

ON THE ESR IDENTIFICATION OF DIPHENYLMETHYL AND 9-FLUORENYL

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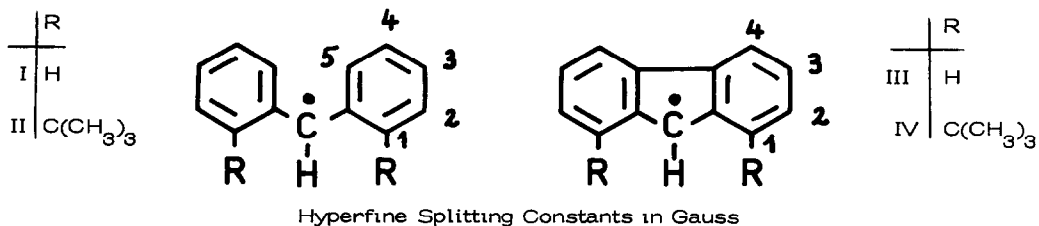
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In connection with our studies of diarylamine and carbazole radical cations we became interested in the isoelectronic neutral free radicals diphenylmethyl and 9-fluorenyl. The literature offers a broad spectrum of esr data concerning such radicals.

The esr study of γ irradiated diphenylmethane crystals yielded an isotropic α -hydrogen splitting constant of 11.9 G for diphenylmethyl ¹⁾. Diphenylmethyl (I) was also generated via thermolysis of different phosphazine and diazo precursors; esr measurements yielded the hfs coupling constants given in the table ^{2, 3)}. However, in comparing these data with the esr results of the o-substituted diphenylmethyl II ⁴⁾, considerable differences appear, which cannot be explained by a simple substitution effect or by differences in the geometrical structure of these radicals. Esr data of 9-fluorenyl obtained either by thermolysis of a diazo precursor ³⁾ or by thermal dissociation of the dimer, 9,9'-bifluorenyl ⁵⁾, again show remarkably small α -hydrogen splittings. A study of irradiated fluorene crystals recently reported by Kotsch ⁶⁾ yielded a very reasonable value for the α -hydrogen coupling constant in 9-fluorenyl, namely 12.9 G.

Considering these various esr data one has the suspicion that radicals of some other structure could be involved in some of the experimental observations. The radicals with the surprisingly small α -hydrogen coupling constants ^{2, 3, 5)} might have a diarylalkylmethyl



	H_a a	$^{13}C_a$ a	H_1 a	H_2 a	H_3 a	H_4 a	H_5 a	Lit.
I	11.9							1)
I ^{+))}	8.36	31.0	3.05	1.22	3.05	1.22	3.05	2, 3)
II	15.92		—	1.37	3.42	1.37	3.42	4)
III ^{+))}	7.0	27.5	3.75	0.49	1.89	0.49	—	3)
III ^{+))}	3.48		3.83	0.84	3.83	0.84	—	5)
III	12.9							6)
IV	13.46		—	0.80	3.90	0.60	—	This work

+) Structural assignment in question

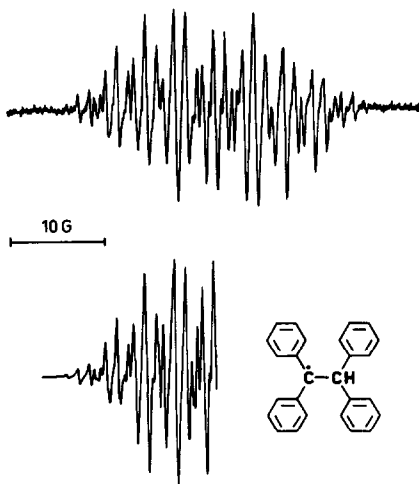


Fig. 1.: ESR spectrum of the 1,1,2,2-tetraphenylethyl radical in benzene at 40°C and its simulation (linewidth 0.35 G).

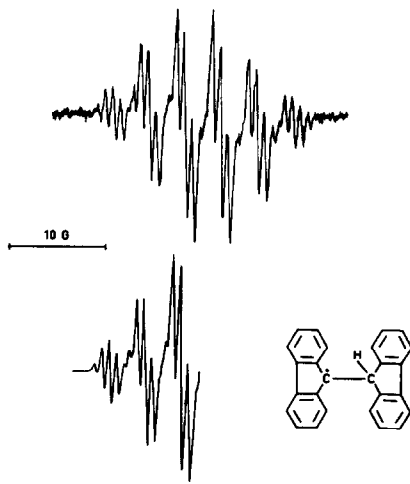


Fig. 2.: ESR spectrum of the 9,9'-bi-fluorenyl-9-yl radical in benzene at 60°C and its simulation (linewidth 0.30 G).

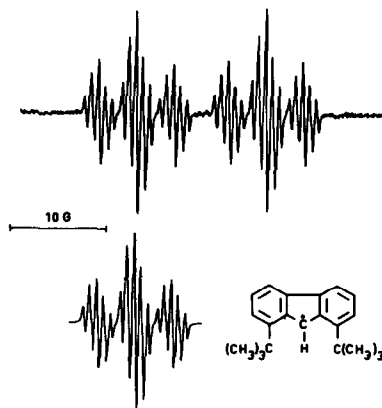


Fig. 3.: ESR spectrum of the 1,8-di-tert-butyl-9-fluorenyl radical (IV) in benzene at 20°C and its simulation (linewidth 0.20 G).

structure, and the single hydrogen splitting may be due to one β -proton. Which radicals of this structure can one expect in the chemical systems studied?

Diphenylmethyl radicals can dimerize to tetraphenylethane, and a subsequent hydrogen abstraction, e.g. by diphenylcarben, would yield the 1,1,2,2-tetraphenylethyl radical. We prepared this radical by reaction of 1-chloro-1,1,2,2-tetraphenylethane ⁷⁾ with sodium and observed the esr spectrum shown in Fig. 1. This spectrum, with the data $a^H = 8.45$ (1H), $a^H = 3.03$ (6H) and $a^H = 1.24$ G (4H), is identical with the esr spectrum obtained in the thermolysis of diphenylazomethane, which was erroneously assigned to diphenylmethyl ^{2, 3)}.

Fig. 2. shows the esr spectrum of the corresponding 9,9'-bifluorenyl-9-yl radical, which was likewise prepared by reaction of 9-bromo-9,9'-bifluorene with mercury. This esr spectrum, with the data $a^H = 3.68$ (1H), $a^H = 3.85$ (2H), $a^H = 3.50$ (2H) and $a^H = 0.76$ G (4H), was also previously observed and erroneously assigned to the 9-fluorenyl radical ⁵⁾.

As early as 1957 Theilacker et al. ⁹⁾ synthesized a 9-fluorenyl radical, namely 1,8-di-tert-butyl-9-fluorenyl (IV). The esr spectrum of IV (shown in Fig. 3.) yielded the coupling constants given in the table. The smaller α -hydrogen splitting with respect to the corresponding coupling constant in the o-substituted diphenylmethyl radical II agrees well with the in-

creased delocalization of the unpaired electron into the planar fluorenyl system and is almost identical with the value obtained by Kotsch⁶⁾ from γ irradiated fluorene crystals.

In addition to these studies we also tried to detect unsubstituted diphenylmethyl and 9-fluorenyl by esr and applied several methods and chemical reactions to the problem. However in no case could we obtain resolved esr spectra of these radicals. Certainly the isotropic esr data of diphenylmethyl and 9-fluorenyl will only deviate to a small extent from the observed data of II and IV; even so, the esr identification of the parent radicals remains a challenge.

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