

Low temperature structural analysis of a TDAE·C₆₀ crystal

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X-Ray single crystal diffraction studies of TDAE·C₆₀ were performed at low temperature and its crystal structure could be solved and analysed on the basis of diffraction data obtained at 7–11 K.

The discovery of organic ferromagnetism in TDAE·C₆₀ by Allemand *et al.*,¹ where TDAE is tetrakis(dimethylamino)-ethylene, with a transition temperature of about 16 K aroused considerable interest in this compound, since it has the highest T_c of any known molecular ferromagnet without transition metal atoms. A number of possible models, such as itinerant ferromagnetism, superparamagnetism, spin-glass like ground state, and spin-canted weak ferromagnetism have been proposed^{1–6} to explain its magnetic behavior at low temperatures. However, despite intensive studies of TDAE·C₆₀, a detailed crystal structure based on single crystal diffraction data has not been published until now. The first structural characterization of TDAE·C₆₀ crystals was conducted on X-ray powder diffraction data by Stephens *et al.*,⁷ on the basis of which it has been shown that TDAE·C₆₀ is a 1:1 charge-transfer complex and that the structure has a *C*-centered monoclinic unit cell. The space group was determined as *C2/m* (or non-centric subgroups *Cm* and *C2*). However, a more recent X-ray study of single crystals suggests a space group of symmetry *C2/c* with a doubling of the unit cell size in the *c*-direction and with TDAE shifted along the *b*-axis by about 0.02 Å perpendicular to the *c*-axis.⁶ A determination of the crystal structure at room temperature is complicated because, as is well known, in most materials based on fullerenes the C₆₀ molecules rotate rapidly or have orientational disorder at room temperature. In TDAE·C₆₀ crystals the fullerene molecules also rotate at room temperature and freeze out below 150 K,⁶ so it is hard to localize carbon atom positions of the molecule in this temperature range.

We have carried out an X-ray single crystal diffraction study of TDAE·C₆₀ compound at low temperatures down to 7 K. As was shown by EPR measurements the freshly grown, un-annealed single crystals are found to be ordered antiferromagnetically below 10 K^{6,8} and do not show a ferromagnetic transition.

For crystal growth we used the diffusion method, originally developed in the 1970s for the crystallization of organic charge-transfer salts.⁹ C₆₀ (Hoechst, gold grade) and TDAE (Aldrich, 95% pure) were used without further purification. The solvent (toluene) was distilled under argon atmosphere and transferred into a glove-box (O₂ concentration < 1 ppm). A toluene solution of C₆₀ (2 mg ml⁻¹) and a mixture of toluene and TDAE (3:1) were prepared inside the glove-box and poured separately into the two compartments of a growing cell separated by fritted glass. The cell was carefully closed and maintained at 8 °C. After six months the crystal growth was completed. The cell was then transferred back to a glove-box, and the crystals were extracted from it, washed with hexane and dried.

The full set of diffraction patterns for structural analysis were obtained using a Weissenberg type X-ray imaging plate at 160,

30, 7 and 11 K. The structure was solved and refined based on the space group *C2/c* for the set of data obtained at 7 K. The same structural parameters were used as initial values for analyzing the intensity arrays collected at other temperatures.

The crystal structure for TDAE·C₆₀ at 160 K shows the presence of significant molecular disorder, with rapid oscillation of the carbon atoms of the C₆₀ molecules around the *b*-axis. This is expressed by the large values of the thermal coefficients for the atoms. Even at the lowest temperatures, the values of B_{eq} remain high, which testifies to the presence of some degree of disorder in the structure. It seems that the degree of orientational ordering depends on the cooling time below 50 K and structural parameters with relatively low thermal coefficients were obtained for data collected at 11 K after cooling at that temperature for about 4 h.[‡]

There are four chemically equivalent C₆₀·C₂(NC₂H₆)₄ units per unit cell. Projections of the structure along the *b* and *c* crystallographic axes are shown in Fig. 1. The packing of the unit cell shows that C₆₀ anions are located at inversion centers with the coordinates (0.5, 0, 0), (0, 0.5, 0), (0.5, 0, 0.5) and (0,

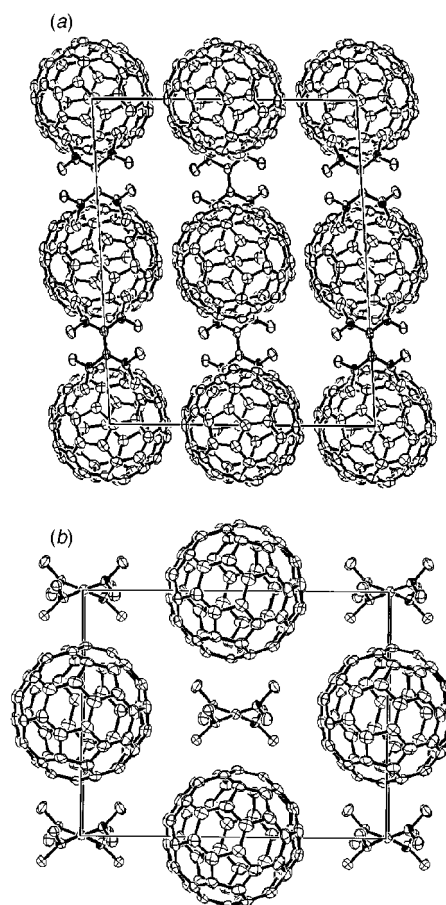


Fig. 1 Projections of the C₆₀·TDAE crystal structure (ORTEP-III, 50% probability) at 11 K along the (a) *b*-axis and (b) *c*-axis.

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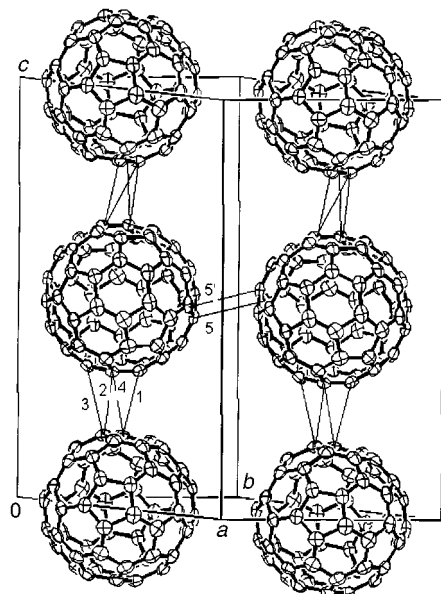


Fig. 2 Shortest $C_{60}\cdots C_{60}$ contacts along the $[001]$ and $[1\bar{1}0]$ directions: (1) $C(16)-C(16') = 3.369(6)$, (2) $C(24)-C(24') = 3.082(6)$, (3) $C(24)-C(28') = 3.373(4)$, (4) $C(16)-C(24') = 3.479(4)$, (5,5') $C(3)-C(14') = 3.471(4)$ Å.

0.5, 0.5). The centers of gravity of the C=C double bonds of the TDAE units are at the two-fold axes and the molecules are located at positions (0, -0.0022, 0.25), (0, 0.0022, 0.75), (0.5, 0.4978, 0.25) and (0.5, 0.5022, 0.75), with the double bonds parallel to the c -axis.

The C_{60} molecules form a chain along the c -axis with the shortest distance between molecular centers equal to 9.915 Å at that temperature. There are several short contacts between adjacent fullerene molecules along the chain: 3.082(6), 3.369(6) and 3.373(4) Å. The intermolecular separation between C_{60} molecules within the ab plane is 10.223 Å and there is a short contact [3.471(4) Å] in the $[1\bar{1}0]$ crystallographic direction, while in the $[110]$ direction all distances are more than 3.60 Å. The $C_{60}\cdots C_{60}$ type short contacts are shown by dashed lines in Fig. 2.

The C-C bonds in the six-membered rings (6:6) of the C_{60} molecule vary from 1.369(5) to 1.409(5) Å, and in the five-membered rings (5:6) they fall in the range 1.433(4)–1.490(4) Å. In the previous reports^{10–16} it was noticed that on going from the neutral molecule C_{60} to the C_{60}^{n-} ($n = 1-6$) anions, the mean 6:6 ring junction bond length tends to increase [1.355(9) Å (for C_{60})¹² \rightarrow 1.389(3) Å (C_{60}^{-})¹³ \rightarrow 1.399(2) Å (C_{60}^{2-})¹⁰], while the mean 5:6 bond tends to decrease [1.467(21) \rightarrow 1.449(3) \rightarrow 1.446(2) Å].[§] The trend of increasing 6:6 bond lengths and decreasing 6:5 bond lengths in the series $C_{60} \rightarrow C_{60}^{n-}$ with increasing n is consistent with successive additions of electrons to the t_{1u} LUMO of C_{60} .^{10,16} The mean 6:6 and 5:6 bond lengths in TDAE- C_{60} are 1.389(5) and 1.453(5) Å, respectively. These values are close to those of C_{60}^{-} and also C_{60} in the molecular complexes $[Fe(C_5H_5)_2]C_{60}$ [1.387(6) and 1.450(6) Å]¹⁴ and $TPDP(C_{60})_2(CS_2)_4$ [1.381(6) and 1.451(6) Å].¹¹

Two symmetrical parts of the TDAE molecule are twisted about the C=C double bond and the dihedral angle between the planes formed by the symmetrically equivalent N-C-N group of atoms is equal to 41.7°. The central C-C bond length is 1.408(6) Å, and distances from the central C atoms to the N atoms of the $N(CH_3)_2$ groups are equal to 1.372(3) and 1.369(3) Å. The N-C type bond lengths within the $N(CH_3)_2$ groups are 1.454(4)–1.461(3) Å. The obtained configurations of TDAE are

in reasonable agreement with predictions,¹⁷ which testifies to a charge state of TDAE of +1. There are several short distances between atoms of C_{60} molecule and methyl groups of TDAE. The two contacts, 3.401(4) and 3.482(4) Å, show that there is close interaction between C_{60} and TDAE.

Low temperature X-ray single crystal diffraction studies have allowed access to detailed structural characteristics of an unannealed sample of TDAE- C_{60} . On the basis of this analysis it has been shown that there are very short contacts (3.082 Å) between adjacent C_{60} molecules along the chain of fullerene molecules as well as the presence of close interactions between C_{60} and TDAE.

Notes and references

‡ Crystal data at 11 K: $C_{70}N_4H_{24}$, monoclinic, space group $C2/c$ (No.15), $a = 15.890(8)$, $b = 12.867(7)$, $c = 19.83(3)$ Å, $\beta = 93.6(2)^\circ$, $V = 4046(5)$ Å³, $Z = 4$, $M = 920.99$, $D_c = 1.51$ g cm⁻³, $F(000) = 1888$, Monochromated Mo-K α radiation, $\lambda = 0.71069$ Å, $\mu = 0.89$ cm⁻¹. Data collection was carried out using an Imaging Plate system (rotating anode) equipped with a liquid helium cooling device. 3309 reflections with $I > 3\sigma(I)$ were used in refinement. Atomic parameters were refined via a full-matrix least-squares procedure with anisotropic temperature factors. Hydrogen atoms were located from a difference Fourier map and refined with isotropic thermal coefficients equivalent to that for the bonded carbon atom. Final parameters were: $R = 0.078$, $R_w = 0.076$, $S = 4.36$, 370 variables, 3309 observed reflections (4874 unique reflections), max./min. peak in final diff. map = +0.56 / -0.47 e Å⁻³. CCDC 182/1309. See <http://www.rsc.org/suppdata/cc/1999/1511/> for crystallographic data in .cif format.

§ All the averaged values of bond lengths given there were obtained via single crystal structure analysis at low temperatures, and their accuracies allow for bond length analysis.

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