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SPIN DENSITY DISTRIBUTION IN FREE RADICALS-IX1)

THE ROLE OF RESONANCE IN TWISTED TRIARYLMETHYLRADICALS

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In a continuation of earlier work2), we now wish to report our results for the tris-(4-phenyl-3,5-di-tert.-butylphenyl)-methyl radical 1. We wanted to determine the effect of the strong mutual twisting of the phenyl rings in the biphenyl system upon the spin density distribution and the resonance stabilisation of the radical in comparison with the unsubstituted Schlenk radical 2. The radical 1 was synthesized according to the scheme (3→4→5→6→7→8→1)3). The addition of phenyllithium to the sterically hindered carbonyl group4) of 35) was achieved in high yield. The resulting quinol-hydrazone 4, when treated with zinc and hydrochloric acid in ethanol, is reduced and cleaved at the N-N bond to produce the crystalline, air-sensitive 5. Thus the 4-phenyl-3,5-di-tert.-butylphenyl system is available via 5 and 6 for further synthetic applications.

A benzene solution of 1 exhibits a reddish-yellow colour and the radical itself is stable for months when kept in the dark, in the absence of oxygen.

The low-field half of its EPR-spectrum is shown in Fig. 1.

The spectrum shows 7 groups of lines (a=0.25mT, see Table), which arise through coupling of the electron with the protons of the inner phenyl rings (H-2). Furthermore, each group consists of at least 11 lines with a coupling constant of 0.01 mT. However, since 1 cannot have 10 equivalent protons (≙ 11 lines),

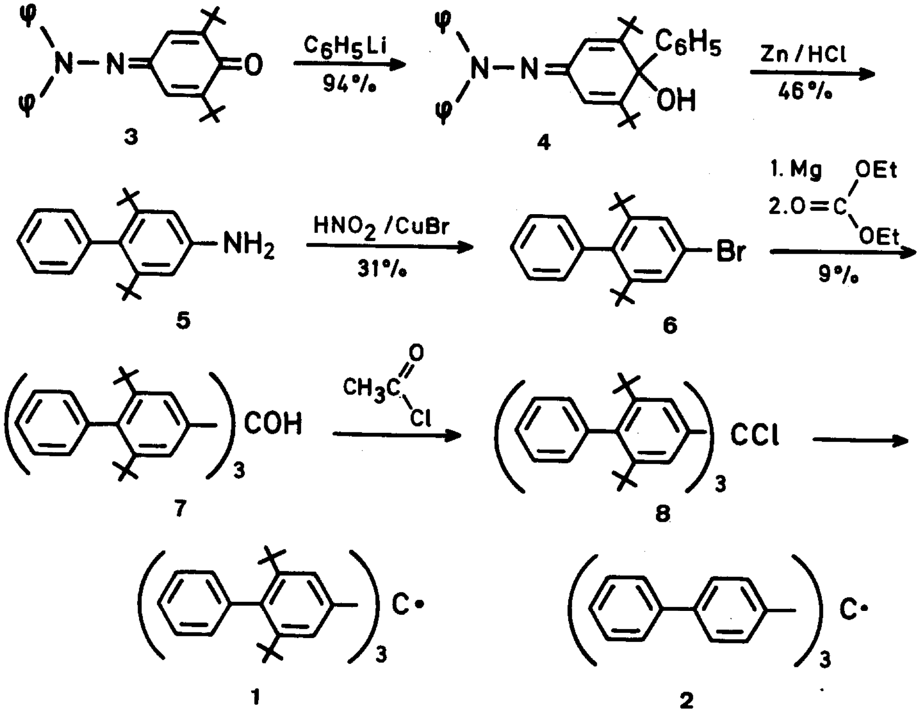
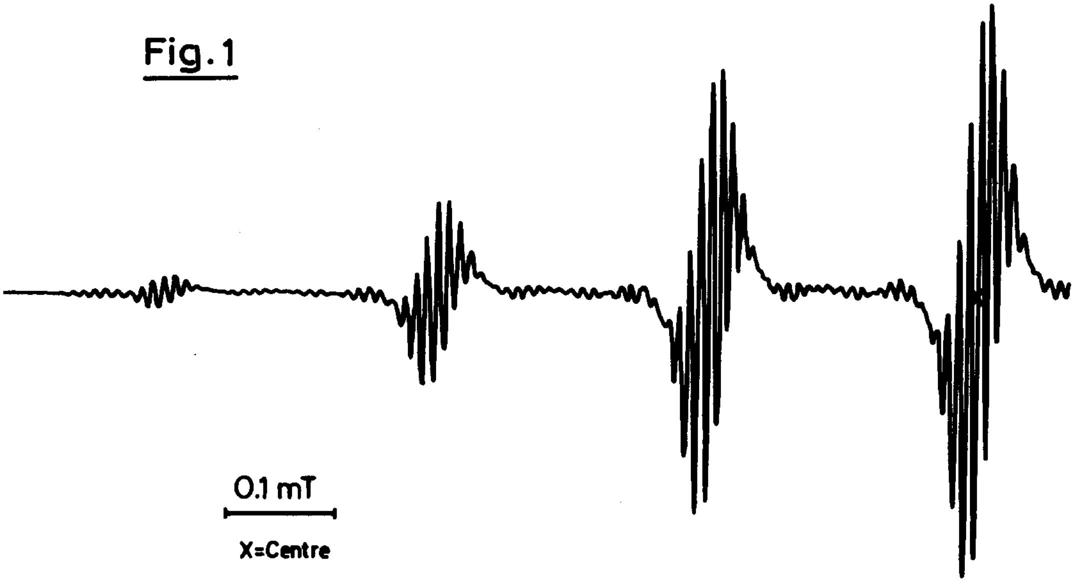
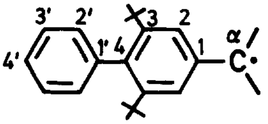
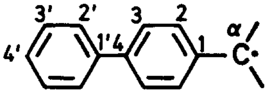
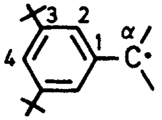

φ
φ
N—N=
=O
3
C_6H_5Li
94%
4
C_6H_5
OH
Zn / HCl
46%
NH_2
5
HNO_2 / CuBr
31%
Br
6
1. Mg
2. O=C(OEt)OEt
9%
COH
7
$CH_3C(=O)Cl$
CCl
8
C·
1
C·
2

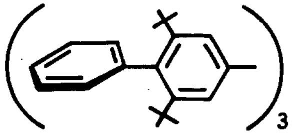
Fig. 1


0.1 mT
X=Centre

it has to be concluded that the splitting arises from 12 equivalent protons (≙ 13 lines). The protons of the outer rings, H-2' and H-3', are the only ones which could be responsible and would therefore have to show the same coupling parameters within the linewidth. Due to their low intensity, the two outer lines of each group are not visible above the noise and the ^{13}C-hyperfine structure. The coupling constant of the proton H-4' is very small and a computer simulation indicated that the best agreement with the experimental value is obtained when a = 0.0020 - 0.0025 mT. The coupling constants of the protons H-2, H-2' and H-3' were confirmed using ENDOR6). The value for H-4' could not be deduced from the ENDOR-spectrum but it was shown that no proton coupling in the range 0.25 mT to 0.01 mT is exhibited by radical 1.

		a^H [mT]						a_α^C [mT]
		2	3	4	2'	3'	4'	
	1	0,25	–	–	0,01	0,01	0,0025	2,29
	2	0,2499	0,1136	–	0,0438	0,0174	0,0438	–
	9	0,255	–	0,277	–	–	–	2,347

Although the complete assignment of the ^{13}C-coupling constants has not yet been achieved, the value of 2.29 mT for the methyl carbon C-α was obtained directly from the spectrum. This value corresponds well with the tris-(3,5-di-tert.-butylphenyl)-methyl radical 9, which was obtained by both Berndt et al.7) and us3) but via somewhat different pathways. The H-2 coupling constant decreases only slightly in going from 9 to 1 and the a-values for the protons H-2', H-3' and H-4' are very small as compared with 2 8). Furthermore, 1 has a reddish-yellow colour whereas 2 is violet. Thus, one can conclude that the phenyl rings in 1 show an angle of torsion of approximately 90°. Molecular models indicate that the twisting of the phenyl rings in the radical 1 should be somewhat greater than the torsion of the phenyl ring relative to the trigonal plane of the methyl-carbon atom in the benzyl radical 10[9]. The tert.-butyl groups in 1 lie more or less above the twisted ring whereas in 10 they



1

10

point away from it. The radical 1 is characterized by the values $a_{H-2'} \sim a_{H-3'} \simeq 4 \cdot a_{H-4'}$ whereas normally $a_{H-ortho} \sim a_{H-para} \sim (2\text{-}3) \cdot a_{H-meta}$ is found for the phenyl ring of a benzyl system (the outer ring of 1 plus C-4 can be considered as being a benzyl type radical[10]). This descrepancy can be explained by assuming hyperconjugative interaction between the p-orbital of C-4 and the C-1'/C-2' bond resulting in the spin density being transfered partially to H-2' and H-3'. This explanation is in good agreement with Berndt's hypothesis[7] and Pople's calculations[11].

Thus, radical 1 shows no significant additional stabilisation due to π-π conjugation relative to 9. The effect of this upon its dissociation and a comparison with the dissociation of the Schlenk radical 2[2] will be the subject of a further paper.

References

1) Part VIII: S. Hauff, P. Krauß and A. Rieker, Chem.Ber. 105, 1446 (1972).
2) H. Kessler, A. Moosmayer and A. Rieker, Tetrahedron 25, 287 (1969).
3) M. Stein, Diplomarbeit, Universität Tübingen 1974.
4) A. Rieker and G. Henes, Tetrahedron Letters, 3775 (1968).
5) A. Mannschreck and B. Kolb, Chem.Ber. 105, 696 (1972).
6) Dr. K. Scheffler kindly measured the spectra.
7) K. Schreiner, A. Berndt and F. Baer, Mol.Phys. 26, 929 (1973).
8) A.H. Maki, R.D. Allendoerfer, J.C. Darner and R.T. Keys, J.Amer.Chem.Soc. 90, 4225 (1968).
9) K. Schreiner and A. Berndt, Angew.Chem. 86, 131 (1974).
10) A. Rieker and K. Scheffler, Liebigs Ann. Chem. 689, 78 (1965).
11) J.A. Pople and D.L. Beveridge, J.Chem.Phys. 49, 4725 (1968).