New complex of fullerene with an organic donor: $(C_{60})_2 \cdot TPDP \cdot (CS_2)$

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The discovery of superconductivity characterized by high temperatures of the superconducting transition[1] in M_3C_{60} salts (M is an alkali metal) and the discovery of ferromagnetic properties in TDAE • C_{60} salts (see Ref. 2) have awakened considerable interest in studying compounds of C_{60} with organic donors. The use of these donors opens up broad possibilities for the synthesis of substances with various packings of C_{60} in the crystal, which finally determines different properties of these compounds. At present, molecular complexes of fullerene with various donors including S- and Te-containing derivatives of tetrathiafulvalene have been prepared.[3,4]

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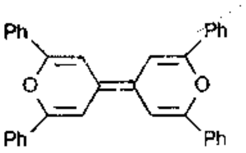
We synthesized the first charge transfer complex of C_{60} with 2,2',6,6'-tetraphenyldipyranylidene (TPDP) as the donor, $(C_{60})_2$ • TPDP • $(CS_2)_4$ (1).



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This compound was obtained by evaporation (for 7 days at ambient temperature under argon) of a solution containing equimolar amounts of TPDP and C_{60} in carbon disulfide, as well-formed black crystals looking as rhombs with a characteristic crater in the middle. Found (%): C. 86.20; H, 0.86; S, 10.88. $C_{158}H_{24}O_2S_8$. Calculated (%): C, 86.00; H, 1.08; S, 11.51.

The TG and DTG curves obtained in thermogravimetric analysis (20 to 700 °C, argon atmosphere) indicate that between 125 °C and 200 °C, this compound loses 12 % of its mass. This corresponds to the complete removal of CS_2 from the complex, which is confirmed by the absence of the band at 1508 cm^{-1} from its IR spectrum. During further heating, in the 320-600 °C temperature range, the donor gradually decomposes; the loss of mass is 15 %. The IR spectrum of the residue (73 % of the total mass) exhibits absorption bands (AB) of the individual C_{60} against the background of a broad band, probably associated with the carbon, resulting from decomposition of TPDP.

The IR spectra (Specord 75-IR, pellets with KBr) contain all the AB corresponding to the components of the complex. The bands at 1425, 1175, 575, and 525 cm^{-1} are due to vibrational modes of C_{60}, their frequencies and the ratios between their intensities are unchanged with respect to individual C_{60}. The band at 1508 cm^{-1} corresponds to v(CS) in CS_2. TPDP is responsible for the AB at 3070, 3038, and 3015 cm^{-1} (v(CH)); 1655, 1592, and 1488 cm^{-1} (v(CC)); 1064 and 911 cm^{-1} (in-plane 5(CCH)); and 755 and 685 cm^{-1} (out-of-plane 8(CH)). As a result of complex formation, the v(CH) and 5(CCH) ,AB shift to the low-frequency region, the v(CC) band is broadened, and the intensity of 8(CH) increases by a factor of 1.5.

The X-ray photoelectron spectrum exhibits no peak associated with the S atom, since CS_2 is removed from the complex during evacuation. The half-widths of C1s peaks exhibited by the complex (1.9 eV) and the initial C_{60} (1.8 eV) are approximately identical, while that exhibited by the donor, TPDP, is somewhat higher (2.2 eV). The charge states of the carbon atoms of TBPD and C_{60} incorporated in the complex are similar, possibly due to the exchange by pi-electrons or due to the fact that fullerene makes the major contribution to the spectrum. The energy of the main plasmon for the complex (hw_p = 25.5 eV) is lower than that for C_{60} (26.1), whic4 is apparently caused by interaction of TPDP (hw_p =21.3 eV) with C_{60}.

The electric conductivity of a single crystal of 1 is 10-7 (Ohm cm)$^{-1}$, which is typical of weak charge-transfercomplexes.

Thus, the (C_{60}) • TPDP • $(CS_2)_4$ compound obtained by us is a molecular complex with weak charge transfer. It is probably formed through pi-pi interaction of the phenyl rings of TPDP with the pi-system of fullerene.

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