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Pentamethylated derivatives of [60]fullerene: X-ray structure of the $C_{60}Me_5H$ and ESR spectroscopy evidence for the stable radical $^{\bullet}C_{60}Me_5$

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ABSTRACT

Single-crystal X-ray study of 6,9,12,15,18-pentamethyl-1,6,9,12,15,18-hexahydro(C_{60}-I_h)[5,6]fullerene ($C_{60}Me_5H$) has been reported. In crystal packing, the stacking self-organization of molecules is realized. It is concluded that the formation of such polar columns is a general rule for crystals of $C_{60}R_5H$ independent of the nature of the R group. An ESR spectrum of the stable fullerenyl radical of the cyclopentadienyl-type, $^{\bullet}C_{60}Me_5$, was observed in a sample of the pentamethylated[60]fullerene. Rotation of methyl groups around C–C bonds is restricted on the ESR scale time and therefore protons within each methyl group are non-equivalent.

1. Introduction

Usually η^2 coordination has been realized in the various fullerene–metal complexes.[1] It turned out that the whole π-electron system of C_{60} and C_{70} can be broken to isolate one cyclopentadienyl ring, which may be coordinated in η^3 or η^5 fashion to a metal.[1] In 1992, we began our investigations of homolytic functionalization of fullerenes and their derivatives.[2–6] One of the tasks to be solved was to elucidate the possibility of modifying the fullerene core by functionalizing it with an uneven number of organic groups by consecutive addition of radical groups. In these studies, we focused on using *P*-centered phosphoryl radicals $^{\bullet}P(O)(OR)_2$. Provided that the successive 1,4-addition occurred selectively, around one of the five-membered rings, a fullerene derivative with an isolated cyclopentadienyl ring could have been obtained. However, the ESR spectra of the reaction mixture from homolytic phosphorylation of [60]fullerene with phosphoryl radicals generated by means of photo-induced decomposition of the corresponding organomercurials $Hg[P(O)(OR)_2]_2$ lacked the signals of the expected 'cyclopentadienylfullerenyl' radical. As a result of multiple homolytic phosphorylations we could observe by ESR spectroscopy the fullerenyl radical of the *allyl* but *not cyclopentadienyl*-type.[4,5] The regioselective multiple functionalization of C_{60} via (homolytic) chlorination followed by electrophilic aromatic substitution of benzene with $C_{60}Cl_6$ has been reported.[7] The general solution of the problem to synthesize fullerene C_{60} with a 'fenced' cyclopentadienyl ring had been found by Nakamura and co-workers.[8–12] The key finding was a remarkably selective fivefold addition of organocopper reagents to the fullerene core.[8] Till present, several X-ray structures of penta*organyl*fullerene hydrides $C_{60}R_5H$ have been reported, but all of them possessed bulky R groups that could be responsible for stacking the conical molecules into polar columns in the crystals. However, the crystal packing of the simple alkyl analogues was not investigated thus far. In this paper, we studied the first penta*alkyl*fullerene hydride structure devoid of bulky addends, the parent compound $C_{60}Me_5H$ (**1**), as well as presented the experimental ESR evidence for the existence of the corresponding free-radical $^{\bullet}C_{60}Me_5$ (**2**).

2. Results and discussion

The direct and simple way of making a fence of five groups around a five-membered ring in C_{60} was found in the copper-catalyzed specific 1,4-addition of organomagnesiums (in fact, the newly formed organocopper reagents) to C_{60}. Optimization of the experimental procedure gave the opportunity to prepare the monohydride $C_{60}Me_5H$ (**1**). We prepared **1** according to that procedure and were able to grow yellow single crystals suitable for X-ray analysis. The compound **1** is air sensitive, especially in solution.

The ^1H NMR spectra of **1** display four sharp singlets in the ratio 3:6:6:1; in C_6D_6: δ (ppm) 2.00 (3H), 2.04 (6H), 2.12 (6H), 3.73 (H–Cp), and in $CDCl_3$: δ (ppm) 2.32 (6H), 2.34 (6H), 2.44 (3H), 4.45 (H–Cp). The ^1H NMR ($CDCl_3$) spectrum of the authentic sample of **1**,

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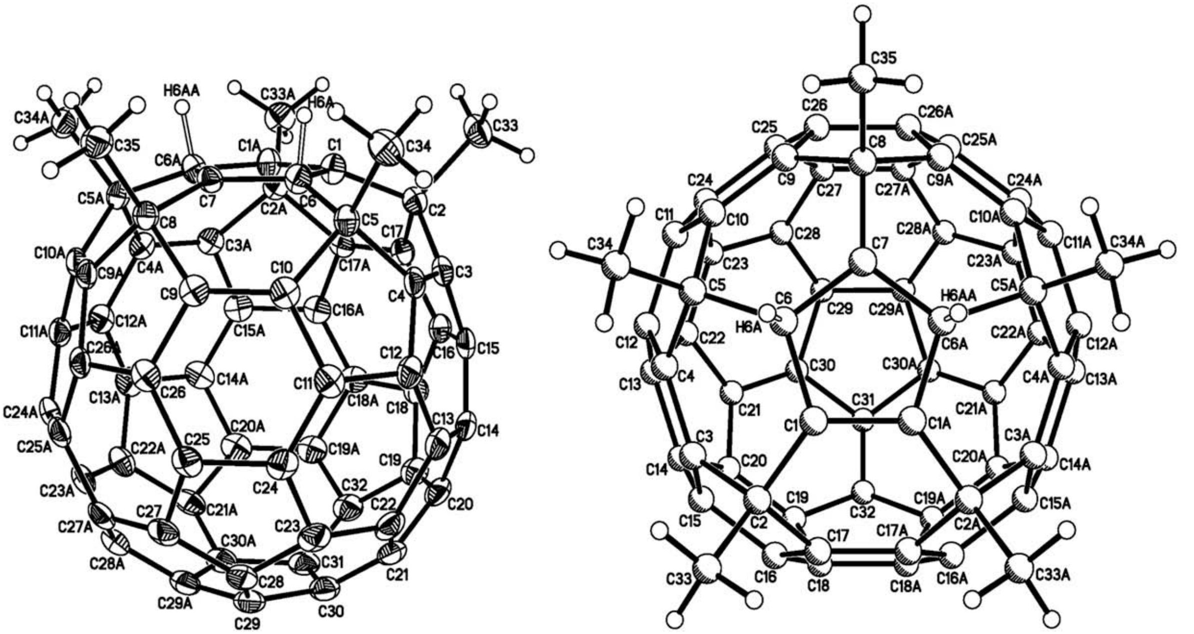


Figure 1. Molecular structure of **1** with thermal ellipsoids drawn at the 30% probability level (side view) and top view of **1**. Nearly spherical form of the thermal ellipsoids for all carbon atoms provides evidence for the absence of any disorder in the fullerene core.

Table 1
Selected bond lengths (Å) and angles (deg.) in molecule **1**

C(1)–C(1A)[a]	1.421(6)	C(14)–C(20)	1.442(4)
C(1)–C(6)	1.448(4)	C(15)–C(16)	1.446(4)
C(1)–C(2)	1.507(4)	C(16)–C(18)	1.393(4)
C(2)–C(3)	1.536(4)	C(16)–C(17)	1.441(4)
C(2)–C(33)	1.540(4)	C(17)–C(17A)	1.371(6)
C(2)–C(17)	1.541(4)	C(18)–C(18A)	1.424(7)
C(3)–C(4)	1.372(4)	C(18)–C(19)	1.452(4)
C(3)–C(15)	1.437(4)	C(19)–C(20)	1.392(4)
C(4)–C(12)	1.430(4)	C(19)–C(32)	1.452(4)
C(4)–C(5)	1.534(4)	C(20)–C(21)	1.447(4)
C(5)–C(6)	1.511(4)	C(21)–C(30)	1.386(4)
C(5)–C(10)	1.535(4)	C(21)–C(22)	1.450(4)
C(5)–C(34)	1.539(4)	C(22)–C(23)	1.395(4)
C(6)–C(7)	1.413(4)	C(23)–C(28)	1.441(4)
C(7)–C(8)	1.502(5)	C(23)–C(24)	1.446(4)
C(8)–C(35)	1.529(5)	C(24)–C(25)	1.436(4)
C(8)–C(9)	1.544(4)	C(25)–C(26)	1.398(4)
C(9)–C(10)	1.374(4)	C(25)–C(27)	1.447(4)
C(9)–C(26)	1.432(4)	C(26)–C(26A)	1.453(6)
C(10)–C(11)	1.436(4)	C(27)–C(27A)	1.390(6)
C(11)–C(24)	1.386(4)	C(27)–C(28)	1.455(4)
C(11)–C(12)	1.457(4)	C(28)–C(29)	1.389(4)
C(12)–C(13)	1.389(4)	C(29)–C(30)	1.445(4)
C(13)–C(14)	1.439(4)	C(29)–C(29A)	1.458(6)
C(13)–C(22)	1.449(4)	C(30)–C(31)	1.454(4)
C(14)–C(15)	1.389(4)	C(31)–C(32)	1.397(6)
C(1A)–C(1)–C(6)	107.4(2)	C(6)–C(5)–C(34)	113.0(2)
C(1A)–C(1)–C(2)	124.0(2)	C(4)–C(5)–C(34)	113.6(2)
C(6)–C(1)–C(2)	122.8(3)	C(10)–C(5)–C(34)	113.6(2)
C(1)–C(2)–C(3)	108.4(2)	C(7)–C(6)–C(1)	108.4(3)
C(1)–C(2)–C(33)	113.3(2)	C(7)–C(6)–C(5)	123.5(3)
C(3)–C(2)–C(33)	112.4(2)	C(1)–C(6)–C(5)	123.6(3)
C(1)–C(2)–C(17)	107.8(2)	C(6)–C(7)–C(6A)	108.2(3)
C(3)–C(2)–C(17)	100.2(2)	C(6)–C(7)–C(8)	124.6(2)
C(33)–C(2)–C(17)	113.8(2)	C(7)–C(8)–C(35)	114.9(3)
C(6)–C(5)–C(4)	107.8(2)	C(7)–C(8)–C(9)	106.4(2)
C(6)–C(5)–C(10)	107.5(2)	C(35)–C(8)–C(9)	113.9(2)
C(4)–C(5)–C(10)	100.3(2)	C(9)–C(8)–C(9A)	99.9(3)

[a] Symmetry transformation x, $-y+1/2$, z was used to generate equivalent atoms labeled with A.

prepared by Nakamura and co-workers,[10] showed also four sharp singlets at 2.30, 2.32, 2.42, and 4.46 (Cp–H) in a ratio 6:6:3:1. It is noteworthy that in the more polar solvent, chloroform, downfield shift of the hydride H is very high, 0.72 ppm. These data indicate the increased polarization of the Cp–H bond. Similar but slighter shifts are observed for methyl groups. In this connection, we emphasize that similar deshielding for methyl protons was observed in the corresponding anion formed by the deprotonation of **1** with KO^tBu.[10] Single crystals for X-ray study of **1** were obtained as a solvate with pentane, $\mathbf{1}\cdot C_5H_{12}$, by slow diffusion of pentane carefully layered over the solution of **1** in *o*-dichlorobenzene at room temperature under argon. The structure of molecule **1** is shown in Figure 1, selected bond lengths and angles are given in Table 1.

In the crystal, molecule **1** occupies a special position on the mirror plane going through C(7), C(8) atoms and the middle of the C(1)–C(1A) bond. A molecule of the solvating pentane also occupies a special position on the mirror plane and as a consequence is disordered over two positions. The attempt to refine structure in the non-centrosymmetric group *Pna*2_1 was not satisfactory (it leads to worse convergence, higher standard deviations of bond lengths and angles, and does not lead to removal of the disorder of a solvate molecule).

The structure of the fullerene core in **1** is similar to that in three $C_{60}R_5H$ previously studied, namely, R=$C_6H_5C_6H_4$ **3**,[11] $C_6H_5(CH_3)_2SiCH_2$ **4**,[12] and $C_6H_5C_6H_4(CH_3)_2SiCH_2$ **5**.[12] In all structures there is an essential pyramidalization of the five carbon atoms bearing organic groups. Hexagons and pentagons incorporating these atoms have conformations of 'boat' and 'envelope' correspondingly. The characteristic peculiarity of all hydrido[60]-fullerenes $C_{60}R_5H$, including **1**, is the planar geometry of the five-membered ring to which the H atom is added; in **1** the maximum deviation from the average plane of atoms C(1)C(6)C(7)C(6A)C(1A) is 0.006 Å.

Planar geometry of the cyclopentadiene ring in hydrido[60]-fullerenes **1**, **3–5** is in contrast to the non-planar conformation of the cyclopentadiene ring in hexamethylfullerene $C_{60}Me_6$ **6** wherein the carbon atom of the pentagon bonded to methyl group goes out of plane with four carbons by 0.25 Å.[13] Planar geometry

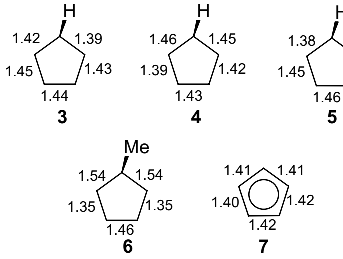
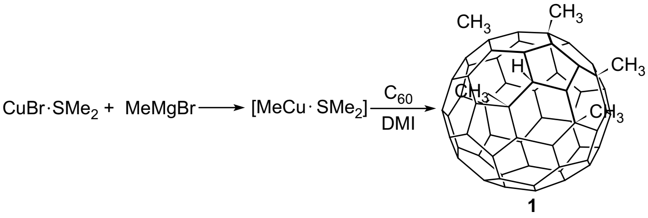


Chart 1.



Scheme 1.

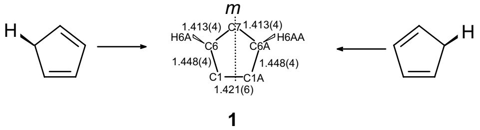


Chart 2.

of this pentagon had been expectedly found in the anion of pentakis(biphenyl-4-yl)[60]fullerene **7**.[14]

In this connection, the question arises about the localization of the hydrogen atom in **1**, **3**–**5**. Previously, the X-ray structures of **3**–**5** had been reported but no comment was done concerning the position of the hydride H that was probably left unidentified.[11,12] We also were not able to localize the hydride atom in **1** from Fourier analysis despite all H atoms in methyl groups having been unambiguously determined from X-ray diffraction data.

Nonetheless, taking into account the high accuracy of determination of all geometric parameters for **1** (Table 1) and using data about structures of **3**–**5**, **6**, and **7**, some conclusions can be drawn about the structures of pentaorganylhydrido[60]fullerenes (Cambridge Structural Database, CSD version 2007, refcodes: TAHTIG (**3**), IQITAD (**4**), IQITEH (**5**), ACUMAM (**6**), JARKUJ (**7**)).

Attention should be paid to the bond lengths in the cyclopentadienyl ring (Chart 1). Thus, double and ordinary bonds are clearly alternated in hexamethylfullerene **6** and all C–C bonds are equal in anion **7** (average value 1.41 Å, shorter than the usual values 1.45 Å for pentagons without addends). The non-equivalency of bond lengths in **3**–**5** is less pronounced relative to **6**; however, this non-equivalency makes **3**–**5** significantly different from **7**. In the structures of **3**–**5** there are three bonds of 1.41 Å and two bonds of 1.45 Å (on average) corresponding to the diene-type fragment.

Obviously, the distribution of bond lengths in **3**–**5** is caused by the presence of a hydride at one carbon of the pentagon. The place of H in Scheme 1 corresponds to the structures given in CSD. From our viewpoint, the position of the H atom corresponds to the distribution of bond lengths only in the case of **4**.

The description of pentadiene ring C(1)C(6)C(7)C(6A)C(1A) in structure **1** is a little more complicated because of the symmetry plane going through the C(7) atom and the midpoint of the C(1)–C(1A) bond. Alternation of bond lengths is also seen in **1** but their positions in the ring probably indicate the superposition of two forms with different placements of the hydride H, namely, at C(6) and C(6A), Chart 2.

This description seems to be reliable taking into account the accuracy of determination of bond lengths for **1**. In addition, all

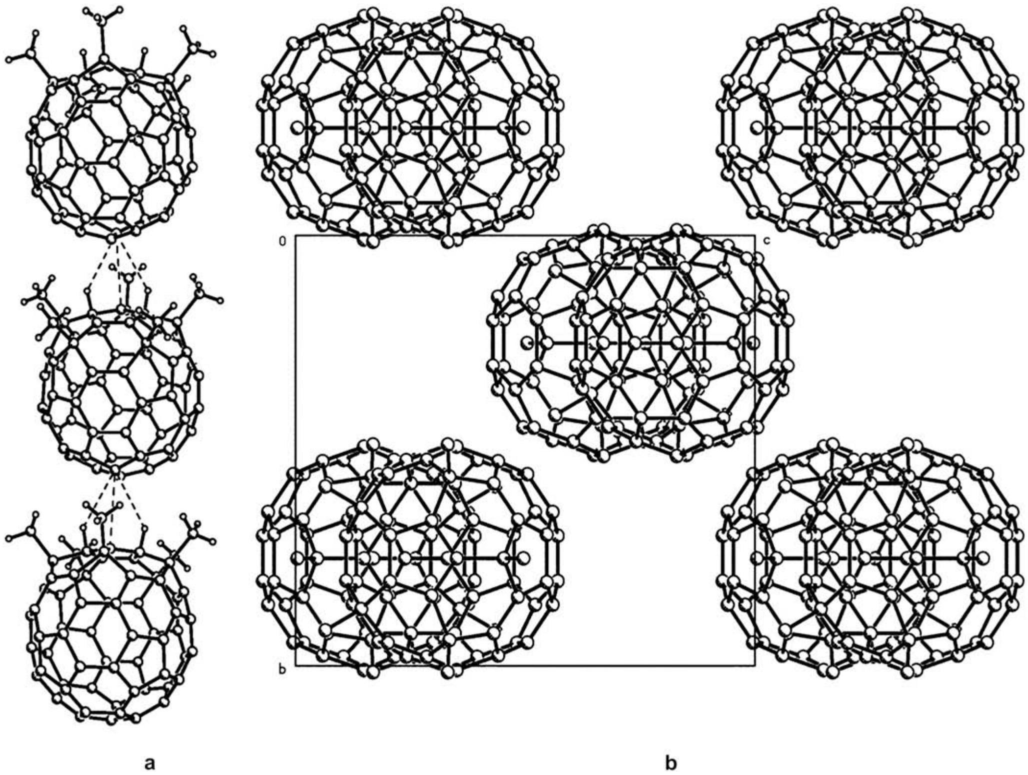


Figure 2. Crystal packing: (a) three stacked molecules of **1** (the stacking period of the molecules within a column is 10.15 Å); (b) fragment of the crystal packing of columns in projection on the *bc* crystal plane (for clarity, solvent molecules and H atoms are omitted).

pentagons without added groups have bonds of equal length, on average 1.446 Å, in agreement with the literature value 1.45 Å.[1]

In crystal packing, molecules of **1** form zig-zag columns along the axis *a* of the crystal with the shortest intermolecular distances $C(7)\cdots C(32)_{-0.5+x,\ y,\ 1.5-z}$ 3.382(4) Å and $H(6A)\cdots C(32)_{-0.5+x,\ y,\ 1.5-z}$ 2.74 Å (Fig. 2a). The distance between two neighbor molecules in the same column (calculated as the distance between two centroids of C_{60} fragments) is 10.15 Å. Each column in a crystal has four parallel neighbor columns with shortest intermolecular contacts $C(23)\cdots C(15)_{0.5-x,\ -y,\ -0.5+z}$ 3.311(4) and $C(23)\cdots C(16)_{0.5-x,\ -y,\ -0.5+z}$ 3.366(4) Å (Fig. 2b).

It is worth noting that there are analogous polar columns in structures **3**–**5** wherein conical molecules with a fullerene apex stack head-to-tail with intracolumnar spacing equal to 11.10, 10.28, and 10.19 Å, respectively. Hence one can conclude that the formation of similar polar columns in crystals of $C_{60}R_5H$ is a general rule independent of the nature of addends R. It is probably determined by the significant polarization of molecules, in part, by the charge shift in the bottom side of the fullerene core.

This hypothesis is confirmed by the data of the structure of σ-bonded dimer $[K^+(THF)_3]_4[Ar_5C_{60}–C_{60}Ar_5^{4-}]$, Ar=$C_6H_4$–Ph (**8**), prepared from anion **7** or from the hydride precursor.[14] In dimer **8** σ-bond C_{60}–C_{60} is formed by the carbon atoms from the bottom sides of two fullerene units.

ESR study of a sample of $C_{60}Me_5H$ in 1,2,4-trichlorobenzene solution at high resolution gives a spectrum (Fig. 3), which is characterized by hyperfine interaction (hfi) of the unpaired electron with three magnetically non-equivalent groups of protons: a_H (5H)=0.17 G; a'_H (5H)=0.334; a''_H (5H)=0.53 G and satellite lines from hfi with two groups of ^{13}C nuclei: a'_C (5 ^{13}C)=6.8 G; a''_C (10 ^{13}C)=0.8 G; g=2.0026. These data demonstrated that the observed picture is a spectrum of the fullerenyl radical of cyclopentadienyl-type ($^{\bullet}C_{60}Me_5$) and in this species the rotation of methyl groups around C–C bonds is restricted on the ESR scale time and protons located in positions, which are not equivalent.

It is not a surprise in the light of fact that rotation of the methyl group in fullerenyl radical $^{\bullet}C_{60}Me$ is hindered. The effects of line broadening in the $^{\bullet}C_{60}Me$ radical in the temperature range 200–275 K were observed. The rate constants for rotation about the Me–C_{60} bond and barrier to rotation were obtained to be 10–100 MHz and ΔH=3.3 kcal mol^{-1}. Analysis of broadening of lines of $Me_3C–C_{60}$ gives the barrier of the hindered rotation: ΔH=7.3 kcal mol^{-1}.[15] In our case we did not observe specific broadening of lines of $^{\bullet}C_{60}Me_5$ in the range 25–350 K and the position of Me-groups is 'frozen' on the ESR time scale. We believe that barrier to rotation of Me-groups in $^{\bullet}C_{60}Me_5$ is remarkably more than in $^{\bullet}C_{60}$–Alk.

Short heating of the sample at 350 K leads to an increase of intensity of signal of $^{\bullet}C_{60}Me_5$, however, more prolonged heating leads to decrease of intensity of signal. Using the usual methods for homolytic abstraction of H from $C_{60}Me_5H$, such as photolysis of a solution of $C_{60}Me_5H$ with di-*tert*-butyl peroxide gives no increase of intensity of the spectra. We believe that the H–C bond in $C_{60}Me_5H$ is polar in the sense $H^{+\delta}–C^{-\delta}$ and relatively stable to homolytic reactions. Possibly, the radical $^{\bullet}C_{60}Me_5$ was formed as a minor product during the synthesis of $C_{60}Me_5H$ through organocopper intermediates.

Similar stability for corresponding homolytic reactions was observed for $C_{60}Ph_5H$. The ESR spectrum of stable $^{\bullet}C_{60}Ph_5$ cyclopentadienyl-type fullerenyl radical was observed only under UV-irradiation of a toluene solution of $C_{60}Ph_5Cl$.[16] Earlier, formation of $^{\bullet}C_{60}Ph_5$ as an intermediate was postulated in the process of electrochemical oxidation of the corresponding dianion.[9] The ESR spectrum of dianion radical $(C_{60}Ph_5)^{2-}$ has an asymmetrical broad line (~20.0 G)[18] in contrast with the relatively narrow line of $^{\bullet}C_{60}Ph_5$ (~1 G).[16]

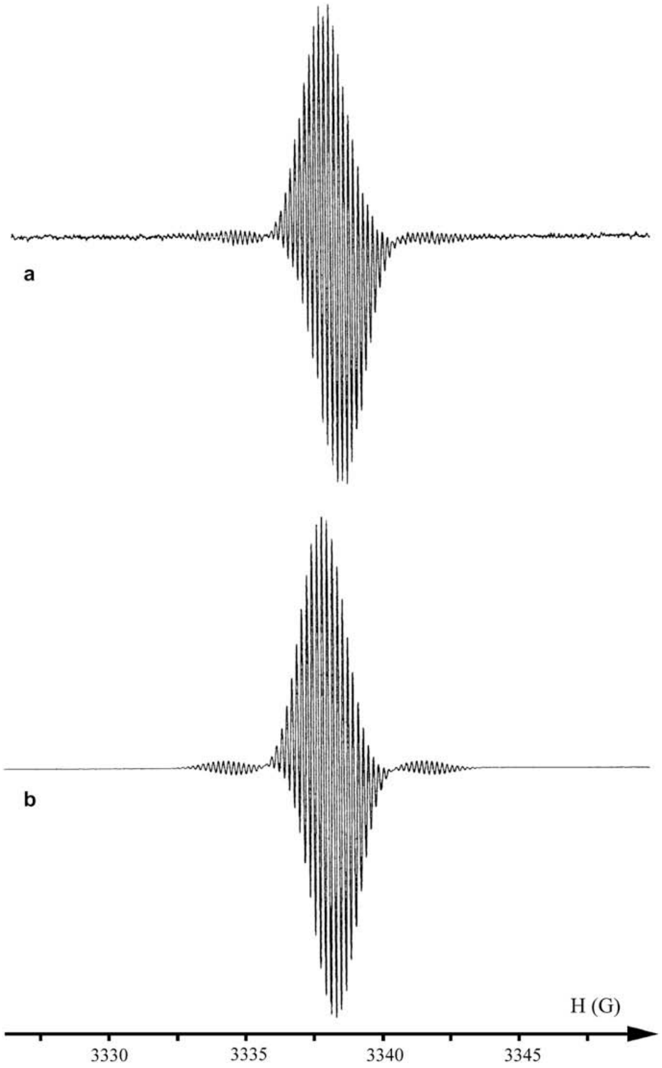


Figure 3. ESR spectra of the radical $^{\bullet}C_{60}Me_5$: (a) experimental spectrum at 290 K (b) simulation.

3. Conclusion

X-ray study of the simplest pentaalkylfullerene hydride $C_{60}R_5H$, R=Me demonstrated that the formation of the polar columns of the 'shuttlecock' type is not determined by overcrowding due to bulky added groups but is a general rule for crystals of $C_{60}R_5H$ independent of the nature of the R group. Simultaneously, we discovered the existence of the stable free radical $^{\bullet}C_{60}Me_5$ admixed to the hydride probably formed during the organocopper reaction. The well-resolved ESR spectrum evidences the non-equivalency of the protons within each methyl group due to the steric hindrance to the rotation around C–C bonds.

4. Experimental

4.1. General comments

All manipulations were carried out under argon using standard Schlenk techniques. 1,2-Dichlorobenzene (ODCB) was dried by distillation under reduced pressure from P_2O_5 and CaH_2. Pentane and THF were distilled from sodium/benzophenone ketyl. The compound $C_{60}Me_5H$ was prepared according to the literature procedure.[10] ^1H NMR spectra (at 400 MHz) were recorded on a Bruker

Avance-400 instrument. The chemical shifts were referenced to residual solvent protons (δ 7.25 ppm for C_6D_6 and $CDCl_3$).

4.2. X-ray structure determination

Single crystals of **1**·C_5H_{12}·were grown from an ODCB/pentane solution at room temperature. The crystals ($C_{70}H_{28}$, M=868.92, crystal size 0.04×0.30×0.35 mm^3) are orthorhombic, space group *Pnma*, at 120 K, a=19.598(4), b=13.183(2), c=14.655(3) Å, V=3786(1) $Å^3$, Z=4, D_{calcd}=1.524 g/cm^3, μ(Mo Kα)=0.87 cm^{-1}. The intensities of 11,637 reflections (4191 independent reflections, R_{int}=0.0810) were measured on a Bruker SMART 1000 CCD diffractometer (graphite monochromated Mo Kα radiation, λ=0.71073 Å, ω-scan technique, $2\theta_{max}$=54°, T=120 K). The SMART 1000 CCD software[17] was used for collecting frames of data, indexing reflections, determination of lattice constants, integration of intensities of reflections, and SHELXTL[18] or space group and structure determination, refinements, graphics, and structure reporting. The structure was solved by direct methods and refined by the full-matrix least-squares technique against F^2 with the anisotropic temperature factors for all non-hydrogen atoms. The H atoms of methyl groups in **1** were located from difference Fourier synthesis; the rest of the hydrogen atoms were placed geometrically and included in the structure factors calculations in the riding motion approximation. The refinement converged to wR_2=0.1556 and GOF=1.016 for all independent reflections [R_1=0.0592 was calculated against F for 1982 observed reflections with $I>2\sigma(I)$], 339 refined parameters. Crystallographic data for the structural analysis of **I** have been deposited with the Cambridge Crystallographic Data Centre, CCDC 682520.

4.3. ESR spectroscopy

ESR spectra were recorded on a Bruker EMX-10/12 X-band (ν=9.4 GHz) digital ESR spectrometer equipped with a Bruker N_2-temperature controller. ESR spectra at high resolution were recorded at microwave power 0.05 mW, 20 kHz magnetic field modulation of 0.01 G amplitude. Digital field resolution was 4096 points per spectrum, allowing all hyperfine splitting to be measured directly with accuracy better than 0.04 G. Spectra processing and simulation were performed with Bruker WIN-EPR and SimFonia Software. 1,2,4-Trichlorobenzene was dried, accurately degassed, and distilled under argon.

Acknowledgements

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