Synthesis and crystal structure of the molecular complex of fullerene C_{60} with 2-(4-thiono-1,3-dithiolan-5-ylidene)-4,5-dimethyl-1,3-diselenol ($C_{60}\cdot 2DTDS$)

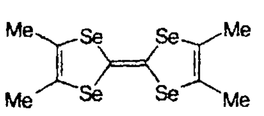
N. G. Spitsina, S. V. Konovalikhin, A. S. Lobach, G. V. Shilov, and O. A. D'yachenko*

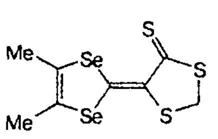
*Institute of Problems of Chemical Physics, Russian Academy of Sciences,
142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: +7 (096) 515 3588. E-mail: spitsina@icp.ac.ru*

A new molecular complex of fullerene C_{60} with 2-(4-thiono-1,3-dithiolan-5-ylidene)-4,5-dimethyl-1,3-diselenol ($C_{60}\cdot 2DTDS$) was synthesized for the first time. The crystal and molecular structures of $C_{60}\cdot 2DTDS$ were established by X-ray diffraction analysis. The crystal structure of $C_{60}\cdot 2DTDS$ is layered: the layers of fullerene C_{60} molecules alternate with those of DTDS molecules. The molecules of C_{60} and DTDS are associated by shortened C...Se, C...S, and C...C contacts forming a three-dimensional network of secondary interactions in the crystal. The $C_{60}\cdot 2DTDS$ crystals have a specific feature: the absence of shortened C...C contacts between the nearest C_{60} molecules despite the short distances between their centers, 9.948(2) and 10.054(2) Å. The electrochemical properties of DTDS were studied by cyclic voltammetry in $CH_2Cl_2/0.05$ *M* Bu_4NPF_6 at room temperature. DTDS undergoes reversible one-electron reduction to a radical anion [$E^\circ = -1.81$ V ($Fc^{0/+}$)] and reversible one-electron oxidation to a radical cation [$E^\circ = +0.37$ V ($Fc^{0/+}$)]. The degree of charge transfer in $C_{60}\cdot 2DTDS$, $\Delta N = 0.18$, calculated from the electrochemical parameters of DTDS and C_{60} indicates that this compound is a molecular complex with a partial charge transfer.

Key words: fullerene C_{60}, 2-(4-thiono-1,3-dithiol-5-ylidene)-4,5-dimethyl-1,3-diselenol (DTDS), electrochemical properties, crystal and molecular structures, X-ray diffraction analysis, intermolecular interactions.

It is known[1—4] that fullerene C_{60} forms charge-transfer molecular complexes (CTC) with organic electron donors. They are of interest as possible starting subjects for doping with alkali metals and as semiconductors with unusual structures and properties. The specific feature of the C_{60} molecule as an acceptor is its spherical shape and high negative reduction potentials.[5] The structures and properties of fullerene CTC considerably depend on the structures and electrochemical redox potentials of the donors. We have previously[3,4] obtained molecular complexes of C_{60} with a symmetrical selenium analog of tetrathiafulvalene, *viz.*, tetramethyltetraselenafulvalene (TMTSF): $2C_{60}\cdot 2TMTSF\cdot C_6H_6$ (**1**) and $C_{60}\cdot TMTSF\cdot 2CS_2$, which have layered structures and are the initial matrices for further doping. However, the question about a possibility of forming layered structures with non-symmetrical systems obtained by the substitution of an unsaturated five-membered sulfur-containing heterocycle for one selenium-containing fragment in the symmetrical TMTSF molecule remained unclear.


TMTSF


DTDS

In this work, we synthesized a new molecular complex of fullerene C_{60} with 2-(4-thiono-1,3-dithiolan-5-ylidene)-4,5-dimethyl-1,3-diselenol (DTDS), $C_{60}\cdot 2DTDS$ (**2**), and solved the structure of its single crystal. The electrochemical properties of non-symmetrical chalcogenide DTDS were studied for the first time. The electrochemical parameters of DTDS and C_{60} were used for the calculation of the degree of charge transfer in the complex synthesized.

Experimental

Measurement of the electrochemical parameters of DTDS. Voltammetric measurements were carried out at room temperature in an atmosphere of dry Ar in CH_2Cl_2, which was purified by refluxing over P_2O_5 and distillation. An 0.05 *M* solution of Bu_4NPF_6 was used as the supporting electrolyte. All measured potentials are presented relative to that of the ferrocene$^{0/+}$ ($Fc^{0/+}$) redox pair by referring the potential of the reference electrode (Ag/AgCl/4 *M* aqueous solution of LiCl), which was separated from the solution under study in the cell by a bridge filled with a solution of the supporting electrolyte, to the potential of the $Fc^{0/+}$ redox transition ($E^\circ = 0.43$ V, SCE in CH_2Cl_2). All cyclic voltammograms were obtained in the absence of Fc, which was added at the end of each experiment. A glassy-carbon disk electrode (diameter of

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3 mm, Tokai, Japan) was used as the working electrode. Voltammetric measurements were carried out using a PAR-175 signal generator with compensation of ohmic losses. Voltammograms were recorded on an RE0074 two-coordinate recorder.

Synthesis of complex 2. Single crystals of 2 were prepared from a benzene solution containing C_{60} and DTDS in a ratio of 1 : 2. Freshly distilled, dehydrated, and degassed benzene was used. Fullerene C_{60} (purity 99.99% according to HPLC) was prepared by the evaporation of graphite rods in an electric arc in an Ar atmosphere and purified by the known procedure.[6] The structure and procedure of the synthesis of the starting DTDS were described earlier.[7] The starting reagents, C_{60} (14.4 mg) and DTDS (14.3 mg), were dissolved separately in 20 mL of benzene, and the solutions were filtered and mixed. The mixture was heated for 30 min at 50 °C in an Ar atmosphere, cooled to room temperature, and exposed to air for 10—15 days. The solvent was slowly evaporated to a volume of 2—3 mL, and small lustrous black prisms were obtained. The crystals were filtered off, washed with acetone, and dried *in vacuo*.

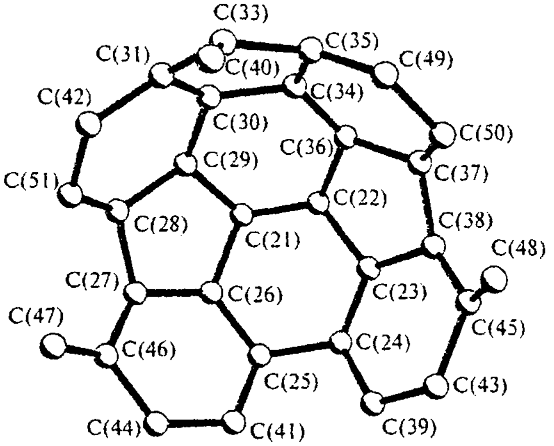

Fig. 1. C_{60} molecule (only atoms arranged in the independent area of the unit cell are designated).

X-ray diffraction analysis. A crystal of 2 (0.20×0.30×0.35 mm) close in shape to a rectangular prism was taken for XRD. The main crystallographic data of 2: $C_{60} \cdot 2C_8H_8S_3Se_2$, molecular weight 1437.09, triclinic system, a = 13.255(2) Å, b = 9.948(2) Å, c = 10.054(2) Å, α = 101.80(2)°, β = 95.05(2)°, γ = 107.50(2)°, V = 1221.7(4) Å^3, space group $P\bar{1}$, Z = 1, d_{calc} = 1.953 g cm^{-3}, $F(000)$ = 704. The measurement of 5027 independent non-zero reflections and determination of the unit cell parameters were performed on a KM-4 four-circle automated diffractometer (Kuma Diffraction) (Cu-Kα radiation, λ = 1.5418 Å, a graphite monochromator, ω/2θ scan mode, 3.54° < θ < 80.09°). The structure was solved by the direct method and a series of subsequent Fourier syntheses by the SHELX-86 and SHELXL-93 programs.[8,9] Hydrogen atoms were revealed from the difference Fourier syntheses. All non-hydrogen atoms were refined by the full-matrix least-squares method in the anisotropic approximation, and H atoms were refined in the isotropic approximation. The finite R factor was equal to 0.0496 from 3291 reflections with the intensities $I \geq 2\sigma(I)$. Absorption was not applied, μ(Cu-Kα) = 64.39 cm^{-1}. The coordinates of atoms in the structure of 2 are

Table 1. Coordinates of Se, S, C (×10^4), and H (×10^3) atoms and equivalent isotropic thermal factors ($U_{iso} \cdot 10^3$/Å^2) in the complex $C_{60} \cdot$2DTDS (2)

Atom	x	y	z	U_{iso}
		DTDS molecule		
Se(1)	−1411(1)	5049(1)	5313(1)	35(1)
Se(2)	76(1)	5477(1)	8084(1)	39(1)
S(1)	−780(1)	2142(1)	7998(1)	51(1)
S(2)	−2672(1)	11(1)	6151(1)	54(1)
S(3)	−2851(1)	1962(1)	4379(1)	58(1)
C(1)	−984(2)	4199(3)	6655(3)	32(1)
C(2)	−1402(2)	2749(3)	6673(4)	34(1)
C(3)	−472(3)	6939(4)	6209(4)	40(1)
C(4)	161(3)	7121(4)	7402(4)	40(1)
C(5)	−513(4)	8107(4)	5510(5)	52(1)
C(6)	942(4)	8535(4)	8254(5)	64(1)
C(7)	−1954(4)	498(4)	7749(5)	68(1)
C(8)	−2260(3)	1677(4)	5714(4)	45(1)
H(1)	−7(5)	906(6)	606(6)	98(20)
H(2)	−31(4)	791(5)	500(5)	62(16)
H(3)	−88(3)	835(4)	585(4)	32(11)
H(4)	94(3)	929(4)	797(4)	56(13)
H(5)	72(5)	892(7)	887(7)	93(26)
H(6)	148(5)	857(9)	860(8)	98(34)
H(7)	−226(2)	65(2)	822(2)	90(6)
H(8)	−164(4)	−10(5)	781(6)	99(20)
		C_{60} molecule		
C(21)	−2614(3)	5676(5)	−1419(5)	61(1)
C(22)	−2793(3)	6969(4)	−1328(5)	56(1)
C(23)	−2692(3)	7940(4)	32(5)	52(1)
C(24)	−2412(3)	7567(4)	1219(5)	54(1)
C(25)	−2210(3)	6198(4)	1128(5)	55(1)
C(26)	−2301(3)	5280(5)	−170(5)	53(1)
C(27)	−2800(3)	3733(5)	−374(6)	60(1)
C(28)	−3426(3)	3178(5)	−1782(5)	60(1)
C(29)	−3309(3)	4393(5)	−2411(4)	53(1)
C(30)	−4203(3)	4458(5)	−3284(4)	52(1)
C(31)	−5197(3)	3304(4)	−3504(4)	49(1)
C(32)	−4371(4)	2111(4)	−2021(5)	60(1)
C(33)	−6032(4)	3949(5)	−3549(4)	60(1)
C(34)	−4373(4)	5818(4)	−3144(4)	54(1)
C(35)	−5536(4)	5531(5)	−3323(4)	56(1)
C(36)	−3706(3)	7035(4)	−2222(4)	53(1)
C(37)	−4142(3)	8042(4)	−1421(4)	51(1)
C(38)	−3527(3)	8605(3)	−21(4)	49(1)
C(39)	−2959(3)	7820(4)	2381(4)	53(1)
C(40)	−6934(3)	3419(5)	−3016(4)	58(1)
C(41)	−2627(3)	5567(5)	2216(4)	52(1)
C(42)	−5267(4)	2135(4)	−2877(5)	55(1)
C(43)	−3757(4)	8430(4)	2319(5)	55(1)
C(44)	−3092(3)	4075(4)	1963(4)	52(1)
C(45)	−4040(3)	8832(3)	1070(5)	50(1)
C(46)	−3184(3)	3158(4)	651(6)	59(1)
C(47)	−4223(3)	1991(4)	411(6)	62(1)
C(48)	−5199(4)	8515(4)	875(6)	62(1)
C(49)	−5940(3)	6492(4)	−2551(4)	58(1)
C(50)	−5227(3)	7780(3)	−1571(4)	52(1)

presented in Table 1, the bond lengths and bond angles in the C_{60} and DTDS molecules are presented in Tables 2 and 3, and designations of atoms in the C[illegible] molecule are indicated in Fig. 1.

Results and Discussion

Oxidation and reduction of DTDS were studied on a glassy-carbon electrode in CH_2Cl_2 at room temperature. Four diffusion-controlled (I_p [illegible]$^{-1/2}$ = const, where I_p is the height of the peak) peaks (A, B, C, and D, Fig. 2) are observed on the cyclic voltammograms (CV) at sweeps of 20—200 mV s^{-1}. As can be seen in Fig. 2, two consecutive one-electron oxidation peaks (A and B) and two reduction peaks (C and D) are observed on CV of DTDS. DTDS undergoes reversible one-electron oxidation to a radical cation (E° = +0.37 V ($Fc^{0/+}$)) ($E^\circ = (E_p^c + E_p^a)/2$, where [illegible], E_p^c, and E_p^a are the formal redox potential and those of the cathodic and anodic responses, respectively) and irreversible oxidation to a dication (E_p^a = −1.[illegible]3 V ($Fc^{0/+}$)). DTDS is reduced in two one-electron successive stages: the first step is reversible reduction to the radical anion (E° = −1.81 V ($Fc^{0/+}$)), and the second stage is irreversible reduction to the dianion (E_p^c = −2.26 V ($Fc^{0/+}$)).

It is known[10] that the degree of charge transfer between a donor (D) and an acceptor (A) in a molecule (AD) formed by the interaction of these compounds in solutions depends on their electrochemical redox potentials.

The degree of charge transfer (ΔN in fractions of an electron) can be estimated from Eq. (1)

$$\Delta N = (\chi_A - \chi_D)/(G_A + G_D), \qquad (1)$$

where χ_A and χ_D are the electrochemical electronegativities of A and D ($\chi = (E^{Ox} + E^{Red})/2$, E^{Ox} and E^{Red} are the reversible oxidation and reduction potentials), and G_A and G_D are the inherent electrochemical gaps (G =

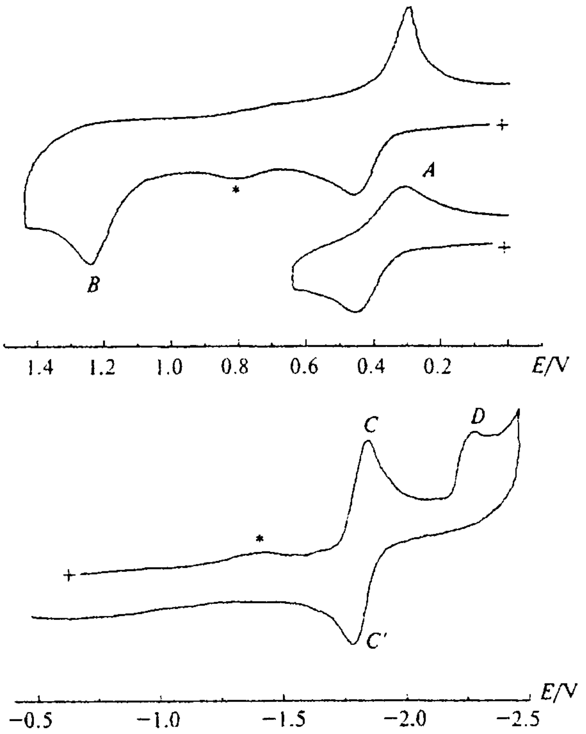

Fig. 2. Cyclic voltammograms of a solution of DTDS ($3 \cdot 10^{-4}$ mol L^{-1}) on a glassy-carbon electrode (v = 200 mV s^{-1}) in CH_2Cl_2/0.05 M Bu_4NPF_6 at −20 °C. The origin of peaks marked with asterisks is not established.

Table 2. Bond lengths (d) in complex **2**

Bond	d/Å	Bond	d/Å	Bond	d/Å
DTDS molecule		C(22)—C(23)	1.473(6)	C(34)—C(35)	1.467(7)
Se(1)—C([illegible])	1.865(4)	C(23)—C(24)	1.373(7)	C(34)—C(36)	1.364(5)
Se(1)—C([illegible])	1.897(3)	C(23)—C(38)	1.452(6)	C(35)—C(49)	1.372(7)
Se(2)—C([illegible])	1.865(3)	C(24)—C(25)	1.452(6)	C(36)—C(37)	1.444(6)
Se(2)—C([illegible])	1.875(4)	C(24)—C(39)	1.446(7)	C(37)—C(38)	1.470(6)
S(1)—C(2)	1.804(4)	C(25)—C(26)	1.403(7)	C(37)—C(50)	1.372(6)
S(1)—C(7)	1.842(4)	C(25)—C(41)	1.440(7)	C(38)—C(45)	1.357(7)
S(2)—C(7)	1.691(6)	C(26)—C(27)	1.444(6)	C(39)—C(40a)	1.476(7)
S(2)—C([illegible])	1.741(4)	C(27)—C(28)	1.482(7)	C(39)—C(43)	1.371(7)
S(3)—C(8)	1.612(5)	C(27)—C(46)	1.344(8)	C(40)—C(41a)	1.452(7)
C(1)—C([illegible])	1.385(4)	C(28)—C(29)	1.449(7)	C(41)—C(44)	1.385(6)
C(2)—C([illegible])	1.420(5)	C(28)—C(32)	1.341(6)	C(42)—C(43a)	1.457(7)
C(3)—C([illegible])	1.349(5)	C(29)—C(30)	1.437(6)	C(43)—C(45)	1.446(7)
C(3)—C([illegible])	1.487(6)	C(30)—C(31)	1.428(6)	C(44)—C(46)	1.414(7)
C(4)—C([illegible])	1.503(5)	C(30)—C(34)	1.418(7)	C(44)—C(49a)	1.465(6)
		C(31)—C(33)	1.438(7)	C(45)—C(48)	1.459(7)
C_{60} molecule		C(31)—C(42)	1.416(7)	C(46)—C(47)	1.472(6)
C(21)—C(22)	1.363(6)	C(32)—C(42)	1.413(7)	C(47)—C(48a)	1.356(7)
C(21)—C(26)	1.454(7)	C(32)—C(48a)	1.494(7)	C(47)—C(50a)	1.444(7)
C(21)—C(29)	1.443(6)	C(33)—C(35)	1.471(6)	C(49)—C(50)	1.448(5)
C(22)—C(36)	1.469(6)	C(33)—C(40)	1.358(7)		

Note. Symmetry matrix for equivalent atoms (a): $-x-1, -y+1, -z$.

Table 3. Bond angles (ω) in complex **2**

Angle	ω/deg
DTDS molecule	
C(1)—Se(1)—C(3)	93.7(2)
C(1)—Se(2)—C(4)	94.7(2)
C(2)—S(1)—C(7)	91.9(2)
C(7)—S(2)—C(8)	99.3(2)
Se(1)—C(1)—Se(2)	114.8(2)
Se(1)—C(1)—C(2)	125.6(2)
Se(2)—C(1)—C(2)	119.6(3)
S(1)—C(2)—C(1)	117.5(2)
S(1)—C(2)—C(8)	116.6(3)
C(1)—C(2)—C(8)	125.9(3)
Se(1)—C(3)—C(4)	118.8(3)
Se(1)—C(3)—C(5)	115.5(3)
C(4)—C(3)—C(5)	125.7(3)
Se(2)—C(4)—C(3)	118.0(2)
Se(2)—C(4)—C(6)	116.1(3)
C(3)—C(4)—C(6)	125.9(4)
S(1)—C(7)—S(2)	112.2(3)
S(2)—C(8)—S(3)	122.0(2)
S(2)—C(8)—C(2)	113.6(3)
S(3)—C(8)—C(2)	124.3(3)
C_{60} molecule	
C(22)—C(21)—C(29)	119.8(4)
C(22)—C(21)—C(26)	119.6(4)
C(26)—C(21)—C(29)	109.4(4)
C(21)—C(22)—C(23)	120.0(4)
C(21)—C(22)—C(36)	119.6(4)
C(23)—C(22)—C(36)	107.8(4)
C(22)—C(23)—C(24)	120.9(4)
C(22)—C(23)—C(38)	108.3(4)
C(24)—C(23)—C(38)	118.9(4)
C(23)—C(24)—C(25)	119.4(4)
C(23)—C(24)—C(39)	119.9(4)
C(25)—C(24)—C(39)	108.4(4)
C(24)—C(25)—C(26)	119.5(5)
C(24)—C(25)—C(41)	109.4(4)
C(26)—C(25)—C(41)	118.9(4)
C(21)—C(26)—C(25)	120.7(4)
C(21)—C(26)—C(27)	108.0(4)
C(25)—C(26)—C(27)	119.2(5)
C(26)—C(27)—C(28)	107.1(5)
C(26)—C(27)—C(46)	121.3(5)
C(28)—C(27)—C(46)	119.7(4)
C(27)—C(28)—C(29)	108.4(4)
C(27)—C(28)—C(32)	119.7(5)
C(29)—C(28)—C(32)	119.8(4)
C(21)—C(29)—C(28)	107.1(4)
C(21)—C(29)—C(30)	120.6(4)
C(28)—C(29)—C(30)	120.3(4)
C(29)—C(30)—C(31)	118.1(4)
C(29)—C(30)—C(34)	118.0(4)
C(31)—C(30)—C(34)	110.9(4)
C(30)—C(31)—C(33)	106.8(4)
C(30)—C(31)—C(42)	119.4(4)
C(33)—C(31)—C(42)	121.8(4)
C(28)—C(32)—C(48a)	120.5(5)
C(42)—C(32)—C(28)	121.6(5)
C(42)—C(32)—C(48a)	106.1(4)
C(31)—C(33)—C(35)	108.7(4)
C(31)—C(33)—C(40)	120.4(5)
C(35)—C(33)—C(40)	119.4(5)
C(30)—C(34)—C(35)	107.2(4)
C(30)—C(34)—C(36)	121.4(4)
C(35)—C(34)—C(36)	120.0(4)
C(33)—C(35)—C(34)	106.3(4)
C(33)—C(35)—C(49)	121.8(4)
C(34)—C(35)—C(49)	119.4(4)
C(22)—C(36)—C(34)	120.7(4)
C(22)—C(36)—C(37)	107.3(4)
C(34)—C(36)—C(37)	120.1(4)
C(36)—C(37)—C(38)	109.5(4)
C(36)—C(37)—C(50)	120.5(3)
C(38)—C(37)—C(50)	117.9(4)
C(23)—C(38)—C(37)	107.0(4)
C(23)—C(38)—C(45)	120.9(4)
C(37)—C(38)—C(45)	119.8(4)
C(24)—C(39)—C(40a)	106.3(4)
C(24)—C(39)—C(43)	121.0(4)
C(43)—C(39)—C(40a)	120.9(4)
C(33)—C(40)—C(39a)	119.1(5)
C(33)—C(40)—C(41a)	118.9(4)
C(39a)—C(40)—C(41a)	109.2(4)
C(25)—C(41)—C(40a)	106.7(4)
C(25)—C(41)—C(44)	119.4(4)
C(44)—C(41)—C(40a)	122.8(4)
C(31)—C(42)—C(32)	120.8(4)
C(31)—C(42)—C(43a)	117.2(4)
C(32)—C(42)—C(43a)	110.1(4)
C(39)—C(43)—C(42a)	120.6(4)
C(39)—C(43)—C(45)	118.8(4)
C(45)—C(43)—C(42a)	108.4(4)
C(41)—C(44)—C(46)	121.4(4)
C(41)—C(44)—C(49a)	118.0(4)
C(46)—C(44)—C(49a)	108.8(3)
C(38)—C(45)—C(43)	120.5(4)
C(38)—C(45)—C(48)	120.9(4)
C(43)—C(45)—C(48)	106.6(4)
C(27)—C(46)—C(44)	119.9(4)
C(27)—C(46)—C(47)	121.4(5)
C(44)—C(46)—C(47)	106.9(4)
C(46)—C(47)—C(48a)	119.1(5)
C(46a)—C(47)—C(50)	109.5(4)
C(48a)—C(47)—C(50a)	118.9(4)
C(32a)—C(48)—C(47a)	119.7(4)
C(45)—C(48)—C(32a)	108.7(4)
C(45)—C(48)—C(47a)	120.1(5)
C(35)—C(49)—C(44a)	119.0(4)
C(35)—C(49)—C(50)	120.4(4)
C(50)—C(49)—C(44a)	108.6(4)
C(37)—C(50)—C(47a)	122.4(4)
C(37)—C(50)—C(49)	119.7(4)
C(49)—C(50)—C(47a)	106.2(4)

Note. Symmetry matrix for equivalent atoms (a): $-x-1, -y+1, -z$.

($E^{\mathrm{Ox}} - E^{\mathrm{Red}}$)) of these molecules. The degree of charge transfer for the donor (DTDS) and acceptor (C_{60})* calculated by Eq. (1) is equal to 0.18. Based on ΔN = 0.18, we may assume that the interaction of DTDS and fullerene C_{60} affords a CTC rather than a radical ionic salt. For example, the degree of charge transfer for the authentic radical ionic salt of C_{60} with cobaltocene[12] ($[Cp_2Co^+] \cdot [C_{60}^-] \cdot PhCN$) calculated by Eq. (1) is equal to 0.58. The XRD data of the $C_{60} \cdot 2DTDS$ crystals confirm this assumption: C...C, C...S, and C...Se contacts of fullerene C_{60} and DTDS molecules are shorter than the sums of van der Waals radii of the C, S, and Se atoms.

A crystal of **2** has a layered structure: the layers of C_{60} molecules and those of DTDS molecules alternate along the *a* axis of the unit cell (Figs. 3 and 4). The nearest environment of each C_{60} molecule is formed of six C_{60} molecules in the fullerene layer and six DTDS molecules (three molecules from each adjacent layer) (see Fig. 4). The C_{60} molecule is associated with four adjacent DTDS molecules by C...C, C...S, and C...Se contacts whose lengths are shorter than the sums of van der Waals radii of the C (1.70 Å), S (1.85 Å), and Se (2.00 Å) atoms.[13] The shortened contacts form a three-dimensional network in the crystal (see Figs. 3 and 4, Table 4). The S(3)...C(4[illegible]) and S(3)...C(49) contacts unify the C_{60} and DTDS molecules in chains parallel to the *b* axis of the unit cell of the crystal (see Fig. 3). The remaining shortened C...C, C...S, and C...Se contacts form a two-dimensional network of contacts in the *ac*

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* The reversible oxidation and reduction potentials of fullerene C_{60} are the following: $E^{\mathrm{Ox}} = +1.26$ V, $E^{\mathrm{Red}} = -1.06$ V ($Fc^{0/+}$) (see Ref. 11).

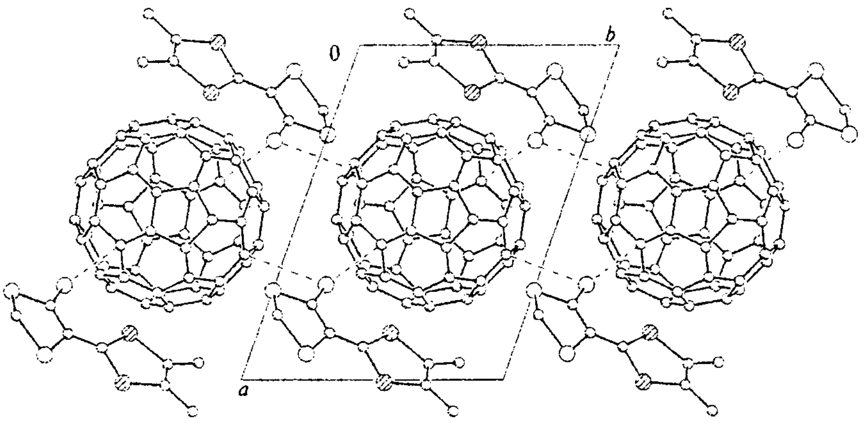

Fig. 3. Projection of crystal structure **2** on the *ab* plane of the unit cell.

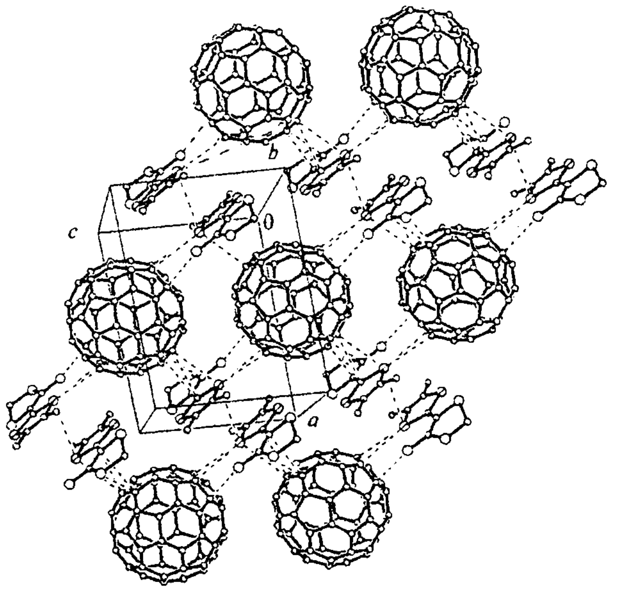

Fig. 4. Shortened intermolecular contacts in crystal **2**.

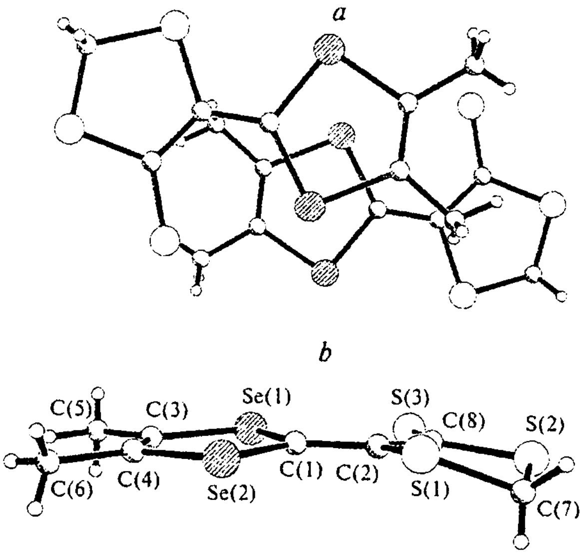

Fig. 5. Overlap of DTDS molecules in the dimer (*a*) and conformation of a DTDS molecule in crystal **3** (*b*).

Table 4. Shortened intermolecular contacts (*d*) in structure **2**

Contact	*d*/Å	Matrix
Se(1)...Se(1)	3.873(3)	$-x$, $1-y$, $1-z$
Se(1)...C(29)	3.549(5)	x, y, $z+1$
Se(1)...C(41)	3.580(5)	x, y, z
Se(1)...C(44)	3.641(5)	x, y, z
S(3)...C(43)	3.484(5)	x, $y-1$, z
S(3)...C(49)	3.232(6)	$-x-1$, $1-y$, $-z$
C(1)...C(29)	3.345(8)	x, y, $z+1$
C(2)...C(28)	3.307(8)	x, y, $z+1$
C(8)...C(28)	3.387(8)	x, y, $z+1$

plane of the unit cell of the crystal (see Fig. 4). The distances between the centers of translationally identical C_{60} molecules are equal to 9.948(8) Å along the *b* axis and 10.054(8) Å along the *c* axis. In molecular complexes of fullerenes, the distances between the centers of the C_{60} molecules usually lie[12,14–18] in the interval of 10.01–10.12 Å, and the C_{60} molecules have several shortened C...C contacts with each other. The only exception is the $2C_{60} \cdot 2TMTSF \cdot C_6H_6$ complex (**1**), in which the distances between the centers of the adjacent C_{60} molecules are equal to 10.06(7) Å, the shortened C...C contacts between them being absent.[3] One of the shortest distances between the centers of the C_{60} molecules, as compared to those in complex **1** and other molecular complexes of C_{60}, was observed in the structure of **2**; however, in complex **2** the shortened $C_{60}...C_{60}$ contacts are absent. Comparison of the geometry of molecular complexes **1** and **2** suggests the following: it is not correct to estimate the efficiency of intermolecular $C_{60}...C_{60}$ interactions using only the data on the distances between the geometric centers of the fullerene molecules; the mutual orientation of the C_{60} molecules should also be taken into account.

In the crystal of **2**, the fullerene C_{60} molecule is centrosymmetric and has a shape close to the sphere: the minimum and maximum distances of the atoms from the center are 3.526(9) and 3.536(9) Å, respectively, and the average radius of the sphere is 3.529(9) Å. In the five-membered cycles, the lengths of 30 C—C bonds of the d_{56} type vary within the 1.418(7)—1.494(7) Å interval, and the average bond length of the d_{56} type is equal to 1.442(8) Å. In the six-membered cycles, 15 C=C bonds of the d_{66} type range from 1.341(6) to 1.413(9) Å, and the average bond length of the d_{66} type is 1.372(9) Å. The C—C—C bond angles in the five-membered cycles range from 106.3(4) to 109.4(5)°, and those in the six-membered cycle vary from 117.2(4) to 122.8(4)°.

In the layer formed by the DTDS molecules, the latter form peculiar dimers bound by a center of symmetry (Fig. 5). Therefore, in the dimers the molecules are parallel and oriented relative to each other according to the "head-to-tail" type. The dimers contain one shortened Se...Se contact (see Fig. 5, *a*, Table 3). Overlap of the DTDS molecules in the dimer is shown in Fig. 5. The distance between the medium planes of the molecules in the dimer is equal to 3.642 Å.

The structure of the DTDS molecule in the crystal of **2** is similar to that in the single crystal of DTDS (**3**).[7] In both **2** and **3** crystals, the Se-heterocycle is planar (the maximum deviation of the atoms from the mean plane of the heterocycle in crystal **2** is less than 0.01 Å), and the bond lengths and bond angles in these heterocycles coincide within experimental errors. The S-heterocycle is non-planar, and only the S(1), C(2), C(8), and S(3) atoms are coplanar. The S(2) atom deviates by 0.32 Å from the mean plane of the heterocycle, whereas the C(7) atom deviates by −0.31 Å. The same conformation was observed for DTDS molecules in crystal **3**. Thus, the involvement of DTDS molecules in intermolecular interactions with C_{60} molecule has no effect on its conformation. The values of the bond lengths and bond angles in the S-heterocycle of the DTDS molecule in crystals **2** and **3** are close, except for the S(2)—C(7) and C(8)=S(3) bonds. In crystal **3**, both bonds are shortened as compared to similar bonds in the DTDS molecule in crystal **2**: the former is shortened by almost 0.08 Å, and the latter is shortened by 0.04 Å. The reasons for this bond shortening are yet unclear.

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