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ESR study of spin-adducts of trimethylaminoboryl radicals with fullerene C_{60}

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It was established by ESR that trimethylaminoboryl radicals formed by UV irradiation of BH_3NMe_3 in the presence of di-*tert*-butyl peroxide in saturated benzene solutions of fullerene C_{60}, add to fullerenes to give $^{\cdot}C_{60}$—BH_2NMe_3 spin-adducts. The latter undergo dimerization with a rate constant of *ca.* $2.5 \cdot 10^6$ L mol^{-1} s^{-1}. A more prolonged photolysis of excess BH_3NMe_3 in a benzene solution of C_{60} results in multiple addition of the trimethylaminoboryl radicals to the fullerene to give stable radicals $^{\cdot}C_{60}[BH_2NMe_3]_n$.

Key words: fullerene, ESR, radical, photolysis, boryl.

Free radicals readily add to polyhedral carbon clusters known as fullerenes to give mono- and polyaddition adducts.[1–5] The structure and reactivity of fullerene spin-adducts depend on the chemical nature of the key atom of the attacking radical and on the structure of the radical. Fullerene monoadducts with alkyl or phosphonyl radicals[3,5] undergo reversible dimerization. Stable allyl and cyclopentadienyl radicals formed by the addition of each subsequent radical at the γ position relative to the previous radical have been detected by ESR[2] in the multiple addition of benzyl radicals to C_{60}. In the case of the multiple addition of phosphonyl radicals to C_{60}, the spin-adducts are stabilized due to steric shielding by the phosphonyl groups located farther from the radical center.[5] The structures of the fullerenyl radicals were deduced by analyzing the hyperfine structure that appears due to the interaction of an unpaired electron with the magnetic nucleus of the key atom of the radical added. Previously[4] we studied for the first time the addition of a boron-centered polyhedral radical, a derivative of metacarborane-12, to a fullerene. Therefore, it was interesting to continue to study spin-adducts of C_{60} fullerene with radicals centered at magnetic boron nuclei, and to study the structure and reactivity of spin-adducts of ligand-bonded boron-centered radicals $^{\cdot}BH_2NMe_3$ with C_{60}.

Results and Discussion

Boryl radicals were first obtained[6] by the Scheme 1.

Scheme 1

$$\mathrm{Bu^tO{-}OBu^t} \xrightarrow{h\nu} 2\,\dot{\mathrm{O}}\mathrm{Bu^t}$$

$$\mathrm{BH_3NMe_3} + \dot{\mathrm{O}}\mathrm{Bu^t} \longrightarrow \underset{\mathbf{1}}{\dot{\mathrm{B}}\mathrm{H_2NMe_3}} + \dot{\mathrm{H}}\mathrm{OBu^t}$$

Radical **1** is characterized by the interaction of an unpaired electron with boron, hydrogen, and nitrogen nuclei: $a_{^{11}B} = 51.3$ G, $a_{2H} = 9.6$ G, $a_N = 1.4$ G, as well as with protons of methyl groups: $a_H = 1.4$ G. Based on the analysis of the hyperfine splitting constants, a pyramidal structure was assigned to radical **1**. The ESR spectra of spin-adducts of the $^{\cdot}BH_2NMe_3$ radical with the substituted alkene $CH_2{=}CHSiMe_3$ have also been studied.[7]

During UV irradiation of a saturated solution of C_{60} in benzene containing $3 \cdot 10^{-2}$ *M* BH_3NMe_3 and di-*tert*-butyl peroxide (10 μL per 0.2 mL of the solution), the ESR signal of a radical ($g = 2.0018$) was recorded. This signal was characterized by the interaction of an unpaired electron with nuclei of the magnetic isotopes ^{10}B (natural abundance 18.8 %), $a_{^{10}B} = 4.2$ G, $S = 3$, seven lines with intensity ratio of 1 : 1 : 1 : 1 : 1 : 1 : 1, and ^{11}B (natural abundance 81.2 %), $a_{^{11}B} = 12.4$ G, $S = 3/2$, four lines with intensity ratio of 1 : 1 : 1 : 1 (Fig. 1, *a*). The data obtained imply the formation of a monoborylfullerenyl radical.

$$\mathrm{C_{60}} + \dot{\mathrm{B}}\mathrm{H_2NMe_3} \longrightarrow \underset{\mathbf{2}}{\dot{\mathrm{C}}_{60}\text{-}\mathrm{BH_2NMe_3}}$$

No hyperfine interaction between protons and the nitrogen nucleus is observed in the ESR spectra of radical **2**, and that with the ^{11}B nucleus is two times

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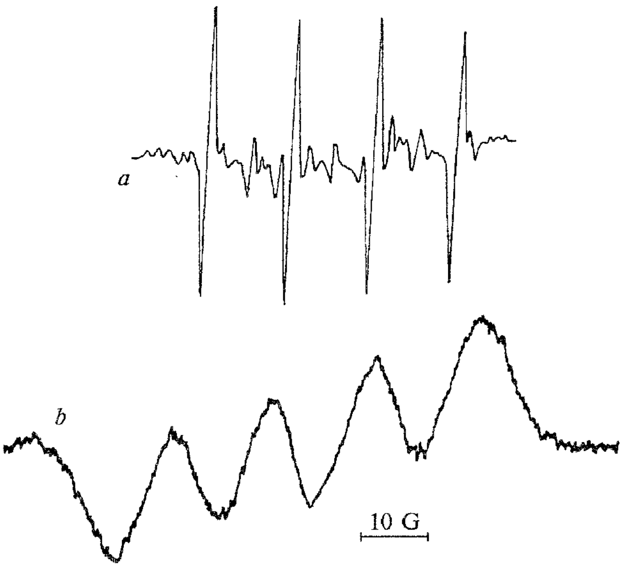


Fig. 1. ESR spectra of radicals at 300 K: *a*, C_{60}—BH_2NMe_3, *b*, C_{60}—$[BH_2NMe_3]_n$.

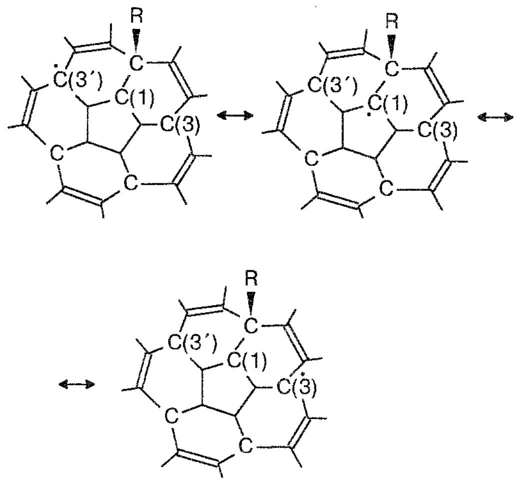
weaker than in the $^{\cdot}CH_2$—$CHSiMe_3BH_2NEt_3$—(**3**) radical ($a_{^{11}B}$ = ~ 25 G). Even if one assumes that the positions of the C—B bonds relative to the $2p_z$ orbital of the lone electron in radicals **1** and **2** are similar, still the difference in the coupling constants for radicals **2** and **3** cannot serve as a measure of the degree of delocalization of the unpaired electron in radical **2**. The coupling constant with the nucleus of a β-atom may also depend on other factors;[7] moreover, in this case delocalization of the unpaired electron seems to be primarily determined by the properties of the fullerene rather than those of the radical added.

When irradiation is switched off, radicals **2** disappear in less than a second, probably due to dimerization. When the solution is irradiated with visible light (620—680 nm), the radicals appear again due to the cleavage of the weak C—C bond in the dimer:

$$2\,\dot{C}_{60}\text{—}BH_2NMe_3 \rightleftharpoons Me_3NBH_2C_{60}\text{—}C_{60}BH_2NMe_3\ .$$

If one irradiates a sample with visible light immediately after preparation, radicals **2** are not detected, since in this case the rate of generation of the *tert*-butoxyl radicals decreases sharply. After 10—15 min of photolysis with UV light resulting in the accumulation of dimers of the borylfullerenyl radicals, irradiation with visible light gives rise to the photo-excitation of the fullerene moiety in the dimer and to facile homolysis of the weak C—C bond (*cf.* Ref. 5). Analysis of the possible structures of the dimers allowed us to assume that, owing to strong steric interaction, the fullerenyl radicals can undergo dimerization only by forming a C—C bond between the C-3 and C-3′ atoms (Scheme 2).

Scheme 2



We measured the rate constant for dimerization of radicals **2** as ~$2.5 \cdot 10^6$ L mol^{-1} s^{-1} by kinetic ESR spectroscopy. We also attempted to study the equilibrium in the radical—dimer system and to estimate its enthalpy. However, when the system was heated to the boiling point of benzene, a steady concentration of radicals **2** could not be reached. It is possible that when heating occurs and the dimer dissociates, the radicals **2** formed react with the methyl radicals resulting from the thermal decomposition of di-*tert*-butyl peroxide. Alternatively, the concentration of borylfullerenyl dimers may be insufficient for observing **2** at low degrees of dimer dissociation. Deuterated boryl radicals react with C_{60} in a similar way. The $^{\cdot}C_{60}$—BD_2NMe_3 radical does not differ from radical **2** either in the ESR spectral pattern or in reactivity.

When the concentrations of BH_3NMe_3 and di-*tert*-butyl peroxide are increased *ca.* fivefold, UV irradiation of the sample for 15—20 min affords the stable $^{\cdot}C_{60}[$—$BH_2NMe_3]_n$ radical ($a_{^{11}B}$ = 13.0 g, *g* = 2.0037, see Fig. 1, *b*). The formation of the stable radical results from multiple addition of boryl radicals to the fullerene. Similarly to the reaction involving phosphonyl radicals,[5] no "concerted" addition to give allyl or cyclopentadienyl radicals, appearing during multiple addition of benzyl radicals to C_{60},[2] occurs in this case. Boryl radicals add to the positions in C_{60} that are more distant from a carbon atom having the maximum spin density. Therefore, hyperfine interaction of the lone electron with several distant nuclei having a spin of 3/2 results in broadening of the lines in the ESR spectrum. A decrease in the rotation rate of the radical due to the increase in its mass, accompanied by an increase in the contribution of the *g*-factor and the hyperfine structure, may be another possible reason for this broadening.

Thus, it has been established by the ESR method that trimethylamineboryl radicals add to C_{60} to give monoaddition spin-adducts capable of dimerization, and stable polyaddition adducts.

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Experimental

ESR spectra were recorded on a Varian E-12A radiofrequency spectrometer. Photolysis was carried out by focused light from a DRSh-1000 UV lamp. The solutions in quartz tubes were thoroughly degassed. Thermostatting was performed using a Unipan-660 temperature-control device.

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