

1960). The closest S...S distance of 3.44 Å is smaller than the expected value by 0.26 Å; such a short distance (3.38 Å) was also found in Zn(EX)₂ (Ikeda *et al.*, 1966). The closest C...C distance of 3.53 Å may be attributed to the small volume of the dithiocarbonic carbon atom. The other distances are normal. It can be seen from the Table that the sulphur-methyl and methyl-methyl contacts are most important in the structure.

The numerical calculations were performed on the FACOM270-30 computer of this Institute, with a universal crystallographic computation program system, UNICS (Sakurai, Ito, Iwasaki, Watanabe & Fukuhara, 1967).

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Studies on Flavin Derivatives. The Crystal and Molecular Structure of 5-Ethyl-3,7,8,10-tetramethylisoalloxazinium Perchlorate

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The crystal structure of 5-ethyl-3,7,8,10-tetramethylisoalloxazinium perchlorate, C₁₆H₁₉ClN₄O₆, has been derived from three-dimensional X-ray diffractometer data. The unit cell is orthorhombic, space group *P*2₁2₁2₁, with the dimensions *a* = 7.768 (3), *b* = 13.255 (4) and *c* = 17.647 (6) Å. There are four formula units in the unit cell. The structure was determined by direct methods. Full-matrix least-squares refinement of the structural parameters gave an *R* value of 0.042 for the 1342 observed reflexions. The isoalloxazinium ring system is nearly planar. The packing of the molecules in the unit cell leads to several very short (2.8 to 3.0 Å) non-bonded C...O and N...O contacts.

Introduction

The structure determination of 5-ethyl-3,7,8,10-tetramethylisoalloxazinium perchlorate (ETIP) reported here is part of a series (Kierkegaard *et al.*, 1971) of structural investigations of flavin derivatives in different states of protonation and oxidation.

A schematic structural formula of ETIP is given in Fig. 1. ETIP is an example of a 5-alkylflavoquinonium ion. The significance of such ions in the catalysis of flavin enzymes has been discussed by Hemmerich, Ghisla, Hartman & Müller (1971).

Experimental

A blackish crystalline specimen of 5-ethyl-3,7,8,10-tetramethylisoalloxazinium perchlorate was kindly supplied by Dr S. Ghisla (University of Konstanz,

Germany). The crystals were examined by X-ray photographic methods (Guinier, oscillation and Weissenberg techniques). The photographs indicated orthorhombic symmetry and the systematic absences among the X-ray reflexions were consistent with the space group *P*2₁2₁2₁. The crystal finally selected had the dimensions 0.04 × 0.12 × 0.36 mm, with the prismatic axis along [011], and was mounted on a goniometer along the *a* axis. The cell parameters were obtained by least-squares refinement of diffractometer measurements with Cu K α radiation (λ = 1.54184 Å).

The crystal data are:

Composition of asymmetric unit = C₁₆H₁₉ClN₄O₆, *a* = 7.768 (3), *b* = 13.255 (4), *c* = 17.647 (6) Å, *V*₀ = 1817.0 Å³, *D*_c = 1.45 g.cm⁻³, *Z* = 4, μ (Cu K α) = 22.6 cm⁻¹, space group *P*2₁2₁2₁.

Three-dimensional X-ray intensity data were collected on a Siemens AED single-crystal diffractometer

with graphite-monochromated Cu *K* radiation and a scintillation detector. The 1737 intensities within $\theta \leq 64^\circ$ were measured with the θ - 2θ scan technique (scan interval 2.0°) and the background intensity was calculated as the average of the intensities measured at each end of the scan. To be able to judge the random counting errors of the data, a plot of the percentage of the collected data with $\sigma(I_{\text{net}})/I_{\text{net}} \leq \sigma_{\text{rel}}$ versus σ_{rel} was performed and is shown in Fig. 2. The calculation of $\sigma(I_{\text{net}})$ was based on conventional counter statistics. The 1342 reflexions (77%) for which $\sigma(I_{\text{net}})/I_{\text{net}} \leq 0.33$ were used in the subsequent calculations. The net intensities were corrected for Lorentz, polarization and absorption effects (the transmission factors varied between 0.77 and 0.91).

Structure determination and refinement

The crystal structure was solved by a computerized application of direct methods (Karle & Karle, 1966)

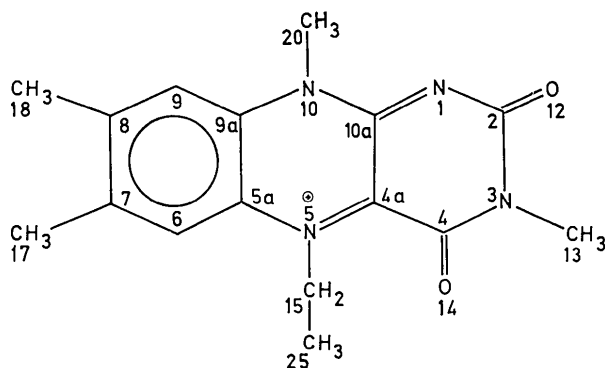


Fig. 1. Schematic drawing of the 5-ethyl-3,7,8,10-tetramethylisalloxazinium ion, with atoms numbered for reference in the text.

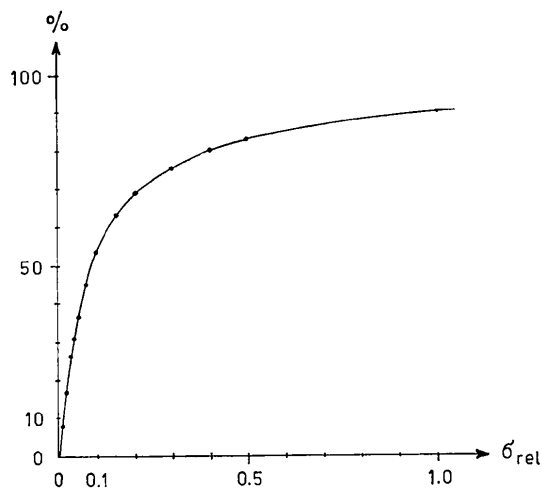


Fig. 2. Percentage of the collected data with $\sigma(I_{\text{net}})/I_{\text{net}} \leq \sigma_{\text{rel}}$ plotted versus σ_{rel} .

utilizing the so called weighted \sum_2 formula for determination and refinement of phases. A detailed description of the phasing computer programs is given elsewhere (Norrestam, 1972).

Approximate overall temperature factor and scale factor were obtained from a usual Wilson plot using a local version of the program *FAME* (Dewar & Stone, University of Chicago). The statistical averages and distributions of the derived normalized structure factors $|E|$ are given in Table 1. From the 205 highest $|E|$ values ($|E|$ greater than 1.5), the 894 best triple relations ($|E(\mathbf{h})| \cdot |E(-\mathbf{k})| \cdot |E(\mathbf{k}-\mathbf{h})|$ greater than 10.8) were derived. Of the 205 reflexions used for generation of triple relations, nine ($|E|$ values below 1.8) did not enter into any relations.

Table 1. Statistical data for the normalized structure factors

	Experimental	Theoretical
$\langle E \rangle$	0.82	0.89
$\langle E ^2 - 1 \rangle$	0.92	0.74
$\langle E ^2 \rangle$	1.00	1.00
$ E > 1$	29.8 %	37.0 %
$ E > 2$	3.9 %	1.8 %
$ E > 3$	0.8 %	0.01 %

The chlorine positional parameters were determined from a three-dimensional Patterson function calculated with $|E|^2$ values, and refined together with an isotropic temperature factor and a scale factor by four cycles of full-matrix least-squares, with only the 778 reflexions

Table 2. Fractional atomic coordinates for non-hydrogen atoms

Estimated standard deviations are given in parentheses

	x	y	z
Cl'	0.5952 (2)	0.6036 (1)	0.3645 (1)
O'(1)	0.6144 (7)	0.5613 (4)	0.4366 (3)
O'(2)	0.7495 (7)	0.6173 (8)	0.3305 (3)
O'(3)	0.4965 (9)	0.5382 (5)	0.3197 (3)
O'(4)	0.5104 (9)	0.6960 (4)	0.3728 (3)
N(1)	0.5457 (4)	0.3186 (3)	0.4573 (2)
C(2)	0.5331 (6)	0.3408 (3)	0.5323 (2)
N(3)	0.6744 (5)	0.3804 (3)	0.5708 (2)
C(4)	0.8246 (6)	0.4119 (3)	0.5370 (3)
C(4a)	0.8350 (5)	0.3892 (4)	0.4541 (2)
N(5)	0.9739 (5)	0.4086 (3)	0.4131 (2)
C(5a)	0.9763 (5)	0.3889 (3)	0.3353 (2)
C(6)	1.1194 (6)	0.4173 (4)	0.2897 (3)
C(7)	1.1213 (6)	0.3973 (4)	0.2137 (2)
C(8)	0.9807 (7)	0.3440 (4)	0.1804 (3)
C(9)	0.8432 (7)	0.3173 (4)	0.2244 (3)
C(9a)	0.8358 (6)	0.3403 (3)	0.3018 (2)
N(10)	0.6953 (5)	0.3167 (3)	0.3455 (2)
C(10a)	0.6868 (5)	0.3408 (3)	0.4200 (2)
O(12)	0.4001 (5)	0.3277 (3)	0.5680 (2)
C(13)	0.6595 (8)	0.3956 (5)	0.6535 (3)
O(14)	0.9354 (5)	0.4536 (3)	0.5724 (2)
C(15)	1.1366 (6)	0.4535 (5)	0.4484 (3)
C(25)	1.1293 (10)	0.5656 (5)	0.4452 (5)
C(17)	1.2698 (9)	0.4313 (5)	0.1658 (4)
C(18)	0.9807 (11)	0.3228 (6)	0.0971 (3)
C(20)	0.5454 (9)	0.2631 (6)	0.3126 (3)

having $\sin \theta/\lambda$ larger than 0.40 included, to an R value ($R = \sum |F|_{\text{obs}} - |F|_{\text{calc}}| / \sum |F|_{\text{obs}}$) of 0.42.

The 87 reflexions having $|E|$ larger than 1.85 and $|F|_{\text{obs}}/|F|_{\text{calc}}$ below 5.0 (where $|F|_{\text{calc}}$ is based only of the chlorine contribution) were used as basis set for solving most of the triple relations. Refinement of all the phases by the weighted \sum_2 formula yielded 127 phases having estimated standard deviations below 30°. An E map based on these 127 phases gave nine reasonable atomic positions. Full-matrix least-squares refinement of the structural parameters gave an R value of 0.46 for all the 1342 reflexions. The 55 reflexions having $|E|$ larger than 1.85 and $|F|_{\text{obs}}/|F|_{\text{calc}}$ below 2.0 at this stage were used as a new basis set for solving the triple relations. An E map based on the phases obtained yielded five more positions; parts of the ring system could now be identified.

Least-squares refinement and subsequent difference electron density calculations revealed the positions of the remaining 12 non-hydrogen atoms in a straightforward way. Least-squares refinement of the obtained structural model, with anisotropic temperature factors for all the 27 non-hydrogen atoms gave an R value of 0.067 for all 1342 reflexions. Reasonable positions for all the 19 hydrogen atoms were obtained from a difference electron density map based on the parameters obtained for the 27 non-hydrogen atoms. At this stage the imaginary component of the anomalous dispersion correction for chlorine (+0.72) as given by Cromer (1965) was included in the structure factor calculation. Refinement of the structural parameters for the two

alternative enantiomorphs with non-hydrogen atoms given anisotropic temperature factors and hydrogens the isotropic value 6 Å², yielded conventional R values 0.042 and 0.047 and corresponding weighted R values [$R = (\sum w|F|_{\text{obs}} - |F|_{\text{calc}}|^2 / \sum w|F|_{\text{obs}}^2)^{1/2}$] 0.055 and 0.062. Hughes's (1941) weighting scheme with $|F|_{\text{obs}, \text{min}} = 4.0$ was used in all the refinements. The ratio 1.13 between the weighted R values for the two different enantiomorphs indicates that the enantio-

Table 4. Fractional atomic coordinates for hydrogen atoms

Estimated standard deviations are given in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
H(6)	1.206 (8)	0.450 (4)	0.311 (3)
H(9)	0.754 (8)	0.296 (4)	0.206 (3)
H(13a)	0.682 (8)	0.341 (4)	0.678 (3)
H(13b)	0.763 (7)	0.414 (4)	0.666 (3)
H(13c)	0.575 (7)	0.455 (4)	0.659 (3)
H(15a)	1.246 (8)	0.436 (4)	0.422 (3)
H(15b)	1.145 (7)	0.426 (4)	0.501 (3)
H(25a)	1.110 (7)	0.598 (4)	0.391 (3)
H(25b)	1.237 (8)	0.577 (4)	0.465 (3)
H(25c)	1.028 (7)	0.594 (4)	0.483 (3)
H(17a)	1.313 (8)	0.379 (4)	0.146 (3)
H(17a)	1.353 (8)	0.451 (4)	0.194 (3)
H(17c)	1.229 (7)	0.478 (4)	0.118 (3)
H(18a)	0.851 (8)	0.297 (4)	0.082 (3)
H(18b)	1.056 (8)	0.286 (5)	0.081 (4)
H(18c)	1.023 (7)	0.388 (4)	0.073 (3)
H(20a)	0.591 (8)	0.204 (4)	0.294 (3)
H(20b)	0.463 (7)	0.258 (4)	0.355 (3)
H(20c)	0.515 (8)	0.289 (4)	0.270 (3)

Table 3. Anisotropic thermal parameters ($\times 10^4$)

The estimated standard deviations are given in parentheses. The temperature factor expression used is

$$\exp [-(h^2b_{11} + k^2b_{22} + l^2b_{33} + hkb_{12} + hlb_{13} + klb_{23})]$$

	<i>b</i> ₁₁	<i>b</i> ₂₂	<i>b</i> ₃₃	<i>b</i> ₁₂	<i>b</i> ₁₃	<i>b</i> ₂₃
Cl'	193 (2)	80 (1)	37 (1)	-15 (2)	-22 (2)	10 (1)
O'(1)	684 (19)	122 (4)	40 (2)	210 (16)	-16 (9)	31 (4)
O'(2)	310 (12)	398 (12)	69 (2)	-239 (23)	67 (9)	-46 (9)
O'(3)	549 (18)	188 (6)	79 (3)	-302 (17)	-90 (12)	-31 (6)
O'(4)	633 (19)	102 (3)	100 (3)	173 (14)	-67 (13)	59 (6)
N(1)	142 (7)	62 (2)	40 (1)	-34 (7)	5 (5)	0 (3)
C(2)	156 (9)	53 (3)	41 (2)	-8 (8)	24 (7)	19 (4)
N(3)	162 (7)	58 (2)	33 (1)	10 (7)	12 (5)	2 (6)
C(4)	151 (7)	63 (3)	35 (2)	-17 (9)	-5 (6)	-1 (4)
C(4a)	126 (7)	59 (3)	31 (1)	-26 (8)	-8 (5)	0 (4)
N(5)	138 (6)	58 (2)	33 (1)	-35 (7)	-13 (5)	-2 (3)
C(5a)	144 (7)	55 (2)	32 (1)	-15 (8)	2 (5)	10 (3)
C(6)	154 (9)	64 (3)	38 (3)	-20 (9)	6 (6)	5 (4)
C(7)	194 (9)	64 (3)	37 (2)	20 (11)	26 (7)	15 (4)
C(8)	230 (11)	61 (3)	35 (2)	22 (10)	-19 (7)	16 (4)
C(9)	189 (9)	67 (3)	32 (2)	-39 (9)	-13 (7)	4 (4)
C(9a)	135 (8)	53 (2)	31 (1)	-17 (8)	-18 (6)	3 (3)
N(10)	140 (6)	57 (2)	33 (1)	-22 (6)	-20 (5)	2 (3)
C(10a)	123 (7)	50 (2)	34 (2)	0 (8)	-6 (6)	4 (3)
O(12)	181 (6)	91 (3)	55 (1)	-46 (8)	60 (6)	11 (3)
C(13)	212 (10)	83 (4)	41 (2)	45 (12)	21 (7)	-8 (5)
O(14)	229 (8)	131 (3)	39 (1)	-120 (9)	5 (6)	-34 (3)
C(15)	126 (9)	109 (5)	41 (2)	-42 (10)	-17 (7)	1 (5)
C(25)	279 (15)	99 (5)	57 (3)	-112 (14)	-5 (11)	-24 (6)
C(17)	237 (13)	96 (4)	44 (2)	-24 (13)	59 (9)	8 (5)
C(18)	313 (17)	105 (5)	34 (2)	-25 (16)	20 (9)	-1 (5)
C(20)	229 (13)	114 (5)	41 (2)	-135 (14)	-14 (9)	-15 (6)

morph giving the lowest R value (0.042) ought to be the correct one (*cf.* Hamilton, 1965), since the hypothesis tested is one-dimensional, the number of re-

finned parameters is 301 and the number of observations is 1342. All parameter shifts in the last cycles were well below the estimated standard deviations.

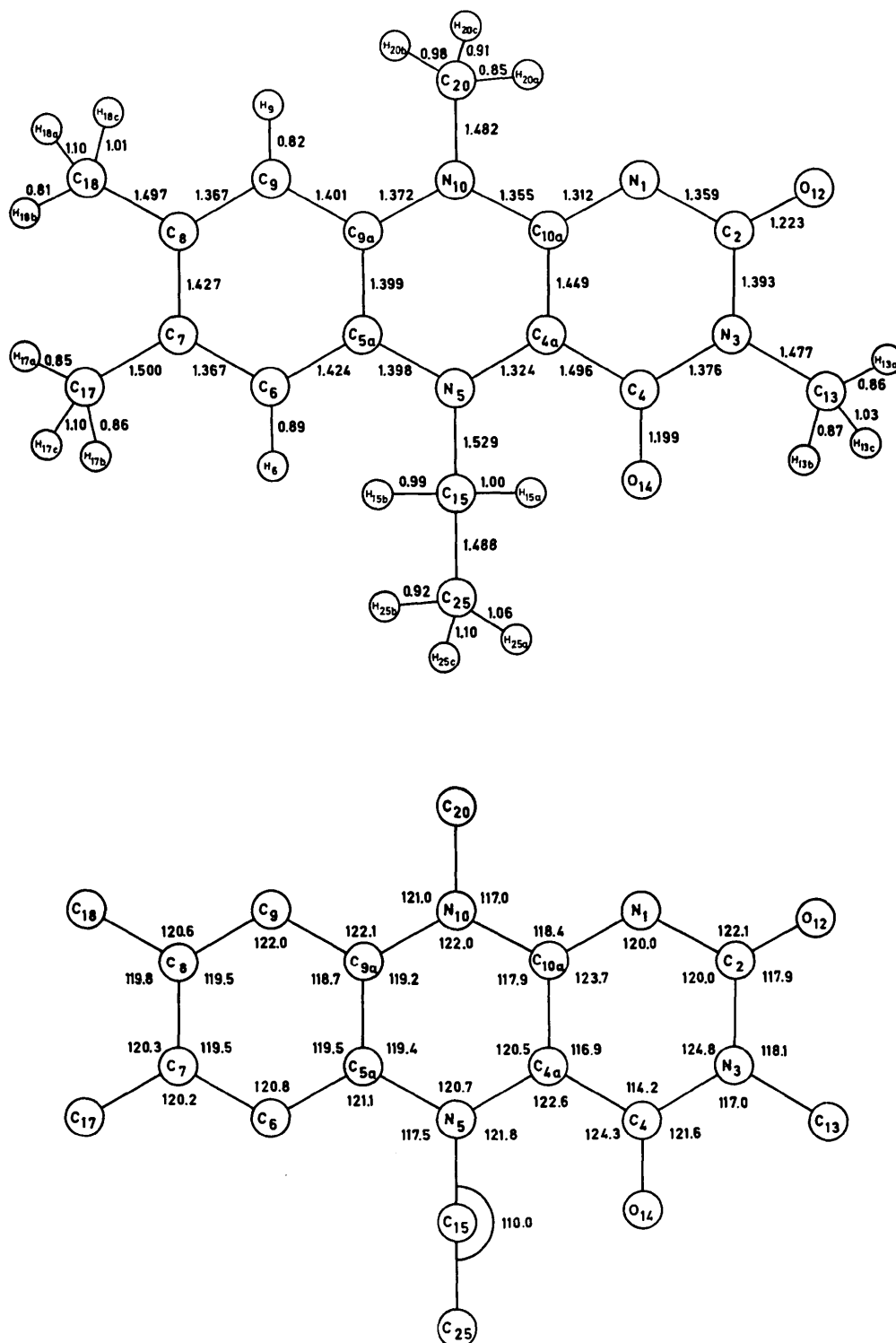


Fig. 3. The intramolecular bond distances, and bond angles between non-hydrogens, in the 5-ethyl-3,7,8,10-tetramethyl-isoalloxazinium ion.

Table 5. Observed and calculated structure factors

Each group of three columns contains h , $10|F_o|$ and $10|F_c|$, and is headed by the values of k and l common to the group.

k	l	h	$10 F_o $	$10 F_c $
1	0	0	100	100
1	0	1	100	100
1	0	2	100	100
1	0	3	100	100
1	0	4	100	100
1	0	5	100	100
1	0	6	100	100
1	0	7	100	100
1	0	8	100	100
1	0	9	100	100
1	0	10	100	100
1	0	11	100	100
1	0	12	100	100
1	0	13	100	100
1	0	14	100	100
1	0	15	100	100
1	0	16	100	100
1	0	17	100	100
1	0	18	100	100
1	0	19	100	100
1	0	20	100	100
1	0	21	100	100
1	0	22	100	100
1	0	23	100	100
1	0	24	100	100
1	0	25	100	100
1	0	26	100	100
1	0	27	100	100
1	0	28	100	100
1	0	29	100	100
1	0	30	100	100
1	0	31	100	100
1	0	32	100	100
1	0	33	100	100
1	0	34	100	100
1	0	35	100	100
1	0	36	100	100
1	0	37	100	100
1	0	38	100	100
1	0	39	100	100
1	0	40	100	100
1	0	41	100	100
1	0	42	100	100
1	0	43	100	100
1	0	44	100	100
1	0	45	100	100
1	0	46	100	100
1	0	47	100	100
1	0	48	100	100
1	0	49	100	100
1	0	50	100	100
1	0	51	100	100
1	0	52	100	100
1	0	53	100	100
1	0	54	100	100
1	0	55	100	100
1	0	56	100	100
1	0	57	100	100
1	0	58	100	100
1	0	59	100	100
1	0	60	100	100
1	0	61	100	100
1	0	62	100	100
1	0	63	100	100
1	0	64	100	100
1	0	65	100	100
1	0	66	100	100
1	0	67	100	100
1	0	68	100	100
1	0	69	100	100
1	0	70	100	100
1	0	71	100	100
1	0	72	100	100
1	0	73	100	100
1	0	74	100	100
1	0	75	100	100
1	0	76	100	100
1	0	77	100	100
1	0	78	100	100
1	0	79	100	100
1	0	80	100	100
1	0	81	100	100
1	0	82	100	100
1	0	83	100	100
1	0	84	100	100
1	0	85	100	100
1	0	86	100	100
1	0	87	100	100
1	0	88	100	100
1	0	89	100	100
1	0	90	100	100
1	0	91	100	100
1	0	92	100	100
1	0	93	100	100
1	0	94	100	100
1	0	95	100	100
1	0	96	100	100
1	0	97	100	100
1	0	98	100	100
1	0	99	100	100
1	0	100	100	100

All least-squares refinements were performed by a local version of the program *LALS* (Gantzel, Sparks & Trueblood, University of California). The scattering factors used for chlorine, carbon, nitrogen and oxygen were those given by Hanson, Herman, Lea & Skillman (1964), and for hydrogen that given by Stewart, Davidson & Simpson (1965).

Final coordinates and temperature factors are listed in Tables 2, 3 and 4. The atomic labels used of the isoalloxazinium ion and the intramolecular bond dis-

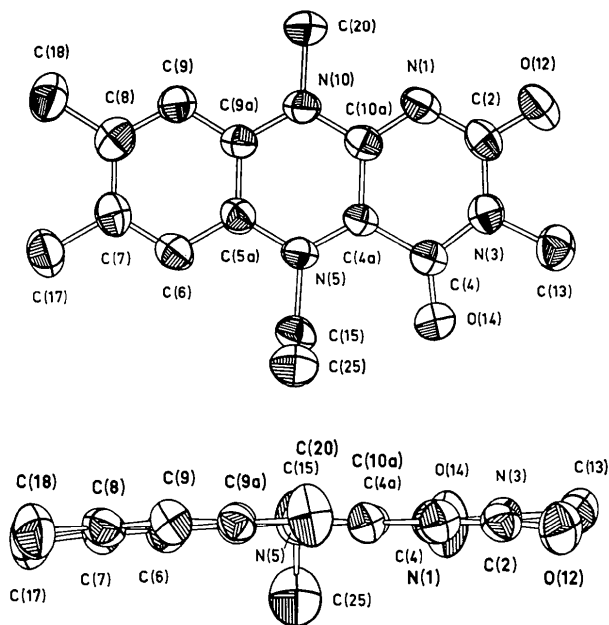


Fig. 4. Conformation of the 5-ethyl-3,7,8,10-tetramethyl-isoalloxazinium ion, as seen perpendicular to and parallel to the molecular plane. Only the non-hydrogens are included and they are represented by their thermal ellipsoids.

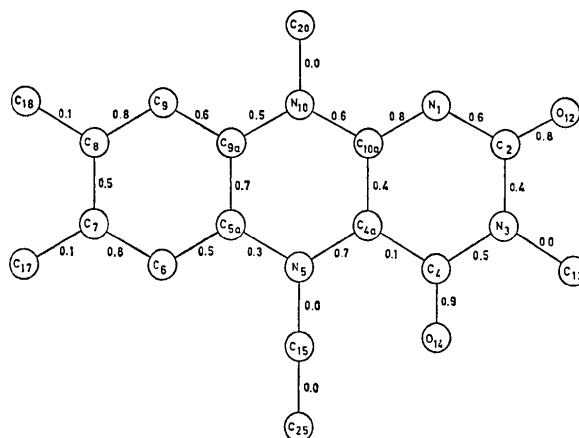


Fig. 5. Estimated π -bond orders in the 5-ethyl-3,7,8,10-tetramethyl-isoalloxazinium ion, obtained from linear bond order-bond distance correlation functions.

tances and angles are shown in Fig. 3. Table 5 comprises h , k , l , $|F|_{\text{obs}}$ and $|F|_{\text{calc}}$ for all the 1342 reflexions used in this study. The bond distances and angles

together with their estimated standard deviations are listed in Tables 6 and 7. No corrections for thermal vibration effects have been made.

Table 6. *Intramolecular bond distances*

The estimated standard deviations are given in parentheses

N(1)—C(2)	1.359 (6) Å	C(15)—H(15a)	1.00 (6) Å
C(2)—N(3)	1.393 (6)	C(15)—H(15b)	0.99 (6)
N(3)—C(4)	1.376 (6)		
C(4)—C(4a)	1.496 (6)	C(25)—H(25a)	1.06 (6)
C(4a)—N(5)	1.324 (5)	C(25)—H(25b)	0.92 (6)
N(5)—C(5a)	1.398 (6)	C(25)—H(25c)	1.10 (6)
C(5a)—C(6)	1.424 (6)		
C(6)—C(7)	1.367 (6)	C(6)—H(6)	0.89 (6)
C(7)—C(8)	1.427 (7)		
C(8)—C(9)	1.367 (7)	C(17)—H(17a)	0.85 (6)
C(9)—C(9a)	1.401 (6)	C(17)—H(17b)	0.86 (6)
C(9a)—C(5a)	1.399 (6)	C(17)—H(17c)	1.10 (5)
C(9a)—N(10)	1.372 (6)		
N(10)—C(10a)	1.355 (6)	C(18)—H(18a)	1.10 (6)
C(10a)—C(4a)	1.449 (6)	C(18)—H(18b)	0.81 (6)
C(10a)—N(1)	1.312 (6)	C(18)—H(18c)	1.01 (6)
C(2)—O(12)	1.223 (6)		
N(3)—C(13)	1.477 (6)	C(9)—H(9)	0.82 (6)
C(4)—O(14)	1.199 (6)		
N(5)—C(15)	1.529 (6)	C(20)—H(20a)	0.85 (6)
C(15)—C(25)	1.488 (9)	C(20)—H(20b)	0.98 (6)
C(7)—C(17)	1.500 (8)	C(20)—H(20c)	0.91 (6)
C(8)—C(18)	1.497 (7)		
N(10)—C(20)	1.482 (8)	Cl'—O'(1)	1.399 (4)
		Cl'—O'(2)	1.352 (6)
C(13)—H(13a)	0.86 (6)	Cl'—O'(3)	1.401 (7)
C(13)—H(13b)	0.87 (6)	Cl'—O'(4)	1.398 (6)
C(13)—H(13c)	1.03 (6)		

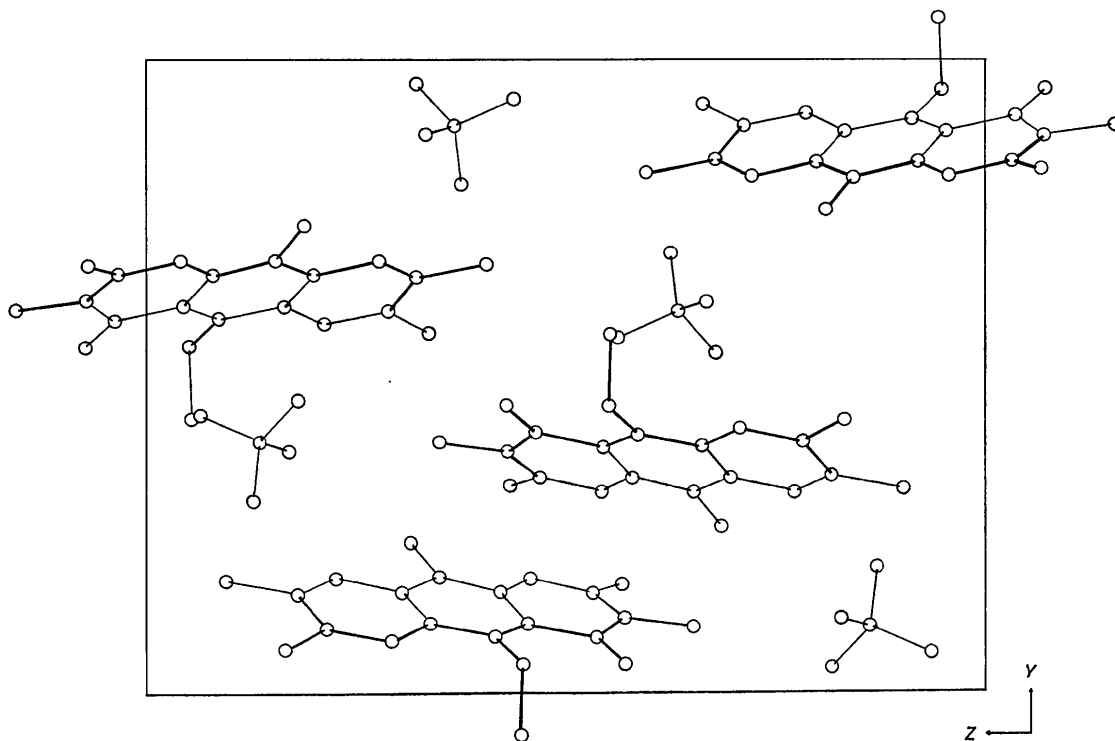


Fig. 6. Packing diagram, excluding hydrogen atoms, viewed along the a axis.

Table 7. *Intramolecular bond angles between non-hydrogen atoms*

The estimated standard deviations are given in parentheses.

C(10a)—N(1)—C(2)	120.0 (4) ^o
N(1)—C(2)—O(12)	122.1 (4)
N(1)—C(2)—N(3)	120.0 (4)
O(12)—C(2)—N(3)	117.9 (4)
C(2)—N(3)—C(4)	124.8 (4)
C(2)—N(3)—C(13)	118.1 (4)
C(13)—N(3)—C(4)	117.0 (4)
N(3)—C(4)—C(4a)	114.2 (4)
N(3)—C(4)—O(14)	121.6 (4)
O(14)—C(4)—C(4a)	124.3 (4)
C(4)—C(4a)—C(10a)	116.7 (4)
C(4)—C(4a)—N(5)	122.6 (4)
C(10a)—C(4a)—N(5)	120.5 (4)
C(4a)—N(5)—C(5a)	120.7 (4)
C(4a)—N(5)—C(15)	121.8 (4)
C(15)—N(5)—C(5a)	117.5 (4)
N(5)—C(5a)—C(9a)	119.4 (4)
N(5)—C(5a)—C(6)	121.1 (4)
C(9a)—C(5a)—C(6)	119.5 (5)
C(5a)—C(6)—C(7)	120.8 (4)
C(6)—C(7)—C(8)	119.5 (4)
C(6)—C(7)—C(17)	120.2 (5)
C(17)—C(7)—C(8)	120.3 (4)
C(7)—C(8)—C(9)	119.5 (4)
C(7)—C(8)—C(18)	119.8 (5)
C(18)—C(8)—C(9)	120.6 (5)
C(8)—C(9)—C(9a)	122.0 (5)
C(9)—C(9a)—C(5a)	118.7 (4)
C(9)—C(9a)—N(10)	122.1 (4)
C(5a)—C(9a)—N(10)	119.2 (4)
C(9a)—N(10)—C(10a)	122.0 (4)
C(9a)—N(10)—C(20)	121.0 (4)
C(20)—N(10)—C(10a)	117.0 (4)
N(10)—C(10a)—C(4a)	117.9 (4)
N(10)—C(10a)—N(1)	118.4 (4)
C(4a)—C(10a)—N(1)	123.7 (4)
N(5)—C(15)—C(25)	110.0 (5)
O'(1)—Cl'—O'(2)	111.3 (4)
O'(1)—Cl'—O'(3)	108.9 (4)
O'(1)—Cl'—O'(4)	107.8 (3)
O'(2)—Cl'—O'(3)	108.6 (4)
O'(2)—Cl'—O'(4)	110.3 (5)
O'(3)—Cl'—O'(4)	110.1 (4)

Discussion

The molecular conformation of the isoalloxazinium ion is shown in Fig. 4, where the atoms are represented by their thermal ellipsoids. The isoalloxazine ring system is almost planar, as seen in Table 8. The largest deviation from the calculated least-squares plane is 0.08 Å. The angle between the normal to the least-squares plane of the benzenoid ring and that to the pyrazinoid ring is 3.0°. The corresponding angle between the normals to the pyrazinoid and the pyrimidinoid planes is 1.3°. These deviations from planarity represent a slight twist of the molecule along its elongation, possibly caused by repulsive forces between the methylene group at C(15) and the keto oxygen atom O(14). It is noteworthy that the bond distance between N(5) and C(15) is 1.529 (6) Å (*cf.* Table 6), compared to the value of 1.47 Å usually found for exocyclic N—C distances (Sutton, 1958).

For an estimate of the π -bond scheme for the iso-

alloxazinium ion consistent with the observed intramolecular distances, bond orders have been evaluated (*cf.* Fig. 5) from the linear π -bond order—bond distance correlation functions suggested by several authors (*cf.* Roos & Skancke, 1967; Fischer-Hjalmars & Sundbom, 1968). Although these functions are intended for the evaluation of bond distances from semiempirical π -electron calculations and are valid only for planar neutral molecules, the obtained approximate bond order scheme more directly visualizes the actual distribution of the π -electrons than does the conventional comparison between the observed distances and various standard bond lengths. As seen in Fig. 5 the highest π -bond orders within the pyrazinoid and pyrimidinoid rings are obtained for the C(4a)—N(5) and the N(1)—C(10a) bonds, 0.7 and 0.8 respectively.

Both of the oxygen atoms, O(12) and O(14), attached to the pyrimidinoid ring are clearly of the keto type. The π electrons of the benzenoid ring are largely delocalized (bond orders ranging from 0.5 to 0.8). This is in accordance with the commonly accepted bond scheme for a 5-alkylisoalloxazinium ion given in Fig. 1. However, the π electrons of the heterocyclic rings are more delocalized than indicated in Fig. 1.

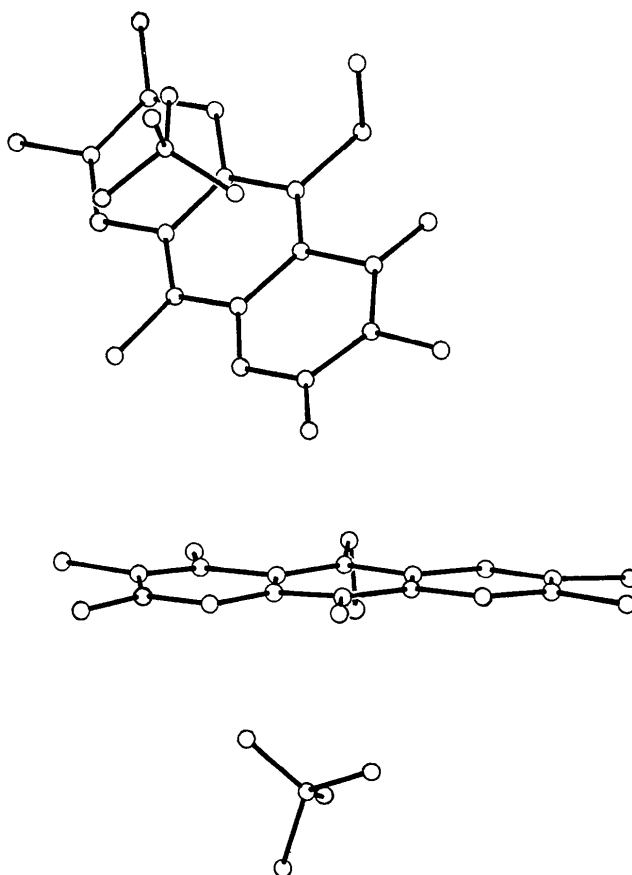


Fig. 7. Part of the crystal structure, showing the mutual geometrical arrangement of the molecules involved in the shortest (below 3 Å) intermolecular contacts.

Thus, the positive charge of the isoalloxazinium ion is probably not located in the N(5) region of the molecule but rather in the C(10a) region. This is also supported by the very short intermolecular contacts (2.8 to 3.0 Å) occurring in the crystal structure, between N(10), C(10a) and C(4a) and various oxygen atoms of adjacent ions.

Within the perchlorate ion, three of the Cl-O distances are 1.40 Å, while the fourth, Cl-O'(2), is 1.35 Å. The O-Cl-O bond angles range from 108 to 111° with an average of 109.6° in agreement with the tetrahedral value 109.5°. The bond lengths have not been corrected for thermal effects, and since the thermal vibrations of the perchlorate oxygens are large (*cf.* Table 3), the significance of the short Cl-O distance is doubtful. Disorder of the perchlorate ion, found in several other structural investigations of perchlorates (see *e.g.* Madaule-Aubry & Brown, 1968), is not indicated by the final electron density map.

Fig. 6 illustrates the molecular packing of the crystal structure, viewed along the *a* axis. The ETIP mol-

ecules lie with their molecular planes perpendicular to the directions [110] and [1 $\bar{1}$ 0]. The lack of suitable hydrogen donors precludes hydrogen bonding in the crystal structure. However, there are several short intermolecular contacts suggestive of electrostatic attractive forces and/or charge-transfer interactions (see Table 9).

Very short intermolecular contacts between the oxygens of the perchlorate group and carbon atoms C(4a) and C(10a), 2.87 and 2.99 Å respectively, indicate that these carbon atoms are more likely to have positive atomic charges than N(5), contrary to Fig. 1. The perchlorate ions involved in these short contacts lie above the C(4a)-C(10a) bond perpendicular to the molecular planes of the ETIP molecules (Fig. 7). Similar packings have been observed in the crystal structures of 1,3,10-trimethylisoalloxazinium iodide and 1,3,7,8,10-pentamethylisoalloxazinium iodide monohydrate (von Glehn, Kierkegaard, Norrestam, Rönquist & Werner, 1970; Norrestam, Torbjörnsson & Müller, 1972). In these structures the iodide ions are

Table 8. *Deviations of atoms from least-squares planes*

The planes are expressed as $AX+BY+CZ=D$, where *X*, *Y*, and *Z* are in Å units relative to the axis *a*, *b*, and *c*. The atoms indicated with asterisks were omitted from the calculations of least-squares planes.

Plane I	Atom	Deviation	Plane II	Atom	Deviation
$A = -0.399$	N(1)	0.043 Å	$A = -0.376$	N(1)	-0.004 Å
$B = 0.893$	C(2)	0.073	$B = 0.905$	C(2)	0.034
$C = -0.206$	N(3)	-0.036	$C = 0.201$	N(3)	-0.040
$D = 0.375$ Å	C(4)	-0.007	$D = 0.611$ Å	C(4)	0.018
	C(4a)	-0.005		C(4a)	0.010
	N(5)	-0.058		C(10a)	-0.017
	C(5a)	-0.017		*N(5)	-0.019
	C(6)	0.043		*N(10)	-0.068
	C(7)	0.076		*O(12)	0.138
	C(8)	0.002		*C(13)	-0.108
	C(9)	-0.048			
	C(9a)	-0.034			
	N(10)	-0.037			
	C(10a)	0.005			
	*O(12)	0.201			
	*C(13)	-0.111			
	*O(14)	0.016			
	*C(15)	-0.159			
	*C(25)	1.203			
	*C(17)	0.192			
	*C(18)	0.054			
	*C(20)	-0.087			

The r.m.s. deviation from the plane of the atoms without asterisks is 0.024 Å.

The r.m.s. deviation from the plane of the atoms without asterisks, is 0.042 Å.

Plane III	Atom	Deviation	Plane IV	Atom	Deviation
$A = -0.391$	N(10)	-0.018 Å	$A = -0.437$	C(9)	-0.007 Å
$B = 0.895$	C(10a)	0.014	$B = 0.878$	C(9a)	0.017
$C = 0.213$	C(4a)	0.010	$C = -0.196$	C(5a)	-0.011
$D = 0.365$ Å	N(5)	-0.028	$D = 0.061$ Å	C(6)	-0.007
	C(5a)	0.023		C(7)	0.017
	C(9a)	0.000		C(8)	-0.010
	*N(1)	0.037		*N(5)	-0.042
	*C(4)	-0.002		*N(10)	0.068
	*C(6)	0.099		*C(17)	0.075
	*C(9)	-0.004		*C(18)	0.031

The r.m.s. deviation from the plane of the atoms without asterisks is 0.018 Å.

The r.m.s. deviation from the plane of the atoms without asterisks is 0.012 Å.

Table 9. Intermolecular distances less than 3.5 Å between non-hydrogen atoms

Estimated standard deviations are given in parentheses
Code for symmetry related atoms

Superscript			
None	x,	y,	z
i	$\frac{3}{2}-x,$	1-y,	$\frac{1}{2}+z$
ii	-1+x,	y,	z
iii	1-x,	$\frac{1}{2}+y,$	$\frac{1}{2}-z$
iv	$\frac{1}{2}+x,$	$\frac{1}{2}-y,$	1-z
v	$\frac{5}{2}-x,$	1-y,	$\frac{1}{2}+z$
vi	1+x,	y	z

O'(1)—N(1)	3.282 (6) Å
O'(1)—C(2)	3.434 (7)
O'(1)—N(3)	3.402 (6)
O'(1)—C(4)	3.119 (7)
O'(1)—C(4a)	2.870 (7)
O'(1)—N(5)	3.474 (8)
O'(1)—C(10a)	2.991 (7)
O'(1)—C(18 ⁱⁱ)	3.304 (8)
O'(2 ⁱ)—C(13)	3.208 (8)
O'(3)—C(6 ⁱⁱⁱ)	3.381 (9)
O'(3)—N(10)	3.349 (8)
O'(3)—C(10a)	3.488 (8)
O'(4)—C(20 ⁱⁱⁱ)	3.418 (9)
N(1)—O(12 ^v)	3.397 (5)
O(14)—C(17 ^v)	3.207 (8)
C(4a)—C(2 ^v)	3.425 (6)
C(4a)—O(12 ^v)	2.946 (6)
N(5)—C(2 ^v)	3.474 (6)
N(5)—O(12 ^v)	3.202 (5)
C(15)—O(12 ^v)	3.380 (7)
C(5a)—O(12 ^v)	3.391 (6)
C(9a)—O(12 ^v)	3.238 (6)
N(10)—O(12 ^v)	2.920 (5)
C(10a)—O(12 ^v)	2.790 (6)

located between the planes of the isoalloxazinium ions, close to the C(4a)—C(10a) bonds, to form molecular stacks with alternating iodide and isoalloxazinium ions. The intermolecular separations, the geometry of the molecular packings and the dark colours of the crystals suggest an extent of axial charge-transfer interactions in these isoalloxazinium iodides.

In the present structure the C(4a) and C(10a) carbon atoms of one ETIP molecule are involved in very short intermolecular contacts with the oxygen atoms of a perchlorate group on one side of the molecular plane, as discussed above, and also to the keto oxygen atom, O(12), of another ETIP molecule (related by $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$) on the other side of the molecular plane, as shown in Fig. 7. The shortest contact distances from this oxygen are 2.79 Å to C(10a), 2.95 Å to C(4a) and 2.92 Å to N(10). The distance from the keto oxygen atom to the least-squares plane of the pyrazinoid ring is 2.68 Å and the angle between the C—O bond direction and the normal to this plane is 124.5°. The symmetry relation ($\frac{1}{2}+x, \frac{1}{2}-y, 1-z$), viz. a twofold screw axis along *a*, implies that the ETIP molecules involved in these short contacts form an infinite helical arrangement. The unit cell contains two such helical arrangements of ETIP molecules. The shortest contact distance, 3.21 Å, between ETIP molecules belonging to different helices occurs between the

keto oxygen atom O(14) of one molecule and the methyl carbon atom C(17) of another.

Thus, the packing of the molecules in the present crystal structure gives rise to several very short non-bonded C···O (and N···O) distances, 2.8 to 3.0 Å, significantly shorter than the sum of the van der Waals radii and of the same order as those found in crystal structures of strong charge-transfer complexes (*cf.* Klug, 1965). In the present study the crystalline specimen is blackish. The dark colour characteristic of organic crystalline charge-transfer complexes has often been attributed to charge-transfer interactions.

Löwdin (1968) has noted that the concept of charge transfer complexes as introduced by Mulliken refers to loosely bound complexes and that the concept, when applied to tightly bound compounds with a large degree of ionic character, as encountered here, needs refinement.

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