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Structure of 4-{8-Ethoxy-10,12-dimethyl-13-(2-quinolyl)-8-azatricyclo[7.3.1.0^{2,7}]trideca-2(7),3,5-trien-11-ylidene}morpholinium Iodide

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Abstract. $C_{29}H_{34}N_3O_2^+.I^-$, orthorhombic, $P2_12_12_1$, a = 16·284 (8), b = 18·798 (9), c = 9·156 (3) Å, Z = 4, D_m = 1·380, D_x = 1·383 Mg m^{-3}. The structure was solved by Patterson and Fourier techniques and refined to a final R value of 0·051 for 2101 measurable reflexions. The crystal structure consists of discrete cationic molecules and iodide anions. The molecular conformation is very similar to that of the cationic molecule in the crystal structure of $C_{30}H_{34}N_3O_2^+.I^-.H_2O$ previously published.

Introduction. In the presence of an acylating agent an aromatic N-oxide reacts smoothly with enamines to give α- or γ-substituted heterocyclic derivatives through the addition–elimination mechanism (Hamana & Noda, 1965, 1966, 1967, 1969; Noda, Narimatsu & Hamana, 1976). When a chloroform solution of N-ethoxyquinolinium iodide (1) and 1-morpholinocyclohexene (2*a*) was allowed to stand overnight at room temperature, however, an unexpected reaction took place to give a novel tricyclic product (3*a*), 4-{8-ethoxy-15-(2-quinolyl)-8-azatetracyclo[7.5.1.1^{10,14}.0^{2,7}]hexadeca-2(7),3,5-trien-16-ylidene}morpholinium iodide, in an excellent yield (Hamana, Noda, Narimatsu & Ueda, 1975) (Fig. 1). The structure of the product, which was consistent with the spectral (IR, NMR and mass) and chemical behavior as well as a reaction-mechanism speculation, was finally established by an X-ray diffraction method (Ueda, Noda & Hamana, 1977). Recently it has become apparent that the enamine of an acyclic ketone, 3-morpholino-2-pentene (2*b*), can also enter into the reaction to yield the same type of a product (3*b*) as 3*a* (Noda, Hamana, Uechi & Ueda, 1982) (Fig. 1). The present study was performed in order to explore the essential feature of this reaction as well as the stability of the product.

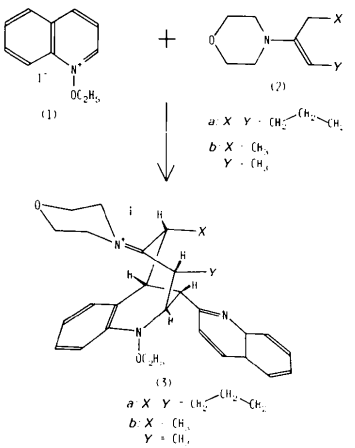

Fig. 1. A diagram for the reaction of N-ethoxyquinolinium iodide (1) with the morpholine enamine of cyclohexanone (2*a*) or 3-pentanone (diethyl ketone, 2*b*).

The crystal used for X-ray work was ground to a sphere of *ca* 0·2 mm in diameter. The density was measured by flotation in an aqueous KI solution. X-ray photographs obtained by the Weissenberg technique showed systematic absences indicating the space group $P2_12_12_1$. The unit-cell parameters and intensity data were measured on a Syntex $P\bar{1}$ automated four-circle diffractometer with monochromated Mo $K\alpha$ radiation. 3309 independent reflexions with a range of $2\theta < 53°$ were collected by the θ–2θ scan technique with a variable scan rate from 4·0 to 24·0° min^{-1}. Of these, intensities of 2101 reflexions were larger than $2{\cdot}0\sigma(I)$, and only these reflexions were used in the least-squares refinement. The large percentage of unmeasurable reflexions was reflected later in determination of the H-atom positions or in high e.s.d.'s for

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the atomic parameters. The intensity data were corrected for Lorentz and polarization effects, but not for absorption and extinction.

The position of the I atom was easily located from a Patterson synthesis, and its z parameter was found to be nearly zero. This effected for this space group a spurious mirror-plane symmetry at $z = 0$ in the Fourier map phased on only the heavy atom. Skeletons of the quinoline and morpholine rings were constructed with peaks appearing on either side of the spurious mirror plane in the Fourier maps. Four models classified by combinations of these parts were assumed as initial trial structures. Least-squares procedures were applied to these models; the Fourier map phased on the model with the lowest R value revealed the positions of all non-H atoms. Refinement was carried out by a block-diagonal least-squares procedure with Cruickshank's weighting schemes (Cruickshank, 1965). Refinement included the H atoms deduced from the difference Fourier maps and calculation was terminated when all shift/e.s.d. ratios for the non-H atoms became less than $\frac{1}{3}$. The final R value was 0·051 for 2101 measurable reflexions. The atomic scattering factors for I^-, O, N and C_{cov}, and also the anomalous-dispersion correction for I, were taken from *International Tables for X-ray Crystallography* (1974). Those for H were adopted from the table of Stewart, Davidson & Simpson (1965). All the calculations were carried out on a FACOM M-200 computer in the Computer Center of Kyushu University, mainly by the use of the *UNICS*-II program system (Sakurai, Iwasaki, Watanabe, Kobayashi, Bando & Nakamichi, 1974). Figs. 2 and 4 were drawn by the use of the *ORTEP* program (Johnson, 1965). The final atomic parameters are listed in Table 1 where the H atoms have been omitted.*

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters*

Numbers in parentheses here and elsewhere in this paper are the e.s.d.'s in the last significant digits.

	x	y	z	B_{eq}* (Å^2)
I	0·10207 (4)	0·01817 (3)	−0·01250 (9)	3·5 (0)
C(1)	0·0811 (6)	0·4158 (5)	−0·1747 (11)	2·9 (3)
C(2)	0·0898 (6)	0·4186 (5)	−0·3278 (11)	3·2 (3)
C(3)	0·1676 (7)	0·4224 (6)	−0·3842 (12)	4·2 (3)
C(4)	0·2356 (6)	0·4237 (6)	−0·2896 (13)	3·9 (3)
C(5)	0·3193 (7)	0·4270 (6)	−0·3375 (14)	5·1 (4)
C(6)	0·3803 (6)	0·4222 (7)	−0·2422 (15)	5·6 (4)
C(7)	0·3645 (7)	0·4182 (7)	−0·0932 (16)	5·9 (4)
C(8)	0·2855 (6)	0·4155 (6)	−0·0382 (16)	4·9 (4)
C(9)	0·2199 (6)	0·4197 (5)	−0·1407 (11)	3·1 (3)
N(1)	0·1420 (4)	0·4173 (4)	−0·0823 (9)	2·7 (2)
C(10)	−0·0065 (6)	0·4134 (5)	−0·1108 (11)	2·6 (2)
C(11)	−0·0073 (5)	0·4183 (5)	0·0541 (10)	2·3 (2)
C(12)	0·0213 (6)	0·3488 (5)	0·1253 (11)	2·9 (3)
C(13)	0·0488 (7)	0·3494 (5)	0·2674 (12)	3·8 (3)
C(14)	0·0719 (8)	0·2875 (6)	0·3345 (13)	5·3 (4)
C(15)	0·0666 (7)	0·2249 (6)	0·2629 (13)	4·6 (4)
C(16)	0·0402 (7)	0·2225 (6)	0·1187 (14)	4·3 (4)
C(17)	0·0178 (5)	0·2850 (5)	0·0489 (11)	2·9 (3)
N(2)	−0·0034 (5)	0·2857 (4)	−0·1017 (9)	2·7 (2)
C(18)	−0·0518 (6)	0·3455 (5)	−0·1521 (10)	2·7 (3)
C(19)	−0·1414 (5)	0·3445 (5)	−0·0917 (10)	2·5 (2)
C(20)	−0·1519 (5)	0·3774 (4)	0·0560 (10)	2·2 (2)
C(21)	−0·0952 (7)	0·4353 (5)	0·1061 (10)	3·0 (3)
C(22)	−0·1272 (5)	0·5086 (5)	0·0621 (11)	3·9 (3)
C(23)	−0·2021 (6)	0·3809 (7)	−0·2007 (13)	4·4 (3)
N(3)	−0·2143 (4)	0·3594 (4)	0·1367 (9)	2·4 (2)
C(24)	−0·2395 (6)	0·3919 (6)	0·2789 (12)	3·4 (3)
C(25)	−0·2421 (7)	0·3358 (7)	0·3947 (11)	4·3 (3)
O(1)	−0·3037 (5)	0·2848 (4)	0·3556 (9)	5·2 (3)
C(26)	−0·2816 (7)	0·2516 (6)	0·2237 (14)	5·0 (4)
C(27)	−0·2757 (6)	0·3047 (5)	0·0995 (12)	3·7 (3)
O(2)	−0·0443 (4)	0·2213 (3)	−0·1431 (8)	3·6 (2)
C(28)	−0·0061 (8)	0·1923 (6)	−0·2687 (15)	5·3 (4)
C(29)	−0·0556 (9)	0·1309 (8)	−0·3201 (17)	7·6 (5)

* The equivalent isotropic thermal parameters were calculated from the deposited anisotropic coefficients following the definition given by Hamilton (1959).

Discussion. The molecular structure has been established by this X-ray study to be that designated in the title. Fig. 2 shows a stereoscopic illustration of the molecule. The bond distances and angles are shown schematically in Fig. 3 together with the atomic-nomenclature scheme. The selected torsion angles are listed in Table 2.

The nearly planar quinoline ring [C(1) through N(1)] is connected to C(10) with considerably strained torsion angles about the C(1)—C(10) bond. The central azatricyclo[7.3.1.0^{2,7}]trideca-2(7),3,5-triene moiety adopts a twin-chair conformation with the rings appreciably distorted from ideal cyclohexane geometry. This distortion is also reflected in the somewhat long distance of the C(18)—C(19) bond or the strained torsion angles about this bond. The benzene-ring [C(12) through C(17)] plane makes an angle of *ca* 85° with the quinoline ring. The morpholine ring has a chair

* Lists of structure factors, anisotropic thermal parameters of non-H atoms, and atomic parameters of H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36684 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Selected torsion angles* (°)

N(1)—C(1)—C(10)—C(11)	4*	O(1)—C(26)—C(27)—N(3)	59
N(1)—C(1)—C(10)—C(18)	−117	C(26)—C(27)—N(3)—C(24)	−56
C(10)—C(18)—C(19)—C(20)	−37	C(27)—N(3)—C(24)—C(25)	60
N(2)—C(18)—C(19)—C(20)	85	C(19)—C(20)—N(3)—C(24)	−173
N(3)—C(24)—C(25)—O(1)	−63	C(19)—C(20)—N(3)—C(27)	4
C(24)—C(25)—O(1)—C(26)	63	C(17)—N(2)—O(2)—C(28)	−129
C(25)—O(1)—C(26)—C(27)	−61	N(2)—O(2)—C(28)—C(29)	−173

* All of the e.s.d.'s are equal to 1°.

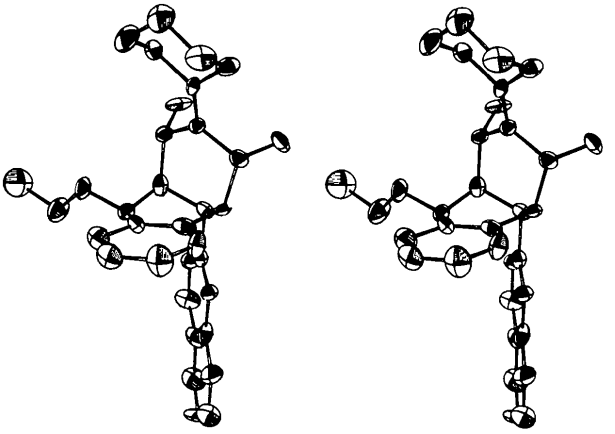

Fig. 2. Stereoscopic illustration of the molecular structure with thermal ellipsoids drawn to enclose 40% probability.

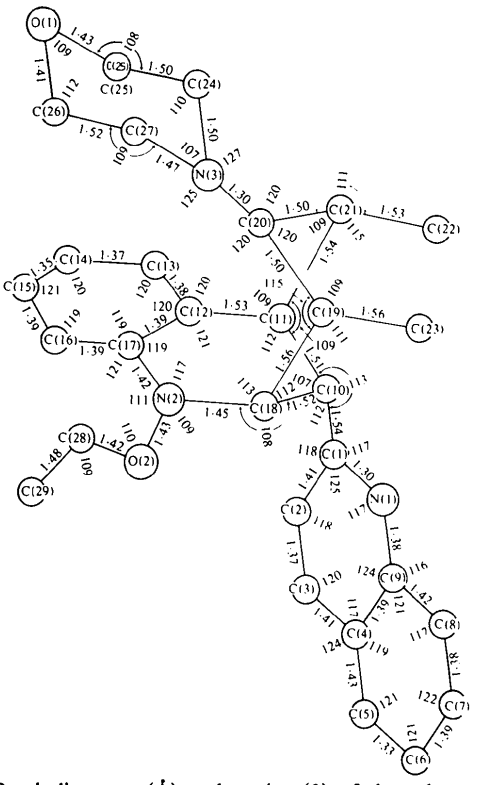

Fig. 3. Bond distances (Å) and angles (°) of the schematically drawn molecule with atomic-nomenclature scheme. The e.s.d.'s in distances range from 0·01 to 0·02 Å and those of all angles are equal to 1°.

conformation with regular torsion angles nearly equal to 60°. C(20), N(3), C(24) and C(27) are nearly coplanar, and the N(3)—C(20) bond of 1·30 (1) Å has a high double-bond character. Thus, it may be assumed that atom N(3) is in sp^2 hybridization to form bonds with distorted angles. It may then be concluded that N(3) is ionized. The ethoxy moiety is attached

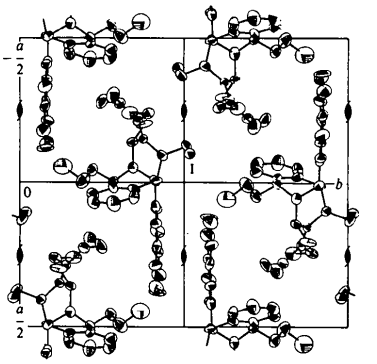

Fig. 4. Projection of the crystal structure on to the *ab* plane.

to N(2) with an antiplanar conformation, and has normal bond distances.

The overall conformation of this molecule is very similar to that of the cationic molecule in the crystal structure of the modification (II) of $C_{30}H_{34}N_3O_2^+.I^-.H_2O$ previously published (Ueda *et al.*, 1977), except that the latter molecule contains the cyclohexane moiety instead of the pentene moiety [C(19) through C(23)] in the present molecule.

Fig. 4 shows the crystal structure projected onto the *ab* plane. The structure consists of discrete cationic molecules and iodide anions. The molecules are so arranged that the normals to their quinoline-ring planes are almost perpendicular to the *b* axis. There are no unusual intermolecular contacts; the molecular packing is due to van der Waals forces only.

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Crystallographic Studies of High-Density Organic Compounds: 5-Fluoro-2,4,6-trinitro-1,3-benzenediamine

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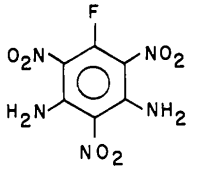
Abstract. $C_6H_4FN_5O_6$, $M_r = 261{\cdot}1$, monoclinic, *Pc*, $a = 7{\cdot}5048$ (4), $b = 5{\cdot}1195$ (3), $c = 11{\cdot}7645$ (6) Å, $\beta = 99{\cdot}625$ (6)°, $D_c = 1{\cdot}95$ Mg m^{-3} for $Z = 2$; Cu $K\alpha$ ($\lambda = 1{\cdot}5418$ Å) diffractometer data; 722 intensities; 713 I's $> 3\sigma$ above background; final $R = 0{\cdot}040$. The effects of the amino and nitro substituents are exhibited by the benzene ring. The nitro groups flanking the F are rotated out of the ring plane by about the same amount, *ca* 20°, while the torsion angle for the third nitro is 3°. All of the H atoms are involved in strong intramolecular hydrogen bonds to adjacent nitro O atoms. Three of the four H atoms participate in weaker intermolecular hydrogen bonds which appear to control the crystal packing. On the basis of crystal-packing-coefficient calculations, it is concluded that the high crystal densities of this compound and of the analagous 3,5-diamino-2,4,6-trinitrophenol are due to efficient intermolecular packing arrangements which minimize free space in the unit cells.

Introduction. The densities of organic crystals containing only C, H, N, O or F atoms average to about 1·3 Mg m^{-3}.* The crystal densities of hydrocarbons are invariably smaller than the average, while the values for molecules containing several N, O or F atoms can be substantially larger. For example, the densities of naphthalene ($C_{10}H_8$), glucose (α-D-glucopyranose, $C_6H_{12}O_6$) and hexanitrobenzene ($C_6N_6O_{12}$) are 1·14, 1·56 and 1·99 Mg m^{-3}, respectively. We are investigating the crystal structures of a number of high-density, polynitro-substituted organic molecules to understand better the relationships between molecular structure, crystal packing and density. The first structure reported (Bhattacharjee & Ammon, 1981) in the series, that of 3,5-diamino-2,4,6-trinitrophenol (DATNP), was characterized by a strong OH···O_2N intramolecular interaction. Herein, we report the structure of a similar compound, *viz* 5-fluoro-2,4,6-trinitro-1,3-benzenediamine (I), which lacks the dominant OH of the phenol.



(I)

The compound, obtained from Dr H. Adolph, Naval Surface Weapons Center, White Oak, Maryland, crystallized as transparent yellow needles from acetonitrile. The space group and approximate cell parameters were obtained from oscillation and Weissenberg photographs with Ni-filtered Cu radiation. Accurate cell parameters were determined and intensity measure-

* Stine (1981) reported an average crystal density of 1·29 Mg m^{-3} for 2051 C, H, N, O or F containing compounds selected from the Cambridge Crystallographic Files.

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