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2-*O*,3-Diethyl-7,8,10-trimethylisoalloxazinium Perchlorate

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Abstract

The crystal structure of 2-*O*,3-diethyl-7,8,10-trimethylisoalloxazinium perchlorate, $C_{17}H_{21}N_4O_2^+ . ClO_4^-$, has been determined from X-ray diffraction data collected at room temperature. The structure is monoclinic, space group $P2_1/c$, with $a = 10.73$ (1), $b = 12.91$ (1), $c = 16.52$ (1) Å, $\beta = 122.18$ (5)°, $V = 1936.9$ Å^3, $Z = 4$ and $D_x = 1.42$ Mg m^{-3}. The derived structural model was refined to a conventional linear R value of 0.056. The structural results confirm the assumed planarity of the alloxazinium ring system of the molecule. The perchlorate ions are located above the central region of the ring system in such a way that discrete alloxazinium perchlorate entities are formed. The perchlorate ions are disordered in a way corresponding to two different orientations of the ions at the same crystallographic site.

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Introduction

2-*O*,3-Diethyl-7,8,10-trimethylisoalloxazinium per-chlorate (DTA perchlorate) is an example of a 2-*O*-substituted flavin (*cf.* Fig. 1), suggested as a model of catalytic intermediates for some flavoenzymes (Hemmerich, Ghisla, Hartman & Müller, 1971). The present investigation is part of a research project for structural studies on flavin derivatives in different states of oxidation and protonation. A crystalline specimen, suitable for X-ray studies, was kindly supplied by P. Hemmerich, University of Konstanz, Switzerland.

Experimental

A single crystal of DTA perchlorate with the dimensions $0.05 \times 0.09 \times 0.32$ mm was selected for X-ray data collection. All independent reflections with $\theta \leq 65°$ were collected at room temperature on a Siemens AED diffractometer, with Cu $K\alpha$ radiation, using the ω–2θ scan technique. The 1023 reflections having estimated $\sigma(I_{net})/I_{net}$ values below 0.20 were considered observable and were used in the subsequent calculations. The net intensities, I_{net}, were corrected for Lorentz, polarization and absorption ($\mu = 2.20$ mm^{-1}) effects. The phases calculated from approximate Cl positions, as derived from a Patterson function, were used to select the proper set of phases generated by a computerized (Norrestam, 1972) symbolic addition procedure (Karle & Karle, 1966). An E map based on these phases revealed most of the alloxazine ring system. Subsequent difference electron density calculations yielded the positions of the remaining non-hydrogen atoms. However, around the Cl atom five peaks (two lower ones) in a trigonal-pyramidal arrangement occurred, suggesting a disordered perchlorate ion having two dominating orientations. To describe these disordered ions all five atomic positions were included in the structural model of the perchlorate ion, and two of these positions [O(4) and O(5)] were given fixed occupancy factors of 0.5. No attempts to refine the occupancy factors were made. The H atoms were located by conventional techniques. In the final refinement, using the weighting scheme suggested by Hughes

(1941), all the nonhydrogen atoms were allowed to vibrate anisotropically, while the H atoms were given isotropic thermal parameters fixed at 5 Å^2. The final linear R value was 0.056 when the parameter shifts were all well below their estimated standard deviations.

The atomic scattering factors used for Cl, O, N and C were those given by Hanson, Herman & Lea Skillman (1964) and for H that of Stewart, Davidson & Simpson (1965). The final atomic coordinates with estimated standard deviations are listed in Tables 1 and 2.* The atomic labelling used for the atoms forming the isoalloxazinium ion is shown in Fig. 1. The intramolecular bond distances and angles are given in Tables 3 and 4.

Discussion

A stereoscopic view of the molecular packing is shown in Fig. 2. As indicated, one positively charged DTA ion

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34201 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates for the C, O, N and Cl atoms*

The estimated standard deviations are given in parentheses.

	x	y	z
N(1)	0.3021 (6)	0.4585 (5)	0.1553 (5)
C(2)	0.2851 (8)	0.3911 (7)	0.2078 (6)
N(3)	0.1801 (7)	0.3161 (5)	0.1770 (5)
C(4)	0.0765 (9)	0.3008 (7)	0.0807 (6)
C(4a)	0.0917 (8)	0.3761 (6)	0.0170 (6)
N(5)	−0.0052 (6)	0.3709 (5)	−0.0745 (5)
C(5a)	0.0124 (8)	0.4366 (6)	−0.1324 (6)
C(6)	−0.0859 (8)	0.4299 (6)	0.2307 (6)
C(7)	−0.0735 (9)	0.4899 (7)	−0.2930 (6)
C(8)	0.0414 (9)	0.5650 (7)	−0.2563 (6)
C(9)	0.1389 (8)	0.5746 (6)	−0.1588 (6)
C(9a)	0.1257 (8)	0.5119 (6)	−0.0951 (6)
N(10)	0.2195 (6)	0.5173 (5)	0.0032 (5)
C(10a)	0.2071 (8)	0.4504 (6)	0.0614 (6)
O(12)	0.3753 (6)	0.3914 (5)	0.3022 (4)
C(13)	0.1804 (8)	0.2415 (7)	0.2459 (6)
O(14)	−0.0152 (6)	0.2356 (5)	0.0520 (4)
C(17)	−0.1750 (9)	0.4804 (8)	−0.3994 (6)
C(18)	0.0605 (9)	0.6326 (7)	−0.3226 (6)
C(20)	0.3366 (9)	0.5960 (7)	0.0452 (6)
C(22)	0.4953 (10)	0.4665 (7)	0.3457 (6)
C(23)	0.2763 (10)	0.1514 (8)	0.2614 (7)
C(32)	0.6203 (11)	0.4250 (9)	0.3467 (6)
O(1)	0.3783 (17)	0.2274 (8)	0.1011 (11)
O(2)	0.4566 (14)	0.3582 (7)	0.0480 (10)
O(3)	0.5038 (16)	0.1911 (8)	0.0260 (10)
O(4)	0.5859 (17)	0.2526 (13)	0.1442 (12)
O(5)	0.3273 (22)	0.2568 (30)	−0.0038 (22)
Cl	0.4553 (3)	0.2568 (3)	0.0637 (2)

Fig. 1. Schematic structural formula for the DTA ion.

and one negatively charged perchlorate ion together form a discrete entity. Within this entity the perchlorate ion is located close to the C(10a) region of the alloxazinium ring system of DTA, yielding fairly short contacts (cf. Table 5). The shortest, 3·04 Å, occur between O(2) of a perchlorate ion and C(10a) and N(10) of the nearest DTA ion. Since there are no possibilities for hydrogen bonds to be formed, the crystal structure can be considered as consisting of neutral entities of DTA perchlorate, separated by mainly van der Waals contact distances. Similar packing patterns have been observed in other isoalloxazinium derivatives (von Glehn, Kierkegaard, Norrestam, Rönnquist & Werner, 1970; Norrestam, Torbjörnsson & Müller, 1972; Norrestam & Tillberg, 1972). The DTA ions shown in Fig. 3 are almost planar; the r.m.s. derivation from a least-squares plane through all 14 atoms forming the alloxazine ring system is 0·033 Å, with the largest deviations of 0·05 Å observed for N(5), N(10) and C(8). Calculations of least-squares planes through each of the three six-membered rings give r.m.s. values of 0·008, 0·017 and 0·004 Å for the benzenoid, pyrazinoid and pyrimidinoid rings respectively. The slight deformation observed for the pyrazinoid ring (towards a boat conformation) is significant as judged by the large deviations from 0° for some of the endocyclic torsion angles, viz 5·2 (1·2)° and −3·6 (1·2)° for the angles formed by C(5a)—N(5)—C(4a)—C(10a) and by C(1a)—C(5a)—N(5)—C(4a) respectively. The two ethyl substituents of the DTA ions are twisted out of the molecular plane: the torsion angles formed by

Table 2. Fractional atomic coordinates for the hydrogen atoms

The estimated standard deviations are given in parentheses.

	x	y	z
H(6)	−0·162 (8)	0·386 (6)	−0·248 (5)
H(9)	0·223 (7)	0·625 (6)	−0·136 (5)
H(13a)	0·074 (8)	0·214 (6)	0·210 (5)
H(13b)	0·233 (7)	0·291 (6)	0·309 (5)
H(17a)	−0·248 (8)	0·434 (6)	−0·414 (6)
H(17b)	−0·243 (8)	0·530 (6)	−0·418 (6)
H(17c)	−0·131 (7)	0·449 (6)	−0·439 (5)
H(18a)	−0·027 (8)	0·679 (6)	−0·360 (5)
H(18b)	0·064 (8)	0·599 (6)	−0·370 (6)
H(18c)	0·167 (8)	0·686 (6)	−0·282 (5)
H(22a)	0·475 (8)	0·472 (6)	0·392 (6)
H(22b)	0·446 (7)	0·547 (6)	0·303 (5)
H(23a)	0·252 (8)	0·117 (7)	0·206 (5)
H(23b)	0·289 (7)	0·088 (6)	0·311 (5)
H(23c)	0·363 (8)	0·164 (6)	0·269 (5)
H(32a)	0·638 (9)	0·370 (6)	0·380 (6)
H(32b)	0·619 (7)	0·424 (6)	0·285 (6)
H(32c)	0·704 (8)	0·463 (6)	0·373 (5)
H(20a)	0·302 (7)	0·658 (6)	0·014 (5)
H(20b)	0·385 (6)	0·595 (6)	0·007 (5)
H(20c)	0·358 (8)	0·604 (7)	0·100 (6)

Table 3. Intramolecular bond distances (Å)

Estimated standard deviations are given in parentheses.

N(1)—C(2)	1·308 (10)	C(6)—H(6)	0·91 (6)
C(2)—N(3)	1·362 (9)	C(9)—H(9)	1·01 (6)
N(3)—C(4)	1·387 (9)	C(13)—H(13a)	1·02 (6)
C(4)—C(4a)	1·503 (10)	C(13)—H(13b)	1·09 (6)
C(4a)—N(5)	1·303 (9)	C(17)—H(17a)	0·91 (7)
N(5)—C(5a)	1·364 (9)	C(17)—H(17b)	0·89 (7)
C(5a)—C(6)	1·390 (10)	C(17)—H(17c)	1·07 (6)
C(6)—C(7)	1·350 (10)	C(18)—H(18a)	1·00 (6)
C(7)—C(8)	1·425 (10)	C(18)—H(18b)	0·91 (6)
C(8)—C(9)	1·383 (10)	C(18)—H(18c)	1·19 (6)
C(9)—C(9a)	1·394 (10)	C(22)—H(22a)	0·91 (6)
C(9a)—N(10)	1·383 (10)	C(22)—H(22b)	1·21 (6)
N(10)—C(10a)	1·352 (9)	C(23)—H(23a)	0·93 (7)
C(10a)—N(1)	1·331 (9)	C(23)—H(23b)	1·12 (6)
C(4a)—C(10a)	1·422 (9)	C(23)—H(23c)	0·88 (6)
C(5a)—C(9a)	1·416 (9)	C(32)—H(32a)	0·86 (7)
C(2)—O(12)	1·327 (9)	C(32)—H(32b)	1·02 (7)
O(12)—C(22)	1·459 (9)	C(32)—H(32c)	0·90 (7)
C(22)—C(32)	1·435 (12)	C(20)—H(20a)	0·92 (7)
N(3)—C(13)	1·488 (9)	C(20)—H(20b)	1·02 (6)
C(13)—C(23)	1·481 (11)	C(20)—H(20c)	0·82 (7)
C(4)—O(14)	1·185 (9)		
C(7)—C(17)	1·501 (9)		
C(8)—C(18)	1·497 (10)		
N(10)—C(20)	1·467 (9)		
Cl—O(1)	1·324 (14)		
Cl—O(2)	1·336 (9)		
Cl—O(3)	1·313 (12)		
Cl—O(4)	1·323 (15)		
Cl—O(5)	1·224 (22)		

Table 4. Intramolecular bond angles (°)

N(1)—C(2)—N(3)	127·2 (7)	N(10)—C(10a)—N(1)	118·3 (6)
C(2)—N(3)—C(4)	121·8 (7)	C(10a)—N(1)—C(2)	115·4 (6)
N(3)—C(4)—C(4a)	113·1 (7)	N(1)—C(2)—O(12)	120·4 (7)
C(4)—C(4a)—C(10a)	117·7 (7)	C(2)—O(12)—C(22)	118·7 (6)
C(4)—C(4a)—N(5)	117·5 (6)	O(12)—C(22)—C(32)	109·4 (7)
C(4a)—N(5)—C(5a)	117·3 (6)	O(12)—C(2)—N(3)	112·4 (7)
C(4a)—C(10a)—N(1)	124·8 (7)	C(2)—N(3)—C(13)	120·6 (6)
C(4a)—C(10a)—N(10)	116·9 (7)	N(3)—C(13)—C(23)	111·0 (6)
N(5)—C(5a)—C(9a)	122·0 (7)	C(13)—N(3)—C(4)	117·3 (6)
N(5)—C(5a)—C(6)	118·6 (6)	N(3)—C(4)—O(14)	123·2 (7)
C(5a)—C(6)—C(7)	122·3 (7)	O(14)—C(4)—C(4a)	123·8 (7)
C(5a)—C(9a)—N(10)	117·7 (6)	C(6)—C(7)—C(17)	122·8 (7)
C(5a)—C(9a)—C(9)	118·7 (7)	C(17)—C(7)—C(8)	118·5 (7)
C(6)—C(7)—C(8)	118·7 (7)	C(7)—C(8)—C(18)	120·7 (7)
C(7)—C(8)—C(9)	120·2 (7)	C(18)—C(8)—C(9)	119·1 (7)
C(8)—C(9)—C(9a)	120·6 (7)	C(9a)—N(10)—C(20)	119·7 (6)
C(9)—C(9a)—N(10)	123·6 (6)	C(20)—N(10)—C(10a)	119·2 (6)
C(9a)—N(10)—C(10a)	121·1 (6)		
O(1)—Cl—O(2)	116·5 (7)	O(2)—Cl—O(4)	96·9 (9)
O(1)—Cl—O(3)	122·7 (7)	O(2)—Cl—O(5)	86·9 (18)
O(1)—Cl—O(4)	96·3 (10)	O(3)—Cl—O(4)	88·6 (9)
O(1)—Cl—O(5)	75·5 (15)	O(3)—Cl—O(5)	96·0 (17)
O(2)—Cl—O(3)	119·5 (8)	O(4)—Cl—O(5)	171·8 (16)

C(2)—O(12)—C(22)—C(32) and by C(2)—N(3)—C(13)—C(23) are −86·2 (1·0)° and 86·5 (1·0)° respectively.

The distribution of bond angles and distances within the DTA rings is consistent with those found in similar compounds (e.g. Norrestam & Tillberg, 1972). The C(4a)—N(5), C(10a)—N(1) and N(1)—C(2) bond
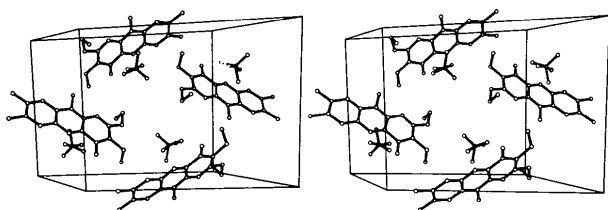
Fig. 2. Stereoscopic packing diagram of the DTA perchlorate structure. The origin is at the lower-left front corner, with **a** pointing into the plane of the paper, **b** upwards and **c** to the right.
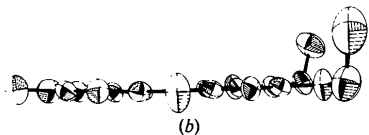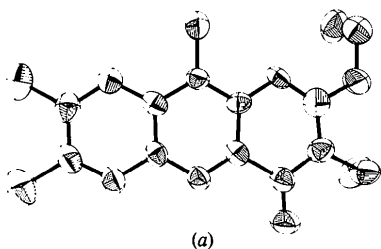

(a)

(b)

Fig. 3. The molecular geometry of the DTA ion, as seen (a) perpendicular to and (b) parallel to the least-squares plane through the molecule. Only the nonhydrogen atoms represented by their thermal ellipsoids are shown.

lengths of 1·303 (9), 1·331 (9) and 1·308 (10) Å indicate appreciable double-bond character for these bonds.

Because of the disorder, the bond lengths and angles within the perchlorate groups are very unreliable and of limited chemical relevance.

Table 5. *Intermolecular distances* (Å) *less than* 3·50 Å *between nonhydrogen atoms and their estimated standard deviations*

Code for symmetry-related atoms

None	x,y,z		(iii)	$1-x, 1-y, -z$
(i)	$-x, 1-y, -z$		(iv)	$x, \frac{1}{2}-y, z-\frac{1}{2}$
(ii)	$-x, y-\frac{1}{2}, -z-\frac{1}{2}$			

N(1)—N(5^i)	3·500 (7)		O(1)—C(4)	3·215 (16)
N(1)—C(5a^i)	3·463 (8)		O(1)—C(4a)	3·244 (14)
N(1)—C(6^i)	3·476 (8)		O(1)—C(10a)	3·288 (12)
C(2)—C(6^i)	3·302 (10)		O(2)—N(1)	3·271 (13)
C(4)—C(9a^i)	3·340 (10)		O(2)—N(10)	3·039 (11)
C(4a)—N(10^i)	3·459 (8)		O(2)—C(10a)	3·044 (13)
N(5)—N(10^i)	3·412 (7)		O(2)—C(20)	3·315 (12)
N(5)—C(10a^i)	3·249 (8)		O(2)—C(20^{iii})	3·361 (14)
N(5)—C(18^{ii})	3·411 (9)		O(3)—O(12^{iv})	3·357 (13)
C(5a)—C(10a^i)	3·462 (9)		O(5)—C(4a)	3·131 (27)
O(1)—N(1)	3·340 (12)		O(5)—N(5)	3·438 (24)
O(1)—C(2)	3·234 (15)		O(5)—C(10a)	3·248 (33)
O(1)—N(3)	3·201 (15)			

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