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X-Ray Crystallographic Studies on Cycloheptadithiophene Compounds and Similar Systems I. The Crystal Structure of Dithieno[2,1-*b*;4,5-*b*′]tropylium Perchlorate

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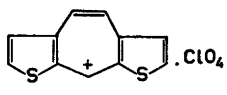
The crystal structure of a dithienotropylium perchlorate



has been investigated by X-ray diffraction methods. The substance is monoclinic, space group $P2_1/n$ with four formula units $C_{11}H_7S_2 \cdot ClO_4$ in a unit cell of dimensions $a = 6.819$, $b = 12.032$, $c = 14.677$ Å and $\beta = 93.60°$. The intensity data were collected by means of an integrating Weissenberg camera and the intensities were estimated visually. The structure was refined to a final R factor of 0.08 for 882 observed reflections. The crystal structure is built up from layers of dithienotropylium cations interleaved by perchlorate ions. As for many other organic salts the oxygen atoms of the perchlorate ion are disordered. The dithienotropylium cation is essentially planar; the largest deviations from the best plane are 0.05 Å and occur for the two sulfur atoms. A few short intermolecular distances exist, one of them being a sulfur–perchlorate oxygen distance of 3.03(3) Å.

The aromaticity of a number of cycloheptadithiophene compounds and also corresponding dithioborepines has been investigated by Gronowitz and co-workers.[1,2] They found that the dithieno[2,1-*b*;4,5-*b*′]tropylium ion was unusually stable, having a pK_{R^+} value of 6.65, while the dibenzotropylium ion has a pK_{R^+} value of only −1.5. They suggested that one of the factors contributing to the higher stability of the thiophene derivative was the absence of *peri* effects between the sulfur atoms and the 9-hydrogen, allowing the three rings to be almost coplanar. Ring strain effects were also assumed to be smaller in the thiophene case. It was therefore of great interest to obtain a detailed knowledge of the bonding distances within the various molecules and ions. One way to obtain the information wanted is to study the solid state of the compounds by means of X-ray diffraction methods. The present and a few following papers will report the results as obtained from studies on single crystals of the various substances.

The present paper deals with the crystal structure of dithieno[2,1-*b*;4,5-*b*′]tropylium perchlorate. For the sake of brevity the actual substance will be called dithienotropylium perchlorate in the following.

X-RAY DIFFRACTION WORK

A small single crystal, kindly supplied by Dr. B. Yom-Tov, was mounted with [001] as rotation axis and the layers 0–10 were registered by means of an integrating Weissenberg camera using Cu$K\alpha$ radiation. The symmetry was found to be monoclinic. The following conditions limiting possible reflections were found:
hkl, no conditions; $h0l$, $h+l=2n$; $0k0$, $k=2n$.
These conditions are characteristic of the space group $P2_1/n$ (No. 14).*

* Orientation different from that given in the International Tables. General point position 4(*e*): x,y,z; $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; $\bar{x},\bar{y},\bar{z}$; $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$.

Table 1. Crystal data for dithienotropylium perchlorate.

Dithienotropylium perchlorate $C_{11}H_7S_2.ClO_4$.
F.W. = 302.7

Monoclinic, $P2_1/n$, $a = 6.819(2)$, $b = 12.032(4)$, $c = 14.667(6)$ Å, $\beta = 93.60(3)°$, $V = 1201(1)$ Å^3.
$Z = 4$.

$D_m = 1.79$, $D_x = 1.68$ g cm^{-3}, $\mu(\mathrm{Cu}K\alpha) = 64.0$

The multiple film technique was used and the intensities were estimated visually using a calibrated scale. The number of observed independent reflections were 882. As the crystal was small and as the value of the linear absorption coefficients was 64.0 cm^{-1}, no absorption correction was performed.

X-Ray powder diffraction photographs were recorded in a Guinier-Hägg focusing camera with $\mathrm{Cu}K\alpha_1$ radiation and potassium chloride ($a = 6.2909$ Å) added as an internal standard. The lattice parameters were obtained with the aid of least-squares calculations. The density of the crystals was determined by flotation. Some crystal data of the compound are given in Table 1.

DETERMINATION AND REFINEMENT OF THE STRUCTURE

The positions of the eight sulfur and four chlorine atoms of the unit cell were deduced from a three-dimensional Patterson function. Using conventional procedures the positions of all non-hydrogen atoms of the cation $C_{11}H_7S_2^+$ and of one of the oxygen atoms (O1) of the perchlorate group were immediately found from difference Fourier maps. As the rest of the perchlorate oxygen atoms did not turn up it was concluded that the perchlorate ion is disordered. The disorder may either be such that the perchlorate ion "rotates" with Cl – O1 as an axis or such that the remaining three oxygen atoms occupy sets of preferred orientations.

Successive least-squares refinements followed by difference Fourier calculations revealed the positions of five more oxygen atoms, *viz.* O2 – O6. The atoms O1, O2, O3, and O4 form one tetrahedron and the atoms O1, O5, and O6 form part of another tetrahedron of oxygens around chlorine. The position of the missing oxygen atom (O7) of the last tetrahedron was deduced by geometrical considerations and was afterwards found to correspond to a peak of moderate height in the last difference Fourier maps.

In a least-squares refinement the isotropic temperature factors found for the oxygen atoms O2 – O7 indicated the occupancy numbers to be 0.6 for O2 – O4 and 0.4 for O5 – O7. No further refinement of the occupancy numbers was made.

A refinement of the positional and thermal parameters of all atoms, using anisotropic temperature factors resulted in a conventional R factor of 0.088. A stereo picture of the perchlorate ion as obtained from the calculations is given in Fig. 1.

Difference Fourier maps based on positional and thermal parameters obtained above revealed the positions of the seven hydrogens of the organic molecule. A least-squares refinement of all atoms using fixed isotropic temperature factors ($B = 4.0$ Å^2) for the hydrogen atoms gave an R factor of 0.080. Thus a small improvement in the discrepancy factor was attained when introducing the positions of the hydrogen atoms in the calculations. However, not all atoms converged at this calculation. Therefore a new refinement was performed where the positions of the hydrogens were fixed at the values obtained above. All parameters of the non-hydrogen atoms now converged. Only small shifts in the parameters were obtained and the R factor did not change.

Fig. 1. Ortep stereoscopic view of the two preferred orientations of the perchlorate ion in dithienotropylium perchlorate.

Table 2. Analysis of the weighting scheme used in the last cycle of least-squares refinement. The averages $w(|F_o|-|F_c|)^2=\overline{w\Delta^2}$ are normalized. $w=(8.0+|F_o|+0.03|F_o|^2)^{-1}$.

Interval $\|F_o\|$	$\overline{w\Delta^2}$	Number of reflections	Interval $\sin\theta$	$\overline{w\Delta^2}$	Number of reflections
0 – 7.9	1.04	89	0.00 – 0.46	1.51	205
7.9 – 10.0	0.98	87	0.46 – 0.59	1.18	206
10.0 – 11.8	0.84	88	0.59 – 0.67	0.82	161
11.8 – 13.7	0.83	88	0.67 – 0.74	1.12	110
13.7 – 16.1	0.74	89	0.74 – 0.79	0.82	78
16.1 – 18.9	0.74	88	0.79 – 0.84	1.03	54
18.9 – 22.7	0.75	88	0.84 – 0.89	1.03	32
22.7 – 26.8	0.81	88	0.89 – 0.93	0.90	22
26.8 – 36.1	1.78	88	0.93 – 0.97	1.51	11
36.1 – 194.4	1.49	88	0.97 – 1.00	0.08	2

Table 3a. Final positional and thermal parameters for dithienotropylium perchlorate. Standard deviations are given within parentheses. All atoms are situated in the general point position 4(*e*) in $P2_1/n$. Anisotropic temperature factors have been used for all non-hydrogen atoms. Their isotropic equivalents are given within brackets. The β_{ij} values are listed separately (Table 3b). Notations of the atoms, *cf.* Fig. 2. The occupancy numbers of the oxygen atoms are 1.0 for O1, 0.6 for O2 – O4 and 0.4 for O5 – O7.

Atom	10^4x	10^4y	10^4z	B(Å^2)
S1	5642(4)	3451(2)	5934(2)	[4.879]
S8	9155(4)	1134(2)	6422(2)	[4.282]
Cl	5404(4)	221(2)	2190(2)	[4.147]
C2	6472(19)	3816(10)	4917(10)	[5.523]
C3	5310(17)	3526(9)	4161(8)	[4.641]
C4	2142(15)	2548(9)	3794(7)	[4.150]
C5	457(16)	1968(9)	3938(8)	[4.253]
C6	7925(15)	1004(9)	4760(9)	[4.200]
C7	7473(16)	719(10)	5592(9)	[4.683]
C9	2288(15)	2289(8)	5947(7)	[3.784]
CII	3602(16)	2835(8)	5383(9)	[3.722]
CIII	3577(14)	2935(8)	4442(8)	[3.576]
CVI	9728(15)	1591(9)	4747(8)	[3.980]
CVII	569(14)	1745(8)	5631(7)	[3.287]
O1	5114(17)	257(10)	1248(8)	[8.768]
O2	6191(46)	−730(18)	2500(25)	[6.619]
O3	6137(45)	1283(17)	2583(13)	[7.188]
O4	3411(30)	263(24)	2416(17)	[9.254]
O5	7507(38)	448(39)	2275(23)	[7.361]
O6	5334(125)	−832(51)	2629(28)	[9.083]
O7	4718(66)	1094(30)	2647(30)	[8.274]

The hydrogen atoms

Atom	10^3x	10^3y	10^3z	B(Å^2)
H2	779(19)	425(10)	472(9)	4.0
H3	566(18)	371(10)	352(10)	4.0
H4	234(17)	286(10)	309(9)	4.0
H5	−25(18)	159(10)	344(10)	4.0
H6	721(18)	94(9)	408(10)	4.0
H7	636(20)	44(11)	537(9)	4.0
H9	259(18)	233(11)	653(10)	4.0

Table 3b. Anisotropic thermal parameters. The temperature factor expression used is $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})]$. The β-values have been multiplied by 10^4.

Atom	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
S1	230(7)	73(2)	81(2)	5(4)	−29(3)	−14(2)
S8	254(8)	84(2)	41(2)	11(3)	14(2)	−3(1)
Cl	230(7)	79(2)	44(2)	3(3)	5(2)	9(1)
C2	282(34)	92(10)	81(11)	24(15)	40(13)	23(7)
C3	306(34)	72(9)	51(9)	26(14)	8(12)	−4(6)
C4	262(31)	95(10)	44(8)	64(15)	−12(10)	20(6)
C5	245(29)	77(9)	45(9)	−4(12)	−16(10)	0(6)
C6	215(28)	72(9)	55(9)	−20(12)	−18(10)	−2(6)
C7	262(30)	99(10)	45(9)	26(14)	1(10)	9(7)
C9	277(28)	71(8)	31(7)	19(12)	1(10)	−6(5)
CII	261(28)	47(7)	55(9)	36(11)	−11(11)	−15(5)
CIII	211(26)	60(8)	40(9)	16(11)	−1(9)	7(5)
CVI	225(27)	75(9)	47(9)	44(13)	1(10)	−9(6)
CVII	249(26)	66(8)	25(7)	19(11)	−14(9)	−5(5)
O1	606(41)	196(12)	64(8)	−28(18)	−37(12)	6(7)
O2	660(92)	62(14)	234(35)	47(33)	−150(40)	73(16)
O3	621(87)	118(18)	95(13)	−166(36)	−63(27)	10(11)
O4	388(57)	233(28)	169(19)	60(38)	161(27)	52(21)
O5	176(57)	267(49)	164(27)	−142(46)	14(29)	9(28)
O6	1909(425)	284(73)	50(22)	−491(150)	−94(67)	78(28)
O7	609(138)	161(37)	216(40)	−88(59)	20(56)	−151(33)

The atomic scattering factors used were those suggested by Hanson, Herman, Lea and Skillman.[3] In the last refinement the expression $w=(8.0+|F_o|+0.03|F_o|^2)^{-1}$ was used for the calculation of the weights. The final weighting scheme is given in Table 2 and the final positional and thermal parameters in Table 3. On request to the author lists of observed and calculated structure factors are available from the Division of Inorganic Chemistry 2.

Table 4. Pertinent distances and angles for the perchlorate group in dithienotropylium perchlorate. *E.s.d.*'s are given within parentheses.

Orientation I Atoms	Distance (Å)	Orientation II Atoms	Distance (Å)
Cl−O1	1.39(1)	Cl−O1	1.39(1)
Cl−O2	1.33(3)	Cl−O5	1.46(3)
Cl−O3	1.47(3)	Cl−O6	1.43(7)
Cl−O4	1.42(3)	Cl−O7	1.35(5)
Atoms	**Angle (°)**	**Atoms**	**Angle (°)**
O1−Cl−O2	114(2)	O1−Cl−O5	99(2)
O1−Cl−O3	113(1)	O1−Cl−O6	118(2)
O1−Cl−O4	99(1)	O1−Cl−O7	116(2)
O2−Cl−O3	119(2)	O5−Cl−O6	102(5)
O2−Cl−O4	109(2)	O5−Cl−O7	101(3)
O3−Cl−O4	101(2)	O6−Cl−O7	115(3)

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The crystal structure of dithienotropylium perchlorate is built up from layers of dithienotropylium cations interleaved by perchlorate ions. The cation layers extend in each unit cell in the planes $z = 0$ and $z = \frac{1}{2}$. The chlorine atoms of the perchlorate ions are situated close to the planes $z = \frac{1}{4}$ and $z = \frac{3}{4}$. The perchlorate oxygen atoms are disordered probably in such a way that two orientations are preferred (*cf.* Fig. 1). Pertinent distances and angles for the perchlorate ion are summarized in Table 4.

As has been stated previously [4] the dithienotropylium cations are nearly planar, the largest deviations from the best plane being about 0.05 Å. A detailed analysis of the planarity of the cation is given in Table 5. Fig. 2 shows the

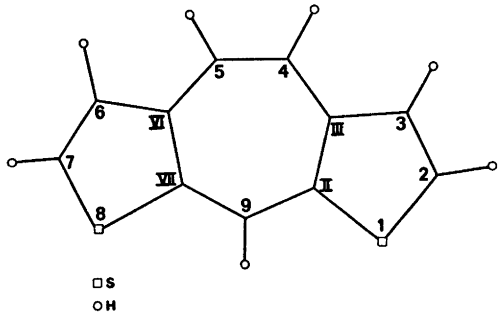


Fig. 2. Applied numbering of the atoms of the dithienotropylium cation.

applied numbering of the atoms of the dithienotropylium cation. The *e.s.d.*'s of the positions of the sulfur atoms are ~0.004 Å and of the carbon atoms ~0.013 Å. It is seen from Table 5 that for each of the separate rings, the thiophene rings and the tropylium ring, respectively, no deviation exceeds 2.0σ for the respective atom. Thus each of the rings now discussed may be considered to be planar. Taking the ring system of the cation as a whole, the carbon atoms deviate at most 3σ from the best plane whereas the sulfur atoms deviate about 10σ. Nearly the same result is obtained if the two sulfur atoms are included in the least-squares calculations of the best planes.

To sum up, each separate ring in the dithienotropylium cation may be considered to be planar but the ring as a whole shows a small deviation from planarity.

Fig. 3 shows the dithienotropylium cation projected perpendicularly on its best plane.

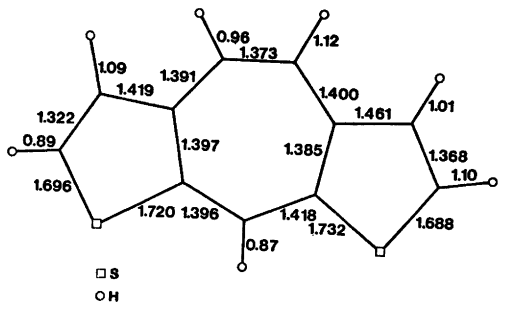


Fig. 3a. Pertinent distances within the dithienotropylium cation. Mean values of the *e.s.d.*'s are 0.012 Å for C–S distances, 0.016 Å for C–C distances and 0.14 Å for C–H distances.

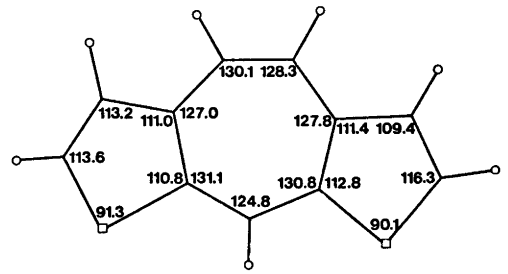


Fig. 3b. Pertinent angles for the non-hydrogen atoms of the dithienotropylium cation. Mean values of *e.s.d.*'s are 0.6° for angles with S at the centre and 1.0° for other angles formed between nonhydrogen atoms.

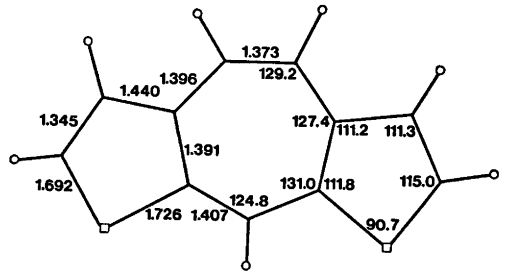


Fig. 3c. Mean values of distances and angles for the two halves of the dithienotropylium cation. For *e.s.d.*'s, *cf.* Table 6.

Table 5. Best least-squares planes through the S1 thiophene ring, the S8 thiophene ring, the tropylium ring and the complete dithienotropylium cation (*cf.* Fig. 2). Distances (Å) of all non-hydrogen atoms to the best plane of the respective ring are given. All non-hydrogen atoms are used to determine the best planes, except for the complete ion where the sulfur atoms are excluded from the calculations. The best planes are calculated according to Blow [10] and the result is given in the form: $lx'+my'+nz'+p=0$. All atoms used for the computations are ascribed unit weights.

Plane	l	m	n	p
S1 ring	0.4963	−0.8671	−0.0435	2.3335
S8 ring	0.5027	−0.8605	−0.0824	2.5419
Tropylium ring	0.5138	−0.8551	−0.0688	2.4369
Total cation	0.5059	−0.8599	−0.0681	2.4452

Atom	Distance to the plane	Atom	Distance to the plane
S1 ring		S8 ring	
S1	−0.006	S8	0.007
C2	−0.003	C6	−0.003
C3	−0.002	C7	−0.003
CII	0.006	CVI	0.009
CIII	−0.003	CVII	−0.010
Tropylium ring		Total cation	
C4	0.004	C2	0.011
C5	−0.011	C3	0.021
C9	0.002	C4	−0.007
CII	−0.015	C5	−0.009
CIII	0.013	C6	−0.006
CVI	0.002	C7	0.011
CVII	0.006	C9	−0.004
		CII	−0.033
		CIII	−0.007
		CVI	0.011
		CVII	0.012
		S1	−0.047
		S8	0.041

Interatomic distances and angles are given in the drawings (Figs. 3a – c)

It is seen from Figs. 3a and 3b that the cation, besides being nearly planar, also has an approximate mirror plane passing through the atom C9 and the midpoint of the line C4 – C5 (*cf.* Fig. 2). Whereas the differences between equivalent distances are at most possibly significant, the angles show one significant difference $\Delta/\sigma=2.5$. The author has, however, chosen to neglect this difference. Mean values and their *e.s.d.*'s have been calculated for the two halves of the cation, which implies an overestimation of the *e.s.d.*'s hitherto used by a factor of about 1.2 (Table 6, Fig. 3c).

Though the precision of the present investigation is not so high, a few conclusions may be drawn from Table 6. The annealed formal double bonds of the thiophene rings (CIII – CII, CVI – CVII) are on the average slightly longer than the other formal double bonds of the ring (C2 – C3, C6 – C7) (*cf.* Fig. 2). The sulfur-tropylium carbon distances (S1 – CII, S8 – CVII) are on the average slightly longer than the thiophenic ones (S1 – C2, S8 – C7). It might be mentioned that the same situation is met with in the crystal structure of the related compound bis-9-(diethieno[2,3-*b*;3′,2′-*f*]borepinyl)ether. (The structure will soon be published by the present author.) Similar disparities of the C – S bonds in thiophene derivatives have, among others, been discussed by Goldberg and Shmueli.[5] They state that the longer of the C – S bonds is that connecting sulphur to the

Table 6. Mean values of distances and angles for the two nearly identical halves of the dithienotropylium cation. *E.s.d.*'s are given within parentheses. A comparison is also made between the distances of the averaged thiophene rings in the present compound and of the thiophene ring in α-thiophenecarboxylic acid.[6] The latter molecule is oriented so that the carbon atom outside the thiophenic ring corresponds to the atom C9 in the present compound.

Atoms	Distance (Å) Mean value	Corresponding value in α-thiophene-carboxylic acid
S1 – C2 S8 – C7	1.692(11)	1.701(10)
C2 – C3 C7 – C6	1.345(15)	1.363(12)
C3 – CIII C6 – CVI	1.440(12)	1.414(11)
CIII – CII CVI – CVII	1.391(14)	1.362(10)
CII – S1 CVII – S8	1.726(9)	1.693(7)
CII – C9 CVII – C9	1.407(12)	
CIII – C4 CVI – C5	1.396(16)	
C4 – C5	1.373(18)	

Atoms	Angle (°) Mean value	
CII – S1 – C2 CVII – S8 – C7	90.7(5)	92.0(4)
S1 – C2 – C3 S8 – C7 – C6	115.0(8)	111.8(7)
C2 – C3 – CIII C7 – C6 – CVI	111.3(9)	111.9(5)
C3 – CIII – CII C6 – CVI – CVII	111.2(8)	112.4(7)
CIII – CII – S1 CVI – CVII – S8	111.8(6)	111.8(6)
C9 – CII – CIII C9 – CVII – CVI	131.0(8)	
CII – CIII – C4 CVII – CVI – C5	127.4(8)	
CIII – C4 – C5 CVI – C5 – C4	129.2(9)	
CII – C9 – CVII	124.8(11)	

carbon atom that seems to be more actively engaged in the π-delocalization (*viz.* the tropylium carbon atoms in the present compound).

The mean values of the distances and angles in the thiophene groups of the present compound are also compared to the corresponding values published for α-thiophene-carboxylic acid [6] in Table 6. It is seen that the averages of the sulfur-tropylium carbon distances are slightly longer than the sulfur – carbon distances in the carboxylic acid. No explanation can at the moment be given for the difference found in the angle at the non-fused thiophenic α-position in the present compound and in the carboxylic acid.

The positive charge of the C9 atom of the present compound is supposed to be delocalized over the whole cation, the β-thiophenic positions (C3, C6) being less positive than the other atoms.[4] More or less ionic interactions would therefore be expected between the perchlorate oxygen atoms and all of the non-hydrogen atoms of the dithienotropylium cation. Fig. 4 shows C – O contacts less than 3.2 Å and S – O contacts less than 3.3 Å for one cation. As seen, the C – O contacts fall in the range 3.06 – 3.11 Å. They are thus slightly shorter than or equal to the sum of the van der Waals radii, 3.1 Å. A somewhat similar situation arises in the crystal structure of succinylcholine perchlorate.[7] Here the positive charges of the quaternary ammonium groups are delocalized from the nitrogen atoms and weak ionic interactions occur between the carbonyl carbon atoms and the oxygen atoms of the perchlorate group. The corresponding C – O distances are 3.05 Å.

One of the distances between sulfur and a perchlorate oxygen atom in the present compound is quite short, 3.03 Å. However, S – O distances of the same magnitude, 3.02 and 3.04 Å, are found in the crystal structure of 5*H*,8*H*-dibenzo[*d*,*f*][1,2]-dithiocin-1,1-dioxide.[8] Likewise, a short S – O distance, 3.04 Å, exists in the crystal structure of phenylamino-2-phenyl-5-thiazolinone-4.[9] In the compounds just discussed the interactions do not seem to be of an ionic character.

Thus if there are ionic interactions between the atoms of the dithienotropylium cation and the perchlorate oxygen atoms, these interactions are weak.

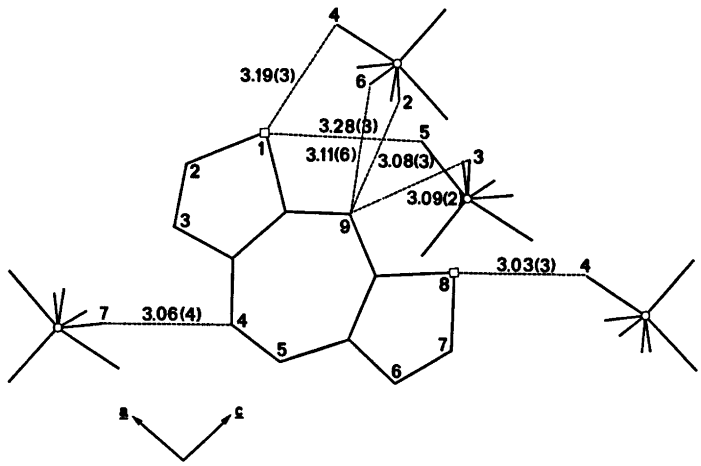


Fig. 4. The atoms of dithienotropylium perchlorate are projected on the *ac* plane along the *b* axis. Short contacts (Å) between the atoms of one dithienotropylium cation and the oxygen atoms of neighbouring perchlorate groups are indicated by dashed lines. The perchlorate oxygen atoms at the ends of the dashed lines are numbered according to Table 3a. *E.s.d.*'s in the distances are given within parentheses.

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