

Data collection

Siemens P4 diffractometer $\theta_{\max} = 30^\circ$
 $2\theta/\omega$ scans $h = 0 \rightarrow 12$
 Absorption correction: none $k = 0 \rightarrow 19$
 3204 measured reflections $l = 0 \rightarrow 22$
 3204 independent reflections 3 standard reflections
 1558 reflections with every 97 reflections
 $I > 2\sigma(I)$ intensity decay: 9.9%

Refinement

Refinement on F^2 $\Delta\rho_{\max} = 0.16 \text{ e } \text{\AA}^{-3}$
 $R[F^2 > 2\sigma(F^2)] = 0.053$ $\Delta\rho_{\min} = -0.16 \text{ e } \text{\AA}^{-3}$
 $wR(F^2) = 0.099$ Extinction correction: none
 $S = 1.046$ Scattering factors from
 3204 reflections *International Tables for*
 274 parameters *Crystallography* (Vol. C)
 H atoms: see below Absolute structure:
 $w = 1/[\sigma^2(F_o^2) + (0.012P)^2]$ Flack (1983)
 where $P = (F_o^2 + 2F_c^2)/3$ Flack parameter = 0.04 (13)
 $(\Delta/\sigma)_{\max} < 0.001$

Table 1. Selected geometric parameters (\AA , $^\circ$)

S—O3	1.4299 (14)	C4—C10	1.563 (3)
S—O2	1.4353 (14)	C5—C6	1.526 (3)
S—N3	1.6281 (15)	C5—C10	1.531 (2)
S—C11	1.768 (2)	C6—C7	1.525 (3)
O1—C2	1.395 (2)	C7—C8	1.540 (3)
O1—C9	1.446 (2)	C8—C9	1.526 (3)
N3—C2	1.471 (2)	C9—C10	1.514 (2)
N3—C4	1.518 (2)	C1'—C2'	1.239 (3)
C2—C1'	1.537 (3)		
O3—S—O2	119.80 (9)	N3—C4—C10	106.16 (13)
O3—S—N3	108.73 (8)	C6—C5—C10	111.1 (2)
O2—S—N3	107.02 (8)	C7—C6—C5	112.6 (2)
O3—S—C11	107.00 (9)	C6—C7—C8	109.0 (2)
O2—S—C11	106.32 (8)	C9—C8—C7	112.5 (2)
N3—S—C11	107.40 (8)	O1—C9—C10	112.23 (14)
C2—O1—C9	116.71 (13)	O1—C9—C8	106.43 (15)
C2—N3—C4	117.83 (13)	C10—C9—C8	111.97 (14)
C2—N3—S	118.94 (11)	C9—C10—C5	109.75 (15)
C4—N3—S	123.18 (12)	C9—C10—C4	112.73 (14)
O1—C2—N3	111.86 (15)	C5—C10—C4	112.51 (15)
O1—C2—C1'	116.1 (2)	C2'—C1'—C2	126.7 (2)
N3—C2—C1'	111.0 (2)		
C9—O1—C2—N3	36.7 (2)	C7—C8—C9—O1	-178.8 (1)
C9—O1—C2—C1'	-92.1 (2)	C7—C8—C9—C10	-55.8 (2)
C4—N3—C2—O1	-58.5 (2)	O1—C9—C10—C5	175.4 (2)
S—N3—C2—O1	119.2 (1)	C8—C9—C10—C5	55.7 (2)
C4—N3—C2—C1'	72.9 (2)	O1—C9—C10—C4	-58.4 (2)
S—N3—C2—C1'	-109.3 (2)	C8—C9—C10—C4	-178.0 (1)
C2—N3—C4—C10	18.3 (2)	C6—C5—C10—C9	-56.3 (2)
S—N3—C4—C10	-159.3 (1)	C6—C5—C10—C4	177.3 (2)
C10—C5—C6—C7	57.4 (2)	N3—C4—C10—C9	36.9 (2)
C5—C6—C7—C8	-54.8 (2)	N3—C4—C10—C5	161.7 (1)
C6—C7—C8—C9	53.7 (2)	O1—C2—C1'—C2'	-12.1 (3)
C2—O1—C9—C10	18.6 (2)	N3—C2—C1'—C2'	-141.3 (2)
C2—O1—C9—C8	141.4 (2)		

The H atoms of the terminal methyl groups were found in the difference Fourier map and refined normally with isotropic displacement parameters. The remaining H atoms were introduced at calculated positions and treated as riding, with C—H = 0.93–0.95 \AA and displacement parameters equal to $1.2U_{\text{eq}}$ of the parent atom. An absorption correction based on the equations of the crystal faces did not improve the results (the R factors were higher). Therefore, it was not included in the calculations. The R factors of the other enantiomeric form were also slightly higher (0.054, 0.100).

Data collection: XSCANS (Siemens, 1996). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXTL (Sheldrick, 1995). Program(s) used to refine structure: SHELXTL. Molecular graphics: SHELXTL. Software used to prepare material for publication: SHELXTL.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1189). Services for accessing these data are described at the back of the journal.

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Propane-1,3-diammonium diperchlorate

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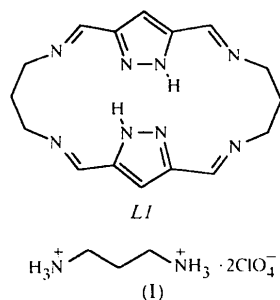
Abstract

The structure of the title compound, $\text{C}_3\text{H}_{12}\text{N}_2^+ \cdot 2\text{ClO}_4^-$, has been determined at 158 K. The extensive network of hydrogen bonds, including two four-centre bonds, is described.

Comment

In the course of our studies of complexes of *LI*, colourless needles of the title compound, (I), were formed

and subsequently characterized by X-ray crystallography (Fig. 1). The data collection was carried out at 158 K and the refinement based on F^2 (Sheldrick & Schneider,



1997), in contrast to the two previous room-temperature data collections which were refined against F (Chen *et al.*, 1991; Pritchard *et al.*, 1992).

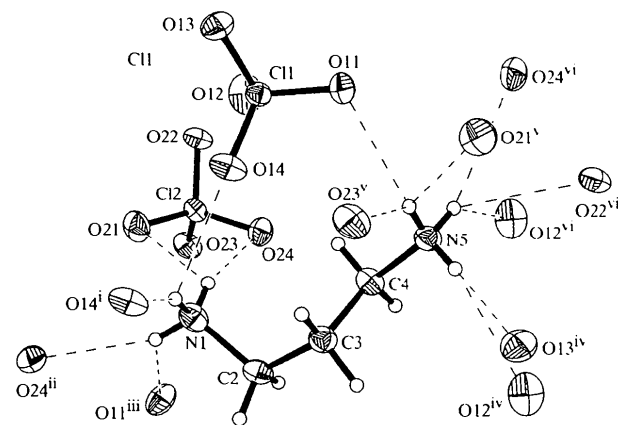


Fig. 1. Perspective view of (1) and the surrounding symmetry-generated atoms showing the hydrogen-bonding environment of the ammonium H atoms. The symmetry codes are as in Table 2. Displacement ellipsoids are at the 50% probability level for non-H atoms.

A notable feature of the structure is the extensive network of hydrogen bonds between the ammonium H and perchlorate O atoms. In examining and describing this network, we considered those contacts which fulfilled the default criteria of the *HTAB* instruction in *SHELXL97* (Sheldrick & Schneider, 1997), rather than the criteria used by Taylor *et al.* (1984). The latter were developed for systems in which the H-atom position is 'normalized' to standard bond lengths (determined by neutron-diffraction studies), not for systems where the H-atom positions were refined freely, as is the case here.

The hydrogen-bonding network involves all of the ammonium H and perchlorate O atoms. Of particular note are two four-centre ('trifurcated') hydrogen bonds to H5B and H5C, both of which incorporate a chelated three-centre ('bifurcated') component (*i.e.* both acceptor O atoms are connected to the same chlorine). Observations of four-centre hydrogen bonds are rare and they

occur only with $N^+—H$ as donors (Taylor *et al.*, 1984). The four remaining ammonium H atoms are each involved in a three-centre hydrogen bond, with two of these being chelated.

One of the perchlorate O atoms (O24) acts as an acceptor in three hydrogen bonds and this O atom is also characterized by an extended Cl—O bond of 1.467 (2) Å [*cf.* 1.439 (2)–1.447 (2) Å]. For the remaining perchlorate O atoms, no correlation is observed between the Cl—O bond lengths and the number of hydrogen bonds (one or two) in which the O atom acts as an acceptor.

Experimental

Colourless needles of the title compound were formed as a by-product when $Pb_2(L1)(ClO_4)_2$ (0.11 mmol) in acetonitrile (60 ml) was mixed with an acetonitrile solution (3 ml) of copper(II) perchlorate (0.24 mmol), stirred under reflux for 5 h, then concentrated under reduced pressure to 10 ml and diffused with diethyl ether. (**Caution:** perchlorate salts are potentially explosive.)

Crystal data

$C_3H_{12}N_2^{3+} \cdot 2ClO_4^-$

$M_r = 275.04$

Monoclinic

$P2_1/c$

$a = 7.292$ (2) Å

$b = 14.454$ (4) Å

$c = 9.643$ (3) Å

$\beta = 96.673$ (3)°

$V = 1009.4$ (5) Å³

$Z = 4$

$D_x = 1.810$ Mg m⁻³

D_m not measured

Data collection

Bruker SMART CCD diffractometer

ω scans

Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)

$T_{min} = 0.49$, $T_{max} = 0.94$

11 221 measured reflections

1719 independent reflections

Refinement

Refinement on F^2

$R(F) = 0.032$

$wR(F^2) = 0.082$

$S = 1.027$

1719 reflections

184 parameters

All H atoms refined

$w = 1/[\sigma^2(F_o^2) + (0.0531P)^2 + 0.5264P]$

where $P = (F_o^2 + 2F_c^2)/3$

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 6123 reflections

$\theta = 2.00$ – 24.81 °

$\mu = 0.673$ mm⁻¹

$T = 158$ (2) K

Needle

$0.90 \times 0.10 \times 0.10$ mm

Colourless

1468 reflections with

$I > 2\sigma(I)$

$R_{int} = 0.039$

$\theta_{max} = 24.81$ °

$h = -8 \rightarrow 8$

$k = -16 \rightarrow 16$

$l = -11 \rightarrow 7$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.245$ e Å⁻³

$\Delta\rho_{min} = -0.556$ e Å⁻³

Extinction correction: none

Scattering factors from *SHELXL97* (Sheldrick & Schneider, 1997)

Table 1. Selected bond lengths (Å)

N1—C2	1.495 (3)	C11—O13	1.4441 (19)
C2—C3	1.521 (3)	C11—O11	1.4463 (18)
C3—C4	1.517 (3)	C12—O21	1.4349 (18)
C4—N5	1.501 (3)	C12—O22	1.4381 (17)
C11—O14	1.4388 (17)	C12—O23	1.4450 (18)
C11—O12	1.4408 (18)	C12—O24	1.4669 (18)

Table 2. Hydrogen-bonding geometry (Å, °)

D—H...A	D—H	H...A	D...A	D—H...A
N1—H1A...O24	0.83	2.41	3.172 (3)	156
N1—H1A...O21	0.82	2.41	2.963 (3)	126
N1—H1B...O14 ⁱ	0.85	2.30	3.100 (3)	156
N1—H1B...O14	0.85	2.54	3.050 (3)	120
N1—H1C...O24 ⁱⁱ	0.87	2.28	3.076 (3)	153
N1—H1C...O11 ⁱⁱⁱ	0.87	2.47	3.074 (3)	127
N5—H5A...O13 ^{iv}	0.82	2.24	3.049 (3)	167
N5—H5A...O12 ^v	0.82	2.49	3.111 (3)	133
N5—H5B...O11	0.79	2.32	2.940 (3)	136
N5—H5B...O23 ^{vi}	0.79	2.56	3.123 (3)	130
N5—H5B...O21 ^{vii}	0.79	2.56	3.103 (3)	127
N5—H5C...O12 ^{viii}	0.85	2.35	3.019 (4)	136
N5—H5C...O22 ^{ix}	0.85	2.49	2.965 (3)	116
N5—H5C...O24 ^x	0.85	2.53	3.229 (3)	141

Symmetry codes: (i) $1-x, 1-y, -z$; (ii) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (iii) $1-x, y-\frac{1}{2}, -\frac{1}{2}-z$; (iv) $1+x, y, z$; (v) $1-x, \frac{1}{2}+y, -\frac{1}{2}-z$; (vi) $1-x, 1-y, -1-z$.

The H atoms were readily located from a difference Fourier map and were allowed to refine freely.

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SAINT* (Siemens, 1995). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990; Sheldrick, 1997). Program(s) used to refine structure: *SHELXL97* (Sheldrick & Schneider, 1997). Molecular graphics: *SHELXL97*. Software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1239). Services for accessing these data are described at the back of the journal.

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Tautomérie de la 4-(hydroxyphénylméthylène) isochroman-1,3 dione à l'état solide

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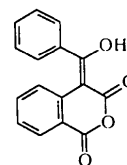
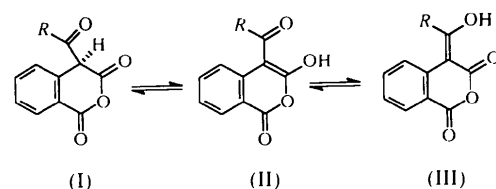
(Reçu le 4 mars 1999, accepté le 13 mai 1999)

Abstract

The crystal and molecular structure of 4-(hydroxyphénylméthylène)isochroman-1,3-dione, C₁₆H₁₀O₄, is presented. The molecular structure is the same as that observed in solution and corresponds to the exocyclic enolic tautomer.

Commentaire

A l'état solide par IR il a été supposé (Schenckenburger, 1965) que les isochroman-1,3 diones présentaient la structure dicarboxylée, (I), alors qu'en solution seule la forme (III) est présente (Saba *et al.*, 1996). Cette étude a été effectuée pour vérifier quel tautomère était effectivement présent dans le cristal de 4-(hydroxyphénylméthylène) isochroman-1,3 dione, (IV).



(IV)