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The Crystal and Molecular Structures of 3-Ethoxy-14-(2-quinolyl)-3-azabenzo[*d*]tricyclo[5.3.1.$1^{2,8}$]dodecan-13-ylidenemorpholinium Iodide Monohydrate

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Three-dimensional X-ray diffraction data collected with an automated diffractometer were used to determine the crystal structures of two modifications of 3-ethoxy-14-(2-quinolyl)-3-azabenzo[*d*]tricyclo[5.3.1.$1^{2,8}$]-dodecan-13-ylidenemorpholinium iodide monohydrate. Crystals of modification I are triclinic, space group $P\bar{1}$, with a = 10·17 (2), b = 16·83 (4), c = 9·41 (2) Å, α = 95·1 (2), β = 105·6 (2) and γ = 74·3 (2)°. Those of modification II are orthorhombic, space group *Pbca*, with a = 17·51 (1), b = 28·85 (1) and c = 10·76 (1) Å. The structures were solved by a combination of minimum-function and heavy-atom methods. They were refined by least-squares calculations to R values of 0·059 and 0·064 for the observed reflexions of modifications I and II respectively. The large cation has five juts, which contact those of adjacent cations in different ways thus causing polymorphism and hollow structures. In the largest vacancy, two anions and two water molecules are trapped. The anions, the water molecules and the cations approach each other by the van der Waals distance. There are neither hydrogen bonds nor ionic short contacts which are often seen in many similar hydrates. The present work established the chemical structures which were not elucidated by chemical trials.

Introduction

In the course of studies on the reactions of aromatic *N*-oxides with enamines in the presence of an acylating agent, it has been established that the reactions are a nucleophilic substitution of the initially formed acyl adduct of the *N*-oxide and proceed by the addition–elimination mechanism (Hamana & Noda, 1965, 1966, 1967). It was expected that the reaction of *N*-ethoxyquinolinium iodide (*a*) with 1-morpholinocyclohexene (*b*) would give 2-(2-quinolyl)cyclohexanone (*A* or *B*) as shown in Fig. 1 (Hamana, Noda, Narimatsu & Ueda, 1975). The many chemical trials were unable to determine the chemical structure. By an X-ray diffraction method the structure was determined as 3-ethoxy-14-(2-quinolyl-3-azabenzo[*d*]tricyclo[5.3.1.$1^{2,8}$]dodecan-13-ylidenemorpholinium iodide, (*C*) in Fig. 1. In this paper the structure analysis for the two modifications of this compound are reported.

Experimental

Samples of the iodide and bromide compounds were prepared by the method reported by Hamana, Noda, Narimatsu & Ueda (1975). Recrystallization gave two crystal modifications for each compound depending on the solvents and seed crystals used as shown in Table 1.

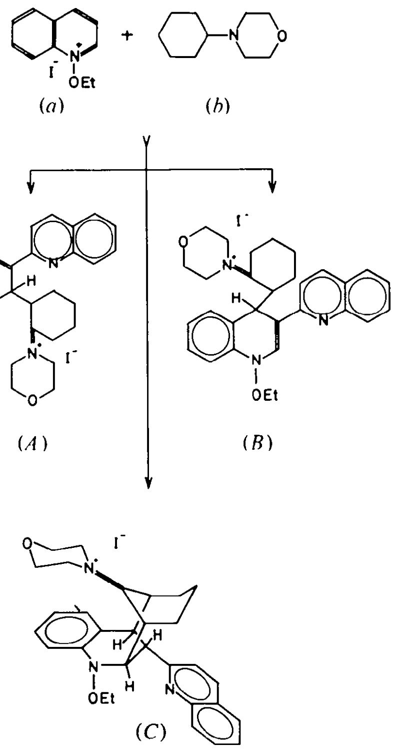

Fig. 1. A diagram for the reaction of *N*-ethoxyquinolinium iodide (*a*) with 1-morpholinocyclohexene (*b*).

Table 1. *Crystal data for the iodide and bromide compounds*

Iodide: $C_{30}H_{34}N_3O_2I.H_2O$

Modification I	Modification II
Triclinic	Orthorhombic
a = 10·17 (2) Å	a = 17·51 (1) Å
b = 16·83 (4)	b = 28·85 (1)
c = 9·41 (2)	c = 10·76 (1)
α = 95·1 (2)°	
β = 105·6 (2)	
γ = 74·3 (2)	
V = 1493 (5) Å^3	V = 5434 (5) Å^3
Space group $P1$	Space group $Pbca$
Z = 2	Z = 8
D_x = 1·432 g cm^{-3}	D_x = 1·499 g cm^{-3}
D_m = 1·448	D_m = 1·483
μ = 12·35 cm^{-1}	μ = 12·31 cm^{-1}
μr = 0·154 (Mo $K\alpha$)	μr = 0·215 (Mo $K\alpha$)
Solvent: dichloromethane	Solvent: acetone

Bromide: $C_{30}H_{34}N_3O_2Br.H_2O$

Modification I	Modification II
Monoclinic	Monoclinic
a = 15·34 Å	a = 22·25 (1) Å
b = 11·68	b = 10·68 (4)
c = 31·68	c = 34·95 (2)
β = 98·8°	β = 97·07 (4)°
V = 5608 Å^3	V = 8243 (3) Å^3
Space group $C2/c$ or Cc	Space group Pc
Z = 8	Z = 12
	D_x = 1·369 g cm^{-3}
	D_m = 1·383
	μ = 25·45 cm^{-1}
	μr = 0·752 (Cu $K\alpha$)
Solvent: dichloromethane	Solvent: acetone

Characteristic features of the IR spectra for these crystals indicated that the modification did not depend on the halogen atom but on the molecular conformation of the cation. Accordingly, it can be expected that there are two types of molecular conformation, notwithstanding that the space groups are different for these four cases. In the case of the iodide, crystals of modification I are yellow parallelepipeds and those of modification II are yellow prisms. The densities were measured by flotation in aqueous potassium iodide solution.

The cell constants and space groups for these compounds were preliminarily decided from Weissenberg photographs. The cell constants were ultimately established from a least-squares procedure using the values of the Bragg angles of 15 reflexions measured on a Syntex $P\bar{1}$ four-circle diffractometer with Mo $K\alpha$ radiation. In the case of modification II, the systematic absences of $0kl$ for k odd, $h0l$ for l odd and $hk0$ for h odd indicate that the space group is $Pbca$. Since the space group is centrosymmetric, the compound having modification II is racemic, which is usual for artificial compounds. For modification I, the space group $P\bar{1}$ was selected by analogy with modification II and was later confirmed in the course of the structure refinement. The crystal data are listed in Table 1.

Single crystals used for intensity measurements were ground to spheres by a method devised by one of us (Ueda, 1974). A spherical crystal of modification I of radius 0·125 mm and a sphere of modification II of radius 0·175 mm were used. Intensity data were collected on a Syntex $P\bar{1}$ automated diffractometer, with Mo $K\alpha$ radiation monochromated by a graphite crystal, using the θ–2θ scan technique to a limit of $2\theta = 45°$. The variable scan rate from 12·0 to 4·8° min^{-1} was adopted. Three reflexions were monitored after every measurement of 97 reflexions. For modification I, 3929 independent reflexions were collected. 1037 reflexions with intensity I less than $2{\cdot}33\sigma(I)$, where σ is the standard deviation, were considered unobserved. For modification II, 3795 independent reflexions were collected of which 1880 reflexions were treated as unobserved. This large percentage (50%) of unobserved reflections is reflected in the determination of the H atoms. Corrections were applied to the data for Lorentz and polarization effects as well as for the absorption effect and variation of the monitored intensities.

Structure determination

For both cases, the iodine atoms were easily located from the three-dimensional Patterson syntheses. The structure factor calculations and subsequent Fourier syntheses were carried out including only the iodine atoms. The results gave a discrepancy index R = 0·70 for modification I and R = 0·52 for modification II. Comparing the map of the minimum function and that of the Fourier syntheses, about 30 light atoms were selected for each case. At this stage, the molecular configuration of the complicated molecular structures could not be presumed. Therefore, the selection was carried out from coincidence of the peaks in both maps and from high peak values of the minimum function. The selection was essentially correct except for a small number of atoms. The refinement step, which contained three cycles of block-matrix least-squares refinement and a subsequent Fourier synthesis, was repeated twice for both modifications. At this step, all the non-hydrogen atoms, including a water molecule, appeared in the Fourier-synthesis maps. R for modification I was 0·26 and for modification II was 0·31 for the observed reflexions.

In the case of modification I, block-diagonal least-squares refinement of the atomic coordinates and isotropic thermal parameters was carried out for eight cycles and the R value was reduced to 0·14. Anisotropic thermal parameters were then introduced and ten additional cycles brought the R value down to 0·088. A difference Fourier synthesis calculated at this stage gave the peaks which corresponded to the expected H atoms and to another position of the water molecule. But the H atoms of the water molecule could not be located. An averaged structure of the two positions for the water molecule was also suggested by the high thermal parameters of the water molecule which were already introduced and by the low electron density at the new position. The last block-diagonal least-squares refinement was carried out for 20 cycles. In the course of the refinement, anisotropic thermal parameters for the new position were introduced and occupation parameters for the two positions were adjusted. The final *R* value was 0·059 for the observed reflexions and 0·081 for all the reflexions. Shifts of the positional and thermal parameters of the non-hydrogen atoms in the last cycle were less than one-tenth of their standard deviations. A final difference Fourier synthesis showed no significant features in the undulations, which varied from −0·3 to 0·3 e Å^{-3}, except in the vicinities of the iodine atom and the water molecule.

The refinement for modification II was carried out in almost the same manner as for modification I. However, some of the H atoms did not appear in the difference Fourier synthesis and their positions were postulated by analogy with the molecular conformation of modification I. The position of the water molecule was uniquely decided. The final *R* value was 0·064 for the observed reflexions and 0·133 for all the reflexions. The final atomic coordinates are given in Tables 2 and 3.*

The weighting scheme of the block-diagonal least-squares method was equal weight for the observed and zero weight for the unobserved reflexions. The atomic scattering factors were taken from *International Tables*

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32488 (41 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Final positional parameters for modification* I

Positional parameters are expressed as fractional coordinates and for I, C, N and O are × 10^4, for H × 10^3. Standard deviations are given in parentheses, here and in the following tables, referring to the last places of the preceding numbers.

	x	*y*	*z*		*x*	*y*	*z*
I	1896·4 (8)	906·7 (5)	3449·5 (9)	O(3)*	3479 (13)	1703 (6)	6998 (11)
C(1)	8472 (8)	4095 (5)	8172 (8)	O(4)*	4166 (18)	989 (11)	7906 (23)
C(2)	9344 (9)	4458 (5)	7614 (9)	H(C2)	999 (9)	412 (5)	701 (10)
C(3)	9288 (9)	5282 (6)	7906 (10)	H(C3)	990 (9)	554 (5)	751 (10)
C(4)	8356 (9)	5768 (5)	8736 (9)	H(C5)	872 (10)	693 (6)	863 (10)
C(5)	8203 (10)	6635 (5)	9059 (11)	H(C6)	720 (10)	765 (6)	1015 (10)
C(6)	7302 (11)	7046 (6)	9918 (11)	H(C7)	592 (10)	695 (6)	1116 (11)
C(7)	6529 (11)	6637 (6)	10486 (11)	H(C8)	604 (9)	550 (5)	1059 (10)
C(8)	6628 (10)	5801 (6)	10168 (10)	H(C10)	900 (9)	293 (5)	894 (9)
C(9)	7551 (9)	5346 (5)	9290 (9)	H(C11)	1029 (9)	276 (5)	703 (10)
C(10)	8494 (8)	3174 (5)	7909 (9)	H(C13)	1025 (9)	283 (5)	438 (10)
C(11)	9268 (8)	2713 (5)	6749 (9)	H(C14)	888 (10)	328 (6)	185 (10)
C(12)	8468 (8)	3080 (5)	5227 (9)	H(C15)	640 (10)	382 (6)	133 (10)
C(13)	9159 (9)	3044 (5)	4098 (10)	H(C16)	515 (10)	391 (6)	321 (10)
C(14)	8407 (10)	3317 (6)	2669 (10)	H(C18)	643 (9)	330 (5)	823 (9)
C(15)	6947 (11)	3633 (6)	2357 (10)	H(C19)	993 (8)	148 (5)	592 (9)
C(16)	6231 (9)	3683 (5)	3448 (9)	H1(C20)	1091 (11)	151 (6)	870 (11)
C(17)	6975 (8)	3410 (5)	4880 (9)	H2(C20)	1044 (11)	73 (6)	789 (12)
C(18)	6976 (8)	3053 (5)	7433 (8)	H1(C21)	953 (12)	165 (7)	1012 (12)
C(19)	9346 (8)	1757 (5)	6682 (9)	H2(C21)	939 (12)	73 (7)	951 (12)
C(20)	10063 (10)	1277 (6)	8158 (11)	H1(C22)	736 (10)	202 (6)	961 (11)
C(21)	9165 (13)	1284 (8)	9162 (12)	H2(C22)	718 (11)	118 (6)	871 (11)
C(22)	7633 (11)	1640 (6)	8763 (10)	H(C23)	595 (9)	210 (5)	687 (10)
C(23)	6964 (8)	2116 (5)	7262 (9)	H1(C25)	577 (9)	66 (5)	447 (9)
C(24)	7820 (8)	1691 (5)	6196 (8)	H2(C25)	522 (9)	161 (6)	514 (10)
C(25)	5808 (9)	1255 (6)	4465 (10)	H1(C26)	510 (10)	221 (6)	288 (10)
C(26)	5211 (10)	1578 (6)	2879 (10)	H2(C26)	416 (10)	151 (6)	248 (11)
C(27)	7477 (11)	1175 (6)	2409 (10)	H1(C27)	800 (10)	85 (6)	166 (10)
C(28)	8150 (10)	827 (5)	3955 (10)	H2(C27)	750 (9)	179 (5)	241 (10)
C(29)	3815 (10)	4170 (7)	5744 (12)	H1(C28)	917 (10)	87 (6)	430 (10)
C(30)	2444 (11)	3947 (9)	5558 (13)	H2(C28)	811 (10)	23 (6)	397 (10)
N(1)	7616 (7)	4514 (4)	8992 (7)	H1(C29)	421 (10)	441 (6)	682 (10)
N(2)	6274 (6)	3515 (4)	6044 (7)	H2(C29)	377 (11)	460 (6)	499 (11)
N(3)	7319 (7)	1299 (4)	5008 (7)	H1(C30)	215 (11)	370 (6)	449 (11)
O(1)	6024 (8)	1120 (4)	1902 (7)	H2(C30)	171 (11)	447 (6)	571 (11)
O(2)	4854 (6)	3410 (4)	5498 (6)	H3(C30)	248 (10)	356 (6)	627 (10)

* The occupancy of the water molecule O(3) is 0·6 and that of O(4) is 0·4.

Table 3. *Final positional parameters for modification* II

Values for I, C, N and O are × 10^4, those for H are × 10^3.

	x	*y*	*z*		*x*	*y*	*z*
I	5736·3 (7)	2393·8 (4)	3025·8 (11)	O(3)	4407 (8)	2323 (5)	383 (16)
C(1)	1088 (7)	1189 (5)	4142 (11)	H(C2)	61 (7)	180 (3)	517 (11)
C(2)	528 (7)	1441 (4)	4828 (12)	H(C3)	−56 (7)	143 (4)	542 (12)
C(3)	−178 (8)	1236 (6)	4953 (12)	H(C5)	−146 (8)	74 (5)	520 (13)
C(4)	−341 (7)	807 (5)	4467 (12)	H(C6)	−168 (8)	−0 (5)	436 (13)
C(5)	−1030 (7)	570 (6)	4645 (14)	H(C7)	−68 (8)	−40 (4)	309 (13)
C(6)	−1146 (8)	154 (6)	4159 (14)	H(C8)	55 (7)	0 (4)	275 (12)
C(7)	−578 (8)	−66 (5)	3452 (14)	H(C10)	176 (7)	174 (4)	339 (12)
C(8)	107 (8)	158 (5)	3266 (14)	H(C11)	223 (7)	95 (4)	265 (12)
C(9)	244 (7)	586 (5)	3791 (11)	H(C13)	301 (7)	27 (4)	293 (13)
C(10)	1864 (7)	1414 (4)	3980 (11)	H(C14)	344 (7)	−34 (4)	438 (12)
C(11)	2466 (7)	1094 (4)	3405 (10)	H(C15)	339 (7)	−20 (4)	658 (11)
C(12)	2687 (6)	709 (4)	4291 (11)	H(C16)	289 (7)	52 (4)	737 (13)
C(13)	2970 (7)	296 (4)	3869 (12)	H(C18)	186 (7)	185 (4)	557 (12)
C(14)	3226 (8)	−43 (5)	4698 (14)	H(C19)	353 (7)	116 (4)	261 (12)
C(15)	3190 (7)	49 (5)	5965 (14)	H1(C20)	248 (7)	183 (4)	194 (12)
C(16)	2906 (7)	457 (4)	6399 (12)	H2(C20)	339 (7)	181 (4)	149 (12)
C(17)	2645 (6)	792 (4)	5578 (11)	H1(C21)	294 (7)	249 (5)	232 (14)
C(18)	2211 (7)	1598 (4)	5171 (11)	H2(C21)	375 (8)	226 (4)	284 (14)
C(19)	3194 (7)	1382 (4)	3040 (12)	H1(C22)	230 (7)	231 (4)	409 (12)
C(20)	3043 (8)	1811 (5)	2215 (12)	H2(C22)	306 (7)	259 (5)	457 (13)
C(21)	3168 (9)	2257 (5)	2852 (14)	H(C23)	321 (7)	191 (4)	580 (12)
C(22)	2853 (8)	2278 (5)	4162 (15)	H1(C25)	505 (7)	182 (4)	563 (12)
C(23)	2984 (7)	1846 (4)	4949 (11)	H2(C25)	417 (7)	181 (4)	634 (12)
C(24)	3519 (6)	1551 (4)	4269 (11)	H1(C26)	435 (7)	96 (4)	673 (11)
C(25)	4547 (8)	1606 (5)	5846 (13)	H2(C26)	505 (8)	127 (4)	734 (13)
C(26)	4799 (9)	1173 (6)	6557 (13)	H1(C27)	539 (8)	56 (5)	427 (14)
C(27)	5003 (9)	754 (6)	4715 (16)	H2(C27)	454 (8)	54 (5)	489 (13)
C(28)	4779 (8)	1176 (5)	3952 (14)	H1(C28)	457 (7)	105 (4)	317 (12)
C(29)	1891 (9)	1362 (5)	8003 (14)	H2(C28)	524 (7)	139 (5)	386 (12)
C(30)	2160 (10)	1453 (6)	9293 (13)	H1(C29)	157 (8)	167 (5)	778 (14)
N(1)	962 (6)	785 (3)	3633 (9)	H2(C29)	163 (8)	105 (5)	796 (14)
N(2)	2273 (5)	1194 (3)	6000 (8)	H1(C30)	249 (8)	119 (5)	947 (12)
N(3)	4199 (6)	1456 (3)	4630 (9)	H2(C30)	175 (9)	158 (5)	982 (15)
O(1)	5327 (6)	908 (4)	5853 (10)	H3(C30)	248 (7)	180 (4)	932 (11)
O(2)	2532 (5)	1330 (3)	7195 (7)				

for X-ray Crystallography (1974). All the calculations were performed on the FACOM 230-75 computer in the Computer Center of Kyushu University with the Universal Crystallographic Computation Program System *UNICS* II (Sakurai, Iwasaki, Watanabe, Kobayashi, Bando & Nakamichi, 1974).

Discussion

Molecular structures

Figs. 2 and 3, respectively, show the crystal structures of modifications I and II projected along the *c* axis with their common numbering scheme. The bond lengths and bond angles of the two modifications are compared in Tables 4 and 5 respectively.

The bond lengths of the quinoline ring almost agree with those of 1-ethyl-2-methylquinolinium iodide (Sakanoue, Kai, Yasuoka, Kasai & Kakudo, 1970). Also those of C(1)–N(1) and C(9)–N(1) agree with the value given in *International Tables for X-ray Crystallography* (1962), within the experimental error. The quinoline ring is planar and seems to have partial double-bond character. In the tetrahydroquinoline ring C(10), C(11), C(18) and N(2) are singly bonded, have a zigzag conformation and deviate from the plane of the benzene ring. The largest deviation occurs at C(10). The bicyclo[3.3.1]nonane moiety consists of twin cyclohexanes in the chair and boat conformations. The bond lengths show considerable deviations from the usual value, 1·54 Å. The unusually long bond distances of C(11)–C(19) and C(18)–C(23) are caused by large steric hindrances between C(10) and C(20), C(22), and also between C(12) and C(24). The former hindrance also adds to the above-mentioned deviation of C(10). The morpholine ring has a chair conformation. The bond lengths and angles can be compared with those of 1,1,2-trimorpholinoethene (Albinati & Zocchi, 1974) and 1-morpholinomethyl-3-methyl-3-phenylpyrrolidine-2,5-dione (Argay & Seres, 1973) and 2*H*-thiopyran *p*-bromobenzyl ester (Smith, Kalish &

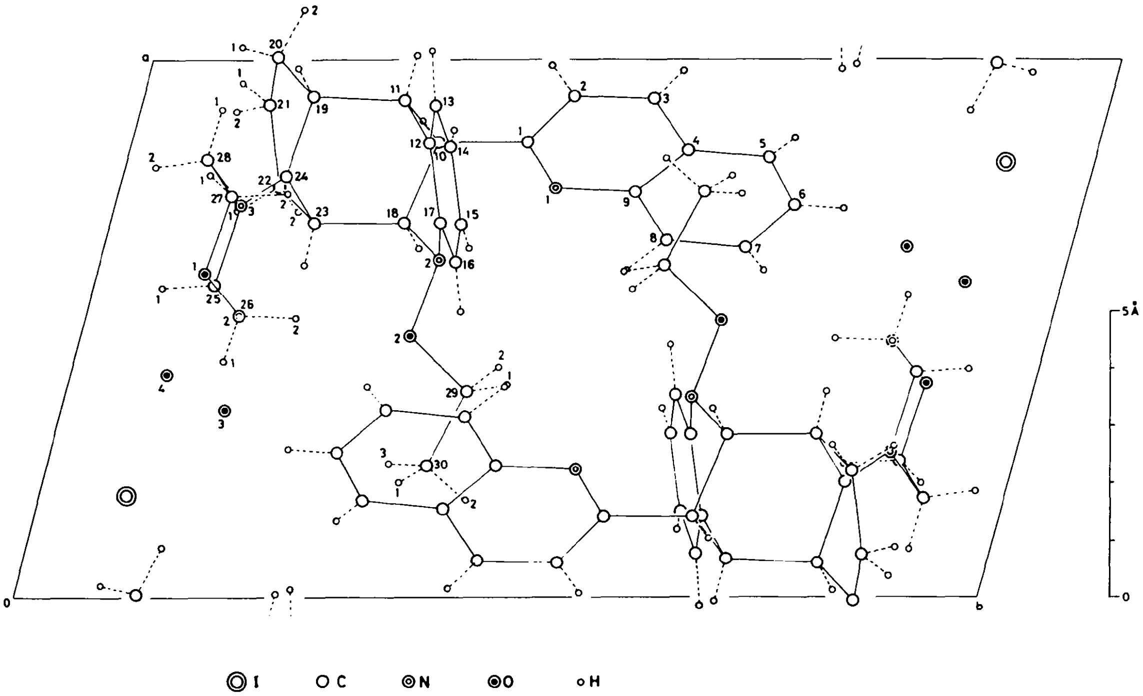


Fig. 2. The crystal structure of modification I projected along **c**.

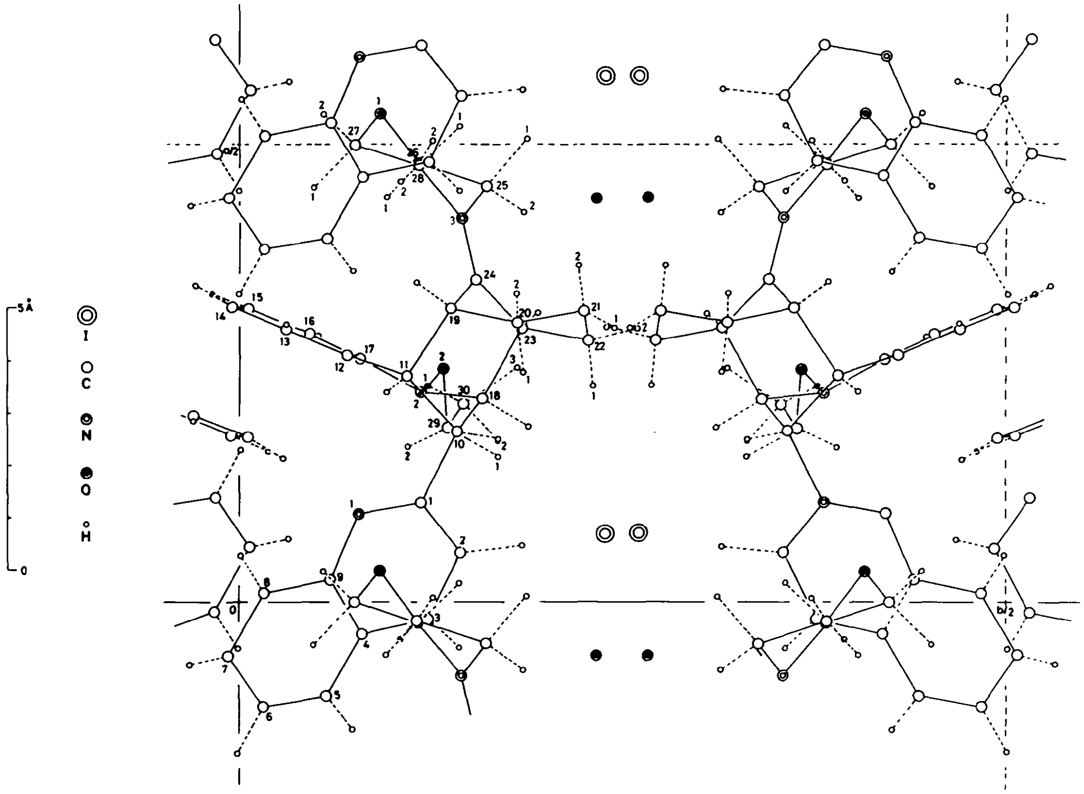


Fig. 3. The crystal structure of modification II projected along **c**.

Table 4. *Intramolecular distances*

Modification	I	II
C(1) -C(2)	1.427(12)Å	1.426(18)
C(1) -C(10)	1.543(12)	1.517(18)
C(1) -N(1)	1.336(11)	1.306(16)
C(2) -C(3)	1.378(13)	1.376(20)
C(2) -H(C2)	1.01(9)	1.10(12)
C(3) -C(4)	1.429(13)	1.374(21)
C(3) -H(C3)	1.00(9)	1.01(13)
C(4) -C(5)	1.438(13)	1.399(21)
C(4) -C(9)	1.435(12)	1.407(19)
C(5) -C(6)	1.388(15)	1.325(23)
C(5) -H(C5)	0.99(10)	1.08(15)
C(6) -C(7)	1.400(15)	1.404(22)
C(6) -H(C6)	1.01(10)	1.06(14)
C(7) -C(8)	1.394(15)	1.376(22)
C(7) -H(C7)	1.02(11)	1.05(14)
C(8) -C(9)	1.437(13)	1.378(20)
C(8) -H(C8)	1.06(10)	1.05(13)
C(9) -N(1)	1.390(11)	1.393(16)
C(10)-C(11)	1.547(12)	1.530(17)
C(10)-C(18)	1.552(12)	1.515(17)
C(10)-H(C10)	1.03(9)	1.15(13)
C(11)-C(12)	1.534(12)	1.514(17)
C(11)-C(19)	1.586(12)	1.571(17)
C(11)-H(C11)	1.02(10)	1.01(13)
C(12)-C(13)	1.412(13)	1.369(18)
C(12)-C(17)	1.424(12)	1.406(17)
C(13)-C(14)	1.404(14)	1.397(20)
C(13)-H(C13)	1.04(9)	1.01(14)
C(14)-C(15)	1.392(15)	1.390(22)
C(14)-H(C14)	1.01(10)	1.00(13)
C(15)-C(16)	1.395(14)	1.360(20)
C(15)-H(15)	1.01(10)	1.04(12)
C(16)-C(17)	1.405(12)	1.387(18)
C(16)-H(C16)	1.03(10)	1.06(14)
C(17)-N(2)	1.434(10)	1.407(15)
C(18)-C(23)	1.573(12)	1.548(17)
C(18)-N(2)	1.484(11)	1.472(15)
C(18)-H(C18)	1.04(9)	1.05(13)
C(19)-C(20)	1.565(13)Å	1.545(19)
C(19)-C(24)	1.528(12)	1.519(17)
C(19)-H(C19)	1.05(9)	0.98(13)
C(20)-C(21)	1.477(17)	1.474(21)
C(20)-H1(C20)	1.04(11)	1.03(13)
C(20)-H2(C20)	0.94(11)	1.00(13)
C(21)-C(22)	1.465(18)	1.515(22)
C(21)-H1(C21)	1.09(12)	0.96(15)
C(21)-H2(C21)	0.97(12)	1.01(15)
C(22)-C(23)	1.578(14)	1.523(20)
C(22)-H1(C22)	1.03(11)	0.98(13)
C(22)-H2(C22)	1.00(11)	1.07(14)
C(23)-C(24)	1.510(12)	1.463(17)
C(23)-H(C23)	1.00(9)	1.01(13)
C(24)-N(3)	1.301(11)	1.283(16)
C(25)-C(26)	1.540(14)	1.529(23)
C(25)-N(3)	1.503(12)	1.507(18)
C(25)-H1(C25)	1.02(9)	1.11(13)
C(25)-H2(C25)	1.03(10)	1.04(13)
C(26)-O(1)	1.435(13)	1.420(21)
C(26)-H1(C26)	1.04(10)	1.02(13)
C(26)-H2(C26)	1.07(11)	1.00(14)
C(27)-C(28)	1.527(15)	1.519(23)
C(27)-O(1)	1.452(14)	1.421(20)
C(27)-H1(C27)	1.02(10)	1.00(15)
C(27)-H2(C27)	1.04(9)	1.03(14)
C(28)-N(3)	1.508(12)	1.489(18)
C(28)-H1(C28)	1.02(10)	0.98(13)
C(28)-H2(C28)	1.02(10)	1.03(13)
C(29)-C(30)	1.502(19)	1.489(23)
C(29)-O(2)	1.467(13)	1.423(18)
C(29)-H1(C29)	1.07(10)	1.08(15)
C(29)-H2(C29)	1.05(11)	1.01(15)
C(30)-H1(C30)	1.05(11)	0.99(14)
C(30)-H2(C30)	1.02(11)	1.00(17)
C(30)-H3(C30)	0.96(10)	1.15(13)
N(2)-O(2)	1.452(9)	1.419(13)

Table 5. *Bond angles for modifications* I *and* II

Modification	I	II
C(2) -C(1) -C(10)	121.9(7)°	117.2(11)°
C(2) -C(1) -N(1)	123.0(8)	123.8(12)
C(10)-C(1) -N(1)	115.1(7)	119.0(11)
C(1) -C(2) -C(3)	119.0(8)	116.6(12)
C(1) -C(2) -H(C2)	121.(5)	124.(6)
C(3) -C(2) -H(C2)	120.(5)	119.(6)
C(2) -C(3) -C(4)	120.5(8)	122.4(14)
C(2) -C(3) -H(C3)	119.(5)	115.(8)
C(4) -C(3) -H(C3)	120.(5)	123.(8)
C(3) -C(4) -C(5)	124.3(8)	124.5(14)
C(3) -C(4) -C(9)	116.6(8)	117.0(13)
C(5) -C(4) -C(9)	119.1(8)	118.4(13)
C(4) -C(5) -C(6)	119.8(9)	121.4(15)
C(4) -C(5) -H(C5)	119.(6)	117.(8)
C(6) -C(5) -H(C5)	121.(6)	122.(8)
C(5) -C(6) -C(7)	121.6(10)	120.9(15)
C(5) -C(6) -H(C6)	119.(6)	116.(8)
C(7) -C(6) -H(C6)	119.(6)	123.(8)
C(6) -C(7) -C(8)	120.2(10)	119.0(14)
C(6) -C(7) -H(C7)	120.(6)	119.(8)
C(8) -C(7) -H(C7)	120.(6)	122.(8)
C(7) -C(8) -C(9)	120.4(9)	120.8(14)
C(7) -C(8) -H(C8)	120.(5)	121.(7)
C(9) -C(8) -H(C8)	120.(5)	118.(7)
C(4) -C(9) -C(8)	118.9(8)	119.4(13)
C(4) -C(9) -N(1)	122.4(8)	122.2(12)
C(8) -C(9) -N(1)	118.7(8)	118.5(12)
C(1) -C(10)-C(11)	116.0(7)	113.9(10)
C(1) -C(10)-C(18)	111.5(7)	114.4(10)
C(1) -C(10)-H(C10)	103.(5)	106.(6)
C(11)-C(10)-C(18)	106.8(7)	106.2(10)
C(11)-C(10)-H(C10)	111.(5)	112.(6)
C(18)-C(10)-H(C10)	109.(5)	104.(6)
C(10)-C(11)-C(12)	109.0(7)	111.3(10)
C(10)-C(11)-C(19)	111.4(7)	109.9(10)
C(10)-C(11)-H(C11)	110.(5)	107.(7)
C(12)-C(11)-C(19)	108.8(7)	109.8(10)
C(12)-C(11)-H(C11)	111.(5)	108.(7)
C(19)-C(11)-H(C11)	107.(5)	111.(7)
C(11)-C(12)-C(13)	121.5(8)	121.5(11)
C(11)-C(12)-C(17)	120.3(7)	118.9(10)
C(13)-C(12)-C(17)	118.0(8)	119.5(11)
C(12)-C(13)-C(14)	121.5(9)	120.9(13)
C(12)-C(13)-H(C13)	117.(5)	115.0(8)
C(14)-C(13)-H(C13)	121.(5)	124.(8)
C(13)-C(14)-C(15)	119.4(10)	118.6(14)
C(13)-C(14)-H(C15)	122.(6)	120.(7)
C(15)-C(14)-H(C15)	118.(6)	121.(7)
C(14)-C(15)-C(16)	120.7(10)	121.3(14)
C(14)-C(15)-H(C15)	120.(6)	119.(7)
C(16)-C(15)-H(C15)	120.(6)	120.(7)
C(15)-C(16)-C(17)	120.3(9)	120.2(12)
C(15)-C(16)-H(C16)	120.(6)	120.(7)
C(17)-C(16)-H(C16)	119.(6)	120.(7)
C(12)-C(17)-C(16)	120.1(8)	119.5(11)
C(12)-C(17)-N(2)	118.6(7)	118.8(11)
C(16)-C(17)-N(2)	121.1(7)	121.4(11)
C(10)-C(18)-C(23)	112.7(7)	112.5(10)
C(10)-C(18)-N(2)	105.6(6)	105.2(9)
C(10)-C(18)-H(C18)	111.(5)	111.(7)
C(23)-C(18)-N(2)	112.9(7)	113.3(10)
C(23)-C(18)-H(C18)	105.(5)	105.(7)
N(2) -C(18)-H(C18)	109.(5)	110.(7)
C(11)-C(19)-C(20)	116.6(7)	115.3(10)
C(11)-C(19)-C(24)	106.3(7)	104.8(10)
C(11)-C(19)-H(C19)	107.(5)	105.(8)
C(20)-C(19)-C(24)	107.3(7)	107.9(10)
C(20)-C(19)-H(C19)	107.(5)	110.(8)
C(24)-C(19)-H(C19)	113.(5)	113.(8)
C(19) -C(20)-C(21)	117.4(9)°	114.0(12)°
C(19) -C(20)-H1(C20)	107.(6)	112.(7)
C(19) -C(20)-H2(C20)	106.(7)	110.(8)
C(21) -C(20)-H1(C20)	110.(6)	103.(7)
C(21) -C(20)-H2(C20)	109.(7)	106.(8)
H1(C20)-C(20)-H2(C20)	107.(9)	111.(10)
C(20) -C(21)-C(22)	122.9(11)	114.4(13)
C(20) -C(21)-H1(C21)	106.(6)	106.(9)
C(20) -C(21)-H2(C21)	107.(7)	99.(9)
C(22) -C(21)-H1(C21)	103.(6)	112.(9)
C(22) -C(21)-H2(C21)	110.(7)	112.(9)
H1(C21)-C(21)-H2(C21)	106.(10)	113.(12)
C(21) -C(22)-C(23)	117.4(10)	115.5(13)
C(21) -C(22)-H1(C22)	109.(6)	107.(8)
C(21) -C(22)-H2(C22)	107.(6)	107.(8)
C(23) -C(22)-H1(C22)	109.(6)	106.(7)
C(23) -C(22)-H2(C22)	108.(6)	115.(8)
H1(C22)-C(22)-H2(C22)	106.(9)	107.(11)
C(18) -C(23)-C(22)	112.7(7)	109.4(11)
C(18) -C(23)-C(24)	109.5(7)	111.6(10)
C(18) -C(23)-H(C23)	106.(5)	107.(7)
C(22) -C(23)-C(24)	107.1(7)	107.1(11)
C(22) -C(23)-H(C23)	110.(5)	114.(7)
C(24) -C(23)-H(C23)	111.(5)	108.(7)
C(19) -C(24)-C(23)	112.6(7)	112.5(10)
C(19) -C(24)-N(3)	123.7(7)	122.9(11)
C(23) -C(24)-N(3)	123.7(7)	124.6(11)
C(26) -C(25)-N(3)	109.1(8)	108.5(12)
C(26) -C(25)-H1(C25)	109.(5)	110.(7)
C(26) -C(25)-H2(C25)	110.(5)	113.(7)
N(3) -C(25)-H1(C25)	109.(5)	107.(7)
N(3) -C(25)-H2(C25)	110.(5)	111.(7)
H1(C25)-C(25)-H2(C25)	109.(8)	108.(10)
C(25) -C(26)-O(1)	111.9(8)	111.2(13)
C(25) -C(26)-H1(C26)	110.(6)	112.(7)
C(25) -C(26)-H2(C26)	108.(6)	108.(8)
O(1) -C(26)-H1(C26)	114.(6)	105.(7)
O(1) -C(26)-H2(C26)	108.(6)	108.(8)
H1(C26)-C(26)-H2(C26)	105.(8)	112.(11)
C(28) -C(27)-O(1)	110.6(9)	108.6(13)
C(28) -C(27)-H1(C27)	111.(6)	112.(8)
C(28) -C(27)-H2(C27)	110.(5)	112.(8)
O(1) -C(27)-H1(C27)	107.(6)	109.(8)
O(1) -C(27)-H2(C27)	109.(5)	110.(8)
H1(C27)-C(27)-H2(C27)	108.(8)	106.(11)
C(27) -C(28)-N(3)	109.7(8)	110.2(12)
C(27) -C(28)-H1(C28)	110.(6)	105.(8)
C(27) -C(28)-H2(C28)	110.(6)	110.(8)
N(3) -C(28)-H1(C28)	110.(6)	111.(8)
N(3) -C(28)-H2(C28)	106.(6)	105.(8)
H1(C28)-C(28)-H2(C28)	110.(8)	115.(11)
C(30) -C(29)-O(2)	106.8(9)	109.3(13)
C(30) -C(29)-H1(C29)	114.(6)	103.(8)
C(30) -C(29)-H2(C29)	114.(6)	110.(9)
O(2) -C(29)-H1(C29)	108.(5)	109.(8)
O(2) -C(29)-H2(C29)	107.(6)	106.(9)
H1(C29)-C(29)-H2(C29)	107.(8)	119.(12)
C(29) -C(30)-H1(C30)	109.(6)	103.(8)
C(29) -C(30)-H2(C30)	107.(6)	111.(10)
C(29) -C(30)-H3(C30)	113.(6)	109.(6)
H1(C30)-C(30)-H2(C30)	111.(9)	129.(13)
H1(C30)-C(30)-H3(C30)	110.(9)	113.(10)
H2(C30)-C(30)-H3(C30)	106.(9)	91.(11)
C(1) -N(1) -C(9)	118.4(7)	118.0(10)
C(17) -N(2) -C(18)	120.1(6)	119.5(10)
C(17) -N(2) -O(2)	111.1(6)	111.9(9)
C(18) -N(2) -O(2)	109.1(6)	110.7(9)
C(24) -N(3) -C(25)	125.0(7)	125.3(11)
C(24) -N(3) -C(28)	125.6(7)	126.9(11)
C(25) -N(3) -C(28)	109.4(7)	107.8(10)
C(26) -O(1) -C(27)	110.3(8)	111.6(12)
C(29) O(2) -N(2)	110.2(6)	108.6(9)

Table 6. *Superposition of the anions of modifications* I *and* II

	Distance	W*	Moiety
C(1)	0·081 Å	1	Quinoline
C(2)	2·391	0	
C(3)	2·251	0	
C(4)	0·255	0	
C(5)	0·526	0	
C(6)	2·969	0	
C(7)	5·294	0	
C(8)	5·082	0	
C(9)	2·556	0	
N(1)	2·442	0	
C(10)	0·026	1	Tetrahydroquinoline
C(11)	0·046	1	
C(12)	0·028	1	
C(13)	0·042	1	
C(14)	0·044	1	
C(15)	0·053	1	
C(16)	0·028	1	
C(17)	0·013	1	
N(2)	0·066	1	
C(18)	0·038	1	
C(19)	0·093	1	Cyclohexane
C(20)	0·186	1	
C(21)	0·417	1	
C(22)	0·105	1	
C(23)	0·062	1	
C(24)	0·077	1	
N(3)	0·137	1	Morpholine
C(25)	0·138	0	
C(26)	0·162	0	
O(1)	0·234	0	
C(27)	0·197	0	
C(28)	0·188	0	
O(2)	0·226	0	Ethoxy
C(29)	0·351	0	
C(30)	0·752	0	

* Weights used for the calculation of the best-fit superposition.

Smutny, 1972). The N(3)–C(25) and N(3)–C(28) bond lengths are considerably longer than the other results. The N(3)–C(24) distances, 1·299 and 1·283 Å, of the two modifications are shorter than the value of 1·335 Å found by Smith, Kalish & Smutny (1972). It might be concluded that electrons are more concentrated between N(3) and C(24) here than in the other case and that the N(3) atoms of the two modifications are ionized.

The molecules of the two modifications may be compared by superposition as rigid molecules to give the best fit. The deviations between the equivalent atoms and the weights used for the calculation of the superposition are listed in Table 6. Because of the large steric hindrance between the tetrahydroquinoline and boat cyclohexane moieties the inner parts of the molecules are firmly constructed and the deviations between the equivalent atoms are fairly small. The quinoline ring may be rotated about the C(1)–C(10) bond. The tilting angle between the two rings is about 120°. This fact is also supported by the IR spectra.

Table 7. *Intermolecular distances shorter than the sum of the van der Waals radii plus* 0·2 Å

Modification I

Reference & Target atoms		Distance	Translation	Symmetry *	D**
I	C(13)	4.018(10)Å	-1,0,0	1	0.168Å
	C(28)	4.002(11)	-1,0,0	1	0.152
	H(C13)	3.37(8)	-1,0,0	1	0.02
	H(C19)	3.37(10)	-1,0,0	1	0.02
	H1(C21)	3.49(10)	-1,0,-1	1	0.14
	H1(C28)	3.10(11)	-1,0,0	1	-0.25
	C(28)	3.984(11)	1,0,1	2	0.134
	H1(C25)	3.38(8)	1,0,1	2	0.03
	H2(C28)	3.22(10)	1,0,1	2	-0.13
C(2)	C(4)	3.586(12)	2,1,2	2	0.186
C(3)	C(9)	3.538(11)	2,1,2	2	0.138
	C(30)	3.441(15)	1,1,1	2	0.041
	H1(C30)	2.77(10)	1,1,1	2	-0.13

Reference & Target atoms		Distance	Translation	Symmetry *	D**
C(4)	C(2)	3.586(12)	2,1,2	2	0.186
C(7)	H3(C30)	2.97(9)	1,1,2	2	0.07
C(8)	H(C15)	2.94(9)	1,1,1	2	0.04
C(14)	H(C3)	2.96(11)	2,1,1	2	0.06
C(22)	H1(C27)	3.03(10)	0,0,1	1	0.13
C(27)	H1(C22)	3.07(11)	0,0,-1	1	0.17
C(30)	H(C2)	3.09(10)	-1,0,0	1	0.19
H(C2)	H2(C30)	2.60(17)	1,0,0	1	0.20
H(C3)	H(C14)	2.57(15)	2,1,1	2	0.17
	H1(C30)	2.53(12)	1,1,1	2	0.13
H(C5)	H(C14)	2.52(15)	2,1,1	2	0.12
H(C7)	H3(C30)	2.59(12)	1,1,2	2	0.19
H(C8)	H1(C29)	2.51(14)	1,1,2	2	0.11

Modification II

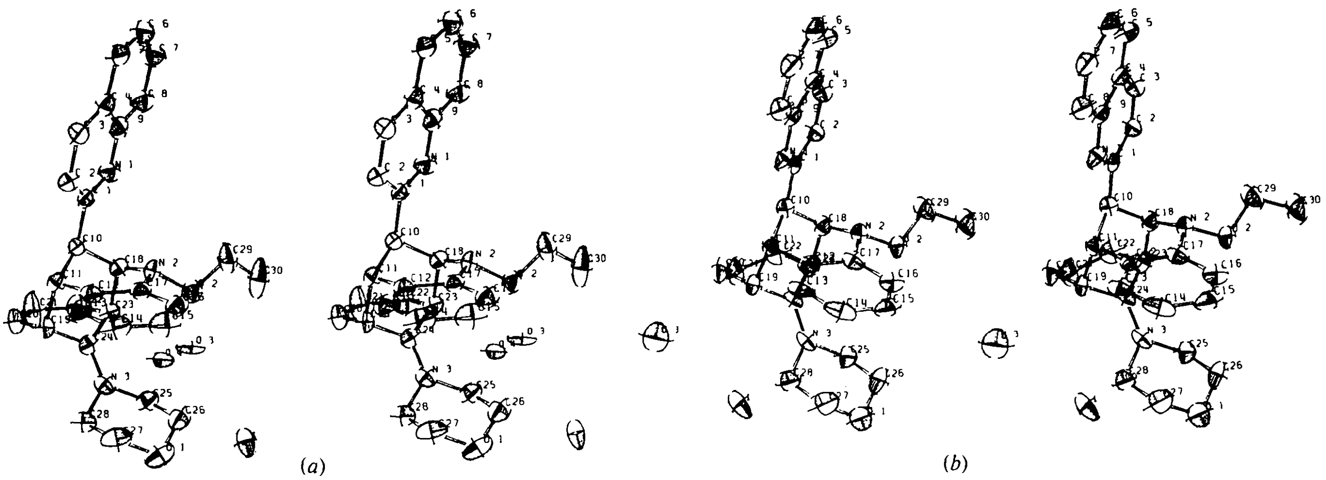
Reference & Target atoms		Distance	Translation	Symmetry *	D**
I	H(C2)	3.05(11) Å	0,0,1	2	-0.30Å
	H(C18)	3.30(13)	0,0,1	2	-0.05
	H1(C29)	3.19(13)	0,0,1	2	-0.16
	O(3)	3.539(15)	0,0,1	7	-0.011
	H(C10)	3.02(12)	1,0,1	8	-0.33
	H1(C20)	3.46(12)	1,0,1	8	0.11
C(2)	O(3)	3.222(19)	0,0,1	8	0.122
C(3)	O(3)	3.239(22)	0,0,1	8	0.139
	H2(C26)	2.94(14)	0,0,2	8	0.04
C(4)	C(7)	3.488(20)	0,0,1	5	0.088
	H1(C28)	2.93(13)	0,0,1	8	0.03
C(5)	C(8)	3.475(21)	0,0,1	5	0.075
	H(C19)	3.07(13)	0,0,1	8	0.17
C(6)	C(8)	3.434(21)	0,0,1	5	0.034
	C(9)	3.452(20)	0,0,1	5	0.052
	C(16)	3.600(18)	0,0,1	5	0.200
	H(C13)	2.72(14)	0,0,1	8	-0.18
C(7)	C(9)	3.375(19)	0,0,1	5	-0.025
	H(C13)	3.05(13)	0,0,1	8	0.15
C(8)	H1(C27)	3.00(14)	0,0,1	8	0.10
C(9)	C(28)	3.503(19)	0,0,1	8	0.103
	H1(C28)	2.77(13)	0,0,1	8	-0.13
C(12)	H(C6)	3.06(13)	0,0,1	5	0.16
C(13)	H(C6)	3.08(14)	0,0,1	5	0.18
C(14)	H(C6)	2.90(13)	0,0,1	5	0.00
	H1(C27)	3.05(14)	1,0,1	5	0.15

Reference & Target atoms		Distance	Translation	Symmetry	D**
C(15)	H(C8)	2.93(13) Å	0,0,0	4	0.03
	H(C6)	2.67(13)	0,0,1	5	-0.23
	H1(C27)	3.05(13)	1,0,1	5	0.15
C(16)	H(C6)	2.65(13)	0,0,1	5	-0.25
C(17)	H(C6)	2.84(13)	0,0,1	5	-0.06
C(22)	O(3)	3.233(20)	0,1,1	7	0,033
	H3(C30)	2.74(12)	0,1,0	7	-0.16
C(25)	O(3)	3.142(22)	0,1,1	7	-0.058
C(29)	O(1)	3.274(18)	0,0,2	8	0.174
C(30)	H1(C20)	3.10(13)	0,0,1	1	0.20
O(1)	H(C14)	2.72(12)	1,0,1	5	0.12
	H2(C29)	2.64(14)	1,0,2	8	0.04
O(3)	H2(C22)	2.53(13)	0,1,0	7	-0.07
	H1(C25)	2.72(12)	0,1,0	7	0.12
	H2(C25)	2.74(12)	0,1,0	7	0.14
	H(C2)	2.65(11)	1,0,1	8	0.05
	H(C3)	2.72(13)	1,0,1	8	0.12
H(C5)	H1(C30)	2.27(19)	0,0,2	8	-0.13
H(C8)	H(C15)	2.32(17)	0,0,-1	4	-0.08
H(C14)	H2(C29)	2.55(18)	0,0,-1	4	0.15
	H1(C27)	2.59(18)	1,0,1	5	0.19
H(C15)	H1(C27)	2.55(18)	1,0,1	5	0.15
H1(C21)	H(C23)	2.43(19)	0,1,0	7	0.03
H1(C22)	H3(C30)	2.60(17)	0,1,0	7	0.20
H2(C22)	H3(C30)	2.03(18)	0,1,0	7	-0.37

* Symmetry operations for modification I: 1=x,y,z; 2=-x,-y,-z.

Symmetry operations for modification II: 1=x,y,z; $2=\frac{1}{2}+x,\frac{1}{2}-y,-z$; $3=-x,\frac{1}{2}+y,\frac{1}{2}-z$; $4=\frac{1}{2}-x,-y,\frac{1}{2}+z$; 5=-x,-y,-z; $6=\frac{1}{2}-x,\frac{1}{2}+y,z$; $7=x,\frac{1}{2}-y,\frac{1}{2}+z$; $8=\frac{1}{2}+x,y,\frac{1}{2}-z$.

**"D" means the difference between the distance and the sum of van der waals radii cited from Pauling (1960).



(a) (b)

Fig. 4. (*a*) A stereoview showing the molecular conformation of modification I. (*b*) A stereoview showing the molecular conformation of modification II.

That is, the two modifications gave slightly different spectra in the solid state but gave identical spectra in chloroform solution. The deviations at C(20), C(21) and C(22) suggest deformation by intermolecular contacts. The deviations at the ethoxy groups suggest that the rotation about the N(2)–O(2) bond is considerably restricted by the molecular configuration. Fig. 4(*a*) and (*b*) show stereo drawings for the molecular configurations and the thermal ellipsoids of the non-hydrogen atoms of modifications I and II drawn with the program *ORTEP* (Johnson, 1965). It is clearly shown that the two molecular conformations differ at the quinoline rings.

Crystal structures

Table 7 shows the intermolecular distances of the two modifications. Some of the distances involving H atoms show unusual values caused by the ambiguous positional parameters for the H atoms. The cation molecule has five juts: the quinoline, tetrahydroquinoline, boat cyclohexane, morpholine and ethoxy moieties. Some of these juts are in contact with those of other molecules by van der Waals interactions. It is clear that the two crystal modifications are caused by different combinations of molecular contacts of these juts. Between the molecules there are enough spaces to accommodate the two water molecules and the two iodide anions. Although they are packed in one space, they and the surrounding atoms are in contact with each other by van der Waals interactions. In the last difference Fourier syntheses the outer rims (about 0·6 e Å^{-3}) around the water molecules and the iodide anions may be caused by a statistical distribution around their positions to account for the loose packing. In fact, the crystals effloresce in extremely dry air and most of the water molecules evaporate from the crystals. For modification I, a water molecule is statistically distributed at the two positions O(3) and O(4) with occupancies 0·6 and 0·4 respectively. It may be concluded that the water molecules exist as structural water in the crystals. On the other hand, the iodide anions are trapped in the space by electrostatic interactions with the azomethinium N atoms N(3). Rather high melting points 216–217 and 208–209° C for modifications I and II probably result from the ionic interactions. In the case of hydrated salts which have azomethinium N atoms, hydrogen bonds are usually found in the crystalline state as follows: proflavine hemisulphate hydrate (Jones & Niedle, 1975), 5-[3-(dimethylamino)propyl]-6,7,8,9,10,11-hexahydro-5*H*-cyclooct[*b*]indole monohydrate (Rodgers, Kennard, Horn & Riva di Sanseverino, 1974), *d*-tubocurarine dichloride pentahydrate (Codding & James, 1973), lidocaine hydrochloride monohydrate (Hanson & Röhrl, 1972), methixene hydrochloride monohydrate (Chu, 1972), histidine hydrochloride monohydrate (Oda & Koyama, 1972), dipyrido[1,2-*a*:2′,1′-*c*]pyrazinium dibromide monohydrate (Derry & Hamor, 1972) and so on. The present results do not indicate any hydrogen bond or any special approach related to a charge-transfer effect between the anions and the charged N atoms. That is, van der Waals contacts and long-range electrostatic forces play the main roles in the crystal formation of the two modifications.

The compounds are relatively stable in acidic or alkaline solution at room temperature, as shown in another paper (Hamana, Noda, Narimatsu & Ueda, 1975). This may be explained partly by the fact that the azomethinium moiety is protected by the hydrogen atoms of C(21), C(25) and C(28) and also by the tetrahydroquinoline moiety. However, the feeble reactivity towards anion exchange cannot be explained from the conformational standpoint. It may be attributed to the difference in the solubilities of halides or to wrapping of the anion by the large cations in solution.

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