

STRUCTURE
OF ORGANIC COMPOUNDS

Supramolecular Architecture of Two Charge-Transfer
Complexes Based
on 2,7-(X,X)-4,5-Dinitro-9-Dicyanomethylenefluorenes
(X = NO₂ or CN) and Tetrathiafulvalene

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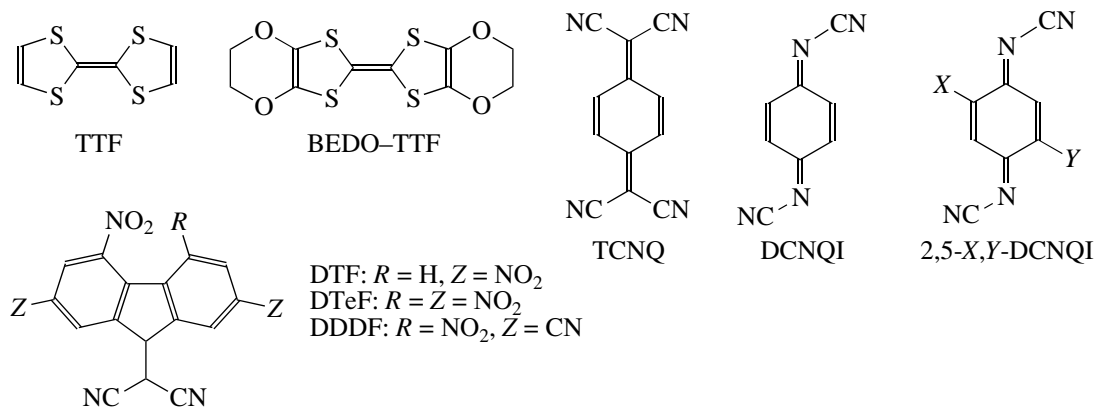
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Abstract—The crystal packings of two charge-transfer complexes based on tetrathiafulvalene and substituted fluorenes—2,4,5,7-tetranitro-9-dicyanomethylenefluorene (in complex **I**) or 2,7-dicyano-4,5-dinitro-9-dicyanomethylenefluorene (in complex **II**)—are analyzed. Crystals of complex **II** involve a third component, namely, C₆H₅Cl solvate molecules. Crystals of both complexes are characterized by the formation of stacks composed of alternating donor and acceptor molecules and sheets in which the molecules are linked through different-type weak interactions. In structure **II**, chlorobenzene molecules occupy cavities that are formed in stacks in the vicinity of the tetrathiafulvalene molecules due to the larger difference in size of the donor and acceptor molecules in complex **II** as compared to that in complex **I**. The chlorobenzene molecules provide a close packing. These molecules are involved in the system of weak interactions to form the Cl...N and C-H...N secondary bonds with the CN groups of the acceptor molecules in the sheets. © 2002 MAIK “Nauka/Interperiodica”.

INTRODUCTION

Molecular organic conductors have been studied extensively over the last two decades [1]. After the discovery of the first stable charge-transfer complex with a metallic conductivity, namely, the complex of

tetrathiafulvalene (TTF) with 7,7,8,8-tetracyanoquinodimethane (TCNQ) [2], a great number of donors—tetrathiafulvalene derivatives—have been synthesized [1–4]. The chemical diagrams of the corresponding compounds are shown in Scheme I.



Scheme I.

However, the structure of acceptors has not been adequately investigated. There had been only a few

works dealing with charge-transfer complexes and radical ion salts that contained acceptors other than TCNQ

molecules [5] until the discovery of the new type of acceptors, namely, *N,N'*-dicyano-1,4-quinodimines (DCNQI) [6–9]. Radical ion salts 2,5-*X,Y*-DCNQI with Li, Na, K, Tl, and Ag possess the properties of metallic semiconductors, whereas the radical ion salts with Cu have an extremely high metallic (three-dimensional) conductivity [10].

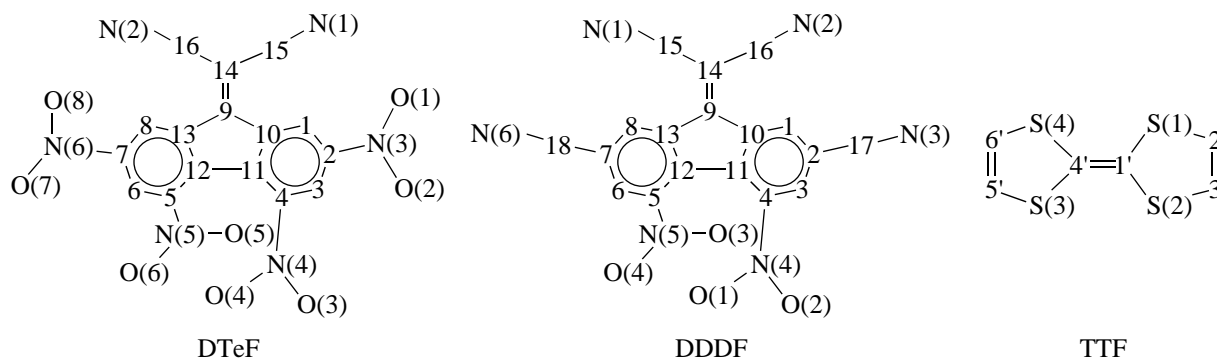
The use of substituted fluorenes with different substituents in the 2- and 7-positions (and in the 4- and 5-positions) as acceptors in charge-transfer complexes makes it possible to change substantially the size and the shape of acceptor molecules, thus affecting the packing of the donor and acceptor molecules in crystals. The electrical conductivity of these charge-transfer complexes can vary by six orders of magnitude [7–10]. Undoubtedly, the electrical conductivity should be governed by the specific features of the supramolecular structure (crystal packing) of charge-transfer complexes. The elucidation of the regularities in the architecture of their crystals is important for the modeling of the structure of charge-transfer complexes with the highest conductivity. Recent investigations into the supramolecular architecture revealed the interrelation between the structure of crystals and their properties [11–16].

In the present work, we analyzed how the replacement of the substituent in the electron-acceptor component of the charge-transfer complex affects its crystal packing by using the example of two fluorene charge-transfer complexes with the same tetrathiafulvalene molecule as a donor component. The properties of these and related charge-transfer complexes either have already been understood or are being investigated intensively. In particular, it was established that the electronic properties of fluorene acceptors are comparable to those of TCNQ and DCNQI derivatives. The fluorene acceptors readily form the charge-transfer complexes with aromatic electron donors [17, 18]. These complexes often possess semiconductor proper-

ties and photoconductivity [17, 19–21]. Recently, Horiuchi *et al.* [22] revealed a metallic conductivity in charge-transfer complexes of bis(ethylene-dioxy)tetrathiafulvalene (BEDO-TTF) with fluorene electron acceptors such as 2,4,7-trinitro-9-dicyanomethylene fluorene (DTF) and 2,4,5,7-tetranitro-9-dicyanomethylene fluorene (DTeF): $\sigma = 65 \text{ S cm}^{-1}$ at 298 K and $\sigma = 390 \text{ S cm}^{-1}$ at 8 K for BEDO-TTF : DTF = 2 : 1 and $\sigma = 18 \text{ S cm}^{-1}$ at 298 K and $\sigma = 32 \text{ S cm}^{-1}$ at 94 K for BEDO-TTF : DTeF = 2 : 1 (pressed pellets).

In this work, we investigated the crystal structures of two charge-transfer complexes based on substituted fluorenes and tetrathiafulvalene. Compound **I** is the tetrathiafulvalene complex with 2,4,5,7-tetranitro-9-dicyanomethylene fluorene (TTF : DTeF = 1 : 1). Compound **II** is the tetrathiafulvalene complex with 2,7-dicyano-4,5-dinitro-9-dicyanomethylene fluorene (DDDF) and chlorobenzene (*Sol*) $\text{C}_6\text{H}_5\text{Cl}$ (TTF : DDDF : *Sol* = 1 : 1 : 1). These charge-transfer complexes differ in degrees of misfit in the shape and size of the donor (*D*) and acceptor (*A*) molecules. Moreover, different substituents (NO_2 and CN groups) in the 2- and 7-positions of the acceptor molecules impose different geometric constraints on the formation of intermolecular secondary bonds that are responsible for the specific features of the molecular packing motif in crystals. At the same time, the DTeF and DDDF fluorene acceptors are closely similar in electron-acceptor properties (the electron affinities are 2.71 and 2.77 eV, respectively) [23]. Therefore, the differences in crystal packings of compounds **I** and **II** can be determined only by the aforementioned factors (different sizes and geometric constraints on the formation of intermolecular secondary bonds).

The synthesis, properties, and X-ray molecular structures of these charge-transfer complexes were described in our earlier work [23]. The donor and acceptor components of the studied complexes with the atomic numbering are shown in Scheme II.



Scheme II.

STACKING MOTIFS IN STRUCTURES **I** AND **II**

Two crystallographically independent solvent molecules in structure **II** are located at the centers of sym-

metry and, hence, are disordered over two positions with the same occupancy. These molecules occupy the centers of symmetry of two different systems (*i* and *j*) and exhibit different types of disordering. The type of

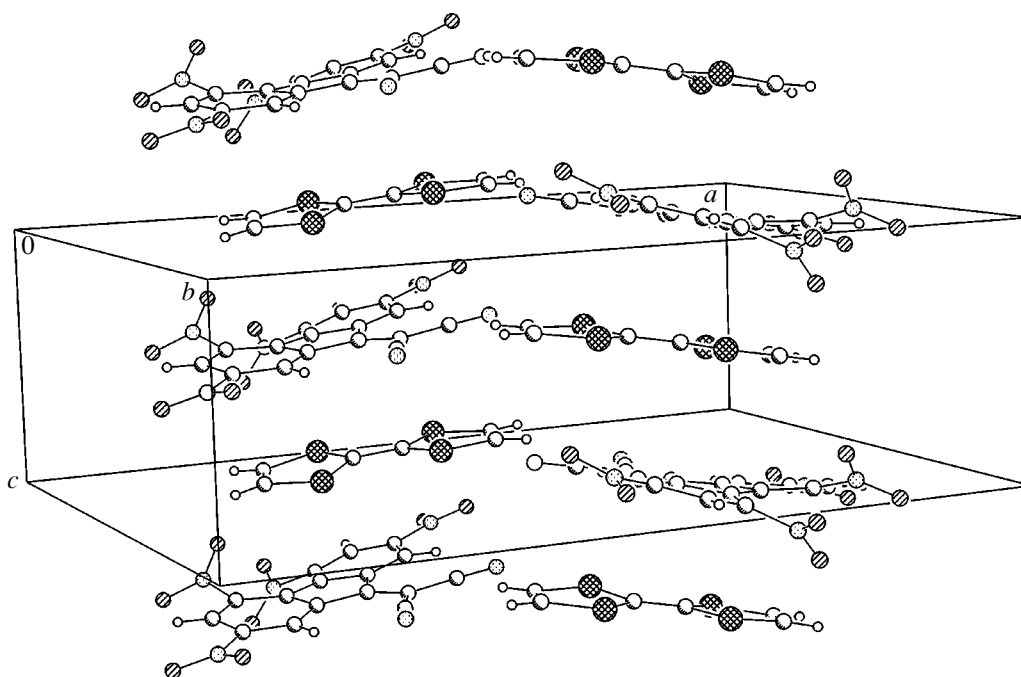
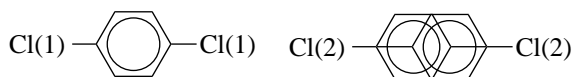


Fig. 1. Stacking structure of charge-transfer complex I.

disordering of the solvent molecules is depicted in Scheme III.



Scheme III.

The molecule at the left is disordered with respect to the symmetry center of the system *i*. This center of symmetry coincides with the center of the benzene ring. The centers of the benzene rings of two disordered components of the molecule at the right are displaced from the symmetry center of the system *j* in opposite directions.

Crystals **I** and **II** are characterized by the same stacking motif of alternating donor and acceptor molecules (Figs. 1, 2), which is typical of charge-transfer complexes. In both crystals, the stacks are aligned along the shortest unit-cell dimension. The nearest-neighbor like molecules inside each stack are related by the translation. The replacement of two NO₂ groups in the 2- and 7-positions of fluorene (in molecule **I**) by the CN groups (molecule **II**) leads to an increase in the linear size of the acceptor molecule. Therefore, in order to provide a close crystal packing, an additional structural block, namely, the solvent molecule, should be introduced into the crystal lattice of compound **II**. The chlorobenzene solvate molecules that belong to the symmetry center system *i* fill part of the free intrastack space and partially occupy cavities between the stacks (Fig. 2). The solvate molecules belonging to the symmetry center system *j* occupy the interstack space and are

arranged at a small angle with respect to the *a* axis in the crystal. However, the structural function of these molecules is not confined only to ensuring a close crystal packing.

In both structures, the mean planes of the donor and acceptor molecules are not strictly parallel to each other. The table presents the short intermolecular distances in the stacking triad with the tetrathiafulvalene molecule sandwiched between two acceptor molecules ("above" and "below"). The mutual orientations of molecules in these triads are shown in Figs. 3 and 4 in projections onto the mean plane of one of the fluorene fragments. It can be seen from these figures that the stacking structures of complexes **I** and **II** differ qualitatively. The acceptor molecules with the tetrathiafulvalene molecule in between are displaced relative to each other in their own planes in structure **II** to a greater extent than in structure **I**. In structures **I** and **II**, the central tetrathiafulvalene molecules are differently located with respect to the fluorene fragments. In structure **I**, the double bond between heterocycles is actually projected outside the tricyclic system. In structure **II**, the double bond predominantly lies between the fluorene tricycles of the upper and lower molecules, even though the chlorobenzene molecule is also located between the two acceptor molecules. This means that the stacking interaction between the donor and acceptor molecules only slightly depends, at least within certain limits, on their mutual displacements and rotations in parallel planes. The data presented in the table also indicate differences in mutual packings of molecules in the stack:

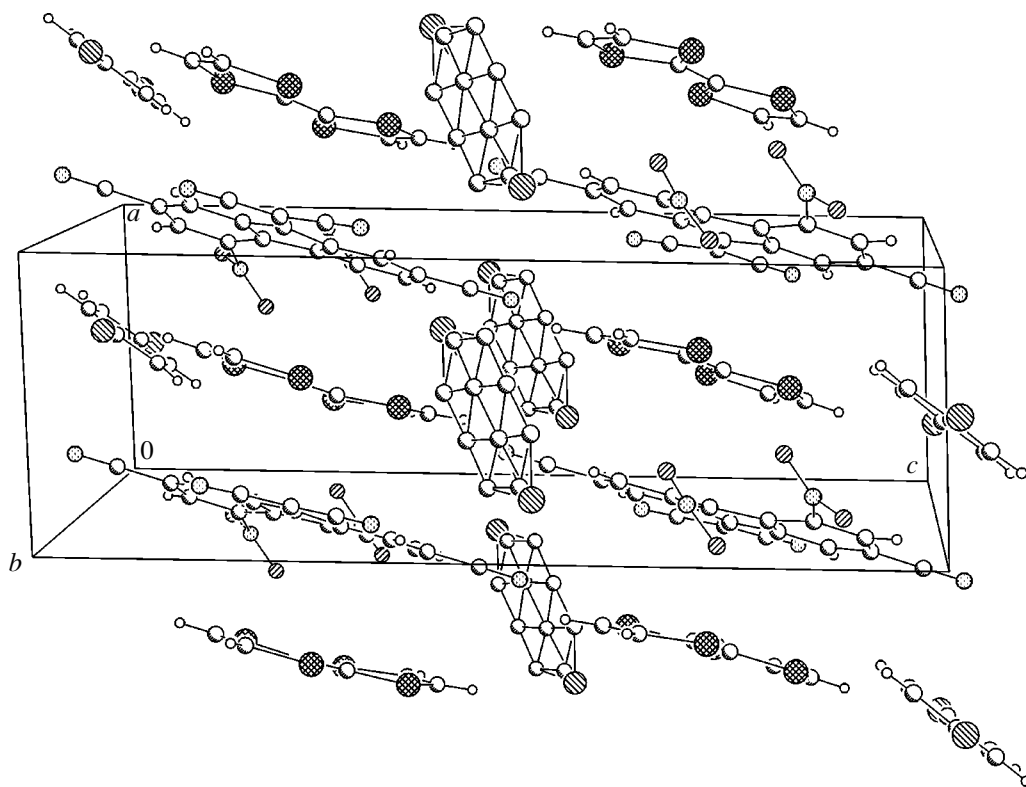


Fig. 2. Stacking structure of charge-transfer complex **II** and location of solvate molecules of both types.

the short intrastack intermolecular contacts in structures **I** and **II** are different.

Compounds **I** and **II** have a common feature in their stacking structure—the intermolecular contacts of the tetrathiafulvalene molecule with one acceptor molecule are generally shorter than those with the other acceptor molecule. This implies that the pair donor–acceptor π – π interactions contribute substantially to the stacking motif of crystal packing.

The described (qualitative and quantitative) differences in the stacking motifs of structures **I** and **II** can be associated with the formation of different systems of intermolecular secondary bonds in the crystals. These bonds are accomplished through different electron–electron interactions (n – σ^* , n – π^* , and p – π^*) with the participation of functional groups of the acceptor and donor molecules. These interactions can change the ratio between the highest occupied and lowest unoccupied molecular orbital levels in the donor and acceptor molecules and, hence, can influence the ability of these molecules to transfer electrons; i.e., these interactions can affect the properties of the charge-transfer complex. In this respect, there is a need to examine the systems of directional secondary bonds and the structural units formed in the crystals as a result of these interactions.

TWO-DIMENSIONAL MOTIFS IN STRUCTURES **I** AND **II**

The crystal structures of both compounds, apart from the stacks, involve infinite sheets of molecules linked through weak interactions. These sheets in structures **I** and **II** differ in appearance and geometry.

Figure 5 shows the puckered sheet of the acceptor and donor molecules linked through different-type secondary interactions in crystal **I**. Each donor molecule forms five short contacts containing three sulfur atoms and two C–H fragments involved in the hydrogen bonds with the CN and NO₂ groups of the neighboring acceptor molecules. Each acceptor molecule is involved in five weak interactions with the neighboring donor molecules through the oxygen atoms of the NO₂ groups and the CN group. The contacts S(1)···O(3) (3.10 Å), S(2)···O(8) (3.20 Å), and S(4)···O(5) (3.24 Å) are somewhat shorter than or comparable to the sum of the van der Waals radii. The O(3) and O(8) oxygen atoms are virtually aligned with one of the S–C bonds of the relevant sulfur atom: the O(3)···S(1)–C(1') angle is equal to 162.8° and the O(8)···S(2)–C(1') angle is 162.2°. The observed geometry of the short contacts is typical [24, 25] and corresponds to the n – σ^* interaction with the participation of the sp^2 orbital of the lone electron pair of the oxygen atom in the NO₂ group and the σ^* orbital of the S–C bond. This geometry is in agreement with the n – π^* interaction involving the p orbital

Short intrastack contacts (Å) between the tetrathiafulvalene molecule and two substituted fluorene molecules located above (molecule *A*) and below (molecule *B*) in structures **I** and **II**

I				II			
TTF-DTeF(A)		TTF-DTeF(B)		TTF-DDDF(A)		TTF-DDDF(B)	
S(1)–C(8)	3.32	S(1)–C(9)	3.63	S(1)–C(4)	3.61	S(1)–C(11)	3.37
S(2)–C(11)	3.22	S(1)–C(13)	3.60	S(2)–C(2)	3.47	S(1)–C(12)	3.42
S(2)–C(12)	3.39	S(2)–C(10)	3.67	S(2)–C(17)	3.55	S(2)–C(10)	3.45
S(2)–O(4)	3.12	S(2)–C(11)	3.66	S(3)–C(10)	3.86	S(2)–C(1)	3.40
S(4)–C(14)	3.20	S(3)–C(1)	3.64	S(3)–C(1)	3.87	S(2)–C(9)	3.73
S(4)–C(16)	3.42	S(3)–O(1)	3.44	S(4)–C(11)	3.72	S(3)–C(14)	3.22
S(4)–C(15)	3.36	S(4)–C(15)	3.64	S(4)–C(12)	3.46	S(3)–C(15)	3.25
C(1')–C(9)	3.29	S(4)–N(1)	3.78	S(4)–C(13)	3.65	S(4)–C(8)	3.25
C(1')–C(13)	3.31	C(1')–C(9)	3.66	C(1')–C(2)	3.75	S(4)–C(13)	3.60
C(1')–C(10)	3.60	C(1')–C(10)	3.63	C(1')–C(3)	3.74	C(1')–C(9)	3.26
C(2')–C(7)	3.52	C(2')–C(13)	3.59	C(1')–C(4)	3.79	C(1')–C(10)	3.38
C(2')–C(6)	3.67	C(2')–C(12)	3.54	C(1')–C(11)	3.84	C(1')–C(13)	3.48
C(3')–C(5)	3.51	C(2')–C(13)	3.59	C(4')–C(10)	3.55	C(2')–C(4)	3.45
C(3')–C(12)	3.45	C(3')–C(11)	3.76	C(4')–C(1)	3.82	C(2')–C(11)	3.63
C(4')–C(9)	3.27	C(3')–C(12)	3.52	C(4')–C(11)	3.72	C(3')–C(1)	3.68
C(4')–C(14)	3.42	C(6')–N(1)	3.50	C(5)–C(14)	3.64	C(3')–C(2)	3.63
C(6')–N(1)	3.38			C(6')–C(9)	3.69	C(4')–C(13)	3.39
				C(6')–C(13)	3.62	C(4')–C(9)	3.29
				C(4')–C(14)	3.48		
				C(5')–C(15)	3.39		

of the lone electron pair of the sulfur atom and the π^* orbital of the NO_2 group. The $\text{O}(5)\cdots\text{S}(4)\text{--C}(4')$ and $\text{O}(5)\cdots\text{S}(4)\text{--C}(6')$ angles are equal to 123.0° and 137.8° , respectively. However, it is evident that one lone electron pair of the $\text{O}(5)$ atom is oriented toward the line aligned with the $\text{S}(4)\text{--C}(6')$ bond.

One further weak interaction with the participation of the donor and acceptor molecules is the $\text{C}\text{--}\text{H}\cdots\text{N}\text{C}$ hydrogen bond. The $\text{N}\cdots\text{H}$ distance (2.47 \AA) and the angles $\text{H}(3')\cdots\text{N}(2)\text{--C}(16)$ (150.7°) and $\text{N}(2)\cdots\text{H}(3')\text{--C}(3')$ (163.5°) have standard values for hydrogen bonds of this type [26]. It is quite probable that there exists one more hydrogen bond, namely, the $\text{C}(2')\text{--}\text{H}(2')\cdots\text{O}(3)$ hydrogen bond with the $\text{H}(2')\cdots\text{O}(3)$ distance equal to 2.53 \AA . However, the short contact between these atoms can be governed by the geometric constraints on the system of weak interactions.

The weak interactions described above are responsible for the formation of zigzag ribbons in the crystal. The ribbons are linked together into puckered sheets due to the $\text{O}\cdots\text{O}$ interactions between the $\text{O}(1)$ and $\text{O}(7)$ oxygen atoms of the NO_2 groups in the adjacent ribbons. The $\text{O}\cdots\text{O}$ distance (2.87 \AA) most likely corre-

sponds to a very weak interaction with a geometry such that the $\text{O}\cdots\text{O}$ line appears to be nearly perpendicular to the planes of both NO_2 groups (with angles of 85.2° and 85.6°). This geometry is most consistent with the $\pi\text{--}\pi^*$ interactions between these groups.

No other specific interactions, except for the aforementioned $\pi\text{--}\pi^*$ interactions, participate in bonding the puckered sheets. The stacking of these sheets results in the formation of the parallel alternating stacks $\dots\text{ADADAD}\dots$.

The system of secondary bonds in structure **II** differs essentially from that in structure **I**. Figure 6 depicts the sheet in structure **II**. The tracery ribbons formed by conjugate centrosymmetric macrocycles involving two pairs of unlike molecules can be distinguished in the sheet of the crystal. It can be seen that macrocycles of two types alternate in the ribbon. A macrocycle of the first type is formed through secondary bonds and has a large cavity that contains the *j*-type solvent molecule. The minimum size of this cavity (i.e., the distance between the acceptor hydrogen atoms oriented toward the interior of the macrocycle) is equal to 6.75 \AA . The cavity is large enough to house the solvent molecule (see Fig. 6). The macrocycle is formed by secondary

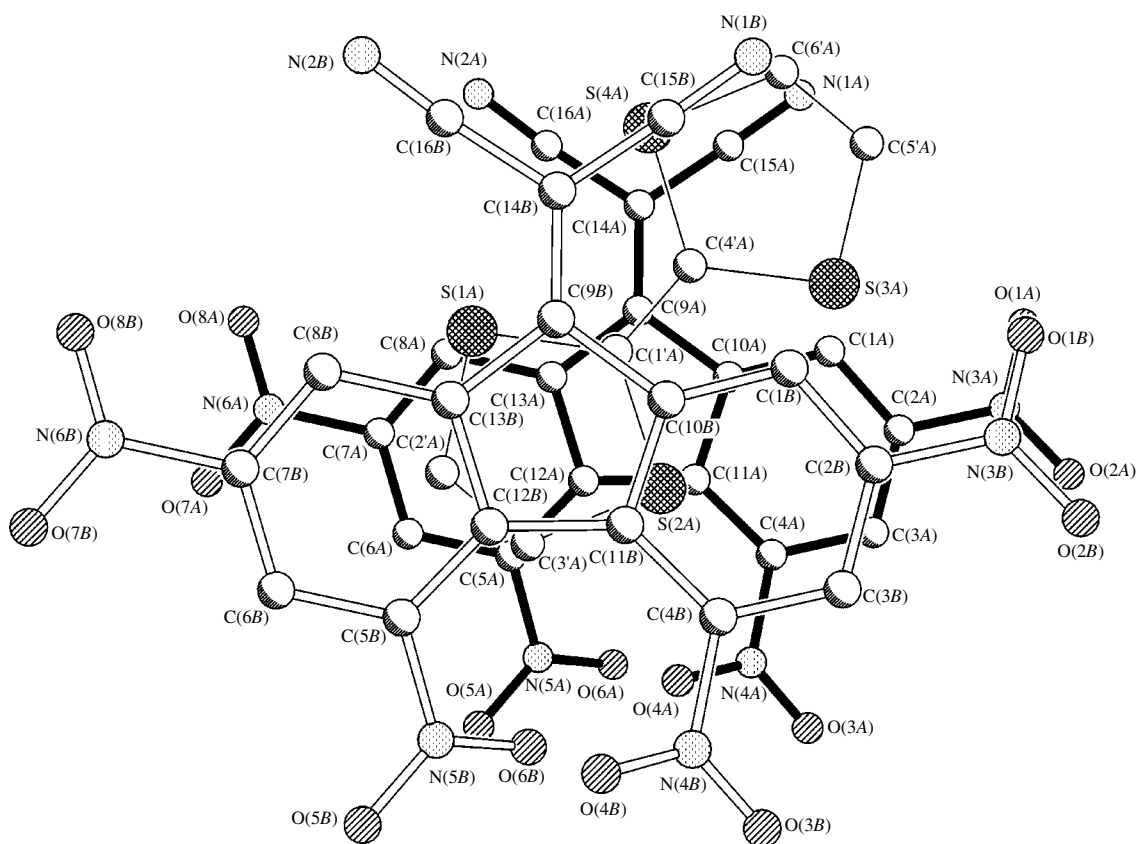


Fig. 3. Mutual arrangement of molecules in the DTef-TTF-DTef triad in a stack of structure I. In atomic numbering, the letter A indicates the basis molecules and B refers to the acceptor molecule related to the basis molecule by the translation z .

bonds of the O...S and N...S types with the participation of the S(3) and S(2) atoms of the tetrathiafulvalene molecules, the O(2) atom of the NO₂ group, and the N(3) atom of the CN group of the acceptor molecules. The S...O and S...N distances are equal to 3.04 and 3.08 Å, respectively. The O(2)...S(3)-C(4'), N(3)...S(2)-C(1'), S(3)...O(2)-N(4), and S(2)...N(3)-C(17) angles are 172.8°, 168.3°, 130.7°, and 173.8°. These parameters are geometrically favorable for the $n-\sigma^*$ and $n-\pi^*$ interactions.

Each tetrathiafulvalene molecule is involved in one more weak interaction: the CH group participates in the formation of the hydrogen bond with the CN group of the acceptor molecule that belongs to the adjacent four-component macrocycle of the second type. The N(6)...H(6') distance is equal to 2.45 Å, and the N(6)...H(6')-C(6') and H(6')...N(6)-C(18) angles are 162.5° and 161.2°, which is typical of hydrogen bonds involving nitrile groups. This macrocycle contains no cavity large enough to house the solvent molecule. Solvent molecules of the *i* type are located outside the ribbons. Each of these molecules participates in the sheet formation through the C-H...NC hydrogen bonds of two centrosymmetrically related acceptor molecules belonging to the adjacent ribbons. These hydrogen bonds have a conventional geometry: the angles at the

H and N atoms are equal to 162.4° and 170.7°, and the N(1)...H(3') distance is 2.49 Å. Moreover, the Cl atom of the chlorobenzene molecule is involved in the secondary interaction with the fluorene molecule. This interaction is rather strong: the Cl...N distance is 3.14 Å, the angle at the Cl atom is 159.5°, and the angle at the N(6) atom is 105.7°. Since the Cl atom in this molecule is disordered over two positions, several alternative descriptions of the crystal structure become possible. For example, one view holds that the Cl atom is statistically disordered over two positions in each sheet. According to other variants, the packing is characterized by different types of local ordering within either ribbons, or sheets, or domains. The crystal packing has defied adequate description only on the basis of X-ray diffraction experiment. However, this is of no fundamental importance, because even the aforementioned hydrogen bonds will suffice to link the ribbons into sheets.

Apart from the weak interaction within the sheet, the Cl atom is involved in the intersheet weak interaction with the N atom of the CN group in the 7-position (see Fig. 7). The Cl(1A)...N(6C) distance is 3.29 Å, and the C(1'A)-Cl(1A)...N(6C) and Cl(1A)...N(6C)-C(18C) angles are equal to 93.9° and 94.4°, respectively. Figure 7 also shows the intersheet short contacts

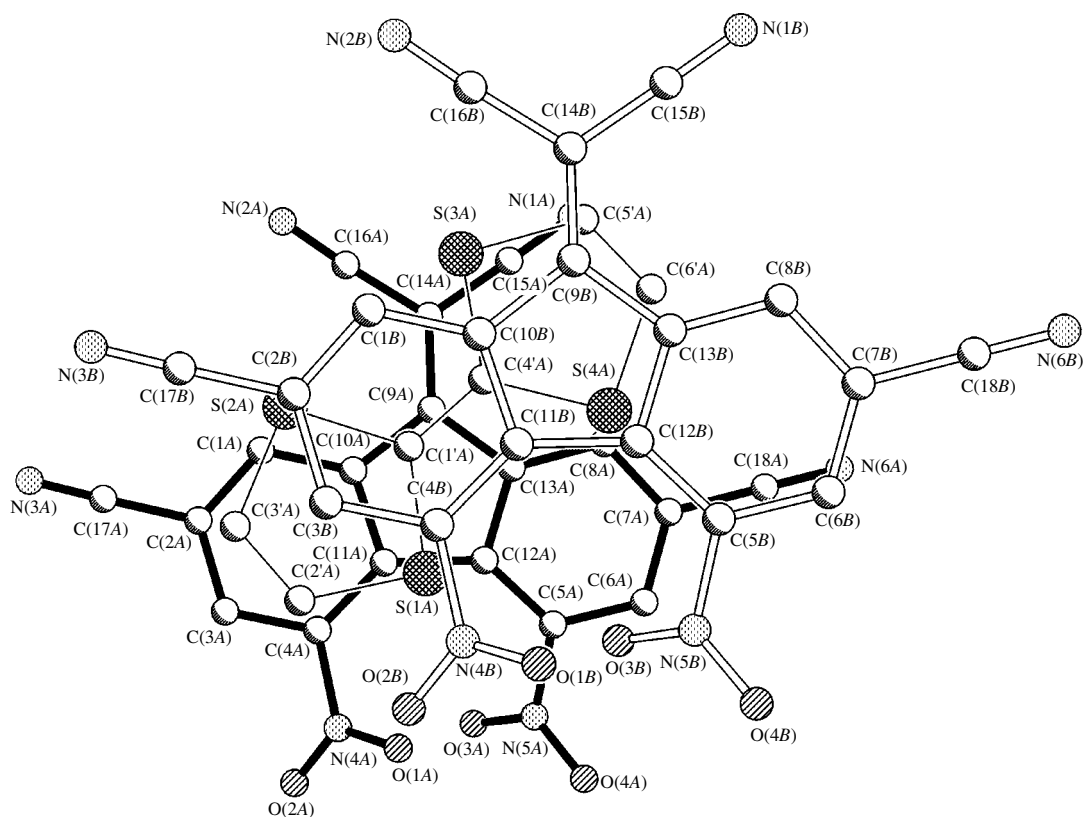
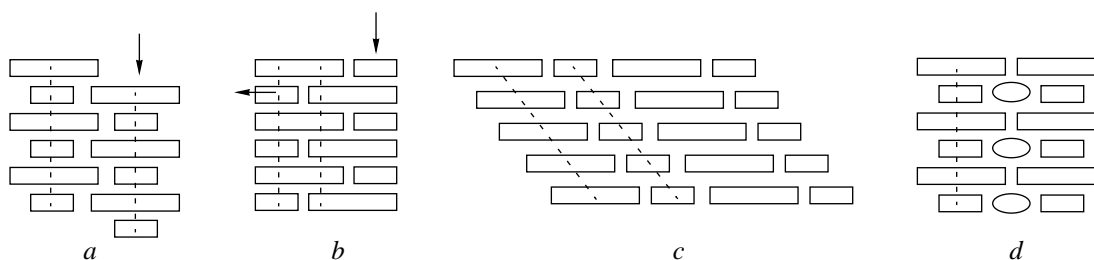


Fig. 4. Mutual arrangement of molecules in the DDDF-TTF-DDDF triad in a stack of structure **II**. In atomic numbering, the letter *A* indicates the basis molecules and *B* refers to the acceptor molecule related to the basis molecule by the translation *x*.

of the *j*-type solvate molecule, whose role is not confined only to filling the macrocycle cavity. The Cl(2A)⋯N(2A) and Cl(2B)⋯N(2B) distances are 3.16 Å, and the angles at the Cl and N atoms are equal to 154.1° and 129.3°, respectively. For these intersheet secondary bonds, there can also arise different-type crystal packings due to the disordering of the Cl atoms. If the Cl atoms of both solvate molecules are statistically disordered, the sheets are cross-linked at random into a three-dimensional framework. In the case when the elements of local ordering of the Cl atoms are present in the structure, there can arise double sheets or a rather ordered cross-linking of the sheets. However, the elucidation of the actual situation calls for further X-ray structure investigation with crystals grown using solvents such as *p*-dichlorobenzene or toluene.

SCHEMATIC REPRESENTATION OF THE STRUCTURE TYPES OF CHARGE-TRANSFER COMPLEXES

As follows from the above analysis of the crystal packing in structures **I** and **II**, the stack ...ADADAD..., which is composed of the alternating donor and acceptor molecules, is a typical structural motif of the charge-transfer complexes under consideration. The ...ADADAD... stacks built up of the acceptor and donor molecules of different sizes can form several genetically related packings. Scheme IV represents four variants of the supramolecular architecture of alternating stacks in the structure of charge-transfer complexes (the large and small rectangles stand for the large-sized acceptor and small-sized donor molecules, respectively; ovals symbolize the molecules of the third component; and dashed lines show the stack orientation).



Scheme IV.

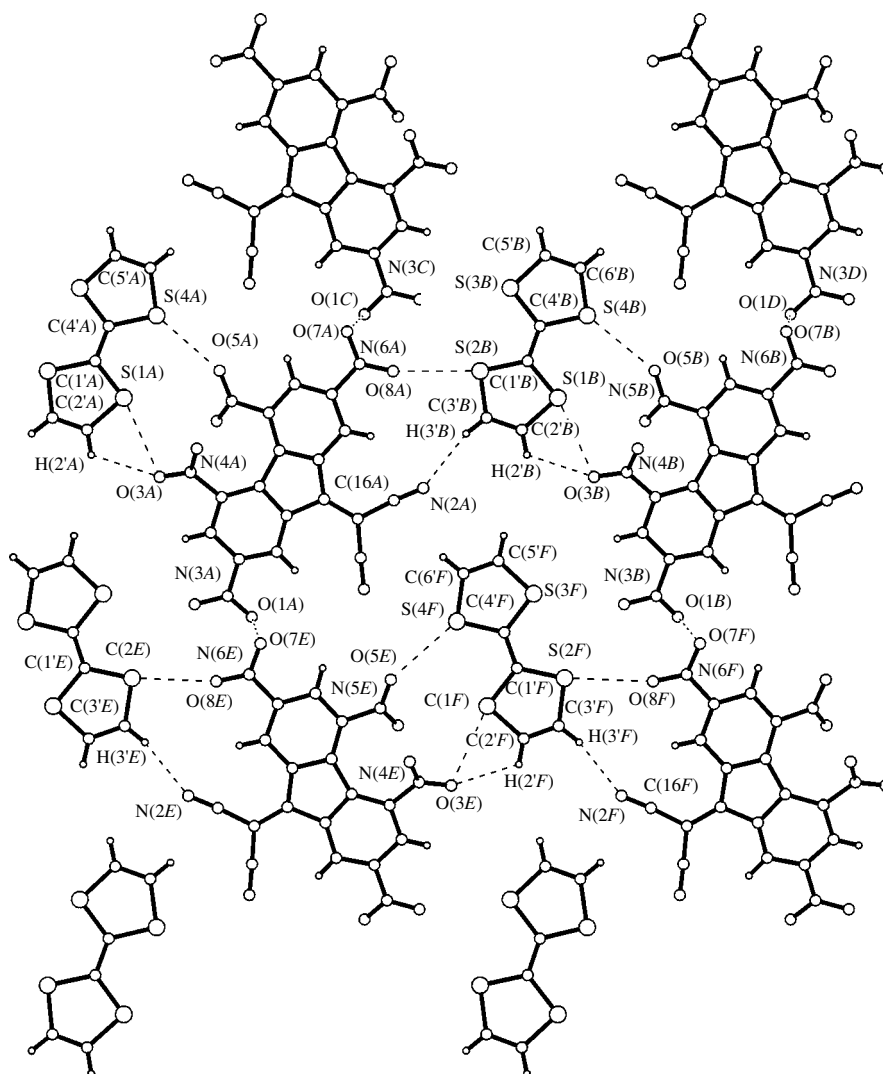


Fig. 5. A sheet of the molecules linked through weak interactions in structure **I**. Letters in atomic numbering indicate different symmetry-related molecules.

In the close packing *a*, one stack is shifted relative to the other stack so that the large-sized acceptor molecules partially fill the interstack space in the vicinity of the small molecule in the adjacent stack. It is this supramolecular architecture that is observed in the charge-transfer complex **I**. As was shown above, the displacement of the small molecules with respect to the large molecules in parallel planes does not affect the π interaction between the acceptor and donor molecules. However, this displacement can result in packing *b*, which is characterized by stacking not only of the type ...ADADAD... but also of the type ...AAA..., i.e., the stacking of large-sized acceptor molecules. It is expected that, in the limit, at a certain size ratio of the acceptor and donor molecules, packing *b* will transform into packing *c* with separate molecular stacks ...AAAA... and ...DDDD... . Packing *c* is especially desirable because it corresponds to the highest (i.e.,

metallic) conductivity [27]. Thus, the description of the packings in the structure of charge-transfer complexes with the use of the graphs considered has revealed their genetic relationship and directed the way to the controlled modification of the supramolecular architecture of these complexes. This can be achieved either by varying the size and shape of the acceptor and donor molecules or by substituting the particular functional groups for the other groups with different geometric constraints on the formation of secondary bonds.

The crystal lattice with packing *d* involves the third component. This packing is characteristic of the structure of complex **II** when solvent molecules of the *j* type are disregarded. Actually, these molecules have no effect on the stacking motif of the crystal, because they are arranged at large angles with respect to the sheets considered above.

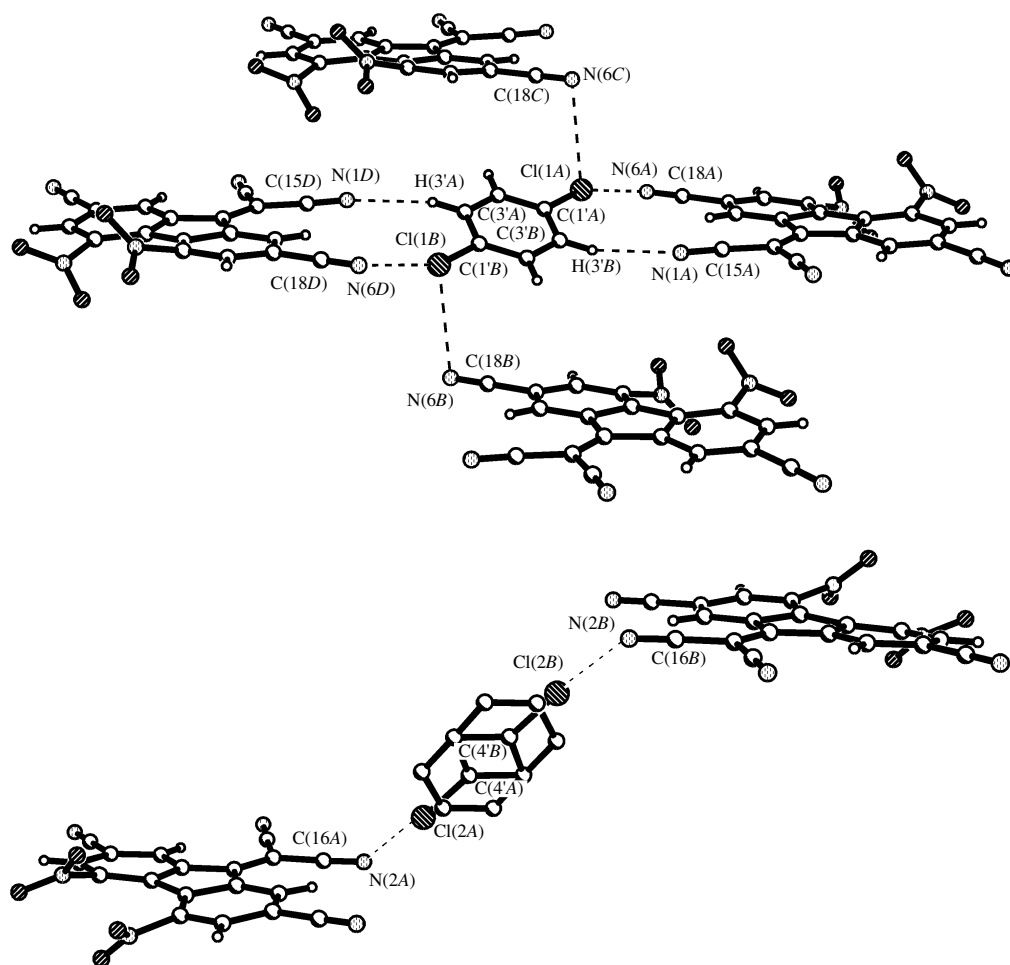


Fig. 7. Weak interactions of the C_6H_5Cl molecules involved in the *i* and *j* systems.

there can also occur more complicated situations, which will be discussed in separate works.

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