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Interaction of Tetrasubstituted Dihalcogenapyranylidenes with Fullerene and Molecular Complex of Fullerene with Tetraphenyldipyranylidene $(C_{60})_2 \cdot TPDP \cdot (CS_2)_4$

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Study of the reaction of new donors, namely tetrasubstituted dihalcogenapyranylidines (DPs) with fullerene was carried out. Molecular complexes of C_{60} with 2,2',6,6'-tetraphenylpyranylidene (TPDP): $(C_{60})_2TPDP(CS_2)_4$ were synthesized. IR-, ESP-, X-ray photoelectron spectra were studied. Thermogravimetrical analysis was carried out. Conductivity of single crystals was 10^{-4} S·cm^{-1} to 10^{-7} S·cm^{-1} for various samples.

The discovery of superconductivity[1] and ferromagnetic properties[2] in fullerene compounds evoked a great interest to the synthesis of fullerene based compounds. Now, C_{60} complexes with various donors are synthesized and described. First of all, they are various S- and Te-containing tetrathiafulvalene derivatives,[3,4] aromatic donors,[5] and some others. All these donors form weak molecular complexes with C_{60}. Fully ionic complexes are synthesized with strong electron donors.[6,7] However, the preparation of complexes and ion-radical salts is somewhat difficult. This is associated with certain peculiarities of C_{60}. Fullerene is a weak acceptor, therefore very strong donors such as alkali metals or TDAE[1,2] are needed for the formation of its ion-radical salts. A high symmetry of C_{60} molecule requires a certain steric structure of a donor molecule. The most suitable are organic donors with a sufficient flexibility, which contain a heteroatom or aromatic substituents.

We report on the study of the reaction of new donors, namely tetrasubstituted dihalcogenapyranylidenes (DPs) with fullerene and the synthesis of a new complex of C_{60} with the donor of this class, 2,2',6,6'-tetraphenylpyranylidene (TPDP): $TPDP(C_{60})_2(CS_2)_4$ (Figure 1).

(DPs) have quite low ionization potentials (I_1). For example, for DP (R = Ph) I_1 value in X = O, S, Se series constitutes 5.80 eV, 5.84 eV, and 6.10 eV, respectively.[8] It is known that the planes of halcogen containing heterocycles may turn by 10° about the central C=C bond. Alkyl and phenyl substituents emerge from the plane of DP skeleton, the dihedral angle between the planes of phenyl rings and the heterocycle in TPDP constitutes 10.2° and 7.6°.[9] These angles increase at the formation of ion-radical salts of DP in TPDP complex, and with iodine they are equal to 25°.[10] All these factors make DPs interesting for the study of their reactions with fullerene.

The C_{60} reaction with DP with X = O, S, Se, R = Me, Ph was used. The equimolar solutions of the starting DP and C_{60} were mixed in CS_2 (the C_{60} concentration was 1 mg/ml - 3 mg/ml) and the solvent was evaporated from the reaction mixture during 3-7 days under argon at room temperature. The reaction mixture was washed with an ethyl alcohol and dried in air. The reaction products were separated under microscope and studied by using IR-spectroscopy. In all cases the starting donor and the adduct of C_{60} with CS_2 (%S=3.2), which is crystallized as extended black plates, were identified. TPDP in addition yielded densed rhomb-like crystals. This reaction was studied in detail. The crystals were found to be attributed to $(C_{60})_2 \cdot TPDP \cdot (CS_2)_4$ complex.

Since TPDP is easily oxidized in air especially in a solution, it was purified by passing the solution, in tetrahydrofuran through an activated Al_2O_3 under argon. The degree of the purity was tested by using thin layer chromatography.

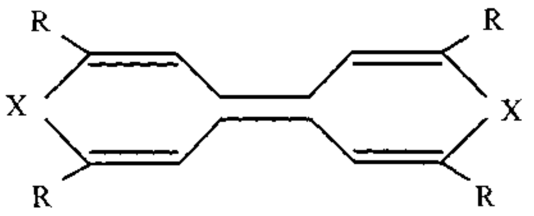

Figure 1 R = Ph, Me, X = Se, S, 0, TPDP: X = 0, R = Ph.

The evaporation of CS_2 from the equimolar solutions of C_{60} TPDP (the concentration of C_{60} was 1 mg/ml - 3 mg/ml) during a week produced black, well-formed rhombic crystals (A) with the length from 1 mm to 2 mm with 50 % yield. The yield of the complex decreased with the time of the solvent evaporation and was equal to 2 % - 5 % for several hours. The basic product of the reaction in this case was the adduct of C_{60} with CS_2.

The elemental analysis of (A) yields the formula $C_{158}H_{24}O_2S_8$ with C = 86.20 %, H = 0.86 %, S = 10.88 %. Calculated values are C = 86.00 %, H = 1.08 %, S = 11.51 %, O = 1.44 %.

If the evaporation of the saturated equimolar solutions of C_{60} (7 mg of C_{60} per 1 ml CS_2) and TPDP is carried out during 20 days, the complex crystallized with 90 % yield. In this case the formation of the crystals of two forms was observed. In addition to rhombic crystals, tetrahedral pyramids (B) 2 mm long were formed. Their yield sharply decreased with a decrease of concentration of the reaction solutions.

The elemental analysis of B yields the formula $C_{158}H_{24}O_2S_8$ with C = 85.12 %, H = 1.5 %, S = 12.52 % . Calculated values are C = 86.00 %, H = 1.08 %, S = 11.51 %, O = 1.44 %.

In both cases the reaction mixture was washed with the ethyl alcohol. The crystals of the complex were separated under a microscope. The complex formation was established by using IR spectra (Figure 2).

The washing of the crystals with heptane and ether results in a partial removal of CS_2 from the surface and the utilization of tetrahydrofuran results in the leaching of TPDP, producing the skeleton of C_{60}.

The thermogravimetric analysis (293 K to 973 K, argon) was carried out. It is seen from TG and DTG curves that A and B losses amount to 12 % of its mass in 398 K - 473 K temperature range, which corresponds to a full removal of CS_2 from the complex and is confirmed by the absence of the 1508 cm^{-1} band in IR spectrum. The further heating in 593 K - 873 K range results in the partial donor decomposition, the loss of the mass being equal to 15 %.

IR spectra of both complexes ("Specord 75IR, tablet in KBr, the error is ±1 cm^{-1}) contain a full set of the absorption bands of the complex components. The frequencies and the ratio of the intensities of the C_{60} bands remain unchanged with respect to the individual C_{60}. The absorption band at 1508 cm^{-1} is attributed to ν_{CS} in CS_2. The complex formation results in the shift of some absorption bands of the donor to a low frequency range. The absorption bands at 1064 cm^{-1} and 911 cm^{-1} are broadened and the intensity of δ_{CH} at 755 cm^{-1} and 685 cm^{-1} increases 1.5 times. The changes of the intensities of the donor absorption bands can be caused by the changes of the dipole moments of CH bonds in TPDP due to π-π interaction of C_{60} and donor.

X-ray photoelectron spectrum (XP) of A shows no peak attributed to sulfur, since CS_2 is removed from the complex during evacuation. The halfwidth of the peak C_1S in the initial C_{60} practically coincides with that in 1A (Table).

This is the evidence that charge states of carbon atoms are approximately equal, probably due to π-electron exchange, but the contribution of C_{60} is the greatest. The energy of the basic plasmon (25.5 eV) is less in A than that in C_{60} (26.2 eV).[11]

Table

	C_1S (eV)	$h\omega_p$ (eV)
C_{60}	1.8	26.1
TPDP	2.2	21.3
1A	1.9	25.5

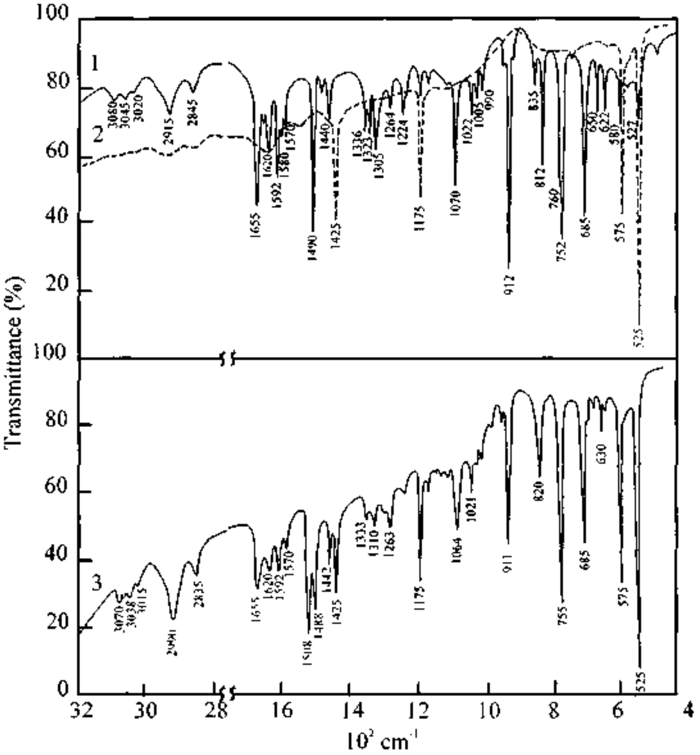

Figure 2 IR-spectra of TPDP (1), C_{60} (2) and of the complex TPDP·$(C_{60})_2$·$(CS_2)_4$ (3) (tablet in KBr, Specord 75 IR).

Conductivity (σ) was measured by a standard four-probe technique. σ of (A) single crystals amounts to 10^{-7} S·cm^{-1} and that for (B) single crystals is equal to 10^{-4} S·cm^{-1}. ESR signal attributed to C_{60} is absent.

Thus, the analysis of IR- and XP-spectra, together with the conductivity measurements shows that the compound obtained, namely, $(C_{60})_2$·TPDP·$(CS_2)_4$ appears as a molecular complex probably formed as a result of the π-π interaction between TPDP and C_{60} phenyl rings. DPs possess a different ability for a complex formation with C_{60} in CS_2. This is, most probably, attributed to the differences in steric factors and ionization potentials of DP. A lower ionization potential of TPDP as compared to other DPs together with the presence of four phenyl substituents promote the formation of TPDP complex with fullerene. The formation of two A and B modifications of the crystals can be associated with different reasons: different orientations of phenyl rings of the donor, the small differences in amount of CS_2 which enters in the complex, and finally the quality and more ordered structure of the crystals.

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