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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]jium 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, $P\bar{1}$, $a = 7{\cdot}7104\,(18)$, $b = 7{\cdot}8210\,(62)$, $c = 25{\cdot}7180\,(77)$ 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]jium 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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(tetrafluoroborate) and DMCTTF (Giral, Fabre & Gouasmia, 1986). The crystals obtained were thin black platelets with a lozenge shape for $(DMCTTF)_2ClO_4$ and $(DMCTTF)_2BF_4$ α-phase, and a spearhead shape for $(DMCTTF)_2ClO_4$ β-phase. Both phases of the perchlorate salt were found in the same batch. All measurements carried out on an Enraf–Nonius diffractometer CAD-4, determination of the unit-cell parameters by least-squares refinement of the setting angles of 24 reflections [$12 < \theta < 70°$ for $(DMCTTF)_2ClO_4$ and $(DMCTTF)_2BF_4$ α-phases, $7 < \theta < 31°$ for the β-phase of $(DMCTTF)_2ClO_4$]. Data-collection characteristics are given in Table 1. Reflection intensity data collected using the $\omega/2\theta$ scan technique. Three standard reflections measured at an interval of 100 reflections, small random variation was observed (±3% for α-ClO_4, ±4% for α-BF_4 and β-ClO_4). Data corrected for Lorentz and polarization factor, also empirical absorption correction (North, Phillips & Mathews, 1968) (transmission range 0·57–0·99). S and Cl atoms located by a Patterson map analysis and the structures completed by the Fourier recycling method using the *MITHRIL* package (Gilmore, 1983). Full-matrix least-squares refinement on *F*, using *SHELX*76 (Sheldrick, 1976), atomic scattering factors with anomalous-dispersion coefficients inlaid. All non-H atoms refined with anisotropic thermal parameters, methylene and methyl groups as rigid groups with a C—H bond length of 1·08 Å and an H—C—H bond angle of 109·5°. The final atomic positional and thermal parameters are given in Table 2 for $(DMCTTF)_2BF_4$ and $(DMCTTF)_2ClO_4$ α-phase and in Table 3 for $(DMCTTF)_2ClO_4$ β-phase.*

Table 1. *Data collection characteristics*

	$(DMCTTF)_2$-BF_4 α-phase	$(DMCTTF)_2$-ClO_4 α-phase	$(DMCTTF)_2$-ClO_4 β-phase
Crystal size (mm)	0·20 × 0·10 × 0·02	0·18 × 0·14 × 0·02	0·20 × 0·11 × 0·03
θ_{min}–θ_{max} (°)	1–70	1–70	0·8–25
Index range *h*	− 18→18	− 18→18	0→9
k	0→9	0→9	− 9→9
l	0→30	0→30	− 30→30
Scan type	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
Scan angle (°)	$2 + 0·15\tan\theta$	$2 + 0·15\tan\theta$	$1·5 + 0·35\tan\theta$
Monochromator	Graphite	Graphite	Graphite
Number of unique reflections	2699	2684	4241
Observed data	2186	2379	2810
Number of parameters	188	188	374
Number of restraints	4	4	3
wR	0·0512	0·0626	0·0471
$w = 1/[\sigma^2(F) + gF^2]$; *g*	0·0001	0·0005	0·001
Goodness of fit, S	2·62	4·17	1·42
$(\Delta/\sigma)_{max}$	0·578	0·625	0·332
Residual e Å^{-3}	0·9	1·0	0·9

Table 2. $(DMCTTF)_2BF_4/(DMCTTF)_2ClO_4$ *α-phase fractional atomic coordinates*

$$U_{eq} = \tfrac{1}{3}(\textstyle\sum_i\sum_j a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j U_{ij}).$$

	x	*y*	*z*	$U_{eq}(\times 10^3 Å^2)$
S1	4422 (1)	2698 (1)	819 (1)	44 (1)
	4426 (1)	2696 (1)	806 (1)	37 (1)
S11	3519 (1)	324 (1)	−226 (1)	44 (1)
	3503 (1)	319 (1)	−230 (1)	37 (1)
S2	3851 (1)	5803 (1)	182 (1)	46 (1)
	3848 (1)	5773 (1)	166 (1)	38 (1)
S12	2939 (1)	3460 (1)	−856 (1)	47 (1)
	2919 (1)	3424 (1)	−863 (1)	40 (1)
C1	4738 (3)	4677 (5)	1134 (2)	43 (3)
	4754 (2)	4666 (4)	1117 (1)	35 (2)
C11	3019 (3)	71 (5)	−916 (2)	41 (3)
	2997 (2)	46 (4)	−916 (1)	35 (2)
C2	4475 (3)	6103 (5)	842 (1)	43 (3)
	4481 (2)	6090 (4)	821 (1)	36 (2)
C12	2760 (3)	1504 (5)	− 1203 (1)	43 (3)
	2740 (2)	1469 (5)	− 1206 (1)	36 (2)
C3	3866 (3)	3596 (5)	200 (1)	42 (3)
	3866 (2)	3562 (4)	192 (1)	33 (2)
C13	3483 (3)	2567 (5)	−238 (2)	43 (3)
	3471 (2)	2547 (4)	−246 (1)	34 (2)
C4	4643 (3)	7950 (6)	1024 (2)	57 (4)
	4668 (3)	7917 (4)	1002 (2)	49 (3)
C14	2343 (4)	1511 (6)	− 1806 (2)	59 (4)
	2319 (3)	1469 (4)	− 1206 (1)	36 (2)
C5	5299 (3)	4630 (6)	1706 (2)	56 (4)
	5314 (3)	4628 (5)	1684 (1)	47 (3)
C15	2908 (3)	− 1739 (5)	− 1145 (2)	49 (4)
	2881 (3)	− 1744 (4)	− 1146 (1)	43 (3)
C16	2115 (6)	−281 (9)	−2005 (2)	96 (8)
	2081 (5)	−313 (7)	−2005 (2)	85 (6)
C17	2641 (6)	− 1690 (8)	− 1764 (2)	98 (8)
	2625 (5)	− 1709 (7)	− 1761 (2)	89 (7)
B	0	4813 (10)	2500	68 (9)
Cl	0	4781 (2)	2500	57 (1)
F1	236 (6)	5652 (6)	2940 (2)	209 (13)
O1	255 (6)	5703 (7)	2958 (2)	195 (12)
F2	− 591 (5)	3616 (11)	2561 (3)	238 (13)
O2	− 590 (5)	3590 (11)	2572 (3)	236 (14)

Discussion. Bond lengths and bond angles of the $DMCTTF^+$ cations are gathered in Table 4, those of BF_4^- and ClO_4^- anions in Table 5. Fig. 1 gives the molecular scheme and atomic labeling of the $DMCTTF^+$, BF_4^- and ClO_4^- ions. The ion conformations are similar in all the structures and are described in the following.

DMCTTF *conformations.* All the bond lengths and angles of the TTF backbone are similar to those found in other TTF derivatives (see, for instance, Liautard, 1984; Thorup, Rindorf, Soling & Bechgaard, 1981). Furthermore, Table 4 shows there is no noticeable dispersion of the bond length values from one compound of the series to another. However, this is not true for the cyclohexene moiety which may adopt two different conformations: these are illustrated in Fig. 2 and correspond to those of the two $DMCTTF^+$ cations of the asymmetric unit in the triclinic ClO_4 β-phase. Conformation *A* differs from conformation *B* by the shortening of the C16—C17 bond (1·40 *versus* 1·54 Å). This supports

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51878 (51 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. $(DMCTTF)_2ClO_4$ *triclinic β-phase fractional atomic coordinates*

$U_{eq} = \frac{1}{3}(\sum_i\sum_j a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j U_{ij})$.

	x	y	z	$U_{eq}(\times 10^3 Å^2)$
S1	4496 (2)	3674 (2)	4231 (1)	45 (1)
S11	2075 (2)	2525 (2)	5259 (1)	43 (1)
S2	7799 (2)	2347 (2)	4794 (1)	42 (1)
S12	5414 (2)	1154 (2)	5814 (1)	45 (1)
C1	6544 (7)	3885 (7)	3892 (2)	45 (6)
C11	1804 (8)	1740 (7)	5918 (2)	43 (6)
C2	8070 (7)	3270 (7)	4151 (2)	38 (5)
C12	3325 (7)	1118 (7)	6177 (2)	43 (6)
C3	5452 (7)	2674 (7)	4809 (2)	38 (5)
C13	4437 (7)	2176 (7)	5240 (2)	36 (5)
C4	9969 (8)	3306 (9)	3952 (2)	56 (7)
C14	3355 (9)	388 (9)	6738 (2)	59 (7)
C5	6386 (10)	4751 (9)	3342 (2)	70 (8)
C15	−100 (8)	1805 (9)	6166 (2)	55 (7)
C16	1444 (13)	737 (19)	7007 (3)	131 (18)
C17	−48 (13)	971 (16)	6719 (3)	117 (13)
S101*	1035 (2)	2633 (2)	698 (1)	53 (1)
S111	3986 (2)	2451 (2)	−375 (1)	51 (1)
S102	−1763 (2)	2669 (2)	45 (1)	59 (1)
S112	1087 (2)	2504 (2)	−997 (1)	60 (1)
C101	−1123 (8)	2646 (8)	1027 (2)	46 (6)
C111	4574 (8)	2356 (7)	−1055 (2)	42 (6)
C102	−2407 (8)	2645 (8)	728 (2)	45 (6)
C112	3253 (8)	2352 (8)	−1338 (2)	46 (6)
C103	485 (8)	2608 (8)	73 (2)	46 (6)
C113	1695 (8)	2538 (8)	−379 (2)	46 (6)
C104	−4336 (8)	2649 (10)	904 (2)	65 (8)
C114	3527 (9)	2193 (10)	−1926 (2)	60 (7)
C105	−1322 (9)	2608 (10)	1620 (2)	65 (8)
C115	6510 (8)	2251 (9)	−1283 (2)	53 (7)
C116	5299 (9)	2544 (10)	−2166 (2)	63 (8)
C117	6925 (9)	1534 (10)	−1832 (2)	61 (8)
Cl	2418 (3)	3487 (3)	2475 (1)	76 (2)
O1	1710 (12)	2138 (11)	2657 (2)	208 (14)
O2	2581 (11)	4430 (11)	2897 (3)	187 (13)
O3	4268 (12)	2675 (12)	2267 (3)	181 (14)
O4	1572 (15)	4633 (14)	2074 (4)	290 (21)

*Numbers greater than 100 label atoms belonging to the $DMCTTF^+$ cations which adopt the *B* (*i.e.* ordered) conformation.

Table 4. DMCTTF *bond lengths* (Å) *and angles* (°)

	BF_4	α-ClO_4	β-ClO_4 (I)	β-ClO_4 (II)
C5—C1	1·507 (6)	1·499 (5)	1·501 (8)	1·509 (8)
C4—C2	1·506 (6)	1·502 (5)	1·490 (9)	1·490 (9)
C2—C1	1·338 (6)	1·350 (5)	1·342 (8)	1·338 (9)
S1—C1	1·744 (4)	1·745 (3)	1·746 (6)	1·752 (6)
S2—C2	1·742 (4)	1·740 (3)	1·747 (5)	1·755 (6)
S1—C3	1·747 (4)	1·733 (3)	1·734 (5)	1·724 (6)
S2—C3	1·709 (4)	1·722 (3)	1·728 (6)	1·728 (7)
C3—C13	1·382 (6)	1·385 (4)	1·369 (7)	1·375 (8)
S11—C13	1·737 (4)	1·735 (3)	1·735 (6)	1·744 (7)
S12—C13	1·737 (4)	1·738 (3)	1·733 (5)	1·727 (6)
S11—C11	1·745 (4)	1·744 (3)	1·750 (6)	1·746 (5)
S12—C12	1·738 (4)	1·741 (3)	1·751 (6)	1·741 (6)
C11—C12	1·336 (6)	1·338 (5)	1·339 (8)	1·335 (9)
C11—C15	1·510 (6)	1·503 (5)	1·500 (9)	1·499 (9)
C12—C14	1·508 (6)	1·507 (5)	1·492 (8)	1·508 (8)
C15—C17	1·513 (7)	1·507 (6)	1·499 (10)	1·523 (9)
C14—C16	1·491 (9)	1·493 (7)	1·476 (13)	1·523 (10)
C16—C17	1·411 (10)	1·424 (8)	1·402 (15)	1·541 (10)
S1—C1—C5	117·2 (3)	117·4 (2)	115·8 (4)	116·5 (4)
S2—C2—C4	116·0 (3)	116·8 (3)	116·3 (4)	115·7 (4)
C5—C1—C2	125·7 (4)	125·9 (3)	127·5 (5)	126·7 (6)
C4—C2—C1	127·3 (4)	126·5 (3)	127·1 (5)	127·9 (6)
S1—C1—C2	117·0 (3)	116·7 (3)	116·7 (4)	116·8 (5)
S2—C2—C1	116·7 (3)	116·7 (3)	116·6 (4)	116·4 (5)
C3—S1—C1	95·1 (2)	95·5 (2)	96·1 (3)	96·0 (3)
C3—S2—C2	96·1 (2)	96·0 (2)	96·3 (3)	96·0 (3)
S2—C3—S1	115·0 (2)	115·1 (2)	114·3 (3)	114·8 (3)
S1—C3—C13	121·4 (3)	122·3 (2)	122·9 (4)	124·5 (5)
S2—C3—C13	123·7 (3)	122·6 (2)	122·8 (4)	120·7 (5)
S11—C13—C3	123·7 (3)	123·1 (3)	122·8 (4)	122·8 (5)
S12—C13—C3	121·4 (3)	122·1 (3)	122·5 (4)	122·9 (5)
S11—C13—S12	114·9 (2)	114·8 (2)	114·7 (3)	114·3 (3)
C11—S11—C13	95·1 (2)	95·4 (2)	95·3 (3)	95·6 (3)
C13—S12—C12	95·4 (2)	95·3 (2)	96·2 (3)	96·1 (3)
S11—C11—C12	117·3 (3)	117·0 (3)	117·7 (4)	116·9 (4)
S12—C12—C11	117·1 (3)	117·2 (3)	115·9 (4)	117·0 (5)
S11—C11—C15	118·1 (3)	118·9 (2)	119·1 (4)	118·8 (4)
S12—C12—C14	119·0 (3)	118·9 (3)	119·1 (4)	118·5 (4)
C12—C11—C15	124·6 (4)	124·1 (3)	123·2 (5)	124·3 (5)
C11—C12—C14	123·9 (4)	123·9 (3)	125·0 (5)	124·5 (5)
C11—C15—C17	110·5 (4)	111·1 (3)	111·8 (6)	109·3 (5)
C12—C14—C16	110·6 (5)	110·9 (4)	111·7 (6)	110·3 (5)
C14—C16—C17	120·3 (6)	119·0 (5)	120·7 (9)	110·8 (6)
C15—C17—C16	117·9 (6)	117·5 (5)	121·5 (9)	111·6 (6)

Table 5. BF_4^- *and* ClO_4^- *bond lengths* (Å) *and angles* (°)

α-Phase			
B—F1	1·264 (7)	F1—B—F2	110·2 (6)
B—F2	1·312 (10)		
Cl—O1	1·340 (6)	O1—Cl—O2	110·3 (5)
Cl—O2	1·321 (9)		
β-phase			
Cl—O1	1·367 (9)	O1—Cl—O2	111·0 (5)
Cl—O2	1·422 (8)	O1—Cl—O3	109·0 (5)
Cl—O3	1·385 (10)	O2—Cl—O3	102·3 (5)
Cl—O4	1·363 (11)	O3—Cl—O4	104·4 (6)
		O1—Cl—O4	115·4 (6)
		O2—Cl—O4	113·5 (6)

the differences in the values of the C14—C16—C17 and C15—C17—C16 angles (~ 120 *versus* ~ 110°). If both C16 and C17 lie on the same side of the mean molecular plane in conformation *A* (Fig. 2*a*), this is no longer the case for conformation *B* (Fig. 2*b*). Conformation *A* is a general feature of the whole $(DMCTTF)_2X$ series. However, in the β-ClO_4 triclinic salt, this conformation is observed in only one type of stack (labelled stack I in the following) while the second one (stack II) is built from molecules which adopt the unusual *B* (*i.e.* ordered) conformation.

Finally, it should be noticed that *U* equivalent thermal parameters of atoms C16 and C17 are twice as large in conformation *A* as in conformation *B*, and therefore that conformation *B* could be considered as embedded in the 'mean statistical' conformation *A*. An attempt to assign two different statistical positions (including those reminiscent of conformation *B*) to each of the C16 and C17 atoms in conformation *A* failed to improve the final least-squares refinement parameters in any of the concerned structures.

Anion conformation. In the monoclinic structures, the B (Cl) atom is located on the twofold axis; thus the whole tetrahedron is generated from the positions of two F (O) atoms. In the ClO_4 β-phase, the

Cl atom is at a general position. The dispersion of bond lengths and angles from an ideal regular tetrahedron may be due to a rotational disorder [large *U* thermal parameters of F (O) atoms] and is a common feature of all the anions. No distinct statistical positions of F or O atoms could be deduced from Fourier-map analyses.

Molecular packing. The crystal structure of all these salts contains two different (DMCTTF) layers (Figs. 3*a* and 3*b*) which are described in the following.

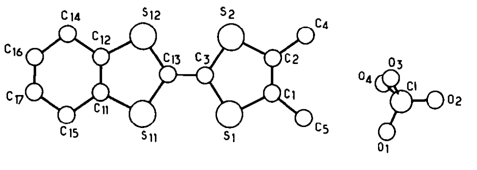

Fig. 1. Molecular scheme and atomic labeling of the DMCTTF molecule and the ClO_4 (BF_4) anion.

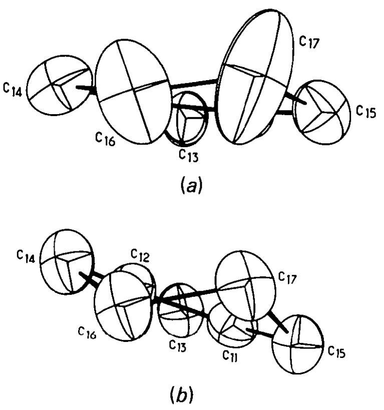

Fig. 2. (*a*) and (*b*). Conformations *A* and *B*: projections of the cyclohexene moieties along the central double bond C3—C13 of the DMCTTF molecules. In (*a*), C11 and C12 ellipsoids are hidden by the strongly disordered C17 and C16 atoms respectively.

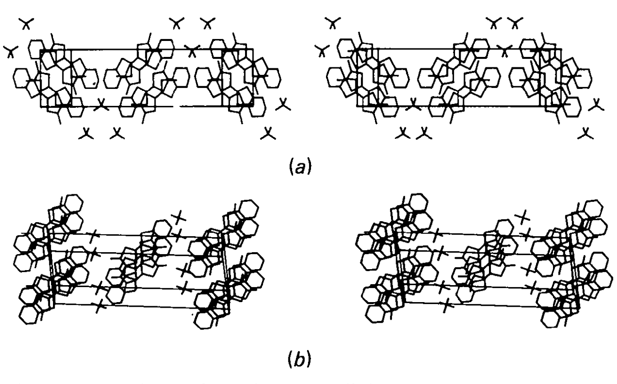

Fig. 3. Stereoviews of (*a*) the monoclinic α-phase structure along the (100) direction; (*b*) the triclinic β-phase of the ClO_4 salt along the *b* axis.

Monoclinic α-phase: (DMCTTF) layers through the twofold axis lie parallel to the *ab* plane (Fig. 3*a*). They are built from centrosymmetric DMCTTF dimers which stack either along the $(a + b)$ or $(a - b)$ directions. The DMCTTF units are oriented so that the longitudinal axes of the molecules of successive layers lie at 109·6 (BF_4) and 110·4° (ClO_4) from each other. Projections of the molecular packing within a single layer are shown in Fig. 4. In the BF_4 (ClO_4) salt, the tilt angle δ between the stacking direction and the mean plane of the DMCTTF units is 32·5° (33·0°). Within a dimer, the interplanar distance d_1 is 3·40 Å (3·39 Å). The overlap is reminiscent of the typical one encountered in the TMTTF series: limited Δl_1 component along the longitudinal axis, quasi-zero transverse Δt_2 component {molecules (I) and $[\bar{\mathrm{I}} + \frac{1}{2}(a + b)]$}. Between dimers, the interplanar distance d_2 of consecutive units is 3·72 Å (3·71 Å) and the overlap much more reduced (large Δl and Δt). All these structural parameters are gathered in

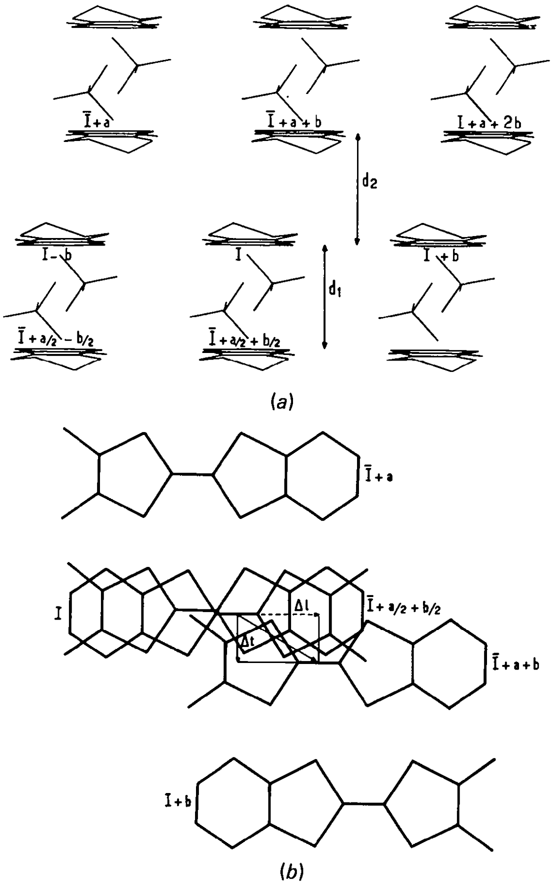

Fig. 4. Monoclinic structures. (*a*) Projection of one single layer of DMCTTF stacks along the central double bond C3—C13. (*b*) Projection of the DMCTTF molecule and its first neighbors in the mean molecular plane: Δl and Δt are, in the mean molecular plane, the longitudinal and transverse components of the vector joining the centers of the C3—C13 double bonds of two DMCTTF molecules.

Table 6 along with similar ones for the ClO_4 *β*-phase structure. This structure suggests a strong electronic localization in the $(a+b)$ direction. If the shortest intermolecular S···S contacts are obtained within the dimer ($d_{S\cdots S}$ = 3·68–3·90 Å), the second relevant ones are observed between molecules (I) and $(\bar{I}+a)$ ($d_{S\cdots S}$ = 4·36–4·40 Å) while contacts between S atoms of molecules (I) and $(\bar{I}+a+b)$ are longer (4·82–4·91 Å). Related transfer integrals have been calculated (Vaca, Coulon, Ducasse, Fritsch, Granier & Gallois, 1989) and clearly corroborate the importance of the molecular overlap between (I) and $(\bar{I}+a)$ units deduced from the crude comparison of the S···S contacts.

Table 6. *Crystal packing geometrical parameters* (Å *and* °)

Definitions of Δl and Δt are given in Fig. 4; for those of d_1, d_2 and δ, see text.

	α-BF_4	*α*-ClO_4	*β*-ClO_4	
			(I)	(II)
d_1	3·40	3·39	3·51	3·50
d_2	3·72	3·71	3·65	3·83
δ	32·47	33·00	23·70	20·20
Δl_1	1·37	1·36	1·39	1·07
Δt_1	0·10	0·10	0·05	0·35
Δl_2	2·83	2·92	1·76	1·97
Δt_2	1·61	1·61	0·05	2·21

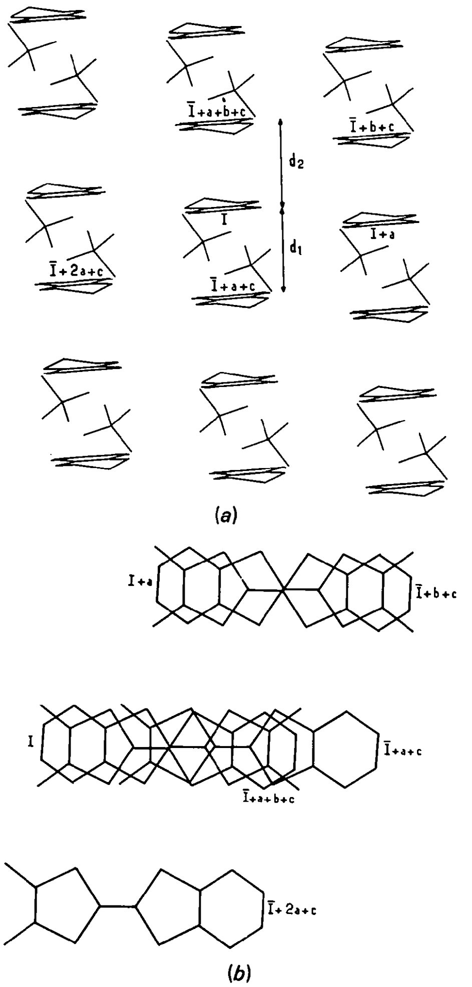

Fig. 5 (*a*) Projection of a type I DMCTTF layer along the central double bond C3—C13. (*b*) Projection of the DMCTTF molecule and its first neighbors in the mean molecular plane.

Triclinic *β*-phase: The DMCTTF units build two independent layers parallel to the *ab* plane. Layers of type I are made of DMCTTF units in conformation *A*, those of type II of molecules in conformation *B*. Their longitudinal axes relative to consecutive layers are only 17·6° apart, while their projections along the *b* direction make an angle of 1·8° only. Data gathered in Table 6 along with Figs. 5 and 6 give the inner layer arrangements of the DMCTTF molecules. In type I layers, dimerization is less important than in the monoclinic salts. Related S···S contacts are 3·77–3·97 Å inside the dimer {(I) and $[\bar{I}+(a+c)]$} and 3·94–5·00 Å between dimers. Moreover, electronic coupling should be limited between adjacent columns since the Δt_1 and Δt_2 components of the overlaps are both much smaller than in the *α*-phase; this type of compact arrangement is close to the $(DMEDTTTF)_2AsF_6$ molecular packing already described (Gallois, Gaultier, Bechtel, Chasseau & Hauw, 1987). In type II layers a stronger dimerization along *b* limits the one-dimensional electronic character along the stacking direction *b* while the large Δl_2 components between dimers [units (I) and

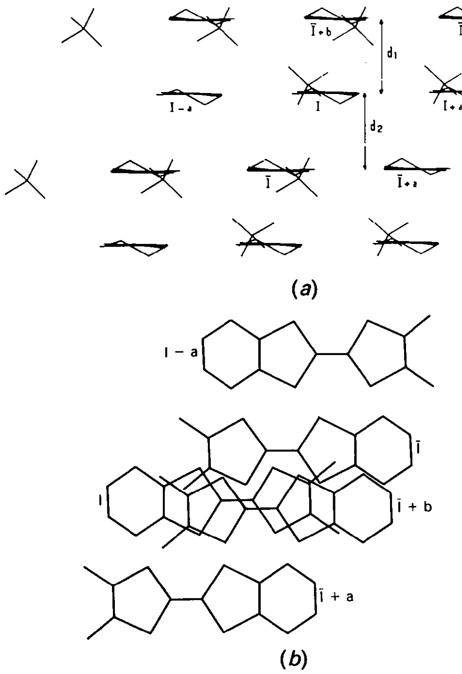

Fig. 6. (*a*) Projection of a type II DMCTTF layer along the central double bond C3—C13. (*b*) Projection of the DMCTTF molecule and its first neighbors in the mean molecular plane.

($\bar{\text{I}}$)] agree with a more enhanced two-dimensional coupling [particularly between (I) and ($\bar{\text{I}} + a$) molecules]. Such a conclusion is reinforced by the existence of short S···S contacts (3·97–4·46 Å) between these latter molecules. These structural features have been recently confirmed by calculations of transfer integrals, the results of which are largely discussed in terms of electronic structure in Vaca, Coulon, Ducasse, Fritsch, Granier & Gallois (1989).

Anion–cation interactions. As a general trend F···C (O···C) contacts are greater than the sum of the van der Waals radii, 3·10 Å (3·30 Å), of the corresponding atoms except in the ClO_4 β-phase structure where distances between O1 and C17 [($\bar{\text{I}} + c$)], O2 and C4 [(I + a)] are 3·31 and 3·38 Å respectively, which is close to 3·30 Å.

The authors are grateful to P. Vaca and C. Coulon for fruitful discussions on structure–physical properties correlations in these compounds.

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Structure of a New Crystalline Form of Famotidine

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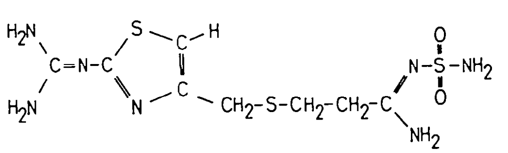
Abstract. 3-{[2-(Diaminomethyleneamino)-1,3-thiazol-4-yl]methylthio}-N^2-sulfamoylpropionamidine, $C_8H_{15}N_7O_2S_3$, M_r = 337·44, monoclinic, $P2_1/c$, a = 11·986 (1), b = 7·200 (1), c = 16·818 (1) Å, β = 99·82 (1)°, V = 1430·1 (5) Å^3, Z = 4, D_x = 1·567 g cm^{-3}, Mo $K\alpha$ radiation, λ = 0·71069 Å, μ = 5·095 cm^{-1}, $F(000)$ = 704, T = 293 (2) K, final R = 0·027 and wR = 0·026 for 3211 contributing reflections. The structure of a new crystalline form of famotidine containing only one intramolecular hydrogen bond of 2·691 (2) Å is presented.

Introduction. Famotidine is a representative of the third generation of stress-ulceration inhibitors. As a specific competitive histamine H_2-receptor antagonist, it inhibits the secretion of histamine-stimulated gastric acid. It differs from the previously described H_2-antagonists in possessing a sulfamoyl amidine function. Like cimetidine it has various crystalline forms (polymorphism) depending on the conditions of the crystallization (Kojić-Prodić, Kajfež, Belin, Toso & Sunjić, 1979). Here we present the crystal and molecular structure of the title compound (I) in a crystalline form different from those already published (Furuya, 1988; Ishida, In, Shibata, Doi, Inoue & Yanagisawa, 1987; Kálmán, 1988).



(I) Famotidine

Experimental. Synthesis of famotidine carried out by KRKA – Chemical and Pharmaceutical Works. Crystals of famotidine obtained by slow evaporation from DMF/H_2O solution. Crystal size: 0·51 × 0·50 × 0·62 mm. Unit-cell parameters and intensity data obtained on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$. Cell dimen-

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