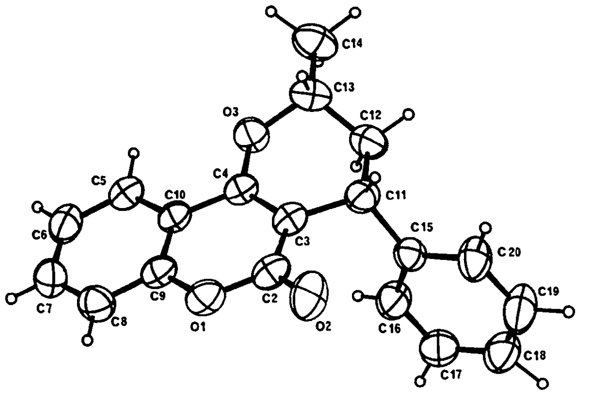

Fig. 2. A drawing of (II) with 50% probability ellipsoids for the non-H atoms.

least diaxial interactions. A plane through the phenyl ring is inclined at 80° with respect to the coumarin ring plane. The dihydropyran ring has a *d,e*-diplanar conformation, with ring displacement asymmetry $\Delta C_2 = 0{\cdot}0569\,(13)$. Intraring bond distances and angles are generally similar to those found in related structures having axial 2-hydroxy groups (Valente, Eggleston & Schomaker, 1987) including the relatively long O—C(sp^3) bond (O3—C13) 1·474 (2) Å. The persistence of this feature suggests that it may be inherent to chroman dihydropyrans. Dihydropyran-ring torsion angles are given in Table 5; a drawing of (II) is given in Fig. 2.

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Structure of the 1:1 Molecular Complex of Durene* with 1,2,4,5-Tetracyanobenzene†

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Abstract. $C_{10}H_{14}.C_{10}H_2N_4$, $Mr = 312{\cdot}4$, monoclinic, $P2_1/a$, $a = 15{\cdot}249\,(6)$, $b = 7{\cdot}750\,(3)$, $c = 7{\cdot}520\,(2)$ Å, $\beta = 105{\cdot}28\,(4)°$, $V = 857{\cdot}3\,(1{\cdot}1)$ Å^3, $Z = 2$, $D_x = 1{\cdot}21$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0{\cdot}41$ cm^{-1}, $T = 293$ K, $F(000) = 328$, $wR = 0{\cdot}038$ for 912 observed reflections. The structure is formed by mixed stacks along **c** with uniformly spaced donor and acceptor molecules. Durene–TCNB is isostructural with the low-temperature phases of anthracene–TCNB and naphthalene–TCNB. The two molecules are ordered on their site. The angle between the long molecular axis and the *ac* plane is 28·2° for durene and 62·7° for TCNB.

Introduction. Formation of weak π-molecular complexes by planar aromatic donors (*D*) and acceptors (*A*) usually leads to columnar structures. This quasi-one-dimensional structure with charge-transfer (CT) forces acting along the *D–A* stack axis is responsible

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* 1,2,4,5-Tetramethylbenzene.

† 1,2,4,5-Benzenetetracarbonitrile.

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for the highly anisotropic physical properties of CT complexes. Recently, interesting order–disorder phase transformations have been found in some of them. In many structural investigations the disorder has manifested itself by large anisotropic thermal motions (Shmueli & Goldberg, 1974).

Among the complexes of 1,2,4,5-tetracyanobenzene (TCNB) the most extensively studied were those with anthracene (Tsuchiya, Marumo & Saito, 1972; Stezowski, 1980; Lefebvre, Odou, Muller, Mierzejewski & Luty, 1989) and naphthalene (Kumakura, Iwasaki & Saito, 1967; Lefebvre *et al.*, 1989). The experimental and theoretical effort devoted to the complexes of TCNB (Luty & Kuchta, 1986; Luty, 1988) allowed the workers to conclude that the presence and nature of the disorder depends on the size and symmetry of the donors embedded in the orientationally ordered TCNB sublattice. The character of the observed disorder may be dynamical (anthracene–TCNB), static (naphthalene–TCNB) or statistically static (pyrene–TCNB).

The aim of this paper is to establish the crystallographic structure of the title compound at room temperature.

Experimental. 1,2,4,5-Tetracyanobenzene was prepared by the method described by Lawton & McRitchie (1959) and purified by vacuum sublimation. Commercially available durene was purified by zone melting. A 1:1 stoichiometric mixture of durene and TCNB was dissolved in pure acetone. Green crystals of the durene–TCNB complex were grown from this solution by slow evaporation at room temperature. The size of the single crystal used was 0·4 × 0·4 × 0·3 mm. Diffraction measurements were performed with a Philips PW 1100 automatic diffractometer using monochromated Mo $K\alpha$ radiation. ω-scan mode used with $2 < \theta < 30°$ $[0{\cdot}05 < (\sin\theta)/\lambda < 0{\cdot}70\ \text{Å}^{-1}]$, scan width 1·5° and scan speed $0{\cdot}015°\ \text{s}^{-1}$. Background counted for half the total scan time on each side of the $K\alpha$ position. Every 2 h three standard reflections ($2\bar{1}1$, $\bar{2}21$ and $21\bar{2}$) were monitored for correction purposes. Their intensities varied within 3%, corrections made using *FSCALE*. 5808 reflections measured with $-21 \leq h \leq 21$, $0 \leq k \leq 10$ and $0 \leq l \leq 10$ (Friedel reflections measured) corresponded to 912 non-equivalent reflections with $I > 3\sigma(I)$. Data corrected for Lorentz and polarization effects. No correction for absorption applied ($\mu = 0{\cdot}41\ \text{cm}^{-1}$). 24 reflections ($6 < \theta < 9°$) used for measuring lattice parameters.

Systematic absences of $h0l$ reflections for $h = 2n + 1$ and $0k0$ reflections for $k = 2n + 1$ suggested $P2_1/a$ as the space group. Initial coordinates of C and N atoms, for the least-squares procedure, were found by direct methods (*MULTAN77*; Main, Lessinger, Woolfson, Germain & Declercq, 1977). Subsequent Fourier syntheses made after several cycles of refinement allowed the H atoms to be localized. In order to prevent extinction effects, nine reflections with a low angle and a high intensity were initially removed. Further refinements (on F) employing anisotropic temperature factors for heavy atoms and isotropic ones for H gave $R = 0{\cdot}050$ $\{wR = 0{\cdot}041$, with weighting scheme $w = [\sigma^2(F) + 0{\cdot}0001F^2]^{-1}\}$. After inclusion of the nine previously removed reflections and introduction of an isotropic extinction factor X, the new calculated structure factor $F^*_{\rm calc}$ became: $F^*_{\rm calc} = F_{\rm calc}(1 - XF^2_{\rm calc}/\sin\theta)$. Then the final refinement reduced the R factor to 0·047 ($wR = 0{\cdot}038$) with $X = 3{\cdot}26\,(6) \times 10^{-6}$. The shifts in atomic parameters in the final cycle were less than $0{\cdot}1\sigma$. $S = 0{\cdot}48$.

An analytical approximation for atomic scattering factors came from *International Tables for X-ray Crystallography* (1974). A final difference synthesis showed extreme values of 0·14 and $-0{\cdot}16\ \text{e}\ \text{Å}^{-3}$. All calculations were carried out with *SHELX76* (Sheldrick, 1976).

Discussion. The final atomic coordinates measured at 293 K are reported in Table 1.† The bond lengths and angles are presented in Table 2. Like most TCNB complexes the structure of durene–TCNB is formed by donor (durene) and acceptor (TCNB) molecules arranged alternately plane-to-plane along the *c* axis. The projection along the *b* axis of the unit cell is presented in Fig. 1. As in the anthracene and naphthalene complexes, molecules of TCNB and/or durene form infinite sheet-like planes perpendicular to the *c* axis. The two molecules in the complex are essentially planar, except for the H atoms of the durene methyl groups. The least-squares best planes through the molecules, in the orthogonal system **a**, **b**, **c***, are as follows: $0{\cdot}1187x - 0{\cdot}3684y - 0{\cdot}9221z$ for durene and $0{\cdot}1038x - 0{\cdot}3661y - 0{\cdot}9248z$ for TCNB with a maximum deviation of 0·004 Å for C(5) in the durene molecule and 0·014 Å for N(9) in TCNB. The two molecules are almost parallel, the dihedral angle between their planes being 0·6°. The mean distance between two consecutive molecules in the stack is 3·457 Å with a minimum atomic approach of 3·481 Å for C(2)–C(10). This interstack distance in the durene–TCNB complex is similar to those found in the room-temperature structures of anthracene–TCNB (3·468 Å) and naphthalene–TCNB (3·440 Å) (Lefebvre *et al.*, 1989). However, in the present case one has to consider the H atoms of the durene

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† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51839 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters* (× 10^4) *and isotropic temperature factors* (Å^2 × 10^3) *for durene–TCNB at room temperature*

$U_{eq} = \frac{1}{3}(\text{trace } \mathbf{U})$.

	x	y	z	U_{eq}/U_{iso}
C(1)	420 (2)	1401 (4)	−464 (4)	54 (4)
C(2)	942 (2)	−16 (4)	251 (4)	47 (4)
C(3)	511 (2)	−1464 (4)	736 (4)	49 (3)
C(4)	1960 (2)	26 (7)	499 (9)	87 (7)
C(5)	1030 (3)	−3074 (5)	1542 (6)	82 (5)
H(1)	721 (16)	2394 (32)	−842 (34)	51 (8)
H(41)	2246 (26)	−181 (50)	1633 (51)	107 (18)
H(42)	2130 (24)	1206 (58)	75 (54)	120 (15)
H(43)	2127 (21)	−915 (48)	−352 (48)	100 (14)
H(51)	471 (29)	−2797 (55)	2581 (56)	138 (19)
H(52)	1373 (21)	−3578 (43)	657 (46)	97 (12)
H(53)	551 (30)	−3897 (62)	1938 (62)	175 (19)
C(6)	−911 (2)	485 (3)	4576 (4)	40 (3)
C(7)	−266 (2)	1620 (3)	4258 (3)	40 (3)
C(8)	650 (2)	1126 (3)	4686 (4)	38 (3)
C(9)	−544 (2)	3300 (4)	3509 (4)	46 (4)
C(10)	1336 (2)	280 (4)	4365 (4)	52 (3)
N(9)	−784 (2)	4636 (3)	2938 (4)	72 (4)
N(10)	1895 (2)	3152 (4)	4139 (4)	76 (4)
H(6)	−1561 (16)	847 (29)	4296 (31)	39 (6)

Table 2. *Bond lengths* (Å) *and bond angles* (°) *for durene–TCNB at room temperature*

The primed atoms are obtained with the inversion centre.

C(1)—C(2)	1.379 (4)	C(5)—H(52)	1·02 (4)
C(1)—C(3′)	1·381 (4)	C(5)—H(53)	1·07 (5)
C(1)—H(1)	0·98 (3)	C(6)—C(7)	1·387 (4)
C(2)—C(3)	1·396 (4)	C(6)—C(8′)	1·382 (3)
C(2)—C(4)	1·514 (5)	C(6)—H(6)	1·00 (3)
C(3)—C(5)	1·516 (5)	C(7)—C(8)	1·401 (4)
C(4)—H(41)	0·86 (4)	C(7)—C(9)	1·437 (4)
C(4)—H(42)	1·02 (5)	C(8)—C(10)	1·444 (4)
C(4)—H(43)	1·04 (4)	C(9)—N(9)	1·143 (4)
C(5)—H(51)	0·91 (4)	C(10)—N(10)	1·135 (4)

C(2)—C(1)—C(3′)	123·4 (3)	C(3)—C(5)—H(52)	111· (2)
C(2)—C(1)—H(1)	118· (2)	C(3)—C(5)—H(53)	106· (3)
C(3′)—C(1)—H(1)	118· (2)	H(51)—C(5)—H(52)	105· (3)
C(1)—C(2)—C(3)	118·6 (3)	H(51)—C(5)—H(53)	108· (4)
C(1)—C(2)—C(4)	119·9 (3)	H(52)—C(5)—H(53)	117· (3)
C(3)—C(2)—C(4)	121·5 (3)	C(7)—C(6)—C(8′)	120·0 (3)
C(2)—C(3)—C(5)	122·3 (3)	C(7)—C(6)—H(6)	120· (2)
C(2)—C(3)—C(1′)	118·0 (3)	C(8′)—C(6)—H(6)	120· (2)
C(5)—C(3)—C(1′)	119·7 (3)	C(6)—C(7)—C(8)	119·8 (2)
C(2)—C(4)—H(41)	111· (3)	C(6)—C(7)—C(9)	119·6 (2)
C(2)—C(4)—H(42)	108· (2)	C(8)—C(7)—C(9)	120·7 (2)
C(2)—C(4)—H(43)	108· (2)	C(7)—C(8)—C(10)	121·0 (3)
H(41)—C(4)—H(42)	112· (4)	C(7)—C(8)—C(6′)	120·2 (3)
H(41)—C(4)—H(43)	110· (4)	C(10)—C(8)—C(6′)	118·8 (3)
H(42)—C(4)—H(43)	108· (3)	C(7)—C(9)—N(9)	178·0 (3)
C(3)—C(5)—H(51)	110· (3)	C(8)—C(10)—N(10)	177·9 (3)

methyl groups which occupy positions out of the molecular plane. There are four such H atoms [H(41), H(43), H(51) and H(52)] whose distances to the neighbouring TCNB plane are 2·62–2·74 Å. These values are smaller than the sum of the van der Waals radius of H and the half depth of a benzene ring (≃2·9 Å); thus these H atoms must be located in the 'holes' of the TCNB molecule. For example, for H(41), the smallest intermolecular atomic distances are H(41)–C(10) = 3·360 Å and H(41)–N(10) = 3·323 Å, and for H(52): H(52)–C(9) = 3·061 Å and H(52)–N(9) = 2·740 Å. For this reason, the durene molecule cannot rotate in its molecular plane, as is the case for anthracene–TCNB and naphthalene–TCNB where the donor molecules librate along the normal to their planes and show orientational disorder. It can also be concluded that there is no rotation of the H atoms around the threefold axis of the methyl groups. The mutual arrangement of durene and TCNB molecules in the complex is shown in Fig. 2, with both molecules viewed along the normal to their mean plane (the H atoms are omitted for clarity). This overlap diagram of the donor and acceptor shows that the CT interactions are not maximized in this complex.

The space group of durene–TCNB is found to be *P*2$_1$/*a*, *i.e.* the same as those of low-temperature phases of the anthracene and naphthalene complexes of TCNB. One may ask whether a high-temperature phase with *C*2/*m* as the space group can exist for the durene–TCNB complex as is the case for anthracene–TCNB and naphthalene–TCNB. In such a case it is necessary to have two molecular sites of 2/*m* symmetry and in order to fulfill this condition,

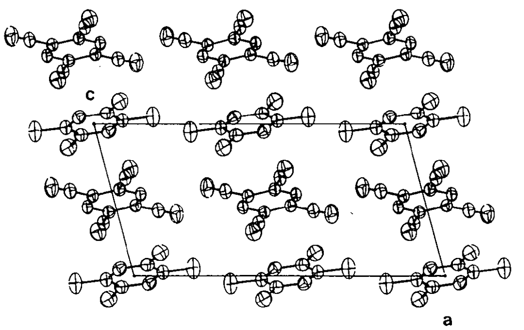

Fig. 1. Packing projection along the *b* axis for durene–TCNB at room temperature.

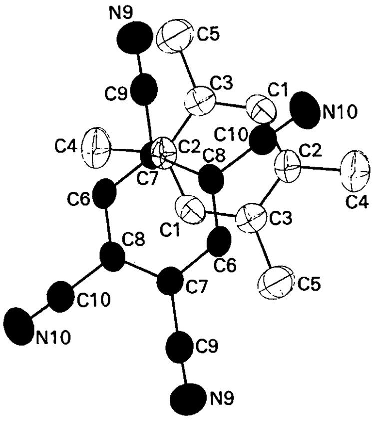

Fig. 2. Projection along the normal to the molecular planes for durene–TCNB (atoms of the TCNB molecule are drawn in black).

the molecular planes have to be perpendicular to the site plane with the long molecular axes perpendicular or along the twofold axis. In the case of durene–TCNB, the normals to the molecular planes make an angle of 21·5° to the *ac* plane and the angles between this plane and the long molecular axes are 28·2 and 62·7° for durene and TCNB, respectively. It seems that rotations of the molecules necessary to obtain their positions for the *C*2/*m* space group are impossible.

In CT crystals, it is interesting to make a comparison between the conformation of molecules in the crystals of the complex and that in the pure compounds. For durene–TCNB no significant differences appear for the durene molecule. Nevertheless, as for the crystal of the pure compound (Prince, Schroeder & Rush, 1973), one can notice a distortion of the benzene ring: the C(2)—C(1)—C(3′) angle is 123·4° [C(1) is bonded to an H atom], whereas the mean value of angles with a central C atom bonded to a methyl group is 118·3°. For the TCNB molecule a distortion of the order of 2° was observed for C—C═N directions with respect to the benzene ring. Namely, the values of the C(8)—C(7)—C(9) and C(7)—C(8)—C(10) angles are 120·7 and 121·0°, respectively. The corresponding mean value for the angle in the direction of the cyano group in the pure compound is 119·0° (Lefebvre *et al.*, 1989).

Analysis of the anisotropic temperature factors (Schomaker & Trueblood, 1968), calculated from *SHELX76*, shows that both molecules can be treated as rigid bodies to a good approximation and that they execute small librational movements. Results of rigid-body analysis of durene and TCNB molecules in the complex are presented in Table 3. The principal axes of the libration tensor L for TCNB lie within 10° of the main molecular axes. One can notice a considerable anisotropy of the eigenvalues of the libration tensor **L**, with the highest value L_1 = 21·7 deg^2, corresponding to the long molecular axis, which is, on the other hand, also the direction of the smallest moment of inertia. For the durene molecule, an even larger anisotropy of the libration tensor is observed: $L_1 = 30{\cdot}4$, $L_2 = 6{\cdot}6$ and $L_3 = 4{\cdot}2$ deg^2, but the situation for its principal axes is not so clear. The direction corresponding to the highest eigenvalue L_1 is close to that defined by the C(3)—C(5) bond but it is also close to the eigendirection of L_1 for the TCNB molecule. The fact that both molecules in the complex have an approximately common eigendirection for their highest eigenvalues of the tensor **L**, allows a nearly constant interstack distance to be maintained when they vibrate in phase. On the other hand, for the durene molecule this direction reduces the thermal displacements of H atoms bonded to C(5), particularly H(52) which has a short atomic contact with TCNB. In general, the state of the thermal vibrations in durene–TCNB is different from that encountered in the many other complexes of TCNB where donor molecules vibrate along the normal to their main molecular planes. The reason for this difference lies in the fact that the molecular packing is governed mainly by dipole–dipole interaction of the C═N groups of TCNB and the relatively large volume of the CH_3 groups of durene. The CT interactions play a minor role in the complex formation. No order–disorder librational-type phase transition can be expected in this complex at higher temperatures.

Table 3. *Rigid-body analysis of durene and TCNB molecules of the durene–TCNB complex*

T_i values are given in Å^2 × 10^4, L_i in deg^2. The orthogonal coordinate system is **a**, **b**, **c***.

	Eigenvalues	Eigenvectors		
TCNB molecule				
T_1	434	0·0979	0·8985	−0·4280
T_2	292	0·9938	−0·0658	0·0892
T_3	276	0·0518	−0·4341	−0·8991
L_1	21·7	0·2065	0·9197	−0·3339
L_2	8·5	0·9059	−0·0508	0·4204
L_3	6·0	0·3697	−0·3893	−0·8437
R.m.s.	0·0032 Å^2			
E.s.d.	0·0034 Å^2			
Durene molecule				
T_1	515	−0·0446	0·9908	−0·1276
T_2	373	−0·9656	−0·0755	−0·2490
T_3	295	−0·2563	0·1121	0·9601
L_1	30·4	0·2356	−0·9532	0·1893
L_2	6·6	0·5201	−0·0408	−0·8531
L_3	4·2	0·8209	0·2994	0·4862
R.m.s.	0·0049 Å^2			
E.s.d.	0·0054 Å^2			

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Structures of Dimethyltetramethylenetetrathiafulvalene Perchlorate, $(DMCTTF)_2ClO_4$, and Tetrafluoroborate, $(DMCTTF)_2BF_4$, Salts

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Abstract. Bis[2-(4,5-dimethyl-1,3-dithiol-2-ylidene)-4,5,6,7-tetrahydro-1,3-benzodithiol]ium perchlorate, $(C_{12}H_{14}S_4)_2ClO_4$, $M_r = 672{\cdot}42$, crystallizes in two phases: α-phase, monoclinic, $C2/c$, $a = 15{\cdot}0612\,(57)$, $b = 7{\cdot}7832\,(8)$, $c = 24{\cdot}9299\,(50)$ Å, $\beta = 101{\cdot}28\,(10)^\circ$, $V = 2865{\cdot}9$ Å^3, $Z = 8$, $D_x = 1{\cdot}56$ g cm^{-3}, $\lambda(\text{Cu}\ K\alpha) = 1{\cdot}54178$ Å, $\mu = 66{\cdot}66$ cm^{-1}, $F(000) = 1396$, $T = 298$ K, $R = 0{\cdot}046$ for 2379 observed reflections $[I > 2{\cdot}5\sigma(I)]$; β-phase, triclinic, $P\overline{1}$, $a = 7{\cdot}7104\,(18)$, $b = 7{\cdot}8210\,(62)$, $c = 25{\cdot}7180\,(77)$ Å, $\alpha = 83{\cdot}76\,(11)$, $\beta = 81{\cdot}77\,(14)$, $\gamma = 68{\cdot}58\,(37)^\circ$, $V = 1426{\cdot}1$ Å^3, $Z = 2$, $D_x = 1{\cdot}57$ g cm^{-3}, $\lambda(\text{Mo}\ K\alpha) = 0{\cdot}71079$ Å, $\mu = 6{\cdot}78$ cm^{-1}, $F(000) = 698$, $T = 298$ K, $R = 0{\cdot}044$ for 2810 observed reflections $[I > 2{\cdot}5\sigma(I)]$. Bis[2-(4,5-dimethyl-1,3-dithiol-2-ylidene)-4,5,6,7-tetrahydro-1,3-benzodithiol]ium tetrafluoroborate, $(C_{12}H_{14}S_4)_2BF_4$, one crystalline phase observed, isometric to the α-phase, $M_r = 648{\cdot}96$, monoclinic, $C2/c$, $a = 15{\cdot}0175\,(22)$, $b = 7{\cdot}7403\,(6)$, $c = 24{\cdot}8673\,(28)$ Å, $\beta = 101{\cdot}154\,(10)^\circ$, $V = 2835{\cdot}9$ Å^3, $Z = 8$, $D_x = 1{\cdot}558$ g cm^{-3}, $\lambda(\text{Cu}\ K\alpha) = 1{\cdot}54178$ Å, $\mu = 59{\cdot}85$ cm^{-1}, $F(000) = 1364$, $T = 298$ K, $R = 0{\cdot}055$ for 2186 observed reflections $[I > 3\sigma(I)]$. Both compounds contain two DMCTTF organic stacks per unit cell: in the α-phase, these are symmetry related through the 2_1 screw axis; in the β-phase the organic stacks are independent; as a general trend, the DMCTTF^+ cations are strongly dimerized and favor electron conduction localization at low temperature.

Introduction. The title compounds belong to a novel series of organic conductors which are based on the new unsymmetrical π-donor derived from the tetrathiafulvalene (TTF) backbone: dimethyltetramethylenetetrathiafulvalene (DMCTTF) and its selenium analogue (DMCTSeF). Since the discovery of superconductivity and antiferromagnetism in the organic Bechgaard salts, intensive research has been devoted to the synthesis of new π-donor molecules. The salts obtained are generally built from columns of these molecules which contain quasi-one-dimensional networks of S···S contacts thus providing the conductivity pathway for the electrons. In order to favor the coupling between the conducting organic stacks, several unsymmetrical derivatives of TTF have been synthesized (Coulon, Amiel, Chasseau, Manhal & Fabre, 1986; Fabre, Giral, Dupart, Coulon, Manceau & Delhaes, 1983). The $(DMCTTF)_2X$ salts, where X is a diamagnetic anion ($X = AsF_6^-$, PF_6^-, BF_4^-, ClO_4^-, ReO_4^-), have been synthesized recently (Giral, Fabre & Gouasmia, 1986) and exhibit remarkable physical properties (Vaca, Granier, Gallois, Coulon, Gouasmia & Fabre, 1988). For all the sulfur compounds of the series an antiferromagnetic ground state is observed at higher temperatures (20–30 K) than in previous series (10–20 K). Finally, the compounds described here present original magnetic behavior, since they are built from two types of chains per unit cell. According to whether these chains are symmetry related or not, they reach the magnetic ground state at the same or two different temperatures.

Experimental. As for all the compounds of the $(DMCTTF)_2X$ series, the above radical cation salts were prepared in tetrahydrofuran using oxidative electrocrystallization at constant current (10 μA), in the presence of tetrabutylammonium perchlorate

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