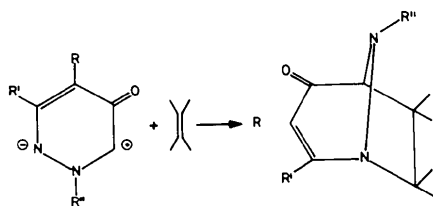Charge distribution on the ring leads one to predict 1,3-dipolar cycloaddition of double and triple bonds, as follows:

The potential 1,3-dipolar character of betaines, such as (II), is as expected (Katritzky & Dennis, 1979).

The type of layered packing arrangement (along **a** with an offset of 0.33 Å) found in (IIa) is associated with relatively small inter-ring dihedral angles. Apparently, sufficient energy is gained in this type of structure relative to some hypothetical arrangement having less planar molecules to offset the increase in intramolecular energy. Only $Br \cdots C(9^i)$ 3.373 (3), $Br \cdots H(9^i)$ 3.01 (3) and $O(6) \cdots H(5^{ii})$ 2.31 (3) Å [(i) $1-x$, $1-y$, $\bar{z}$; (ii) $\bar{x}$, $1-y$, $1-z$] are considerably shorter

than the sum of the van der Waals radii (Br 1.95, C 1.70, N 1.50, O 1.40, H 1.20 Å) (Pauling, 1960).

References

Amit, A. G. & Hope, H. (1966). *Acta Chem. Scand.* **20**, 835–844.
Ballard, R. E. & Norris, E. K. (1975). *Acta Cryst.* B**31**, 626–628.
Bar, I. & Bernstein, J. (1981). *Acta Cryst.* B**37**, 569–575.
Caristi, C., Gattuso, M., Ferlazzo, A. & Stagno D'Alcontres, G. (1983). *Tetrahedron Lett.* **24**, 1285–1288.
Chang Sun Choi & Abel, J. E. (1972). *Acta Cryst.* B**28**, 193–201.
Churchill, M. R. (1973). *Inorg. Chem.* **12**, 1213–1214.
Dewar, M. J. S. & Schmeising, H. N. (1968). *Tetrahedron*, **11**, 96–120.
Domenicano, A., Mazzeo, P. & Vaciago, A. (1976). *Tetrahedron Lett.* pp. 1029–1032.
Domenicano, A., Vaciago, A. & Coulson, C. A. (1975). *Acta Cryst.* B**31**, 221–234.
Hamor, M. J. & Hamor, T. A. (1978). *Acta Cryst.* B**34**, 863–866.
International Tables for X-ray Crystallography (1968). Vol. III, p. 270. Birmingham: Kynoch Press.
International Tables for X-ray Crystallography (1974). Vol. IV, pp. 99–101, 149–150. Birmingham: Kynoch Press.
Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
Katritzky, A. R. & Dennis, N. (1979). *Recent Progress in the Cycloaddition Reactions of 3-Oxidopyridinium Betaines and Analogous Compounds* in *New Trends in Heterocyclic Chemistry.* Amsterdam: Elsevier.
Kelemen, J., Kormány, G. & Rihs, G. (1982). *Dyes Pigments,* **3**, 249–271.
Lofthus, A. (1959). *Mol. Phys.* **2**, 367–371.
Molecular Structures and Dimensions (1972). Vol. A1, edited by O. Kennard, D. G. Watson, F. H. Allen, N. W. Isaacs, W. D. S. Motherwell, R. C. Pettersen & W. G. Town, p. S2. Utrecht: Oosthoek.
Moreiras, D., Solans, J., Solans, X., Miravitlles, C., Germain, G. & Declercq, J. P. (1981). *Acta Cryst.* B**37**, 737–739.
Pauling, L. (1960). *The Nature of the Chemical Bond,* 3rd ed., p. 260. Ithaca: Cornell Univ. Press.
Trombetti, A. (1968). *Can. J. Phys.* **46**, 1005–1011.

Structure of 1'-(p-Bromophenyl)-3'-ethyl-1',3',4',5'-tetrahydro-1,2-dideoxy-D-*glycero*-L-*gluco*-heptofuranoso[1,2-d]imidazole-2'-thione,* $C_{16}H_{21}BrN_2O_5S$

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Abstract. $M_r = 433.3$, orthorhombic, $P2_12_12_1$, $a = 8.466$ (2), $b = 27.136$ (5), $c = 7.776$ (5) Å, $V = 1786$ (1) Å³, $Z = 4$, $D_m = 1.60$ (1), $D_x = 1.61$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.7107$ Å, $\mu = 2.42$ mm⁻¹, $F(000) = 888$, 300 K, $R = 0.045$ for 1196 observed independent reflexions. The sugar ring adopts a $^4T_3$ conformation and the dihedral angle in the bicycle is 72.2 (4)°. Intermolecular hydrogen bonds link molecules related by a screw axis to give helical chains parallel to |001|.

* IUPAC name: 6-(p-bromophenyl)-4-ethyl-3-hydroxy-2-(1,2,3-trihydroxypropyl)-2,3,3a,5,6,6a-hexahydrofuro[2,3-d]imidazole-5(4H)-thione.

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Introduction. The structure determination of the title compound
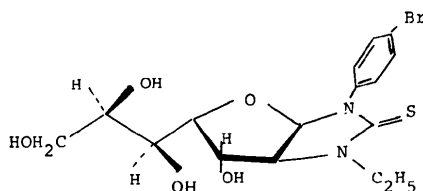
was undertaken as part of a wider research project involving compounds obtained by reaction of 2-deoxy-2-ethyl(propyl)aminohexose(heptose) with aryl (alkyl) isothiocyanates (García Gonzalez, Galbis-Pérez, Fernandez-Garcia-Hierro & Fernández-Bolaños, 1979; Galbis-Pérez, Pinto Corraliza, Román-Galán & Goméz-Guillén, 1979), whose principal aim is to establish the conformational details of the molecular structure in the solid state. The furanoid structure for the sugar moieties of these compounds is now well confirmed (Conde, López-Castro & Márquez, 1978). The title compound has been prepared (Galbis-Pérez, Palacios, Jiménez-Requejo, Avalos & Fernández-Bolaños, 1983) by condensation of 2-amino-2-deoxy-D-glycero-L-gluco-heptose (Galbis-Pérez, Pinto Corraliza, Román-Galán & Goméz-Guillén, 1979) and fractioned crystallization separation. Its chemical nature was established from elemental analysis and spectroscopic data and the X-ray analysis was carried out to define the structural details.

Experimental. Single crystals in the form of prisms elongated along [001] prepared in the Organic Chemistry Department of the University of Extremadura and kindly supplied by Professor J. Galbis; D_m by flotation; crystal $0.07 \times 0.09 \times 0.12$ mm, unit-cell parameters by least squares from 44 reflexions, Enraf–Nonius CAD-4 diffractometer, $2\theta_{max} = 60°$ ($h \le 11$, $k \le 38$, $l \le 10$), ω–2θ scan, three reflexions monitored, variation less than 1% of mean intensity, 2961 independent reflexions measured, 1765 unobserved, $I < 2\sigma(I)$, Lorentz–polarization but no absorption ($\mu R \sim 0.2$) or extinction corrections; structure solved by Patterson function and heavy-atom method with initial set of phases based on the Br-atom positon; full-matrix least-squares refinement on F, anisotropic; difference Fourier synthesis (calculated up to sin $\theta/\lambda = 0.5$ Å^{-1}) revealed 21 H-atom positions; isotropic temperature factor for each H atom equal to that of the atom bonded to it, further refinement including H positional parameters and anomalous dispersion for Br and S (*International Tables for X-ray Crystallography*, 1974), $wR = 0.057$, weighting scheme based on a statistical count criterion; the enantiomorphic form of the molecule was considered and final $wR = 0.045$ to give absolute configuration; crystallographic programs

of XRAY70 (Stewart, Kundell & Baldwin, 1970) used throughout.*

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* (Å$^2 \times 10^3$)

$$U_{eq} = \frac{1}{3}\sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j \cos (\mathbf{a}_i, \mathbf{a}_j).$$

|	x	y	z	U_{eq}
Br	1950 (2)	7530 (<1)	9420 (2)	74 (1)
S	9034 (3)	6561 (1)	6712 (4)	43 (1)
O(1)	4969 (7)	5846 (2)	3244 (10)	39 (2)
O(2)	6459 (8)	5537 (2)	126 (9)	44 (2)
O(3)	6162 (8)	4576 (2)	2779 (9)	41 (2)
O(4)	4222 (9)	4921 (2)	5709 (10)	49 (3)
O(5)	2449 (9)	4318 (2)	2079 (10)	50 (3)
N(1)	6451 (10)	6462 (3)	4666 (12)	37 (3)
N(2)	8635 (9)	6152 (3)	3612 (11)	34 (3)
C(1)	8055 (13)	6383 (3)	4970 (14)	39 (4)
C(2)	5943 (12)	6267 (3)	3048 (14)	35 (3)
C(3)	7510 (12)	6097 (3)	2224 (14)	38 (4)
C(4)	7172 (12)	5559 (3)	1770 (13)	34 (3)
C(5)	5987 (12)	5420 (3)	3160 (13)	34 (3)
C(6)	4980 (13)	4968 (3)	2717 (15)	34 (3)
C(7)	3667 (12)	4897 (3)	4048 (15)	41 (4)
C(8)	2884 (14)	4386 (4)	3800 (14)	47 (4)
C(9)	5407 (12)	6706 (3)	5822 (14)	33 (3)
C(10)	5156 (13)	6537 (4)	7461 (15)	39 (4)
C(11)	4111 (14)	6776 (4)	8528 (14)	39 (3)
C(12)	3290 (14)	7186 (4)	7923 (14)	41 (4)
C(13)	3521 (13)	8352 (3)	6293 (15)	46 (4)
C(14)	4573 (13)	7111 (3)	5219 (14)	40 (4)
C(15)	10335 (13)	6065 (4)	3349 (16)	48 (4)
C(16)	11151 (15)	6492 (5)	2513 (19)	69 (5)
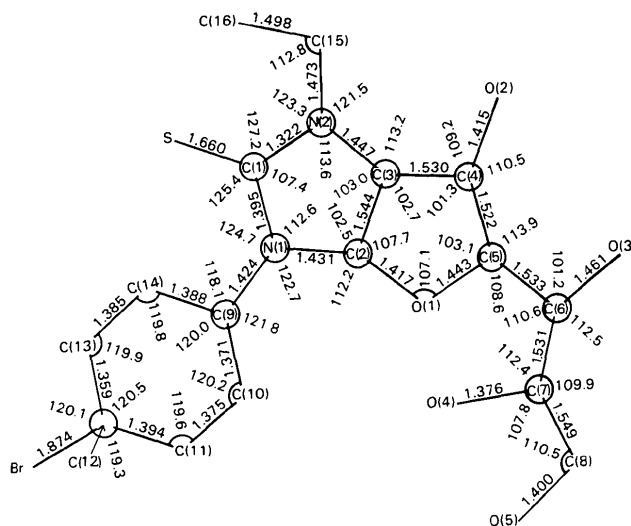
Fig. 1. Bond lengths and angles in the molecule (e.s.d.'s are in the ranges 0.011–0.017 Å and 0.8–1.0°, respectively).

Discussion. Fractional atomic coordinates and equivalent isotropic temperature factors are given in Table 1. Bond lengths and angles involving non-hydrogen atoms are shown in Fig. 1. C—H bond distances range from 0·82 (10) to 1·17 (10) Å with an average value of 1·01 (10) Å. The average O—H bond length is 0·79 (11) Å.

Bond distances and angles in the imidazolidine ring agree well with the mean values reported for analogous glucofuranoimidazolidine-2-thione compounds (Conde, López-Castro & Márquez, 1978). However, the N(1)—C(2) and N(1)—C(1) bond lengths deviate significantly from the reported mean values 1·351 (3) and 1·471 (2) Å, respectively, being close to the values reported for 1'-phenyl-1',3',4',5'-tetrahydro-1,2-dideoxyglucofuranoso[1,2-d]imidazol-2-one (Conde, Bernier & Márquez, 1980).

The observed asymmetry for the N(1)—C(1) and N(2)—C(1) bonds should indicate that the resonance form
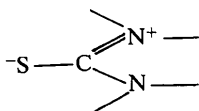
is important and, perhaps, the substituted groups at N(1) and N(2) should influence the resonance system. The imidazolidine ring is not planar; the ring atoms shift significantly from the least-squares plane [the value of the total puckering amplitude (Cremer & Pople, 1975) is $Q = 0·087$ (9) Å] and this feature has not been found for monosubstituted [only at N(1)] glucofuranoimidazolidine compounds.

Bond lengths and angles in the furanosyl ring agree with mean values reported for these compounds. The asymmetry of the endocyclic bonds O(1)—C(2) and O(1)—C(5), due to anomeric effects, observed in analogous compounds is difficult to establish in this case because of the high e.s.d.'s. The glucofuranose ring is not planar, as shown by the deviations from the least-squares plane through the five atoms of the ring. In terms of the ring-puckering coordinates (Cremer & Pople, 1975), the amplitude and phase magnitudes are $Q = 0·40$ (1) Å and $\varphi = 131·9$ (9)° for the sequence O(1)—C(2)—C(3)—C(4)—C(5) and the resulting conformation $^4T_3$ is intermediate between envelope ^4E and twist ^4_3T forms. The values of the pseudo-rotational parameters τ_m and P correspond to one of the zones of high population density in the conformational wheel defined in a statistical study, performed over a large number of sugar rings (Murray-Rust & Motherwell, 1978). The small value of the C(4)—C(3)—C(2)—O(1) = 8 (1)° torsion angle observed in this and analogous compounds may be attributed to distortion of the furanosyl ring due to the ring fusion.

The two rings show a *cis* form of coupling (Fig. 2) for which $\beta = v_1 - \delta$ and $\lambda = \mu_1 - \delta$, v_1 and μ_1 being

projected valency angles and β, γ and δ torsion angles. The relation $\beta = \gamma$ derived for a *cis* fusion involving only ternary or quaternary C atoms (Geise, Altona & Romers, 1967) holds in this case. As observed in similar compounds (Conde, López-Castro & Márquez, 1978), bonds of the C(2) and C(3) carbon atoms are nearly eclipsed. The dihedral angle between the least-squares planes of imidazolidine and furanosyl rings is 72·2 (4)°.

The phenyl ring, planar as expected, and with an average C—C distance of 1·38 (1) Å and C—C—C angle of 120 (1)°, forms a dihedral angle of 56·2 (3)° with the imidazolidine ring. This value agrees with those observed in analogous compounds studied previously in which the dihedral angle ranges from 60 to 80°, except for the value 15·1 (6)° observed in one case (Conde, Bernier & Márquez, 1980), and may indicate a significant contribution of intramolecular interaction.

Fig. 3 shows the contents of the unit cell viewed down the c axis. The structure consists of helical chains parallel to [001]. In these chains each molecule is linked by hydrogen bonds O(2)···O(3) ($\frac{3}{2} - x$, $1 - y$, $-\frac{1}{2} + z$) and O(4)···O(5) ($\frac{1}{2} - x$, $1 - y$, $\frac{1}{2} + z$) to two nearest neighbours related by a twofold screw axis. Details of the geometry of these bonds are: O(2)—H(O2) = 0·91 (12), H(O2)···O(3) = 1·87 (12) Å, O(2)—H(O2)···O(3) = 159 (10)° and O(4)—H(O4) = 0·74 (12), H(O4)···O(5) = 2·10 (12) Å, O(4)—H(O4)···O(5) = 142 (13)°. No other intermolecular contacts significantly shorter than the sum of the van der Waals radii have been detected.
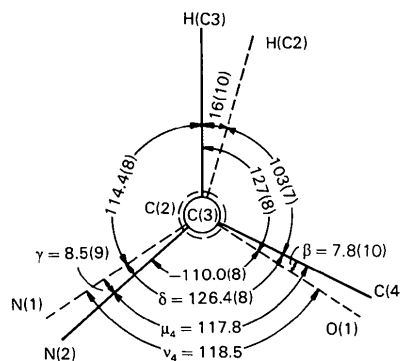

Fig. 2. Newman projection along the C(2)—C(3) bond illustrating the ring fusion (angles in deg).
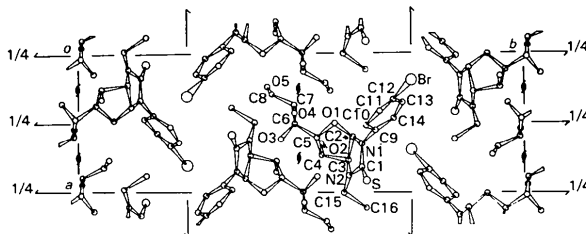

Fig. 3. A view of the cell down the c axis.

References

CONDE, A., BERNIER, F. & MÁRQUEZ, R. (1980). Acta Cryst. B36, 3048–3052.

CONDE, A., LÓPEZ-CASTRO, A. & MÁRQUEZ, R. (1978). Rev. Iberoam. Crist. Miner. Metalog. 1, 23–36.

CREMER, D. & POPLE, J. A. (1975). J. Am. Chem. Soc. 97, 1354–1358.

GALBIS-PÉREZ, J. A., PALACIOS, J. C., JIMÉNEZ-REQUEJO, J. L., AVALOS, M. & FERNÁNDEZ-BOLAÑOS, J. (1983). Unpublished results.

GALBIS-PÉREZ, J. A., PINTO CORRALIZA, R. M., ROMÁN-GALÁN, E. & GOMÉZ-GUILLÉN, M. (1979). An. Quím. 75, 387–391.

GARCÍA GONZALEZ, F., GALBIS-PÉREZ, J. A., FERNANDEZ-GARCIA-HIERRO, J. I. & FERNÁNDEZ-BOLAÑOS, J. (1979). An. Quím. 75, 1002–1004.

GEISE, H. J., ALTONA, C. & ROMERS, C. (1967). Tetrahedron, 23, 439–463.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

MURRAY-RUST, P. & MOTHERWELL, S. (1978). Acta Cryst. B34, 2534–2546.

STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The XRAY70 system. Univ. of Maryland, College Park, Maryland.

Structure of (2-Ethoxyethyl)trimethylammonium Iodide, C7H18NO+.I−

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Abstract. $M_r = 259 \cdot 1$, monoclinic, $P2_1/n$, $a = 16 \cdot 060\ (7)$, $b = 13 \cdot 231\ (6)$, $c = 10 \cdot 610\ (6)$ Å, $\beta = 94 \cdot 8\ (1)°$, $Z = 8$, $U = 2247\ (2)$ Å^3, $D_m = 1 \cdot 53$, $D_x = 1 \cdot 532$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0 \cdot 7107$ Å, $\mu = 2 \cdot 84$ mm^{-1}, $F(000) = 1024$, $T = 298$ K. Final $R = 0 \cdot 070$ for 2477 observed reflections. The overall conformation of the cations, described by the torsion angles N–C–C–O, does not markedly differ from that found in many muscarinic agents.

Introduction. We have performed the single-crystal X-ray analysis of the structure of the title ethoxy substituted choline iodide, as a part of an investigation into the conformational properties of some muscarinic agents, which we are examining in an attempt to correlate molecular conformation and biological activity. The title compound, which possesses remarkable muscarinic activity, has been considered in an extensive structure–activity analysis (Pratesi, Villa & Grana, 1968; Pratesi, Villa, Ferri, De Micheli, Grana, Santagostino Barbone, Silipo & Vittoria, 1981).

Experimental. Compound obtained by condensation of potassium ethoxide with (dimethylamino)ethyl chloride hydrochloride, distillation of resulting product and subsequent quaternization (Pratesi et al., 1968); single crystals obtained by slow evaporation of a solution in absolute ethanol, under reduced constant pressure in a dry atmosphere. D_m measured by flotation. Approximate unit-cell parameters estimated from preliminary Weissenberg and precession photographs. Prismatic crystal ~0·3 × 0·3 × 0·5 mm. Philips PW 1100 four-circle diffractometer, graphite monochromator. Accurate unit-cell parameters and crystal orientation matrices (together with their estimated standard errors) obtained from least-squares refinement of 2θ, ω, χ and φ values of 20 carefully centered high-angle (θ range 15–20°) reflections. θ–2θ scan, scan speed $0 \cdot 03°$ s^{-1}, 2θ range 4–50° ($-18 \leq h \leq 18$, $0 \leq k \leq 15$, $0 \leq l \leq 11$). Two standard reflections ($\bar{3}11$, $3\bar{1}\bar{1}$) every 180 min with no significant intensity variation during data collection. 3902 data measured, 2477 with $I \geq 3\sigma(I)$, R_{int} for 216 equivalent reflections (only $hk0$) being 0·062. Lorentz and polarization corrections, intensities placed on an absolute scale by Wilson's method, experimental

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