five-membered ring, and also to the planar configuration of the molecule, which produces some unusual bond lengths and angles. The planarity of the fluoranthene moiety is found to be similar for compounds (I), (III) and (IV), whilst it is significantly non-planar in (II).

Fig. 2 shows the content of the unit cell projected down **b**. The molecules are packed in layers, but are displaced with respect to one another to relieve short intermolecular contacts, so that packing forces are unlikely to influence the geometry of the molecule to any appreciable extent.

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Endoannular Reactions and Ring–Chain Tautomerism. Structure of 1-(2-Hydroxyethyl)-3-methyl-2,4(1*H*,3*H*)-quinazolinedione

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Abstract. $C_{11}H_{12}N_2O_3$, $M_r = 220{\cdot}2$, tetragonal, $P\bar{4}2_1c$, $a = 17{\cdot}008\ (5)$, $c = 7{\cdot}081\ (3)$ Å, $V = 2048\ (1)$ Å^3, $Z = 8$, $D_x = 1{\cdot}43$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}5418$ Å, $\mu(\mathrm{Cu}\ K\alpha) = 0{\cdot}9$ mm^{-1}, $F(000) = 928$, room temperature, $R = 0{\cdot}044$ for 1023 reflections. The reaction of 2-(2-bromoethyl)isatoic anhydride with methylamine affords the title compound, which is the ring–chain tautomer of 2,3-dihydro-6-methyl-4,1,6-benzoxadiazonine-5,7(1*H*,6*H*)-dione. The side-chain hydroxyl group is disordered in the crystal assuming two conformations, approximately *trans* and *gauche**, both involved in the hydrogen-bonding network of the crystal packing.

Introduction. In order to investigate the endoannular interactions and ring–chain tautomerism in medium-sized heterocycles (Pinnen, Zanotti & Lucente, 1982; Zanotti, Pinnen, Lucente, Cerrini, Gavuzzo & Mazza, 1983; Pinnen, Zanotti, Lucente, Cerrini, Fedeli & Gavuzzo, 1985) we tried to synthesize the nine-membered system 2,3-dihydro-6-methyl-4,1,6-benzoxadiazonine-5,7(1*H*,6*H*)-dione (I) by reacting 2-(2-bromoethyl)isatoic anhydride with methylamine according to the procedure of Barcza, Coppola & Shapiro (1979). The nine-membered ring of compound (I) contains in fact a free amino group and a potentially reactive *N*-acylurethane carbonyl suitably located to study the endoannular reaction and related tetrahedral intermediates. As previously reported (Pinnen, Lucente, Mazza & Pochetti, 1987) this reaction leads to

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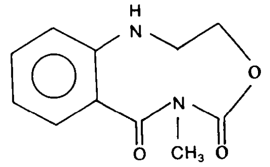
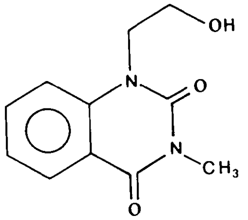
1-(2-hydroxyethyl)-3-methyl-2,4(1*H*,3*H*)-quinazolinedione (II), the ring–chain tautomer of (I). This has been proved by the crystallographic analysis of the reaction product which is here reported in detail. Conventional chemical methods are generally not very reliable for the determination of ring–chain tautomers and NMR data do not allow unequivocal distinction between forms (I) and (II).



(I)



(II)

Experimental. The compound was synthesized as described in the *Introduction.* Melting point, IR absorptions and ^{1}H NMR data of the reaction product are in accordance with those previously reported by Barcza, Coppola & Shapiro (1979). Crystals in the shape of thin needles were obtained from ethyl acetate by slow evaporation at room temperature. Approximate unit-cell dimensions and space group were determined from oscillation and Weissenberg photographs. A crystal $0{\cdot}5 \times 0{\cdot}2 \times 0{\cdot}1$ mm was used for intensity measurements on a Syntex $P2_1$ automatic diffractometer equipped with graphite monochromator and Cu $K\alpha$ radiation. Refined unit-cell parameters were derived from a least-squares fit of the angular settings of 15 reflections in the range $10 < \theta < 30°$. Intensities were recorded up to a maximum value 2θ of 138° by the θ–2θ scan technique. Two standard reflections, 201 and 021, measured after every 80 showed only small random deviations from their means. Out of the 1142 independent reflections recorded, 1025 with $I > 1{\cdot}5\sigma(I)$ were considered observed and used for the calculations ($h\,0\to20$, $k\,0\to13$, $l\,0\to8$). Lorentz and polarization corrections were applied, but intensities were not corrected for extinction or absorption.

The structure was solved by direct methods using the program *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). 247 reflections and 5946 $\sum_2$ relationships were used in the phase-determining procedure. An *E* map computed with the phases of the set having the best combined figure of merit revealed all the non-hydrogen atoms and these were refined isotropically by full-matrix least-squares methods. A difference Fourier map computed at this stage showed a residual electron density peak of *ca* 2 e Å^{-3} in the vicinity of the hydroxyl O(11), making a reasonable valence bond length and angle with C(11). This was interpreted as due to a minor conformation assumed in the crystal by the terminal hydroxyl of the 2-hydroxyethyl side chain. Therefore two different positions for the hydroxylic oxygen were assumed with 0·75 and 0·25 occupancy factors respectively; the position with the lower occupancy factor is identified as O(99) in the tables. All the atoms were then anisotropically refined except for O(99), which was isotropically refined. The quantity minimized was $\sum w(|F_o|-|F_c|)^2$ where $w=(a+|F_o|+c|F_o|^2)^{-1}$ with a and c equal to $2F_{o\min}$ and $2/F_{o\max}$ respectively. A difference Fourier map revealed all the H atoms in stereochemically feasible positions, except the H bound to O(99). These H positional parameters together with isotropic thermal values deduced from the carrier atoms were included and kept fixed in the refinement. The two reflections 002 and 020 were omitted because they were judged to be severely influenced by extinction or absorption. At convergence $(\Delta/\sigma)_{\max}=0{\cdot}5$, $S=0{\cdot}8$, $R=0{\cdot}044$ and $wR=0{\cdot}065$ for all the observed reflections. The residual electron density in the final difference Fourier map is within $\pm0{\cdot}2$ e Å^{-3}. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). All the calculations were carried out on the D.G. ECLIPSE MV/8000 II of the CNR Research Area (Montelibretti) using local programs. The refined atomic parameters are listed in Table 1.*

Discussion. The atomic numbering scheme together with a perspective view of the major conformer found in the crystal are shown in Fig. 1, and the valence bond lengths and angles are reported in Table 2. The atom connectivity unequivocally establishes that the reaction product is 1-(2-hydroxyethyl)quinazolinedione (II), the ring–chain tautomer of 4,1,6-benzoxadiazonine (I). The two N atoms are completely sp^2 hybridized, as shown by the sums of the bond angles around N(1) and N(3) which are 360·0 (2) and 359·9 (1)° respectively and by the displacements of these atoms from the plane of their three substituents, which are 0·023 (3) and 0·017 (3) Å respectively. The atoms of the two fused rings are coplanar: the largest deviation from the mean plane through these atoms is 0·039 (3) Å for N(3). The mean plane of the heterocyclic system is approximately

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* Lists of structure factors, anisotropic thermal parameters and H positional parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44690 (99 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final fractional coordinates and B_{eq} values of the non-*H *atoms with e.s.d.'s in parentheses*

$$B_{\rm eq} = \tfrac{4}{3}\textstyle\sum_i \sum_j b_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$(Å^2)
O(2)	−0·0153 (1)	0·1728 (1)	0·2958 (5)	5·1
O(4)	0·2455 (1)	0·1251 (1)	0·2185 (5)	4·8
O(11)	−0·0972 (2)	0·4202 (2)	0·2634 (6)	4·5*
O(99)	−0·0107 (6)	0·4229 (6)	0·1280 (15)	4·5 (2)*
N(1)	0·0667 (1)	0·2776 (1)	0·3131 (4)	3·0
N(3)	0·1152 (1)	0·1500 (1)	0·2513 (4)	3·5
C(1)	−0·0006 (2)	0·3275 (2)	0·3704 (5)	3·5
C(2)	0·0516 (2)	0·1996 (2)	0·2878 (5)	3·4
C(3)	0·0984 (2)	0·0660 (2)	0·2262 (8)	5·6
C(4)	0·1933 (2)	0·1738 (2)	0·2438 (5)	3·3
C(5)	0·2828 (2)	0·2879 (2)	0·2477 (5)	3·5
C(6)	0·2960 (2)	0·3683 (2)	0·2666 (6)	3·8
C(7)	0·2331 (2)	0·4182 (2)	0·2965 (5)	3·6
C(8)	0·1569 (2)	0·3902 (2)	0·3119 (5)	3·2
C(9)	0·2059 (2)	0·2586 (2)	0·2635 (5)	2·9
C(10)	0·1426 (2)	0·3088 (2)	0·2955 (4)	2·8
C(11)	−0·0413 (2)	0·3645 (2)	0·2038 (6)	4·2

* Disordered with occupancies 0·75 and 0·25 for O(11) and O(99) respectively.

Table 2. *Valence bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses for the non-*H *atoms*

N(1)—C(1)	1·481 (4)	C(5)—C(6)	1·393 (4)
N(1)—C(2)	1·363 (4)	C(5)—C(9)	1·404 (4)
N(1)—C(10)	1·402 (4)	C(6)—C(7)	1·381 (4)
C(2)—O(2)	1·226 (4)	C(7)—C(8)	1·386 (4)
C(2)—N(3)	1·396 (4)	C(8)—C(10)	1·411 (4)
N(3)—C(3)	1·468 (4)	C(9)—C(10)	1·393 (4)
N(3)—C(4)	1·389 (4)	C(11)—C(1)	1·506 (5)
C(4)—O(4)	1·228 (4)	C(11)—O(11)	1·406 (5)
C(4)—C(9)	1·465 (4)	C(11)—O(99)	1·242 (12)

C(1)—N(1)—C(2)	116·7 (2)	C(6)—C(5)—C(9)	119·3 (3)
C(1)—N(1)—C(10)	121·3 (2)	C(5)—C(6)—C(7)	119·6 (3)
C(2)—N(1)—C(10)	122·0 (2)	C(6)—C(7)—C(8)	121·6 (3)
O(2)—C(2)—N(1)	122·0 (3)	C(7)—C(8)—C(10)	119·5 (3)
O(2)—C(2)—N(3)	120·2 (3)	C(4)—C(9)—C(5)	118·6 (2)
N(1)—C(2)—N(3)	117·8 (2)	C(4)—C(9)—C(10)	120·3 (2)
C(3)—N(3)—C(2)	117·4 (2)	C(5)—C(9)—C(10)	121·1 (3)
C(3)—N(3)—C(4)	117·6 (2)	C(8)—C(10)—N(1)	121·5 (3)
C(2)—N(3)—C(4)	124·9 (2)	C(8)—C(10)—C(9)	118·8 (3)
O(4)—C(4)—N(3)	120·1 (3)	N(1)—C(10)—C(9)	119·7 (3)
O(4)—C(4)—C(9)	124·8 (3)	N(1)—C(1)—C(11)	112·3 (3)
N(3)—C(4)—C(9)	115·1 (2)	C(1)—C(11)—O(11)	110·9 (3)
		C(1)—C(11)—O(99)	118·7 (7)

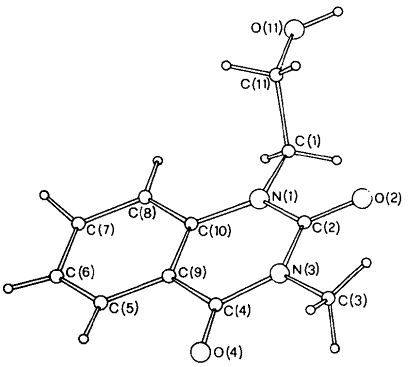

Fig. 1. A perspective view of the major conformer of the title compound together with the atomic numbering scheme.

perpendicular to the fourfold axis, the angle being 80·3 (1)°.

The hydroxyl oxygen O(11) forms with the sp^3 C(11) a bond length and a valence angle respectively of 1·406 (5) Å and 110·9 (3)°, in agreement with the expected geometry of this functional group. The corresponding geometrical values involving O(99) are affected by the poor accuracy of localization of this atomic position. However, the ^{1}H NMR spectrum in $(CD_3)_2SO$ solution reveals the presence of a single exchangeable proton coupled to a CH_2 group (triplet centred at δ 4·9); on the other hand, the ^{13}C NMR spectrum in $CDCl_3$ solution, in addition to eight signals corresponding to the sp^2 C atoms, shows the signal of the methyl group (quartet at δ 28·42) and two peaks attributable to the two CH_2 groups (triplets at δ 60·6 and 46·0).

The conformation of the 2-hydroxyethyl side chain is described by the following torsion angles: C(10)—N(1)—C(1)—C(11) = 89·9 (3), C(2)—N(1)—C(1)—C(11) = −93·2 (3), N(1)—C(1)—C(11)—O(11) = −171·5 (3), N(1)—C(1)—C(11)—O(99) = −78·2 (7)° computed according to the convention of Klyne & Prelog (1960). The hydroxyl O assumes a *trans* and a *gauche** conformation in the major and minor conformer respectively and gives rise to intermolecular hydrogen bonds in both cases.

A view of the crystal packing along the short axis including the possible hydrogen-bonding network is shown in Fig. 2. *n*-Glide-related molecules stack their mean planes one on top of another, making an angle of 0·2 (1)°, and extend their side chains on the same side.

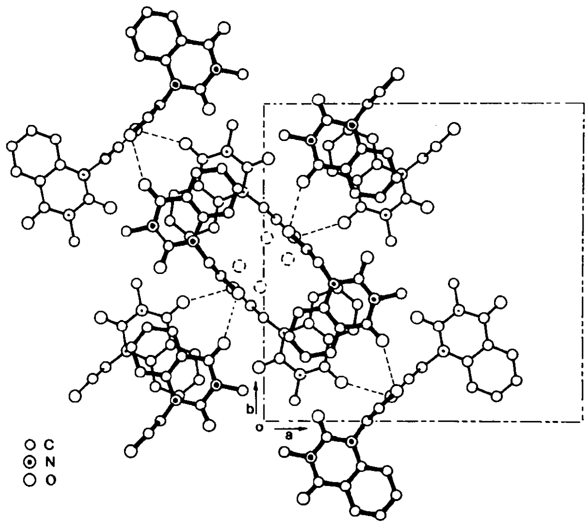

Fig. 2. The crystal packing shown along the *c* axis. Heavier and lighter bonds indicate molecules at higher and lower heights respectively. Dashed lines represent intermolecular hydrogen bonds between the carbonylic and *trans* hydroxylic oxygens. Broken circles represent the possible positions of the hydroxylic oxygens when assuming the *gauche** conformation.

Although most of the atoms of these rings do not superimpose on each other, the distance between their mean planes is 3·468 (2) Å, a value slightly larger than would be expected for an appreciable charge-transfer complex to be present. Dipole–dipole interactions may play an essential role in stabilizing this system. Couples of *n*-glide-related molecules form aggregates of four molecules around the twofold axes and the space between their protruding side chains may be filled by the hydroxyl group when assuming the minor conformation. The 0·25 occupancy factor attributed to O(99) may be accounted for by assuming a statistically disordered hydroxyl group for each set of four molecules so arranged. The four broken circles in Fig. 2 represent the four possible positions that may be occupied in turn by O(99).

The hydroxyl group plays an important role in the hydrogen-bond network, acting as a donor in both conformations. O(11) of a molecule at *x*, *y*, *z* forms an intermolecular hydrogen bond with the carbonylic O(4) of another molecule at $-\frac{1}{2}+x$, $\frac{1}{2}-y$, $\frac{1}{2}-z$ with the following geometrical features: O(11)···O(4) = 2·786 (3), H···O(4) = 1·87 (3) Å, O(11)—H···O(4) = 154 (0), C(4)—O(4)···H = 142 (0), C(4)—O(4)···O(11) = 151·0 (3), C(11)—O(11)···O(4) = 118·5 (3), [O(11)—H—O(4)—C(4)] = −168 (1)°, where H represents the hydrogen bound to O(11) found in the final difference Fourier. The hydroxyl O(11) at *x*, *y*, *z* is also an acceptor of an intermolecular hydrogen bond with the hydroxylic O(99) of another molecule at $-\frac{1}{2}+y$, $\frac{1}{2}+x$, $\frac{1}{2}+z$ with the following geometrical features: O(11)···O(99) = 2·86 (1) Å, C(11)—O(11)···O(99) = 117·9 (4) and O(4)···O(11)···O(99) = 100·8 (3)°; the values including the H atom have not been computed since this could not be detected from the final difference Fourier.

The disordered hydroxyl group does not cause weakening of the crystal packing forces. In fact, when an O(11) atom is replaced by an O(99) atom, the O(4)···O(11) hydrogen bond is replaced by the energetically similar O(11)···O(99) hydrogen bond. Furthermore, while the hydrogen bond between the hydroxylic and carbonylic groups allows the packing of the molecules in the *ab* plane, that between the hydroxyl groups of the two different conformers has a large component perpendicular to this plane.

The ^{13}C NMR spectrum was recorded on the Bruker WP 200 of the CNR Research Area (Montelibretti). Mr M. Viola is thanked for the drawings. Financial support from the Ministero della Pubblica Istruzione is also acknowledged.

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Structure of (*R*)-Norfenfluramine Dichloroacetate*

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Abstract. $C_{10}H_{13}F_3N^+.C_2HCl_2O_2^-$, $M_r = 332·16$, monoclinic, $P2_1$, $a = 13·359\ (5)$, $b = 6·810\ (3)$, $c = 8·447\ (3)$ Å, $\beta = 107·55\ (2)°$, $V = 732·7\ (6)$ Å^3, $Z = 2$, D_m (by flotation) = 1·509, $D_x = 1·506$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 4·17$ cm^{-1}, $F(000) = 340$, $T = 294$ K, final $R = 0·058$ for 1793 observed reflections with $I > 3\sigma(I)$. The conformation of the protonated amine is extended. The poisoned faces (100) and ($\bar{1}00$) of the enantiomeric crystal in racemic supersaturated solutions contain the achiral anion and the group $-NH_3^+$.

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* Norfenfluramine is α-methyl-3-(trifluoromethyl)benzeneethanamine (*Chemical Abstracts* name).

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