for computing facilities, and the authors of the computer programs used.

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X-ray Crystallographic Studies on Cycloheptadithiophene Compounds and Similar Systems.

XI. The Structure of 9*H*-Cyclohepta[2,1-*b*: 4,5-*b'*]dithiophen-4-ylium Perchlorate at 173 K

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Abstract

$C_{11}H_7S_2^+.ClO_4^-$ is monoclinic, space group $P2_1/c$, with a = 10·4615 (18), b = 25·7202 (26), c = 26·8840 (23) Å, β = 94·657 (10)° at 173 K, and Z = 24. The structure was refined to an R of 0·12 for 3794 non-zero counter reflexions at 173 K. The cations are approximately planar. Aromatic character is indicated by the relatively uniform C–C lengths. The S–C bonds are equal. The structure is built up of columns of cations with the anions in between. There is orientational disorder, and diffuse scattering is observed in Weissenberg photographs. A comparison with another phase of the same compound and a similar compound is made.

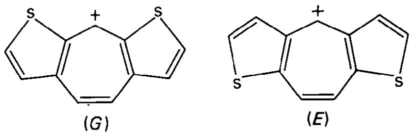

Fig. 1. Schematic drawings of molecules *G* (9*H*-cyclohepta[2,1-*b*:4,5-*b'*]dithiophen-4-ylium perchlorate), and *E* (4*H*-cyclohepta[1,2-*b*:5,4-*b'*]dithiophen-4-ylium tetrafluoroborate).

Introduction

The title compound is composed of cycloheptadithiophenylium cations and ClO_4^- anions ($G.ClO_4^-$, Fig. 1); it has two modifications. Aurivillius (1974) determined the crystal structure of the phase with a small unit cell (phase I, *G* I) and found the cation to be approximately planar. The present crystal structure is that of another phase with a large unit cell (phase II, *G* II). The structure of a corresponding compound, 4*H*-cyclohepta[1,2-*b*:5,4-*b'*]dithiophen-4-ylium tetrafluoroborate (*E*), has been determined and its molecular structure related to a series of similar compounds (Andersson, 1979). The cation *G* has an even higher degree of aromaticity than *E* (Yom-Tov, 1972).

The packing of the present compound has been studied, and compared between the two phases and the corresponding compound mentioned above. The structure was determined at 173 K.

Experimental

Crystals were formed when a saturated solution of $G.ClO_4^-$ in boiling acetonitrile was cooled to room temperature. By cooling in air, plate-like crystals (phase I) were formed and, by using ice-water, needles (phase II) were obtained.

It was possible to transform phase II to phase I by heating to 458 K for some days, or by shaking the crystals in their saturated solution at room temperature, but not the reverse. When a single crystal of II was transformed to I, it retained its habit, but the

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Table 1. *Crystal data* (*G* II)

$C_{11}H_7S_2^+.ClO_4^-$, M_r = 302·8, monoclinic, space group $P2_1/c$, Z = 24, D_m = 1·7, D_x = 1·66 Mg m^{-3}

	173 K	295 K
a	10·4615 (18) Å	10·5565 (8) Å
b	25·7202 (26)	25·7669 (11)
c	26·8840 (23)	26·8556 (10)
β	94·657 (10)°	94·465 (6)°
V	7210 (3) Å^3	7283 (3) Å^3
μ(Mo $K\alpha$)	0·66 mm^{-1}	
λ(Mo $K\alpha_1$)	0·70930 Å	
λ(Cu $K\alpha_1$)		1·54051 Å

extinction observed with polarized light did not persist. It was concluded that II is metastable at the temperatures used.

X-ray diffraction work

A single crystal (part of a needle), with a volume of 6 $\times 10^{-3}$ mm^3, was used. Cell dimensions and intensities were determined on a four-circle diffractometer (Enraf–Nonius CAD-4) with equatorial geometry and graphite-monochromatized Mo K radiation (λ = 0·71073 Å). The temperature was kept at 173 K by a flow of cold nitrogen gas (Danielsson, Grenthe & Oskarsson, 1976). Some crystal data are given in Table 1. The intensities of 7410 reflexions, of which 3794 had $I > 3\sigma_c(I)$, were measured. Further details of the measurements are similar to those in Andersson (1978).*

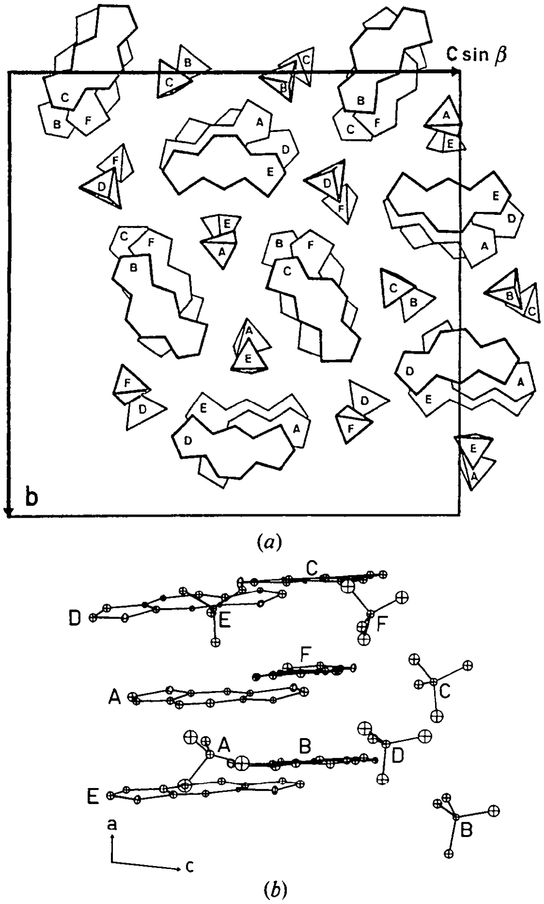
Determination and refinement of the structure

The intensities were corrected for Lorentz and polarization effects but not for absorption (μ = 0·66 mm^{-1}). Systematic extinctions at 173 K were $h0l$ with $l = 2n + 1$ and $0k0$ with $k = 2n + 1$. Weak intensities were found for some $h0l$ reflexions with l odd, but could be discarded.* Thus, space group $P2_1/c$ was considered.

The structure was solved by symbolic addition (*MULTAN*, Germain, Main & Woolfson, 1971). Subsequent electron-density syntheses and least-squares refinements gave the positions of all atoms except H. In some ClO_4^- groups the O positions were uncertain due to disorder.

In the final full-matrix refinement, the function minimized was $\sum w(\Delta|F|)^2$, where $\Delta|F| = |F_o| - |F_c|$. The weight function was $w^{-1} = \sigma_c^2(|F_o|) + 0{\cdot}000625|F_o|^2 + 0{\cdot}10$. Scattering factors were those of Doyle & Turner (1968). All atoms were not refined simultaneously, and H atoms could not be refined. Some of the ClO_4^- groups were disordered, and probably additional orientations were possible but were not accounted for. Anisotropic temperature factors were refined for the S atoms,* but not for the Cl atoms.

The final $R = \sum|\Delta|F||/\sum|F_o| = 0{\cdot}122$ and $R_w = [\sum w(\Delta|F|)^2/\sum w|F_o|^2]^{1/2} = 0{\cdot}164$. The goodness of fit $S = [\sum w(\Delta|F|)^2/(m - n)]^{1/2} = 1{\cdot}01$, where m is the number of observations and n the number of parameters. The final coordinates are given in Table 2.* The maximum residual electron density was 1·65 e Å^{-3}. The thermal parameters of some ClO_4^- groups were large, indicating disorder. For some reflexions $\Delta|F|/\sigma(\Delta|F|)$ values were very large.* Weissenberg photographs showed diffuse intensities, indicating disorder.



(*a*)

(*b*)

Fig. 2. Projections of (*a*) *G* II in the direction of **a** (H omitted), and (*b*) the asymmetric unit of *G* II in the direction of **b** (H omitted).

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* Additional experimental details, anisotropic thermal parameters, lists of structure factors, additional least-squares planes, angles in cations, and distances and angles in ClO_4^- have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35694 (38 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* See deposition footnote.

Table 2. *Positional parameters* ($\times 10^4$) *and isotropic thermal parameters with e.s.d.'s in parentheses* (173 K, *G* II)

The expression for the isotropic temperature factor is $\exp[-8\pi^2 U(\sin\theta/\lambda)^2]$. For S the equivalent isotropic temperature factors $8\pi^2 U_{\rm eq}$ (Å^2) are given. $U_{\rm eq} = \frac{1}{3}\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	$8\pi^2 U$ (Å^2)		x	y	z	$8\pi^2 U$ (Å^2)
S(1)*A*	5906 (8)	5598 (3)	−278 (3)	2·8 (5)	C(2)*B*	6063 (29)	5563 (11)	2564 (11)	2·2 (6)
S(2)*A*	6419 (8)	6490 (3)	1525 (3)	2·8 (5)	C(3)*B*	6253 (34)	5980 (13)	2921 (12)	3·4 (7)
S(1)*B*	6138 (8)	4101 (3)	3084 (3)	2·4 (5)	C(4)*B*	6368 (32)	5968 (12)	3431 (12)	3·2 (7)
S(2)*B*	6582 (9)	5698 (4)	4373 (3)	3·7 (5)	C(5)*B*	6539 (33)	6436 (13)	3723 (12)	3·5 (7)
S(1)*C*	504 (8)	6520 (3)	6951 (3)	2·4 (5)	C(6)*B*	6602 (32)	6345 (13)	4200 (12)	3·3 (7)
S(2)*C*	53 (9)	4887 (3)	5716 (3)	2·9 (5)	C(7)*B*	6440 (29)	5519 (11)	3758 (11)	2·4 (6)
S(1)*D*	1670 (8)	2278 (3)	5950 (3)	2·7 (5)	C(8)*B*	6358 (28)	4982 (11)	3651 (10)	2·3 (6)
S(2)*D*	676 (7)	2037 (3)	3977 (3)	2·1 (5)	C(9)*B*	6209 (27)	4774 (10)	3160 (10)	1·6 (5)
S(1)*E*	7465 (8)	2740 (3)	3733 (3)	2·8 (5)	C(10)*B*	5888 (31)	4147 (12)	2430 (11)	2·6 (7)
S(2)*E*	8282 (8)	2777 (3)	5727 (3)	2·4 (5)	C(11)*B*	5963 (27)	4656 (10)	2273 (10)	1·6 (6)
S(1)*F*	2658 (8)	1008 (3)	7603 (3)	2·0 (5)	C(1)*C*	585 (27)	5603 (10)	7387 (10)	1·7 (6)
S(2)*F*	2776 (9)	−1068 (3)	7809 (3)	2·8 (5)	C(2)*C*	569 (29)	5078 (12)	7507 (11)	2·4 (6)
Cl*A*	3675 (8)	8934 (3)	320 (3)	3·3 (2)	C(3)*C*	453 (29)	4672 (11)	7187 (11)	2·2 (6)
Cl*B*	7788 (7)	4829 (3)	1078 (3)	1·9 (1)	C(4)*C*	345 (25)	4657 (10)	6661 (9)	1·2 (5)
Cl*C*	2861 (8)	5211 (3)	1430 (3)	2·5 (2)	C(5)*C*	218 (29)	4168 (11)	6397 (11)	2·3 (6)
Cl*D*	5337 (8)	2652 (3)	2110 (3)	3·2 (2)	C(6)*C*	90 (30)	4241 (12)	5911 (11)	2·7 (6)
Cl*E*	1016 (7)	3462 (3)	4662 (3)	1·9 (1)	C(7)*C*	309 (24)	5090 (9)	6336 (9)	0·9 (5)
Cl*F*	658 (8)	2893 (3)	7374 (3)	2·6 (2)	C(8)*C*	317 (30)	5610 (11)	6416 (11)	2·5 (6)
O(1)*A*	2370 (34)	8877 (14)	−46 (12)	11·6 (9)	C(9)*C*	498 (25)	5833 (10)	6904 (9)	0·9 (5)
O(2)*A*	3334 (34)	8822 (14)	762 (13)	13·8 (9)	C(10)*C*	769 (30)	6493 (12)	7601 (11)	2·4 (6)
O(3)*A*	4122 (23)	9449 (9)	247 (8)	4·0 (5)	C(11)*C*	824 (30)	6008 (12)	7786 (11)	2·6 (6)
O(4)*A*	4311 (34)	8572 (14)	76 (13)	12·2 (9)	C(1)*D*	1124 (25)	1322 (10)	5659 (9)	1·4 (5)
O(1)*B*	7123 (21)	4366 (8)	1220 (8)	3·4 (5)	C(2)*D*	804 (26)	863 (10)	5389 (10)	1·5 (6)
O(2)*B*	7449 (26)	4914 (10)	545 (10)	5·6 (6)	C(3)*D*	559 (28)	806 (11)	4880 (10)	2·1 (6)
O(3)*B*	7367 (21)	5274 (8)	1351 (8)	3·1 (5)	C(4)*D*	559 (29)	1187 (11)	4493 (11)	2·4 (6)
O(4)*B*	9160 (21)	4772 (8)	1181 (8)	3·4 (5)	C(5)*D*	198 (27)	1026 (10)	3990 (10)	1·8 (6)
O(1)*C*	2155 (23)	5180 (9)	947 (8)	4·0 (5)	C(6)*D*	267 (32)	1463 (12)	3666 (12)	2·9 (7)
O(2)*C*	2140 (25)	5558 (10)	1734 (9)	5·2 (6)	C(7)*D*	849 (24)	1737 (9)	4566 (9)	0·8 (5)
O(3)*C*	3008 (22)	4699 (8)	1649 (8)	3·6 (5)	C(8)*D*	1089 (26)	2031 (10)	4971 (10)	1·7 (6)
O(4)*C*	4113 (30)	5411 (12)	1374 (11)	7·3 (7)	C(9)*D*	1252 (28)	1834 (11)	5484 (10)	2·1 (6)
O(1)*D*	4555 (35)	2979 (14)	2311 (13)	13·6 (9)	C(10)*D*	1736 (32)	1791 (13)	6407 (12)	3·2 (7)
O(2)*D*	5186 (22)	2134 (9)	2304 (8)	3·7 (5)	C(11)*D*	1375 (30)	1302 (12)	6213 (11)	2·7 (6)
O(3)*D*	4854 (36)	2584 (13)	1565 (13)	11·5 (9)	C(1)*E*	7377 (0)	1842 (0)	4157 (0)	1·7 (0)
O(4)*D*	6682 (30)	2799 (11)	2163 (11)	7·1 (7)	C(2)*E*	7294 (0)	1418 (0)	4508 (0)	2·9 (0)
O(1)*E*	2202 (22)	3223 (8)	4621 (8)	4·0 (5)	C(3)*E*	7606 (0)	1405 (0)	5037 (0)	2·0 (0)
O(2)*E*	470 (18)	3274 (7)	5110 (7)	2·4 (4)	C(4)*E*	7801 (0)	1829 (0)	5348 (0)	2·6 (0)
O(3)*E*	212 (19)	3316 (7)	4240 (7)	2·7 (4)	C(5)*E*	7967 (0)	1809 (0)	5886 (0)	1·9 (0)
O(4)*E*	1149 (22)	4009 (9)	4686 (8)	3·9 (5)	C(6)*E*	8229 (30)	2251 (12)	6119 (11)	2·7 (6)
O(1)*F*	−271 (36)	2761 (14)	7718 (13)	9·6 (9)	C(7)*E*	7958 (29)	2390 (11)	5193 (11)	2·3 (6)
O(2)*F*	−40 (30)	2872 (12)	6925 (11)	7·0 (7)	C(8)*E*	7827 (28)	2627 (11)	4735 (10)	1·9 (6)
O(3)*F*	1144 (23)	3400 (9)	7502 (8)	4·3 (5)	C(9)*E*	7584 (25)	2375 (9)	4270 (9)	0·9 (5)
O(4)*F*	1575 (30)	2507 (11)	7445 (11)	7·3 (7)	C(10)*E*	7117 (33)	2233 (13)	3361 (12)	3·4 (7)
C(1)*A*	5500 (28)	6596 (11)	−273 (11)	2·3 (6)	C(11)*E*	7070 (0)	1754 (0)	3622 (0)	2·6 (0)
C(2)*A*	5385 (31)	7119 (12)	−146 (11)	2·7 (7)	C(1)*F*	2971 (24)	681 (9)	8529 (9)	0·7 (5)
C(3)*A*	5569 (32)	7385 (13)	312 (12)	3·5 (7)	C(2)*F*	3253 (31)	377 (12)	8982 (11)	2·5 (6)
C(4)*A*	5810 (27)	7127 (11)	795 (10)	2·0 (6)	C(3)*F*	3313 (28)	−151 (11)	9024 (10)	1·9 (6)
C(5)*A*	5892 (28)	7423 (11)	1235 (10)	2·1 (6)	C(4)*F*	3107 (28)	−543 (11)	8650 (11)	1·8 (6)
C(6)*A*	6302 (36)	7131 (14)	1675 (13)	4·2 (8)	C(5)*F*	3224 (32)	−1077 (13)	8774 (12)	3·2 (7)
C(7)*A*	6081 (28)	6581 (11)	902 (10)	2·1 (6)	C(6)*F*	3051 (32)	−1396 (12)	8374 (12)	3·0 (7)
C(8)*A*	6052 (29)	6159 (11)	563 (11)	2·4 (6)	C(7)*F*	2943 (26)	−467 (10)	8141 (10)	1·5 (5)
C(9)*A*	5850 (27)	6180 (11)	42 (10)	1·8 (6)	C(8)*F*	2838 (29)	−14 (11)	7831 (11)	2·2 (6)
C(10)*A*	5513 (32)	5928 (13)	−826 (12)	3·2 (7)	C(9)*F*	2874 (28)	491 (11)	8026 (10)	2·0 (6)
C(11)*A*	5377 (29)	6446 (12)	−770 (11)	2·2 (6)	C(10)*F*	2694 (29)	1457 (11)	8089 (11)	2·2 (6)
C(1)*B*	6067 (29)	5029 (11)	2680 (11)	2·2 (6)	C(11)*F*	2888 (27)	1228 (10)	8543 (10)	2·3 (6)

Discussion of the structure at 173 K (*G* II)

The present structure has six independent units, consisting of a cycloheptadithiophenylium cation (*G* in Fig. 1) and a ClO_4^- ion, in the unit cell. It is built up of columns of cations along **a** with ClO_4^- ions in between (Fig. 2*a*). A view of one asymmetric unit is shown in Fig. 2(*b*). The best planes of the cations have

Table 3. *Angles* (°) *between the best planes of the cations* (*G* II)

Within a column		Between columns			
D–A	161·6 (5)	*D–C*	170·8 (6)	*E–C*	173·3 (7)
A–E	163·6 (6)	*–F*	168·6 (8)	*–F*	170·9 (10)
E–D	177·5 (7)	*–B*	171·0 (6)	*–B*	173·5 (7)
C–F	176·5 (20)	*A–C*	169·4 (5)		
F–B	175·6 (21)	*–F*	172·7 (13)		
B–C	179·1 (5)	*–B*	168·6 (5)		

Table 4. *Intermolecular distances* (Å) *at* 173 K (*G* II)

Van der Waals radii (Bondi, 1964) and upper limits are given. These are followed by the atoms and the distances between them at 173 K. Distances between columns are marked with an asterisk. For notation see Fig. 4*b*.

Distances between cations

VdW 3·5	<3·82
S(2)*A*–S(2)*D*	3·70 (2)
S(1)*B*–S(1)*F*	3·77 (2)
S(1)*C*–S(1)*E**	3·49 (2)
S(1)*D*–S(2)*E*	3·77 (2)
VdW 3·45	<3·74
S(1)*A*–C(2)*D*	3·55 (4)
S(2)*A*–C(6)*D*	3·55 (4)
S(1)*B*–C(9)*C*	3·52 (3)
–C(9)*F*	3·56 (4)
–C(1)*F*	3·66 (4)
S(2)*B*–C(6)*C*	3·63 (4)
S(1)*C*–C(10)*F*	3·34 (4)
S(1)*D*–C(6)*E*	3·67 (4)
S(2)*D*–C(9)*E*	3·50 (3)
–C(1)*E*	3·56 (1)
–C(4)*A*	3·69 (4)
S(1)*E*–C(5)*A*	3·61 (4)
S(2)*E*–C(6)*F**	3·59 (4)
–C(5)*F**	3·65 (4)
S(1)*F*–C(10)*B*	3·47 (4)
–C(1)*C*	3·55 (3)
–C(9)*C*	3·68 (3)
–C(11)*C*	3·71 (4)
S(2)*F*–C(3)*B*	3·63 (4)
VdW 3·4	<3·5
C(1)*A*–C(3)*E*	3·40 (4)
–C(4)*E*	3·49 (4)
C(2)*A*–C(4)*E*	3·42 (4)
C(4)*A*–C(1)*E*	3·43 (4)
C(5)*A*–C(10)*E*	3·45 (5)
C(1)*B*–C(8)*F*	3·44 (5)
C(4)*B*–C(5)*F*	3·50 (5)
C(7)*B*–C(4)*F*	3·48 (5)
C(8)*B*–C(3)*F*	3·44 (5)
–C(7)*C*	3·49 (4)
C(8)*C*–C(1)*F*	3·46 (4)
C(4)*D*–C(2)*E*	3·47 (3)
C(6)*D*–C(11)*E*	3·42 (4)

Distances between anions

VdW 3·0	<3·87
O(1)*A*–O(2)*E*	3·34 (5)
O(4)*A*–O(1)*E*	3·78 (5)
O(3)*B*–O(4)*C*	3·43 (4)
O(4)*B*–O(1)*C*	3·41 (4)
O(1)*D*–O(4)*F*	3·41 (6)
O(4)*D*–O(1)*F*	3·70 (5)
O(3)*A*–O(3)*A**	3·69 (5)

Distances between different ions

VdW 3·3	<3·40
O(2)*A*–S(1)*B*	3·19 (4)
–S(1)*E*	3·24 (4)
O(2)*B*–S(1)*A*	3·17 (4)
O(3)*B*–S(2)*A*	3·33 (3)
O(2)*C*–S(2)*F*	3·19 (3)
O(3)*C*–S(1)*F*	3·19 (3)
O(2)*E*–S(2)*E*	3·20 (3)
VdW 3·2	<3·24
O(1)*B*–C(10)*A*	2·97 (4)
O(1)*E*–C(3)*A*	3·17 (4)
O(2)*F*–C(6)*E*	3·15 (5)

approximately the same direction. The cations of column *C*, *F*, *B* are approximately in the direction of **a**; *D*, *A*, *E* are somewhat more tilted. The cation *A* in column *D*, *A*, *E* deviates slightly, being tilted relative to *D* and *E* (Table 3), and correspondingly *F* relative to *C* and *B*. The greatest angle between planes is *A–D*, 161·6 (5)°. Within a column the distance between the planes is approximately $a/3 = 3{\cdot}487$ Å.

The shortest contacts between the cations are given in Table 4. Most of these contacts are within the columns. Of the $\mathrm{ClO_4^-}$ ions, *A*, *D* and *F* seem to be disordered, having high temperature factors for the O atoms. Short distances between $\mathrm{ClO_4^-}$ ions are within the columns. Between the columns, the distances are, in general, considerably longer. The distances between cations and anions are short relative to the van der Waals distances and the distances between ions of the same charge.

Of the disordered $\mathrm{ClO_4^-}$ ions, *D* has no short contact to cations and *F* only one, in contrast to *B*, *C* and *E* which have at least two short contacts to different O atoms. $\mathrm{ClO_4^-}$ ion *A*, which is also disordered, has two short contacts, but to the same O atom. The short contacts to a cation are preferably to the S atoms. There are not short contacts to all cations.

Comparison with phase I (*G* I)

This phase, with a small unit cell and only one independent unit, was determined at 295 K by Aurivillius (1974). It has a significantly smaller volume per molecule, 300·3 (4) Å^3, compared to that of phase II at room temperature, 303·4 (2) Å^3 (Tables 1,5). Here there are layers of cations with layers of $\mathrm{ClO_4^-}$ in between (Fig. 3). Within a layer the cations are parallel and the distance between the best planes is 3·443 Å.

Short contacts between cations are within the layers (Table 6, Fig. 4*a*). As phases I and II are studied at

Table 5. *Crystal data* (*G* I *and E*)

	$\mathrm{C_{11}H_7S_2^+.ClO_4^-}$, *G* I, monoclinic, $P2_1/n$	$\mathrm{C_{11}H_7S_2^+.BF_4^-}$, *E*, triclinic, $P\bar{1}$
a	6·819 (2) Å	7·1949 (12) Å
b	12·032 (4)	8·7203 (12)
c	14·677 (6)	9·5967 (20)
α		105·787 (15)°
β	93·60 (3)°	99·074 (13)
γ		96·817 (13)
V	1201 (1) Å^3	536·8 (6) Å^3
Z	4	2
T	295 K	143 K

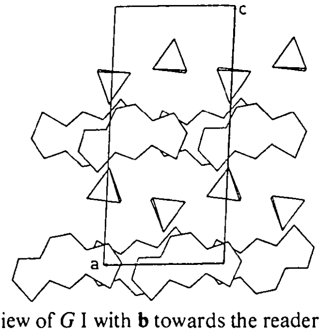

Fig. 3. A view of *G* I with **b** towards the reader (H omitted).

Table 6. *Intermolecular distances* (Å) *at* 295 K (*G* I)

Van der Waals radii (Bondi, 1964) and upper limits are given. These are followed by the atoms and the distances between them. Distances between layers are marked with an asterisk (*cf.* Fig. 4*a*).

Distances between cations	
VdW 3·5	<4·0
S(1)–S(8)	3·716 (4)
VdW 3·45	<3·77
S(1)–C(7)	3·563 (12)
–C(3)	3·696 (11)
S(8)–C(6)	3·745 (12)
VdW 3·4	<3·53
C(6)–C(VII)	3·521 (15)
C(7)–C(VI)	3·426 (16)
C(2)–C(VI)	3·497 (16)
C(2)–C(2)	3·503 (25)

Distances between anions	
VdW 3·0	<4·0
O(1)–O(1)*	3·709 (24)
Distances between different ions	
VdW 3·3	<3·42
O(4)–S(8)	3·028 (25)
–S(1)	3·190 (25)
O(5)–S(1)	3·275 (33)
VdW 3·2	<3·24
O(2)–C(9)	3·081 (33)
O(3)–C(9)	3·094 (23)
O(6)–C(9)	3·106 (62)
O(7)–C(4)	3·058 (43)

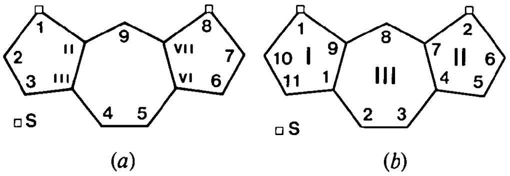

Fig. 4. Schematic diagrams (*a*) of the cycloheptadithiophenylium ion in *G* I showing the numbering of the atoms (*cf.* Table 6), and (*b*) defining the numbering of atoms and planes for molecules *A* to *F* in *G* II (*cf.* Table 4). In the following diagrams the molecules are oriented in the same way.

different temperatures it is not possible to make a direct comparison of short distances. ClO_4^- is disordered and is represented by two orientations. The shortest distance between anions, 3·7 Å, is between the anion layers.

The ClO_4^- ion has several short contacts to cations from its two orientations, preferably to the S atoms and C(9).

Comparison with *E*

This ion (Fig. 1) is similar to *G*. The volume per unit is smaller than for *G* I and *G* II, 281·9 (3) Å^3 at 173 K (Table 5). The parallel cations form layers with the anions in between (Fig. 5). Within a layer the distance between the cations is 3·347 Å.

Most of the short contacts between cations are within a layer. The BF_4^- ion is disordered (two orientations) with the shortest contacts within the layers.

The distances from the BF_4^- ion to the cations are short and mainly to the S atoms.

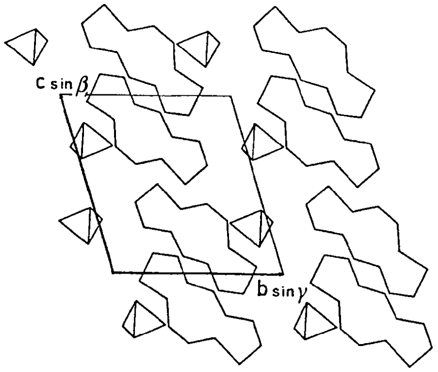

Fig. 5. A view of *E* with **a** towards the reader (H omitted).

Table 7. *Least-squares planes* (*G* II)

Deviations (Å × 10^3) of the atoms from the best planes of the molecules, and angles (°) between planes (I) and (II) are given. Weights proportional to the atomic numbers are used. The e.s.d.'s for the deviations of S and C are 8 and 32 (Å × 10^3) respectively (*cf.* Fig. 4*b*).

	X = *A*	*X* = *B*	*X* = *C*	*X* = *D*	*X* = *E*	*X* = *F*
S(1*X*)	7	22	33	13	−3	−41
S(2*X*)	2	−24	4	−11	6	47
C(1*X*)	−34	−20	26	11	44	37
C(2*X*)	−14	−39	47	6	−38	−49
C(3*X*)	55	20	40	−9	70	−63
C(4*X*)	−29	−4	−15	−23	−5	20
C(5*X*)	−45	50	1	36	−48	−17
C(6*X*)	52	−12	−14	6	−27	16
C(7*X*)	−10	19	−52	−42	26	−24
C(8*X*)	−36	12	−1	35	−3	−72
C(9*X*)	17	14	−21	24	26	−59
C(10*X*)	−6	−57	−40	−54	−32	97
C(11*X*)	24	21	−70	6	−22	97

Planes	*A*	*B*	*C*
(I)–(II)	178·6 (12)	178·1 (14)	178·7 (13)
	D	*E*	*F*
(I)–(II)	179·1 (10)	176·9 (8)	174·8 (27)

Conformation

From a statistical point of view (Table 7, Fig. 4*b*) each of the cations except *F* is planar and only ring (III) in *F* is non-planar.* The angle between planes (I) and (II) is significant for *E* and the mean of the angles between planes (I) and (II) is 178 (2)°.

Bond distances (Fig. 6) and angles* indicate that the e.s.d.'s are correctly estimated and that systematic deviations occur between the left and right sides of *A*, *B*, *C*, and *E* (Hamilton, 1974). The mean values are given in Fig. 7(*a*). The S–C bonds are equal. In the central ring the C–C lengths are about the same, and in the thiophene rings differ more. Some angles differ from

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* See deposition footnote.

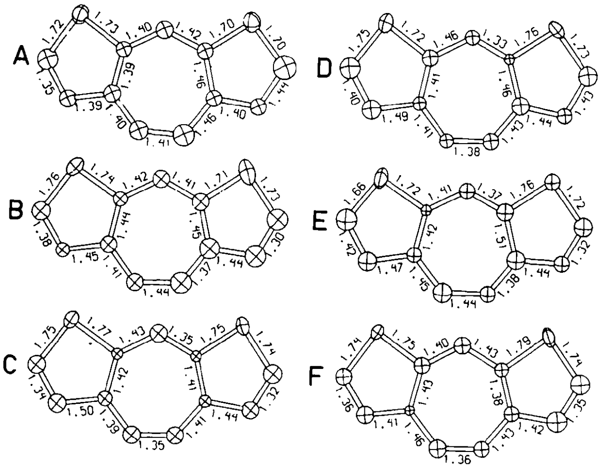
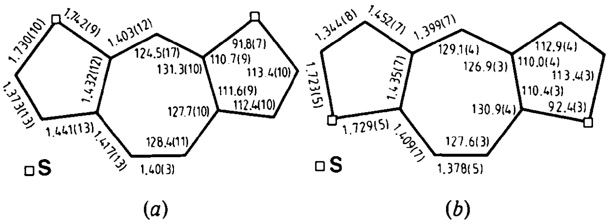


Fig. 6. The cycloheptadithiophenylium ions *G* II at 173 K. Distances (Å) for non-hydrogen atoms are presented. The e.s.d's are for C—S 0·033 and for C—C 0·045 Å. The numbering of the atoms and the ring system is as in Fig. 4(*b*) and 50% probability ellipsoids are shown.



(*a*) (*b*)

Fig. 7. Mean values of bond distances (Å) and angles (°) for (*a*) the cycloheptadithiophenylium ions *G* II at 173 K (the numbering of the atoms is as in Fig. 4*b*), and (*b*) the cycloheptadithiophenylium ion *E* at 143 K.

the ideal values for five- and seven-membered rings. H atoms were not determined. The e.s.d.'s of the ClO_4^- ions are underestimated for *A*, *D* and *F* and the mean Cl—O distance is 1·43 (4) Å.*

Comparison with *G* I

The structure *G* I was determined at 295 K, in contrast to the present structure *G* II, and with one exception the bond lengths in the cation are shorter, probably due to thermal motion. The angles agree. The conformations in *G* I and *G* II are similar. Each separate ring is planar but not the molecule as a whole. The angle I–II is 177·7 (4)°.

Comparison with *E*

E was determined at 143 K, and the cation has a boat conformation with 175·3 (4)° between planes (I) and (II). The average distances and angles are given in Fig. 7(*b*). Comparable distances agree well with the distances of *G* II, although the differences between the shortest and longest distances in the seven- and five-membered rings are larger for *E* than for *G* II. This is in accordance with a lower degree of aromaticity for *E* than for *G*.

In the seven-membered ring the top angle is larger. In both *E* and *G* the angle nearest the S atom is the largest.

Disorder

Areas with diffuse intensity appear in Weissenberg photographs around **b** and **c** at 295 and 173 K (Cu *K̄*) on every third bow near and across *h* ($h = 3, 6, 9; -6 \leq l \leq 4; |k| \leq 3$) and at 204. This is also where the strongest reflexions are situated and they have diffuse intensity at their sides. Around **a** the disorder is observed as streaks in 3*kl* at low θ values. The diffuse bows have their centers of intensity on **a** and thus represent the direction of **a** while 204 gives another direction. As there are three cations, with their planes perpendicular to **a** and separated by *a*/3 in the columns along **a**, but only two ClO_4^- ions, it is assumed that the diffuse rows are caused by some disorder of the cations and the diffuse area at 204 by the ClO_4^- ions.

The normals to the cation planes point approximately in the direction of **a**, which is the direction the diffuse intensity represents. This might be an indication of orientational disorder, and another indication comes from the location of the residual electron density. There are peaks, mainly at the midpoints of bonds, which fit well with a rotated molecule, although this is not the only explanation. Thus, a fraction of the cations are probably rotated by 180°. There are high peaks near the ClO_4^- ions *A*, *D* and *F*, which also have high temperature factors for the O atoms, indicating a high degree of orientational disorder.

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* See deposition footnote.