Tetrahedron Letters No. 49, pp 4871 - 4874.
©Pergamon Press Ltd. 1978. Printed in Great Britain.

0040-4039/78/1201-4871$02.00/0

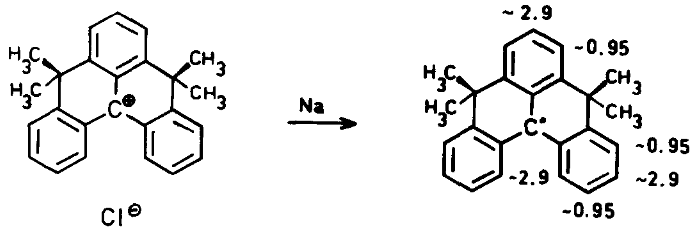
E.S.R. STUDY OF 12,12c-DIHYDRO-4,4,8,8,12,12-HEXAMETHYL-4H,8H-DIBENZO[cd,mn]PYREN-12c-yl, A PLANAR TRIPHENYLMETHYL

Franz A. Neugebauer*, Dieter Hellwinkel** and Gerhard Aulmich

Max-Planck-Institut für Medizinische Forschung, Abt. Organische Chemie,
Jahnstr. 29, D-6900 Heidelberg*, and

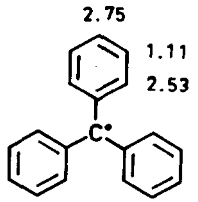
Institut für Organische Chemie der Universität Heidelberg,
Im Neuenheimer Feld 270, D-6900 Heidelberg, West Germany**

In connection with our study on triarylamine radical cations and derivatives [1], in which the aryl substituents have been connected by ortho isopropylidene bridges, we were particularly interested in the isoelectronic neutral C-centered species 4. As a reference system 4 can contribute to the understanding of the results in the triarylamine radical cation series.

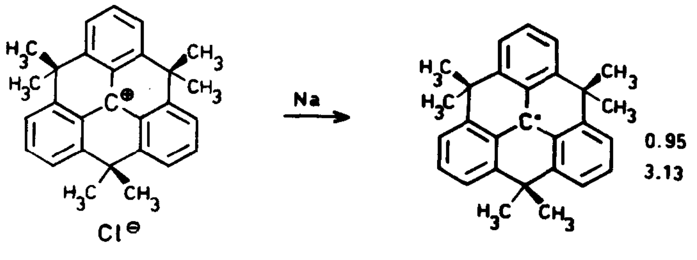


1

3[G]

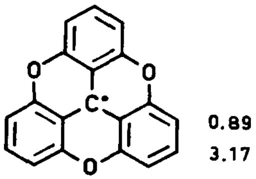


5[G] 3)



2

4[G]



6[G] 4)

Reduction of the carbenium chlorides 1 [2] and 2 [2] suspended in benzene with alkali metals (sodium or potassium mirror) in the absence of oxygen yielded the yellow brown radicals 3 and 4. According to the temperature behaviour of the e.s.r. spectra both radicals seem to be monomeric. The e.s.r. spectrum of 4 (Figure) is nicely resolved and can be easily analyzed in terms of two groups of 3 and 6 hydrogens with the coupling constants $a(H_{"para"})$ = 3.13 and $a(H_{"meta"})$ = 0.95 G. Concentrated solutions of 4 additionally yield a ^{13}C splitting of 18.23 G, which certainly represents the central methyl carbon of 4. The intensity ratio of the satellite to the main lines is 0.5:100 in agreement with one ^{13}C atom. The derivative 3 with only two isopropylidene bridges gave a moderately resolved e.s.r. spectrum, which may be analyzed in terms of two groups of 5 and 6 hydrogens equivalent within the linewidth of about 0.5 G. The assignment of the data is indicated in the formula. The g values of 3 (2.0025) and 4 (2.0025) have the expected magnitude.

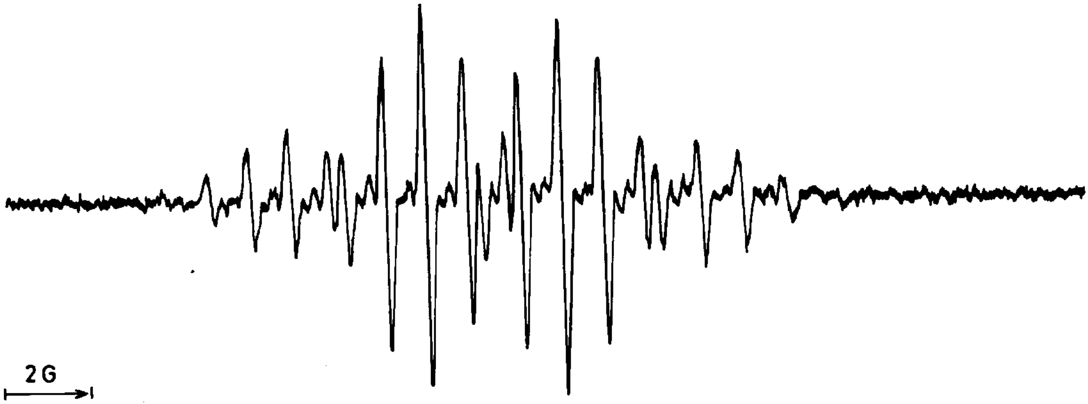
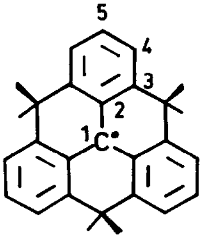


Figure. E.s.r. spectrum of 4 in benzene at room temperature

The propeller configuration of triphenylmethyl (5) is well established. The magnitude of the twist angle about the central C-aryl bond (~30°) depends somewhat on the experimental situation (gas phase 5), solid state 6), solution 7)). The larger "ortho" and "para" proton hfs constants of 3 with respect to the data of triphenylmethyl point out that the magnitudes of the twist angles in 3 are reduced to some extent (~20°). The framework molecular model of 3 shows a helically twisted structure with axial and equitorial methyl groups, the axial ones pointing to opposite directions. Unfortunately, we were not able to identify the central ^{13}C splitting (natural abundance), which would have given a more accurate estimate of the twist angle. In the completely bridged triphenylmethyl derivative 4 a twisted structure is no more possible, but still one has to consider two structures, a planar and a bowl shaped one. A planar geometry would lead to a better delocalization of the unpaired electron, thus one expects a larger "para" hydrogen and a smaller central ^{13}C splitting as compared to the data of triphenylmethyl. On the other hand a bowl shaped structure should give a considerably larger central ^{13}C splitting due to the deviation from trigonal planarity at the central carbon ($\dot{C}H_3$, a(^{13}C) = 38.34 G $^{9)}$; $\dot{C}F_3$, a(^{13}C) = 271.6 G $^{10)}$). The e.s.r. results of 4 clearly indicate a planar structure within the e.s.r. time scale.

In the literature there are quite a number of more or less elaborate calculations of the spin density distribution in triphenylmethyl $^{19)}$. Looking for the trends in the series 5, 3, and 4 McLachlan spin densities $^{13,14)}$ for a twisted triphenylmethyl (~30°) and the planar triphenylmethyl are compared with the experimental results in the tables. The calculated coupling constants of the planar triphenylmethyl are in good agreement with the experimental data of 4, particularly the central ^{13}C splitting. It is known that

	a(i)exp.[G]	a(H)calc.[G]$^{a,11,12)}$	a(^{13}C)calc.[G]$^{b,12)}$	$\rho_C$calc.$^{c)}$
1	18.23 (^{13}C)		17.8	0.419
2			-9.2	-0.048
3			5.2	0.109
4	0.95 (H)	-1.05	-4.0	-0.039
5	3.15 (H)	2.75	4.8	0.102

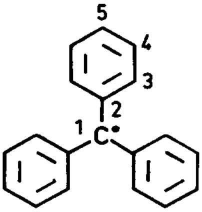


a) Q^{H}_{C-H} = -27 [G]

b) a(^{13}C) = 38.6 ρ_C - 11.6 $\rho_{C'}$, [G]

c) McLachlan spin density calculation of planar triphenylmethyl: λ = 1.2; $\beta_{C-1,C-2}$ = β_{CC} $^{14)}$.

	a(H)exp.[G]$^{3)}$	a(^{13}C)exp.[G]$^{d,8)}$	$\rho_C$exp.$^{8)}$	$\rho_C$calc.$^{e)}$
1		23.5$^{f)}$	0.525	0.520
2		11.3	0.078	-0.049
3	2.53	6.5	0.095	0.096
4	1.11	3.2	0.029	-0.036
5	2.75	4.1	0.104	0.089



d) Data from tris(3,5-di-tert-butylphenyl)methyl.

e) McLachlan spin density calculation: λ = 1.2; $\beta_{C-1,C-2}$ = 0.87 β_{CC} $^{14)}$.

f) Perdeuteriotriphenylmethyl: a($^{13}C_1$) = 23.86 G $^{15)}$; the corresponding value of triphenylmethyl seems to be 23.0 ± 0.8 G $^{16)}$; there are, however, also other data: 26 $^{17)}$ - 20.1 G $^{18)}$.

McLachlan calculations do not predict the correct ordering of the ortho and para coupling constants. The planar 4 is closely related to the sesquixanthydryl radical 6 (4), which, however, exists as a dimer at room temperature. The monomeric state of 4 is obviously due to the spatial requirements of the isopropylidene bridges, which make it sterically impossible for 4 to dimerize.

Acknowledgement

We thank the Deutsche Forschungsgemeinschaft for the support of our work.

References

1) S. Bamberger, D. Hellwinkel, and F. A. Neugebauer, Chem. Ber. 108, 2416 (1975).
2) D. Hellwinkel and G. Aulmich, in preparation, G. Aulmich, Dissertation, Heidelberg 1978; for the corresponding hydrocarbons see: D. Hellwinkel, G. Aulmich, and M. Melan, Chem. Ber. 109, 2770 (1976); Tetrahedron Lett. 1976, 4137.
3) S. V. Kulkarni and C. Trapp. J. Am. Chem. Soc. 92, 4801 (1970).
4) E. Müller, A. Moosmayer, A. Rieker, and K. Scheffler, Tetrahedron Lett. 1967, 3877.
5) Electron diffraction of 5 in the gas phase yielded 40-50°; P. Andersen, Acta chem. Scand. 19, 629 (1965).
6) X-ray crystallographic analysis of tris(4-nitrophenyl)methyl gave 30° and 40°; P. Andersen and B. Klewe, Acta chem. Scand. 21, 2599 (1967).
7) ^{13}C e.s.r. results of tris(3,5-di-tert-butylphenyl)methyl agree with 24-26° 8).
8) K. Schreiner, A. Berndt, and F. Baer, Mol. Phys. 26, 929 (1973).
9) R. W. Fessenden, J. Phys. Chem. 71, 74 (1967).
10) R. W. Fessenden and R. H. Schuler, J. Chem. Phys. 43, 2704 (1965).
11) H. M. McConnell, J. Chem. Phys. 24, 632, 764 (1956).
12) E. T. Strom, G. R. Underwood, and D. Jurkowitz, Mol. Phys. 24, 901 (1972).
13) A. D. McLachlan, Mol. Phys. 3, 233 (1960).
14) A. H. Maki, R. D. Allendoerfer, J. C. Danner, and R. T. Keys, J. Am. Chem. Soc. 90, 4225 (1968).
15) H.-J. Fey, W. Lubitz, H. Zimmermann, M. Plato, K. Möbius, and R. Biehl, Z. Naturforsch. 33a, 514 (1978).
16) M. J. Sabacky, C. S. Johnson, Jr., R. G. Smith, H. S. Gutowsky, and J. C. Martin, J. Am. Chem. Soc. 89, 2054 (1967).
17) P. B. Ayscough, A. P. McCann, and R. Wilson, Proc. Chem. Soc. 1961, 16; S. I. Weissman and J. C. Sowden, J. Am. Chem. Soc. 75, 503 (1953); F. C. Adam and S. I. Weissman, ibid. 80, 2057 (1958).
18) B. Mohos, F. Tudos, and L. Jokay, Acta Chim. Acad. Sci. Hung. 55, 73 (1968).
19) For literature see 8) and Landolt-Börnstein, New Series II/9b, Magnetic properties of Free Radicals, A. Berndt, page 718; Springer Verlag Berlin-Heidelberg-New York 1977.

(Received in Germany 18 September 1978)