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Crystal Structure of C_{70} Molecular Complex with 9,9'-*trans*-Bis(telluraxanthenyl): *BTX* · C_{70} · $(CS_2)_{0.5}$

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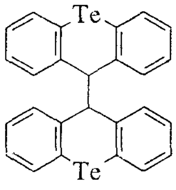
Abstract—The structure of molecular complex *BTX* · $C_{70}(CS_2)_{0.5}$ ($C_{96.5}H_{18}Te_2S$) is determined by single-crystal X-ray diffraction [$a = 10.927(3)$, $b = 21.068(5)$, and $c = 24.147(7)$ Å; $V = 5558.9$ Å^3; space group $Pbc2_1$; and $Z = 4$]. The characteristic feature of the structure is the presence of layers composed of the C_{70} molecules that alternate with layers consisting of the *BTX* donor and CS_2 solvent molecules along the c-axis.

Considerable recent interest has been expressed in investigations into a new allotropic form of carbon—fullerenes [1–4]. Among the fullerene family, the C_{70} molecule is the second most stable and frequently encountered member after C_{60}. Unlike the spherical C_{60} molecule ("football"), the C_{70} molecule is slightly extended ("Rugby-ball") and has the molecular symmetry D_{5h} (Fig. 1). At room temperature, the C_{70} fullerene in the solid state exhibits a close-packed structure with an abnormal c/a ratio due to the elongation along one of the molecular axes. Many properties of C_{70} itself are similar to those of C_{60}, for example, the tendency to packing defects, the occurrence of phase transitions associated with an orientational disorder inherent in these fullerenes, the ability of crystals to incorporate solvent molecules, etc. [1, 5–9].

However, the C_{70}-based materials differ in properties from the C_{60} -based compounds, even though they have about the same chemical nature. Indeed, the fullerides M_3C_{70} (where M is an alkali metal) are not superconductors, and unlike *TDAE* · C_{60} [*TDAE* is tetrakis(dimethylamino)ethylene], *TDAE* · C_{70} does not possess ferromagnetic properties [10–12].

It should be mentioned that the C_{70} fullerenes have been studied to a considerably lesser extent than C_{60}. This is primarily explained by the smaller yield of C_{70} in the syntheses by the standard procedures. Moreover, the purification of C_{70} proved to be rather complicated, and, in actual fact, some experimental works were carried out with a mixture of C_{60} and C_{70}. The preparation of single crystals based on C_{70} is even more difficult than that based on C_{60}. At present, there are only several works dealing with the structure of C_{70}-based compounds [13, 14].

In this work, we undertook the single-crystal X-ray investigation on the molecular complex of C_{70} with organic donor 9,9'-*trans*-bis(telluraxanthenyl), namely, *BTX* · C_{70} · $(CS_2)_{0.5}$.



BTX

The synthesis of the above molecular complex is described in [15].

The main crystal data are as follows: $C_{96.5}H_{18}Te_2S$; $a = 10.927(3)$, $b = 21.068(5)$, and $c = 24.147(7)$ Å; $V = 5558.9$ Å^3; space group $Pbc2_1$; $Z = 4$; $F(000) = 2868$; $M = 1464.4$; $d_{calc} = 1.75$ g/cm^3; and $\mu(MoK_\alpha) = 11.5$ cm^{-1}.

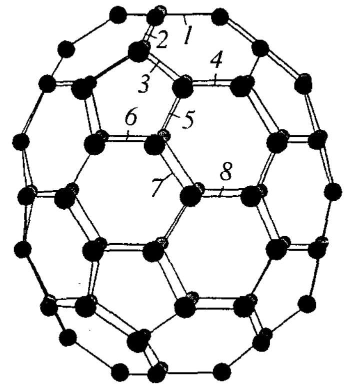


Fig. 1. The C_{70} molecule with the numbering of characteristic bonds (the bond numbering corresponds to that given in [18]).

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Atomic coordinates and the isotropic thermal parameters U_{iso} (Å^2)

Atom	*x*/*a*	*y*/*b*	*z*/*c*	U^*_{iso}
		BTX		
Te(1)	1.2738(4)	0.4237(2)	0.2507(1)	0.055(1)
Te(2)	0.7241(4)	0.5767(2)	0.2798(1)	0.059(1)
C(1)	1.257(2)	0.518(2)	0.273(2)	0.06(1)
C(2)	1.353(2)	0.556(1)	0.293(1)	0.01(1)
C(3)	1.340(3)	0.621(1)	0.304(1)	0.03(1)
C(4)	1.226(3)	0.650(1)	0.294(2)	0.05(1)
C(5)	1.131(2)	0.618(1)	0.269(1)	0.01(1)
C(6)	1.153(2)	0.554(1)	0.260(1)	0.01(1)
C(7)	1.136(2)	0.431(1)	0.187(1)	0.01(1)
C(8)	1.045(2)	0.477(1)	0.194(1)	0.02(1)
C(9)	0.968(3)	0.474(1)	0.148(1)	0.02(1)
C(10)	0.974(3)	0.428(1)	0.106(1)	0.03(1)
C(11)	1.072(3)	0.387(2)	0.105(1)	0.05(1)
C(12)	1.159(3)	0.386(1)	0.147(1)	0.03(1)
C(13)	0.748(3)	0.475(2)	0.264(1)	0.03(1)
C(14)	0.864(3)	0.450(2)	0.273(2)	0.07(1)
C(15)	0.838(4)	0.386(2)	0.260(2)	0.09(2)
C(16)	0.737(3)	0.354(2)	0.239(2)	0.05(1)
C(17)	0.637(4)	0.393(2)	0.230(2)	0.08(2)
C(18)	0.634(4)	0.457(2)	0.245(3)	0.11(2)
C(19)	0.855(6)	0.577(3)	0.342(2)	0.12(2)
C(20)	0.948(4)	0.532(2)	0.343(2)	0.06(1)
C(21)	1.039(5)	0.516(2)	0.382(2)	0.08(2)
C(22)	1.035(5)	0.556(2)	0.428(2)	0.08(2)
C(23)	0.949(4)	0.603(2)	0.435(2)	0.08(2)
C(24)	0.869(4)	0.612(2)	0.390(2)	0.06(1)
C(25)	1.032(2)	0.525(1)	0.241(1)	0.02(1)
C(26)	0.970(3)	0.492(2)	0.292(1)	0.05(1)
		C_{70}		
C(27)	0.522(5)	0.653(2)	0.157(3)	0.12
C(28)	0.429(5)	0.699(2)	0.160(3)	0.13
C(29)	0.420(5)	0.761(2)	0.131(2)	0.13
C(30)	0.527(5)	0.784(3)	0.105(2)	0.13
C(31)	0.631(5)	0.743(2)	0.119(2)	0.13
C(32)	0.634(5)	0.682(2)	0.138(3)	0.13
C(33)	0.693(6)	0.622(2)	0.123(2)	0.13
C(34)	0.769(6)	0.627(2)	0.076(2)	0.13
C(35)	0.776(6)	0.692(2)	0.059(2)	0.13
C(36)	0.707(6)	0.746(3)	0.070(2)	0.13
C(37)	0.630(5)	0.561(3)	0.126(2)	0.13
C(38)	0.782(5)	0.583(2)	0.030(2)	0.13
C(39)	0.658(6)	0.526(3)	0.079(2)	0.13
C(40)	0.519(5)	0.584(2)	0.153(3)	0.13
C(41)	0.328(5)	0.591(2)	0.147(3)	0.12
C(42)	0.719(4)	0.528(2)	0.025(2)	0.13
C(43)	0.438(5)	0.498(3)	0.087(2)	0.13
C(44)	0.421(5)	0.547(3)	0.133(3)	0.13
C(45)	0.325(5)	0.659(2)	0.160(3)	0.12
C(46)	0.654(4)	0.794(3)	0.032(2)	0.13
C(47)	0.225(6)	0.570(3)	0.114(3)	0.12
C(48)	0.166(6)	0.631(2)	0.118(2)	0.13
C(49)	0.215(5)	0.532(3)	0.068(2)	0.12
C(50)	0.111(7)	0.648(2)	0.070(2)	0.13

Table (Contd.)

Atom	*x*/*a*	*y*/*b*	*z*/*c*	U^*_{iso}
C(51)	0.555(5)	0.486(3)	0.062(2)	0.13
C(52)	0.157(4)	0.543(2)	0.014(3)	0.13
C(53)	0.099(5)	0.598(2)	0.027(2)	0.13
C(54)	0.327(5)	0.494(3)	0.059(2)	0.12
C(55)	0.783(6)	0.691(2)	−0.002(2)	0.13
C(56)	0.788(6)	0.626(2)	−0.018(2)	0.13
C(57)	0.219(5)	0.692(2)	0.134(3)	0.13
C(58)	0.232(5)	0.751(2)	0.110(2)	0.13
C(59)	0.332(5)	0.797(3)	0.102(2)	0.13
C(60)	0.098(7)	0.629(2)	−0.027(2)	0.13
C(61)	0.353(4)	0.480(3)	0.001(2)	0.12
C(62)	0.251(4)	0.516(3)	−0.022(2)	0.12
C(63)	0.537(4)	0.818(3)	0.052(2)	0.13
C(64)	0.260(5)	0.708(2)	−0.109(3)	0.13
C(65)	0.097(6)	0.698(2)	−0.028(2)	0.13
C(66)	0.090(5)	0.699(2)	0.032(2)	0.13
C(67)	0.449(4)	0.663(2)	−0.133(3)	0.13
C(68)	0.558(5)	0.479(3)	0.000(2)	0.13
C(69)	0.452(5)	0.521(3)	−0.086(2)	0.13
C(70)	0.353(5)	0.621(2)	−0.126(3)	0.13
C(71)	0.234(5)	0.644(2)	−0.108(3)	0.13
C(72)	0.455(4)	0.481(3)	−0.035(2)	0.12
C(73)	0.658(5)	0.510(3)	−0.029(2)	0.13
C(74)	0.148(5)	0.747(3)	0.063(2)	0.13
C(75)	0.168(5)	0.726(3)	−0.068(2)	0.13
C(76)	0.739(6)	0.734(3)	−0.040(2)	0.13
C(77)	0.162(5)	0.603(3)	−0.071(2)	0.13
C(78)	0.727(6)	0.619(2)	−0.068(2)	0.13
C(79)	0.664(5)	0.788(3)	−0.024(2)	0.13
C(80)	0.658(5)	0.661(2)	−0.105(3)	0.13
C(81)	0.303(4)	0.825(3)	0.047(2)	0.13
C(82)	0.198(4)	0.794(2)	0.024(2)	0.13
C(83)	0.424(4)	0.835(3)	0.030(2)	0.13
C(84)	0.550(5)	0.803(3)	−0.050(3)	0.13
C(85)	0.542(5)	0.755(3)	−0.093(3)	0.13
C(86)	0.659(5)	0.723(3)	−0.087(3)	0.13
C(87)	0.555(5)	0.624(2)	−0.125(3)	0.13
C(88)	0.552(5)	0.560(2)	−0.103(3)	0.13
C(89)	0.666(5)	0.558(3)	−0.070(2)	0.13
C(90)	0.350(5)	0.558(3)	−0.105(3)	0.13
C(91)	0.245(5)	0.549(3)	−0.070(2)	0.13
C(92)	0.331(5)	0.765(3)	−0.096(2)	0.13
C(93)	0.326(5)	0.799(3)	−0.044(2)	0.13
C(94)	0.437(4)	0.825(3)	−0.031(2)	0.13
C(95)	0.433(5)	0.731(2)	−0.117(3)	0.13
C(96)	0.201(5)	0.779(3)	−0.032(2)	0.13
		CS_2**		
C(97)	0.841(3)	0.746(2)	0.241(2)	0.02(1)
S(1)	0.938(2)	0.737(1)	0.198(1)	0.05(1)
S(2)	0.724(3)	0.751(2)	0.277(2)	0.15(1)

* Thermal atomic parameters for the C_{70} molecule were refined under the restrictions: their variations were specified within the standard deviation (0.01) from the mean value (0.13).

** Occupancy factors for atomic sites in the CS_2 molecule are equal to 0.5.

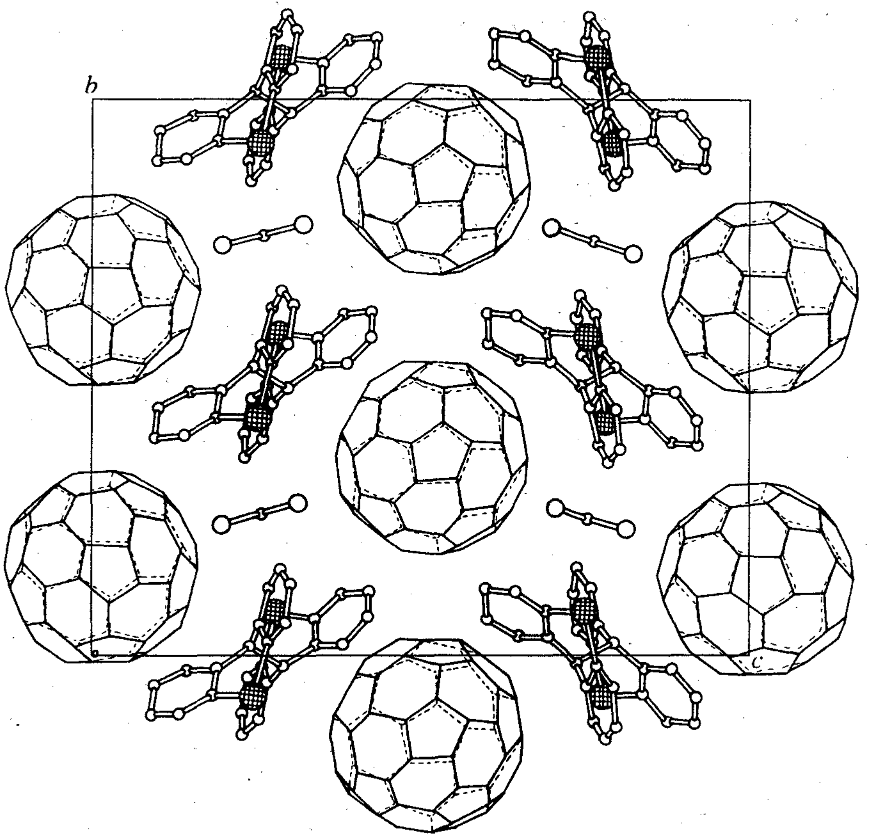

Fig. 2. Projection of the structure along the *a*-axis.

The experimental data (11 280 reflections) were collected with a single crystal 0.175 × 0.15 × 0.7 mm in size on an Enraf–Nonius CAD-4 automated diffractometer (MoK_α radiation, graphite monochromator, ω scan mode, $\sin\theta/\lambda \leq 0.481$ Å^{-1}). After the averaging of equivalent reflections, the set of diffraction data included 1869 independent reflections with $F \geq 4\sigma(F)$.

The structure was solved by the direct method followed by the electron-density syntheses according to the AREN program package [16] and was then refined by the least-squares procedure in the anisotropic approximation for the Te atoms and in the isotropic approximation for the remaining atoms to $R = 0.090$ with the use of the SHELXL93 software package [17]. The positions of the hydrogen atoms were determined geometrically and were not refined. The final coordinates and isotropic thermal parameters for the nonhydrogen atoms are listed in the table.

Note that the narrow diffraction range is characteristic of fullerene crystals and many C_{60}- and C_{70}-based molecular complexes: the reflections at large angles are smeared because of the large thermal vibrations of carbon atoms incorporated into the fullerene molecule. As a consequence, the experimental data are limited in number. In this work, 1865 independent reflections were used in the refinement, which is insufficient in comparison with the total number of the parameters to be refined (405 parameters for 101 symmetry-independent non-hydrogen atoms in the structure). Therefore, for the structure refinement, it was necessary to impose certain restraints on the C–C bond lengths in the fullerene molecule. In order to correctly introduce the restraints, we analyzed the available data on the bond lengths in the free C_{70} molecule [18, 19] and in the structure of $C_{70}S_{48}$ [13]. According to these data, the bond lengths were specified as follows: 1.37(3) Å for bonds 4 and 2; 1,40(3) Å for bond 7; 1.45(3) Å for bonds 1, 3, 5, and 6; and 1.48(3) Å for equatorial bond 8 (Fig. 1). This procedure of structure refinement makes an analysis of the bond lengths and angles in the C_{70} molecule impossible. In this respect, we considered only the general packing of the C_{70}, *BTX*, and CS_2 molecules in the crystal; shortest intermolecular contacts; and changes in the conformation of the *BTX* molecule upon complex formation.

Figure 1 displays the projection of the structure onto the *bc* plane. This structure is characterized by the layers that consist of C_{70} molecules and are aligned perpendicular to the *c*-axis of the crystal. Despite the fact that the $BTX \cdot C_{70} \cdot (CS_2)_{0.5}$ complex is similar in composition to the *BTX* complex with C_{60} ($BTX \cdot C_{60} \cdot CS_2$) [20], these two complexes are not isostructural.

The unit cell parameters of the *BTX* · C_{60} · CS_2 crystals are as follows: a = 10.309(1), b = 10.988(3), and c = 12.011(1) Å; α = 85.20(2)°, β = 71.85(1)°, and γ = 79.83(2)°; V = 1271.9 Å^3; and space group $P\bar{1}$. In the structure of this complex, the C_{60} molecules form chains along the a-axis. The fullerene molecules in the acceptor layer of the C_{70} complex are closer-packed than those in the C_{60} complex, as evidenced by a larger number of short intermolecular contacts. Indeed, there are five short contacts between the C_{70} molecules: two contacts [3.30(9) and 3.42(9) Å] along the chains and three contacts [3.18(8), 3.22(8), and 3.37(8) Å] between the molecular chains in the (001) plane. At the same time, the *BTX* · C_{60} · CS_2 complex has no short contacts between the C_{60} molecules, and all the C···C distances are larger then the sum of the van der Waals radii of the carbon atoms (3.60 Å) [21]. The number of the *BTX*···C_{70} contacts {three Te···C contacts [3.67(6), 3.79(6), and 3.88(5) Å] and twenty-two C···C contacts [3.26(6)–3.54(6) Å] is equal to approximately the number of the *BTX*···C_{60} contacts. Furthermore, there are four slightly shortened C_{70}···CS_2 and *BTX*···CS_2 contacts. The shortest distance between the centers of C_{70} molecules is observed in the (001) plane and is equal to 10.621 Å.

The *BTX* molecule (Fig. 3) has a butterfly conformation and is close in geometry to the molecules in the structure of free *BTX* (**I**) [22] and also in the complexes of *BTX* with *TCNQ* (**II**) [23] and *BTX* with C_{60} (**III**) [20]. The central heterocycle adopts a boat conformation: the Te(1) and C(25) atoms [Te(2) and C(26)] deviate from the plane of the remaining four atoms of the cycle in the same direction by 0.71 and 0.56 Å (0.43 and 0.49 Å), respectively. The planes of the benzene rings deviate, on the average, by 20.4° from the planes passing through four atoms of the central heterocycle in the direction opposite to the deviation of the Te(1) and C(25) [Te(2) and C(26)] atoms. The folding angle of the tricyclic system along the Te(1)–C(25) [Te(2)–C(26)] line is equal to 142.2° (137.2°), which is close to the corresponding angles in structures **I**, **II**, and **III** (138.8°, 140.5°, and 135.5°, respectively). The mean value of the Te–C_{sp2} bond length [2.12(4) Å] is close to that in **I** [2.100(6) Å], **II** [2.112(4) Å], and **III** [2.110(6) Å].

A priori, it would be expected that the C_{70} and C_{60} molecular complexes with *BTX* (1 : 1) should exhibit similar structures, as it is observed, for example, in the complexes $[(C_6H_5)_4P]_2[C_{70}][I]$ [a = 12.682(4) and c = 21.660(3) Å, V = 3484(1) Å^3, space group $P4/nnc$, and Z = 2] and $[(C_6H_5)_4P]_2[C_{60}][I]_x$ [a = 12.588(2) and c = 20.134(2) Å, V = 3190.5(7) Å^3, space group $P4/nnc$, and Z = 2] [14, 24] or in crystals of the C_{60} and C_{70} solvates with pentane: a = 10.14(3), b = 10.08(3), and c = 16.5(5) Å and β = 107.73(3)° for $C_{60} \cdot n\text{-}C_5H_{12}$ and a = 10.618(6), b = 10.529(7), and c = 17.33(1) Å and β = 107.70(3)° for $C_{70} \cdot n\text{-}C_5H_{12}$ [25]. However, in our case, the structures proved to be quite different.

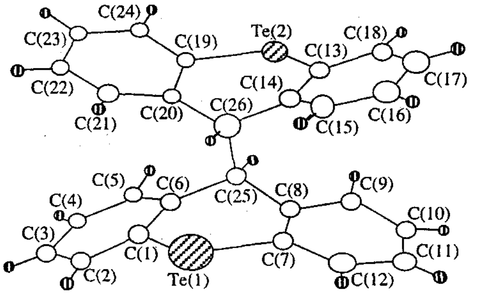

Fig. 3. The 9,9'-*trans*-bis(telluraxanthenyl) donor molecule.

As for the majority of the compounds based on C_{60} and C_{70} fullerenes, the structure of the *BTX* · C_{70} · $(CS_2)_{0.5}$ complex is likely characterized by the orientational disorder. This manifests itself in the comparatively large values of thermal parameters (see table). In order to decrease the thermal atomic parameters and thus to increase the intensity and the number of independent reflections, we attempted to perform the measurements at a low temperature. Unfortunately, our expectations were not realized: a decrease in temperature from 293 to 160 K did not lead to a substantial increase in the intensity of the control reflections (the intensity increased by 10–15%). It seems likely that the orientational disorder in the crystal retains at a low temperature. At 160 K, the unit cell parameters are as follows: a = 10.786(5), b = 21.13(1), and c = 21.94(1) Å. It is worth noting that the b parameter increases with a decrease in temperature; i.e., the thermal expansion coefficient along this axis is negative.

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