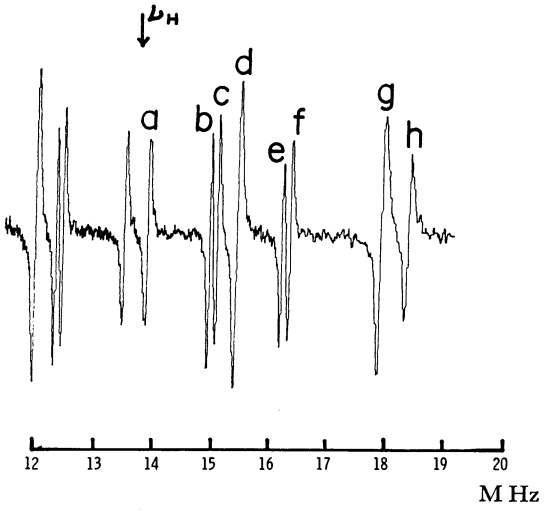

Fig. 2. ENDOR spectrum of 2-methoxytriphenmethyl [IV] recorded at −70 °C.

Table 1. Proton hyperfine coupling constants for triphenylmethyl (in G)

	A					B					C					$-OCH_3$
	2	3	4	5	6	2'	3'	4'	5'	6'	2''	3''	4''	5''	6''	
I	2.56	1.16	2.81			2.56	1.16	2.81			2.56	1.16	2.81			
II	2.59	1.03				2.59	1.14	2.86			2.59	1.14	2.86			0.34
III	2.57	1.03				2.57	1.03				2.57	1.03				0.33
IV		0.89	1.83	0.98	1.74	2.93	1.22	3.26			2.93	1.22	3.26			0.13
V		1.01	2.57	1.13	2.57		1.01	2.57	1.13	2.57		1.01	2.57	1.13	2.57	0.18
VI		0.66	0.84			3.22	1.27	3.58			3.22	1.27	3.58			0.08
VII		0.91	1.17				0.91	1.17			4.09	1.51	4.67			0.11
VIII		1.07	2.35				1.07	2.35				1.07	2.35			0.16

of the substituted phenyl (A), respectively. The larger splitting of either (b) or (c) is assigned to position 5, since the methoxyl substitution causes a small reduction in the spin density at position next to the carbon atom, to which the methoxyl group is bonded. The coupling constants for the ring and the methoxyl protons under the same assumptions are summarized in Table 1, where splittings' assignments, in particular, those for the hindered triphenylmethyls IV and VIII are based on the prediction of the McLachlan MO calculation.

MO Calculation and the Steric Hindrance. In the HMO or McLachlan calculations for triphenylmethyls previously described, the value of the Coulomb integral for the central methyl carbon atom was taken to be equal to that of the aromatic ring carbon atom. This leads to equal spin densities at the ortho- and para-positions, which is contrary to experimental observations.

An improved choice of the parameter was proposed by Kulkarni, who employed the less electronegative value, $\alpha_{Me}=\alpha-1.2\beta$,[6] for the Coulomb integral of the methyl carbon atom. The resonance inhibition between the central methyl and the twisted phenyl $2p_\pi$ orbitals is represented by $\beta\cos\theta$ in which θ is the twisting angle.

In the present work, the inductive effect of the methoxyl group was ignored everywhere, and the hindrance of the phenyl group due to the ortho-substitution was taken into account. As an example, the dependence of the spin densities on the twisting angle (θ) calculated for VII suggested that the spin-density distribution on the substituted phenyls (A) and (B) decreases, but that on the non-substituted phenyl (C) increases, as the degree of steric hindrance in (A) and (B), θ, increases. The MO spin densities are in excellent agreement with the observed values obtained from the McConnel relation ($a^H=Q^H\rho^\pi$, $Q^H=-27$ G), under the assumption that each phenyl, A, B, and C, of VII is twisted outward by 65, 65, and 30°, respectively. The twisting angles of other hindered methyls shown in Table 2, give a satisfactory linear relation between the observed ring proton splitting and the MO spin densities calculated in the same manner, as is shown in Fig. 3. From the slope of the plot, the average value $|Q^H|$ was estimated to be 27.4 G, where the average value $|Q^{OCH_3}|$ is found to be 3.17 G, assuming $a^{OCH_3}=Q^{OCH_3}\cdot\rho^\pi_C$.

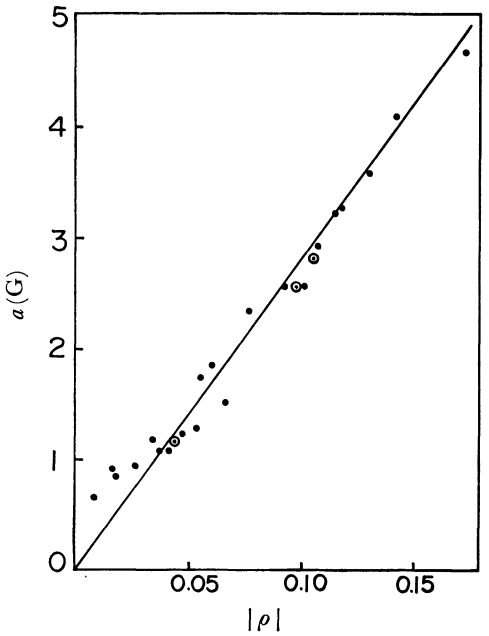

Fig. 3. Relation between the observed proton hyperfine coupling constants and the MO spin densities.
⊙ denotes the plots for mother triphenylmethyl.

Table 2. Twisting angles and MO π-bond orders for triphenylmethyl

	Twisting angle (θ)			Bond order		
	A	B	C	1-7	1'-7	1''-7
I	30°	30°	30°	0.333	0.333	0.333
IV	50°	30°	30°	0.249	0.338	0.338
V	35°	35°	35°	0.317	0.317	0.317
VI	70°	30°	30°	0.134	0.342	0.342
VII	65°	65°	30°	0.168	0.168	0.348
VIII	45°	45°	45°	0.278	0.278	0.278

Of interest is the fact that the twisting angle of the substituted phenyls of high symmetry [VIII] is much smaller than those seen for low symmetrical substitutions, such as VI and VII. This supports the hypothesis that an intramolecular odd-π-electron delocalization does affect the degree of steric hindrance in these molecules. In fact, the HMO bond order cited in Table 2 justifies the fact that the lowest value is predicted between the central methyl and the adjacent ring carbon of the substituted phenyl in derivative VI. On the other hand, the bond order for the non-substituted phenyl is increased by asymmetrical ortho-substitution. This means that the non-substituted phenyl of

derivatives VI and VII may have a more planar conformation compared with that of the parent triphenylmethyl in the true situation. Although the Kulkarni parameter predicts adequate spin densities, a rigorous explanation for the assumption of such a high electronegativity for the central methyl carbon still requires further investigation.[7,8] Other improved calculations for the triphenylmethyl were recently reported,[9,10] in which the resonance integral was chosen by taking into account the bond length of the triphenylmethyl perchlorate determined by X-ray analysis.[11] A tentative calculation for the present derivatives gave a qualitative explanation, but the agreement between the theoretical and experimental spin densities was not sufficient in comparison with the calculation of Kulkarni.

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