Transient EPR Studies of Excited Triplet States in Polyadducts of C_{60} and Bis(ethoxycarbonyl)methylene

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Abstract: Transient EPR spectra of the excited triplet states in polyadducts of C_{60} with bis(ethoxycarbonyl)methylene were measured. The equatorial−equatorial−equatorial (eee) and trans-3, trans-3, trans-3 (t3t3t3) trisadducts together with tetrakis-, pentakis-, and hexakisadduct obtained by equatorial successive addition were examined. zfs parameters *D* and *E* and spin polarization carried by the triplet species were determined by spectrum simulation. *D*, *E* values for tetrakis-, pentakis-, and hexakisadducts are very well differentiated, which makes their identification quite easy. Additionally, polarized EPR spectra of the eee and t3t3t3 trisadducts exhibit an impressive difference also in the line shape (absorption/emission polarization of eee reverts into emission/absorption for t3t3t3), accounted for by a sign reversal of *D*. Changes in strength of *D* and *E* values are described in terms of a simple model calculation previously applied to C_{60} and monoadducts.

Introduction

There is an increasing interest in the synthesis and characterization of C_{60} polyadducts[1−3] with defined three-dimensional structure in view of fullerene derivatives with important biological[4] or material properties.[5]

UV−vis and ^1H and ^{13}C NMR spectroscopic methods have been applied to single out the different isomers.[1−3] However, the electronic absorption spectra are poorly resolved, and NMR spectra give mainly information on the symmetry of the multiple adducts.

In a previous report[6] we have shown that EPR spectra of the photoexcited triplet state can be used successfully to assign the structure to isomeric bisadducts. Line shapes of triplet EPR spectra in a magnetic field are characterized by the *D* and *E* zero field splitting (zfs) parameters accounting for the electron−electron dipolar interaction between the two unpaired electrons in the triplet state. The *D* and *E* values depend on the triplet state wave function which can be used as a sensitive probe to identify the structure of the polyadducts.

EPR spectra of the excited triplet species are often spin polarized, probing the circumstance that the populations of the triplet sublevels deviate from the values at thermal equilibrium. Besides the *D* and *E* parameters, also the populations p_x, p_y, and p_z of the triplet sublevels in the absence of the magnetic field also enter the spectrum simulation. Such populations represent an additional set of spectroscopic parameters that monitor the properties of the triplet wave function and can be used for a better identification of the structure of the adduct.

Here, we report the results of a study on the photoexcited triplet state of C_{60} and bis(ethoxycarbonyl)methylene polyadducts. In particular, we report on the C_3-symmetrical equatorial−equatorial−equatorial (eee) and the D_3-symmetrical trans-3, trans-3, trans-3 (t3t3t3) trisadducts, the C_s-symmetrical tetrakisadduct (tetra), the C_{2v}-symmetrical pentakisadduct (penta), and the T_h-symmetrical hexakisadduct (hexa) (Chart 1).

Experimental Section

The synthesis of the polyadducts shown in Chart 1 has been already reported.[1,2] The trisadducts eee and t3t3t3 were obtained as main products of the cyclopropanation of e and trans-3 bisadducts, respectively. Tetrakis-, pentakis-, and hexakisadduct were synthesized by successive equatorial additions to the starting eee isomer.

The samples were prepared as toluene solutions of the fullerene adducts (5×10^{-4} M). Polystyrene (5% w/w) was added to improve the optical properties of the matrix at low temperaure. The sample was degassed before sealing under vacuum in a quartz tube of 3 mm inner diameter.

Details regarding EPR instrumentation used to detect transient EPR spectra reported in this paper have been described in ref 6.

Results and Discussion

The transient EPR spectra of eee and t3t3t3 trisadducts recorded at 10 K are reported in Figure 1 together with their

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Chart 1

R = COOEt
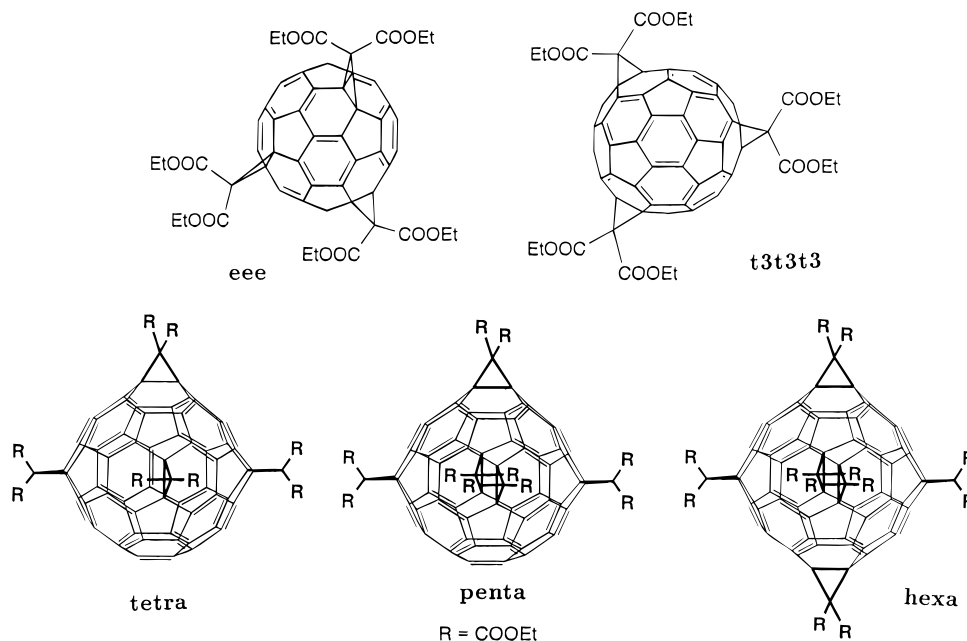
computer simulations. The zfs parameters D and E (for their definition, see refs 7 and 8), and ratios of the zero field populations p_x, p_y, and p_z are listed in Table 1.

The difference in line shape of the two spectra is impressive and gives clear evidence of how useful the triplet EPR spectroscopy can be to identify a trisadduct isomer of C_{60}. The most important spectral features that emerge from the analysis of the spectra are as follows: (i) the zfs parameters of the excited triplet are much larger than those observed for C_{60}[9] and for monoadducts;[10] (ii) the two spectra exhibit an opposite trend of the polarized lines. In the eee adduct, the low-field part of the spectrum is in absorption and the high-field one in emission as in C_{60}. On the contrary, in the t3t3t3 adduct the low-field

Table 1. D and E zfs Parameters (in Gauss) and Population Ratios of the Lowest Excited Triplet State in Tetrakis-, Pentakis-, and Hexakisadducts of C_{60} and Bis(ethoxycarbonyl)methylene[a]

adduct	D	E	$(p_x - p_z):(p_y - p_z)$
monoadduct[b]	−99	−2	1:0.33
e[b]	−199	−17	1:0.10
eee	−301	−83	1:0.05
t3t3t3	+256	+16	1:0.95
tetra	−276	−52	1:0.23
penta	−102	−13	1:0.54
hexa	−204	−21	1:0.05

[a] E is assumed to have the same sign as D. [b] Data for the monoadduct and the equatorial e bisadduct reported in ref 6 are also shown for comparison. Estimated error limit of D, E values is ±1 G.

part of the triplet spectrum is in emission and that at high field is in absorption.

As we reported previously,[10] the transient EPR spectra of the photoexcited triplet state in C_{60} and in C_{60} monoadduct were simulated by using very similar sets of D, E values and populating rate constants. Since the C_{60} molecule belongs to I_h symmetry group and the monoadduct to C_{2v} in their ground state, the above result indicates that a symmetry lowering from I_h to C_{2v} (or C_2) group must occur to the C_{60} molecule when it passes into the excited singlet state. It also suggests that such a distortion is transferred into the excited triplet state by intersystem crossing.

We apply the same argument to reproduce the EPR spectra of eee and t3t3t3 trisadducts. The polarized EPR spectrum of t3t3t3 excited triplet reported in Figure 1 has been simulated by allowing for a sign reversal of the D parameter with respect to that of the eee triplet which has been taken negative as for $^3C_{60}$. With that choice of the D sign, the zero level populations maintain the same pattern observed for $^3C_{60}$ with one or both zero field x and y spin levels mostly populated.
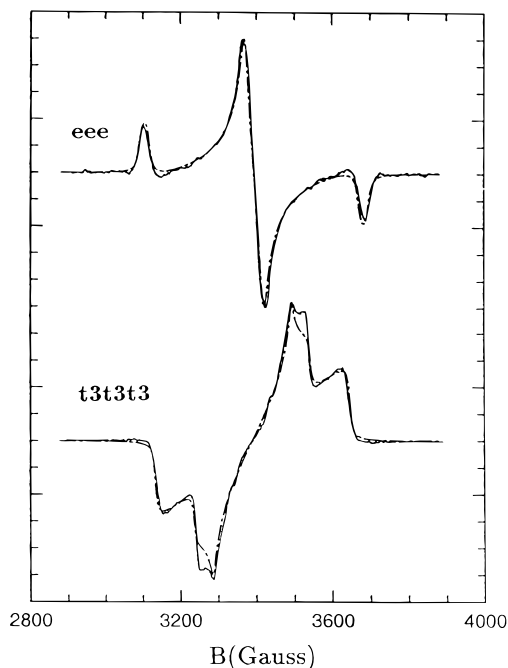
Figure 1. Field-swept DD-EPR spectra (solid line) of excited triplet states for eee and t3t3t3 trisadducts and their computer simulation (dash-dotted line). Signals are detected 0.5 μs after the laser pulse at the temperature of 10 K.

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We note that the EPR spectra of t3t3t3 and eee triplets show a nonvanishing E parameter, which is a clear evidence that the symmetry of their ground state (D_3 for t3t3t3 and C_{3v} for eee) is not preserved in their triplet state because of a Jahn−Teller distortion that lowers that symmetry.[11] Group symmetry considerations suggest that t3t3t3 distorts probably from D_3 to C_2 and eee from C_{3v} to C_s.[12]

The assignment of a positive D sign for the triplet state of t3t3t3 is in agreement with experimental evidence and theoretical calculations that the triplet wave function of $^3C_{60}$ is mainly concentrated near the equatorial plane perpendicular to the axis z carrying the largest zfs component $Z\ (=-^2/_3D)$. With such a wave function the sign of the D parameter was found to be negative.[13] Recently, we have performed a calculation of D based on a model of fully localized double bonds distributed over the fullerene surface.[14] It was found that when the triplet wave function is mainly confined at double bonds near the equatorial plane, a negative D is expected, as for $^3C_{60}$, whereas the wave function that extends near the poles of the fullerene sphere gives a positive D value. The same argument can be applied here to account for the variation in the D values of the eee and t3t3t3 chiral trisadducts with respect to C_{60}.

In the case of the eee isomer, the z axis with the largest zfs component lies on the C_s symmetry plane, possibly in the neighborhood of substituents where the major deformation of the sphere is produced by successive additions. If so, the triplet wave function is more concentrated near the plane normal to the z axis, spreading over 6-6 C−C double bonds not engaged by addends. As a result, the D value is expected to be enhanced and of the same sign as in C_{60}, which is exactly what we observe.

In the case of t3t3t3, because of lowering of the D_3 symmetry of the molecule into C_2 in the excited triplet state, the C_2 symmetry axis with the largest zfs component should be normal to the plane that bisects the double bonds attached by the triple addition. In this case the triplet wave function is pushed toward the poles giving a positive contribution to the D value. This picture allows us to assign a positive sign of D to t3t3t3 and a negative one to the eee trisadduct.

The triplet EPR spectra of tetrakis-, pentakis-, and hexakisadduct are reported in Figure 2 together with their computer simulations.

They display similar line shapes, characterized by the low-field part of the spectrum in absorption and the high-field part in emission. However, simulation of their spectra gives D and E values completely different from one adduct to another. This makes the identification of each multiple adduct very reliable when based on the triplet EPR spectrum. The comparison of the D values for tetrakis-, pentakis-, and hexakisadduct needs further considerations to give a reasonable interpretation.

The tetrakisadduct is C_s-symmetrical, and no additional symmetry loss is expected to occur in the excited state to produce the spectrum with the $E \neq 0$ asymmetry parameter. The situation is similar to that seen for the equatorial bisadduct.[6] According to the scheme outlined above concerning the strength and the sign of D, one expects that the z principal axis of the electron dipolar tensor should lie in the C_s plane and that plane perpendicular to the axis z should host the maximum of
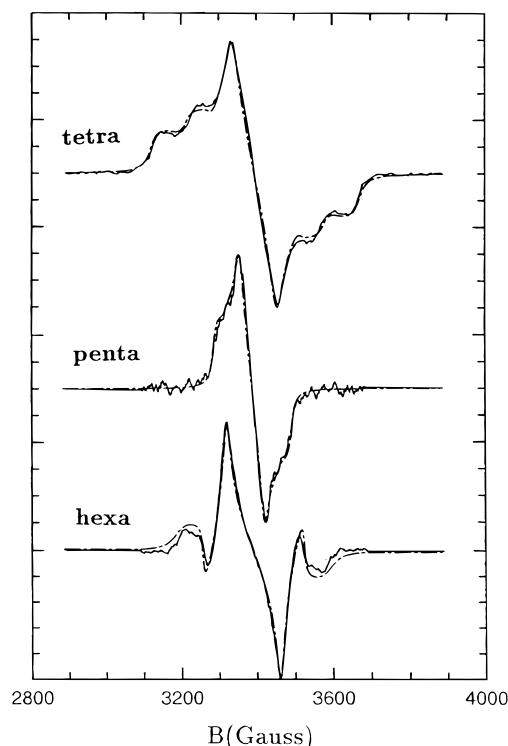
Figure 2. Experimental (solid line) and computer-simulated (dash-dotted line) DD-EPR spectra of the excited triplets for tetrakis-, pentakis-, and hexakisadduct. Signals are detected 0.5 μs after the laser pulse at the temperature of 10 K.

the triplet wave function. The data reported in the table show that the D value is large and positive as expected.

In the C_{2v}-symmetrical pentakisadduct the z principal axis coincides with the C_2 axis. In this case the plane perpendicular to z is easily identified, as that one passing through two double bonds attached by addends and crossing the other two. The D and E values are similar to those of the monoadduct,[6] which belongs to the same C_{2v} symmetry group.

For the hexakisadduct, which possesses T_h symmetry, the fact that the triplet EPR spectrum gives a nonvanishing E value indicates that in the excited triplet state a symmetry loss has occurred. Distorted structures possible for the excited molecule are D_{2h} or C_{2v} subgroups, although subgroups of even more reduced symmetry like C_2 or C_s are possible.[12]

It is well assessed that the nonzero D and E values of the $^3C_{60}$ state are due to a Jahn−Teller distortion of the icosahedral symmetry I_h of C_{60} in its ground state.[15−19] Therefore, it is likely that the origin of the symmetry loss in the eee, t3t3t3, and T_h-symmetrical hexakisadduct must be the same.

The zfs parameters reported in the table indicate that the distorted excited triplet state in all the examined polyadducts has a symmetry compatible with a nonvanishing value of E (lower than C_3). A comparison of the negative D values, which give information on the degree of localization of the triplet wave function in the equatorial plane normal to the z axis, shows that such a degree may be largely different. t3t3t3 represents an exception in that the contribution to the positive D value arises

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from the triplet wave function localized at the double bonds near the poles of the spherical fullerene molecule.

Conclusion

We have shown that the triplet wave function, probed through the measurement of the electron-electron dipolar zfs *D* and *E* parameters by transient EPR spectroscopy, is a very sensitive tool to identify the regioselective polyadducts of C$_{60}$ and bis-(ethoxycarbonyl)methylene.

According to the spectrum interpretation for the eee and t3t3t3 trisadducts, their *D* values differ both in sign and absolute value.

They are from 2 to 3 times larger than that for ^{3}C$_{60}$, giving a clear indication of how much the triplet wave function is modified by the triple addition.

For the higher polyadducts the *D* values maintain the same sign, but they are well distinguished and can be safely used to unambigously identify the structure of the adduct.