Acta Cryst. (1969). B25, 1119

The Crystal and Molecular Structure of Quinuclidinyl Benzilate Hydrobromide

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(*Received* 4 *June* 1968)

Crystals of quinuclidinyl benzilate hydrobromide, $C_{21}H_{23}O_3N.HBr$, are orthorhombic, space group $P2_12_12_1$ with four formula units in a cell having the dimensions $a=11{\cdot}17$, $b=19{\cdot}41$, $c=9{\cdot}01$ Å. The crystal structure was solved by the heavy-atom method and refined by three-dimensional least-squares to a final R value of 0·069. The two benzene rings make an angle of 102° to each other and the ester bridge connecting the benzene rings with the quinuclidine is almost planar. The quinuclidine skeleton is slightly twisted about its threefold axis. The short distance between the hydroxyl oxygen and the carboxyl oxygen strongly suggests an intramolecular hydrogen bond. Furthermore, both the quinuclidine nitrogen and the hydroxyl oxygen seem to be hydrogen-bonded to bromine atoms.

Introduction

Quinuclidinyl benzilate $C_{21}H_{23}O_3N$, is a psychotomimetic drug with anticholinergic potency. The crystal structure of its hydrobromide has been solved as a part of our program on the correlation between molecular configuration and pharmacological action. One of the important factors in psychoactive drugs is the availability of a free electron pair on a nitrogen atom presumed to attach an electrophilic center of the acceptor site (Gabel & Abood, 1965). Consequently it would have been even more interesting to clarify the molecular structure of the base. However, the structure determination of this substance has not yet been successful, but is in progress. The angle between the benzene rings and the presence of hydrogen bonds are other factors which are probably of importance for the adaption to the receptor. Thus, Mashkovsky & Zaitseva (1967) found that the replacement of the hydroxyl group by a methyl group in quinuclidinyl benzilate and related compounds decreased the cholinolytic activity.

A schematic drawing of the quinuclidinyl benzilate molecule (Fig. 1) shows the labelling of the atoms to be referred to later in this paper.

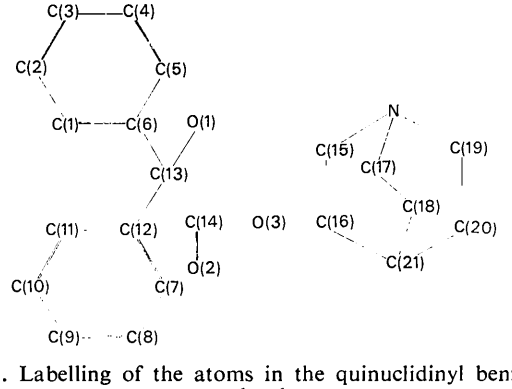

Fig. 1. Labelling of the atoms in the quinuclidinyl benzilate molecule.

Experimental

Quinuclidinyl benzilate hydrobromide was obtained from Hoffman–La Roche, Switzerland, and recrystallized in colourless, clear crystals by A. Flormark at the Research Institute of National Defence, Sweden.

The unit-cell dimensions of the crystals were determined from Weissenberg photographs with silicon as an internal standard and from automatic diffractometer measurements. The density of single crystals was determined by flotation in mixed solvents.

Crystal data

Quinuclidinyl benzilate hydrobromide,
$C_{21}H_{23}O_3N.HBr$, M.W. 418·34
$a=11{\cdot}172\pm0{\cdot}005$ Å
$b=19{\cdot}410\pm0{\cdot}009$ Å
$c=9{\cdot}014\pm0{\cdot}005$ Å
$V=1954{\cdot}7$ Å^3
$D_m=1{\cdot}423\pm0{\cdot}002$ g.cm^{-3}
D_x $(Z=4)=1{\cdot}421\pm0{\cdot}002$ g.cm^{-3}
Absent reflexions $h00$ when h is odd
$0k0$ when k is odd
$00l$ when l is odd
Space group $P2_12_12_1$

Intensity data were collected in two ways. With the use of the usual multiple film and equi-inclination technique, integrated Weissenberg photographs were recorded with Ni-filtered Cu $K\alpha$ radiation for the 0–7 layers about the c axis and the zero-layer about the a axis. The crystal used for this purpose was trimmed to $0{\cdot}40\times0{\cdot}34\times0{\cdot}41$ mm. There were 2122 independent reflexions, of which 1670 were assigned intensities greater than zero. The unobserved reflexions were given half the intensity of the treshold value. The photographic density of the reflexions and corresponding background was measured in a microdensitometer. The intensities were corrected for α_1–α_2 separation, Lorentz and polarization factors, but not for extinction or absorption.

Data from 98 observed reflexions occurring in both the zones [100] and [001] were cross-correlated so that all reflexions could be put on a common scale. Finally the structure factors were placed approximately on an absolute scale by the method due to Wilson (1942).

The second set of intensity data was collected with an automatic diffractometer (PAILRED), using Mo $K\alpha$ radiation. The crystal, having the dimensions $0{\cdot}20\times 0{\cdot}23\times 0{\cdot}17$ mm, was oriented about the a axis and 12 layers corresponding to the entire Cu sphere were recorded. These 2758 reflexions were corrected for the same factors as the Weissenberg data. All calculations were performed on an IBM 7090 computer with our program system.

Determination of the structure

The Patterson projection calculated from the initially recorded set of Weissenberg $hk0$ data made it possible to locate a Br–Br rotation peak. The first calculation of structure amplitudes for this centrosymmetric projection was based on the bromine position only. When the signs obtained were used, the electron density map showed, beside the strong bromine maximum, four additional peaks which were used for further Fourier refinement. After eight cycles of refinement the electron density map contained 26 prominent maxima and the probability index R ($R=\Sigma\,|F_o-F_c|/\Sigma\,|F_o|$) had decreased from the initial 0·54 to 0·19. Nevertheless, it was not possible to fit the projection of the anticipated configuration of the quinuclidinyl benzilate molecule onto the map. After several trials it was recognized that some maxima were false and that one of the benzene rings overlapped two carbon atoms and, moreover, was perpendicular to the plane of projection. It also became evident that the quinuclidine part of the molecule had its axis of symmetry almost perpendicular to the (001) plane. After a two-dimensional least-squares refinement with an over-all temperature factor, $B=4{\cdot}5$ Å^2, the R value dropped to 0·12.

From the projected bond lengths and from a (001) projection, refined to $R=0{\cdot}16$, preliminary z coordinates were obtained for the 26 non hydrogen atoms.

Refinement procedure

The structure was refined by a full-matrix three-dimensional least-squares program (Busing, Martin & Levy, 1962). Initially only Weissenberg data were used and the structure amplitudes were given unit weight. The atomic scattering factors were those listed in *International Tables for X-ray Crystallography* (1962), that for N^+ was interpolated from the scattering factors of O^+ and B^+. No dispersion correction was made for anomalous scattering of Br^-. The first cycles of refinement involving non-hydrogen atoms only and isotropic temperature factors yielded an R value of 0·144. A Fourier difference map prepared at this stage showed heavy extra maxima surrounding the bromine atom and it was not possible to locate the hydrogen atoms. The introduction of hydrogen atoms at probable positions caused only a very slight drop in the R value and there was no significant decrease in the standard deviation of the atomic coordinates. Since the refinement program could not accommodate all non-hydrogen atoms simultaneously when assigned anisotropic temperature factors, it was decided to exclude the hydrogen atoms from calculations. The rather time-consuming refinement procedure with anisotropic thermal parameters resulted after two cycles of refinement in an R value of 0·072. However, the calculated bond lengths were not satisfactory and a three-dimensional electron density map prepared at this stage still showed strong diffraction ripples surrounding the bromine atoms, thereby interfering with the positional parameters of some of the light atoms.

The diffractometer data which were recorded for comparison showed on closer inspection small deviations from the photographic data. Thus, the strongest reflexions in the diffractometer recording exhibited a relatively higher intensity, whereas the weakest reflexions had a larger uncertainty due to too short a scanning time. After scaling, the two sets of data were mixed so that the strongest reflexions were taken from the automatic diffractometer data while the rest were Weissenberg data. A last refinement cycle with all variables included resulted in an R value of 0·069 for 1670 observed reflexions and 0·084 for the entire material, 2122 independent reflexions. The positional and thermal parameters for the final structure are given in Tables 1 and 2 respectively. The observed and calculated structure factors are given in Table 3.

Table 1. *Final fractional atomic coordinates and their standard deviations (in parenthesis)*

	x/a	y/b	z/c
C(1)	0·4136 (9)	0·3841 (7)	0·9004 (13)
C(2)	0·4489 (12)	0·4490 (8)	0·9550 (19)
C(3)	0·4106 (12)	0·5134 (7)	0·8923 (21)
C(4)	0·3285 (12)	0·5112 (6)	0·7714 (18)
C(5)	0·2901 (12)	0·4464 (5)	0·7063 (15)
C(6)	0·3330 (7)	0·3855 (5)	0·7726 (11)
C(7)	0·1721 (12)	0·2918 (6)	0·4741 (13)
C(8)	0·1702 (12)	0·2864 (6)	0·3143 (15)
C(9)	0·2756 (14)	0·3047 (6)	0·2336 (14)
C(10)	0·3759 (13)	0·3261 (7)	0·3111 (15)
C(11)	0·3799 (10)	0·3326 (5)	0·4671 (12)
C(12)	0·2729 (9)	0·3157 (5)	0·5499 (12)
C(13)	0·2842 (10)	0·3160 (5)	0·7185 (11)
C(14)	0·1621 (9)	0·3046 (5)	0·7899 (12)
C(15)	−0·0360 (11)	0·3517 (6)	0·9877 (13)
C(16)	−0·0377 (9)	0·3534 (5)	0·8179 (12)
C(17)	−0·0723 (14)	0·4776 (7)	0·9946 (16)
C(18)	−0·0518 (12)	0·4816 (6)	0·8357 (13)
C(19)	−0·2436 (11)	0·3962 (12)	0·9740 (16)
C(20)	−0·2370 (10)	0·4066 (8)	0·8088 (15)
C(21)	−0·1000 (9)	0·4176 (6)	0·7584 (12)
O(1)	0·3640 (6)	0·2638 (3)	0·7633 (9)
O(2)	0·1334 (7)	0·2557 (3)	0·8604 (10)
O(3)	0·0883 (6)	0·3588 (3)	0·7628 (8)
N	−0·1195 (9)	0·4099 (5)	1·0392 (11)
Br	−0·2002 (1)	0·3872 (1)	0·3742 (1)

Description and discussion of the structure

The geometry of the molecule

The configuration of the molecule is illustrated in Fig. 2, which also shows the ellipsoids of thermal motion scaled to include fifty per cent probability. This figure is redrawn from a plot made on a Calcomp 580 plotter using the *ORTEP* program written by Johnson (1965). The best planes through the two benzene rings C(1)–C(6) and C(7)–C(12) calculated according to Blow (1960) are given by the equations:

$$-0{\cdot}7817X-0{\cdot}0029Y+0{\cdot}6236Z=1{\cdot}4189$$

and,

$$0{\cdot}3208X-0{\cdot}9444Y+0{\cdot}0725Z=-4{\cdot}4355,$$

respectively.

The deviations of the atoms from these planes are seen in Table 4. The angle between the ring normals is

Table 2. *Anisotropic parameters and standard deviations (in parenthesis)*

β_{ij} are the coefficients in the expression: $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	0·0054 (10)	0·0051 (5)	0·0130 (22)	−0·0015 (7)	−0·0002 (12)	−0·0054 (9)
C(2)	0·0078 (13)	0·0051 (6)	0·0225 (29)	−0·0005 (8)	−0·0026 (17)	−0·0055 (11)
C(3)	0·0100 (15)	0·0045 (6)	0·0271 (41)	−0·0022 (8)	0·0077 (23)	−0·0058 (14)
C(4)	0·0097 (15)	0·0029 (4)	0·0241 (33)	−0·0017 (6)	0·0081 (18)	−0·0030 (9)
C(5)	0·0093 (12)	0·0016 (3)	0·0180 (21)	0·0001 (5)	0·0038 (16)	−0·0005 (6)
C(6)	0·0045 (8)	0·0023 (3)	0·0074 (15)	0·0001 (4)	0·0007 (9)	−0·0019 (6)
C(7)	0·0103 (14)	0·0031 (4)	0·0074 (20)	0·0008 (6)	−0·0042 (13)	−0·0004 (6)
C(8)	0·0105 (16)	0·0025 (4)	0·0142 (25)	0·0011 (6)	−0·0034 (15)	−0·0002 (7)
C(9)	0·0136 (17)	0·0029 (4)	0·0113 (21)	0·0014 (7)	−0·0036 (17)	0·0002 (7)
C(10)	0·0104 (15)	0·0035 (5)	0·0132 (24)	0·0012 (7)	0·0042 (15)	0·0006 (8)
C(11)	0·0083 (11)	0·0022 (3)	0·0067 (18)	0·0006 (5)	0·0030 (11)	0·0000 (6)
C(12)	0·0048 (9)	0·0016 (3)	0·0096 (16)	0·0006 (4)	−0·0009 (9)	−0·0003 (5)
C(13)	0·0060 (9)	0·0019 (2)	0·0052 (15)	0·0005 (4)	−0·0033 (10)	0·0004 (4)
C(14)	0·0057 (9)	0·0021 (3)	0·0075 (18)	−0·0003 (4)	−0·0014 (10)	0·0004 (6)
C(15)	0·0109 (13)	0·0036 (4)	0·0067 (18)	0·0033 (6)	0·0033 (12)	0·0033 (7)
C(16)	0·0043 (8)	0·0026 (3)	0·0071 (17)	0·0000 (5)	0·0022 (9)	−0·0007 (6)
C(17)	0·0149 (18)	0·0028 (4)	0·0166 (31)	−0·0003 (7)	−0·0026 (19)	0·0011 (9)
C(18)	0·0120 (14)	0·0022 (3)	0·0101 (24)	0·0001 (6)	0·0003 (14)	0·0009 (7)
C(19)	0·0055 (12)	0·0114 (10)	0·0099 (21)	0·0018 (9)	−0·0004 (12)	0·0035 (12)
C(20)	0·0058 (10)	0·0054 (7)	0·0104 (23)	0·0022 (7)	−0·0013 (11)	0·0004 (9)
C(21)	0·0048 (9)	0·0033 (4)	0·0064 (17)	0·0010 (5)	−0·0010 (10)	0·0008 (6)
O(1)	0·0064 (7)	0·0022 (2)	0·0114 (13)	0·0013 (3)	−0·0016 (8)	0·0001 (4)
O(2)	0·0089 (8)	0·0023 (2)	0·0163 (15)	0·0003 (3)	0·0026 (11)	0·0023 (5)
O(3)	0·0046 (6)	0·0016 (2)	0·0129 (13)	0·0006 (3)	0·0011 (7)	0·0005 (4)
N	0·0083 (10)	0·0037 (3)	0·0093 (15)	0·0017 (5)	0·0024 (10)	0·0012 (6)
Br	0·0147 (1)	0·0024 (0)	0·0085 (1)	0·0000 (1)	0·0017 (2)	−0·0002 (1)

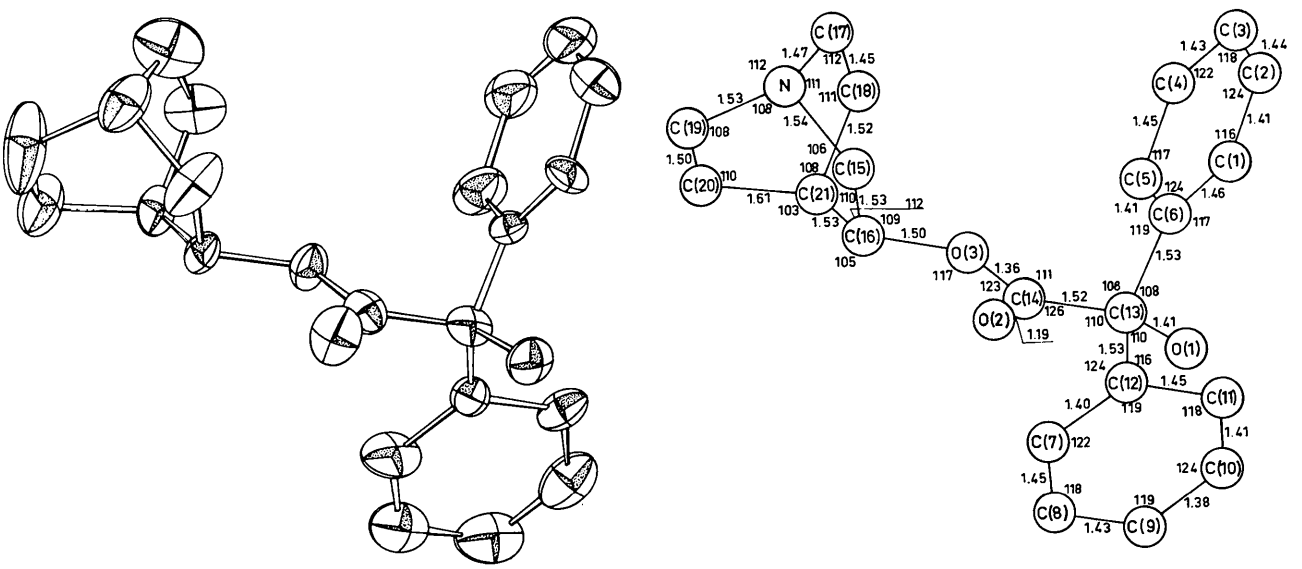

Fig. 2. A perspective drawing of the quinuclidinyl benzilate molecule, showing the ellipsoids of thermal motion with a probability of 50% (left). To the right: bond distances (Å) and angles (°).

Table 3 *Observed and calculated structure factors*

Table 3 (*cont.*)

102°. The benzene ring C(7)–C(12) is almost perpendicular to the (001) plane and so is the axis through C(21) and N of the quinuclidine nucleus, which is quite symmetric in shape. When seen along its axis of symmetry, C(21)–N, it exhibits, however, a slight distortion, the mean angle of twist being 5° ± 1° (Fig. 3). The ester bridge connecting the quinuclidine part of the molecule with the benzene rings is approximately planar. A schematic drawing, Fig. 4, of this part of the molecule shows the deviation of the atoms from the best plane having the equation: $0{\cdot}2843X+0{\cdot}4677Y+0{\cdot}8369Z=9{\cdot}2557$.

Table 4. *Deviations from the best planes through the benzene rings*

C(1)	+0·009 Å	C(7)	+0·012 Å
C(2)	+0·003	C(8)	+0·001
C(3)	−0·018	C(9)	−0·011
C(4)	+0·020	C(10)	+0·008
C(5)	−0·007	C(11)	+0·005
C(6)	−0·007	C(12)	−0·015

The bond lengths and bond angles and their e.s.d.'s are listed in Tables 5 and 6 and illustrated in Fig. 2. The mean aromatic C–C distance, 1·426 Å, is a trifle higher than the standard value but the difference is not significant. The deviation of the aromatic carbon–carbon distances (Table 5) from the mean value seems to be quite large (±0·04 Å) but even this difference is not significant according to the criteria given by Cruickshank (1953). The mean paraffinic C–C distance, 1·526 Å, and the mean C–N⁺ distance, 1·513 Å, are both very close to normal values and so are the C=O and C–O bond lengths. The rather large deviation in the bond lengths from the standard values, especially in one of the benzene rings and the quinuclidine residue, is possibly due to influence on the atomic coordinates by the strong diffraction ripples surrounding the Br atoms. The valency angles are all within the normal range.

Table 5. *Interatomic distances and standard deviations (in parenthesis)*

C(1)—C(2)	1·408 (17)	C(13)–O(1)	1·409 (11)
C(2)—C(3)	1·437 (21)	C(14)–O(2)	1·186 (12)
C(3)—C(4)	1·425 (22)	C(14)–O(3)	1·359 (11)
C(4)—C(5)	1·454 (15)	C(16)–O(3)	1·496 (11)
C(5)—C(6)	1·409 (14)		
C(6)—C(1)	1·463 (15)	C(15)–C(16)	1·531 (17)
		C(17)–C(18)	1·452 (19)
C(7)—C(8)	1·445 (17)	C(19)–C(20)	1·504 (20)
C(8)—C(9)	1·429 (19)	C(16)–C(21)	1·525 (14)
C(9)—C(10)	1·383 (18)	C(18)–C(21)	1·523 (16)
C(10)–C(11)	1·413 (17)	C(20)–C(21)	1·611 (16)
C(11)–C(12)	1·447 (15)	C(15)–N	1·537 (14)
C(12)–C(7)	1·396 (15)	C(17)–N	1·472 (16)
		C(19)–N	1·529 (16)
C(6)—C(13)	1·533 (13)		
C(12)–C(13)	1·525 (14)	O(1)···O(2)	2·726 (10)
C(13)–C(14)	1·524 (14)	O(1)···Br′	3·262 (7)
		N·····Br	3·182 (10)

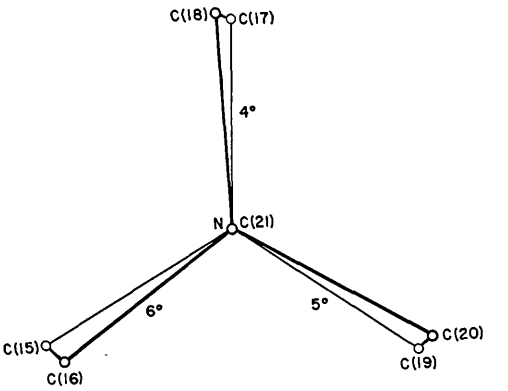

Fig. 3. The quinuclidine part of the molecule seen along its threefold axis, showing the angle of twist between the upper and lower halves.

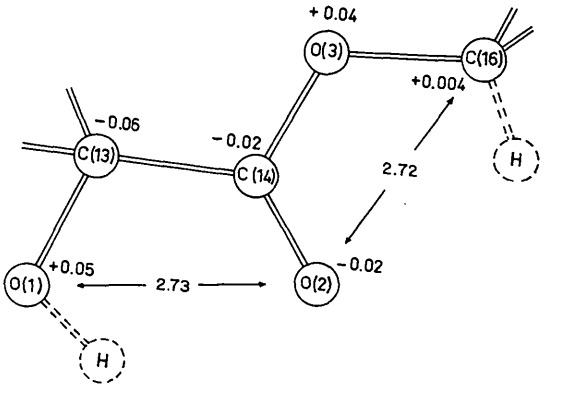

Fig. 4. The planar ester bridge part of the molecule, showing the deviation of the atoms (Å) from the best plane.

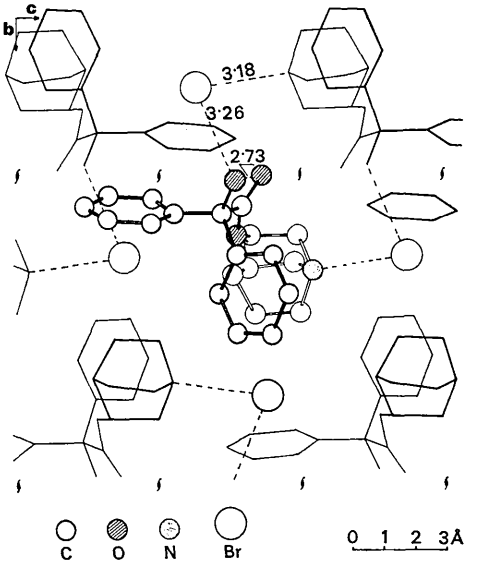

Fig. 5. Quinuclidinyl benzilate. Projection of the structure seen along the *a* axis, showing the packing of the molecules and hydrogen bonds (Å).

The cagelike quinuclidine structure, common to all bicyclo[2,2,2]octanes, is undoubtedly the most interesting part of the molecule. The question about the symmetry of these cage molecules is apparently still under discussion. A more detailed comparison with previous studies may therefore be justified even if no structure determination seems to have been carried out on quinuclidine itself (1-azabicyclo[2,2,2]octane) or any of its derivatives. The crystal structure of 1,4-diazabicyclo[2,2,2]octane (triethylenediamine) was initially determined by Wada & Kishida (1960) and later also by Weiss, Parkes, Nixon & Hughes (1964). While the first investigation indicated that the molecule possessed the highest possible symmetry, $\bar{6}m2$ (D_{3h}), the latter revealed that the lower $32(D_3)$ symmetry was also conceivable. The twist about the threefold axis should in that case be about 10°. However, a final decision between the two point group symmetries could not be made. From microwave spectra of 1-chloro and 1-bromobicyclo[2,2,2]octanes Nethercot & Javan (1953) concluded that the angle of twist should be very small, $0° \pm 4°$. In a recent crystal structure determination of bicyclo[2,2,2]octane-1,4-dicarboxylic acid, Ermer & Dunitz (1968) found no significant deviation from the higher D_{3h} symmetry. The present finding of a torsion angle of 5° is significant and indicates that the general shape of the quinuclidine molecule possesses a D_3 symmetry.

The molecular structure of a diphenyl compound, methadon (6-dimethylamino-4,4-diphenylheptan-3-one) has been determined by Hanson & Ahmed (1958). The benzene rings in this substance are connected with an sp^3 hybridized carbon atom and is therefore comparable to the benzilate part of the present structure. The angle between the benzene plane normals, calculated from the data given by Hanson & Ahmed, is 116° while it is slightly less, 102°, in the present molecule.

Hydrogen bonds and packing of the molecules

There is one short intramolecular oxygen–oxygen distance, 2·73 Å, indicating a hydrogen bond O(1)···O(2) which certainly contributes to the observed planarity of the connecting ester bridge shown in Fig. 4. The existence of this bond is supported by infrared spectroscopy (Östman, Wallerberg & Larsson, 1968).

The packing of the molecules in the unit cell and their relation to the bromine atoms is shown in Fig. 5. which is a projection onto (001). The short N···Br distance, 3·18 Å, and the favourable direction of the hydrogen indicate a $\overset{+}{\text{N}}\text{H}\cdots\text{Br}^-$ hydrogen bond. There is in addition one short intermolecular distance namely O(1)···Br, 3·26 Å, which makes it probable that the hydroxyl group not only participates in the above mentioned intramolecular hydrogen bond but may also form a hydrogen bond with the bromine ion. All other intermolecular distances are in accordance with ordinary packing requirements.

The molecular structure seems to agree with the theory of Gabel & Abood (1965). The molecule is oriented with the nitrogen atom free from steric hindrance of the other parts of the molecule.

The temperature factors

The thermal parameters of the atoms given in Table 2 and illustrated in Fig. 2 are all acceptable. The carbon atoms of the benzene rings in *para* and *meta* positions have, as could be expected, comparatively great thermal motions. In the quinuclidine residue the atoms C(15),C(17) and C(19) around the nitrogen exhibit pronounced elongated ellipsoids indicating oscillation about the axis of symmetry.

The authors gratefully acknowledge the help and interest given this study by all the members of the crystallographic group at the Department of Medical

Table 6. *Interatomic angles and standard deviations (in parenthesis)*

C(1)—C(2)—C(3)	123·9 (13)	C(12)–C(13)–C(14)	110·3 (9)
C(2)—C(3)—C(4)	117·8 (12)	O(1)—C(13)–C(14)	109·9 (7)
C(3)—C(4)—C(5)	121·6 (13)	C(13)–C(14)–O(2)	125·8 (9)
C(4)—C(5)—C(6)	117·1 (12)	C(13)–C(14)–O(3)	110·7 (8)
C(5)—C(6)—C(1)	123·9 (10)	O(2)—C(14)–O(3)	123·5 (10)
C(6)—C(1)—C(2)	115·6 (13)	C(14)–O(3)—C(16)	117·1 (7)
C(1)—C(6)—C(13)	117·0 (10)	O(3)—C(16)–C(15)	108·8 (10)
C(5)—C(6)—C(13)	118·8 (8)	O(3)—C(16)–C(21)	104·8 (8)
		C(15)–C(16)–C(21)	112·0 (9)
C(7)—C(8)—C(9)	118·5 (13)	C(16)–C(21)–C(18)	110·2 (8)
C(8)—C(9)—C(10)	119·0 (12)	C(16)–C(21)–C(20)	103·0 (9)
C(9)—C(10)–C(11)	123·7 (13)	C(18)–C(21)–C(20)	108·4 (10)
C(10)–C(11)–C(12)	117·8 (12)	C(21)–C(18)–C(17)	110·6 (11)
C(11)–C(12)–C(7)	119·3 (10)	C(21)–C(20)–C(19)	110·1 (10)
C(12)–C(7)—C(8)	121·6 (13)	C(16)–C(15)–N	106·2 (9)
C(7)—C(12)–C(13)	123·8 (11)	C(18)–C(17)–N	112·0 (12)
C(11)–C(12)–C(13)	116·4 (10)	C(20)–C(19)–N	108·3 (11)
		C(15)–N——C(17)	110·9 (10)
C(6)—C(13)–C(12)	110·5 (8)	C(17)–N——C(19)	112·0 (12)
C(6)—C(13)–O(1)	108·4 (8)	C(19)–N——C(15)	107·8 (12)
C(6)—C(13)–C(14)	108·2 (8)		
C(12)–C(13)–O(1)	109·6 (9)	Br——N——C(21)	167·5 (5)

Physics, Karolinska Institutet. We also wish to thank Dr L. Larsson, Research Institute of National Defence, Department 1, for valuable criticism of the manuscript Our sincere thanks are due to Hoffman–La Roche Co., Basel, Switzerland for supplying the substance and to A. Flormark, Research Institute of National Defence, Department 1, for preparing single crystals. The work was in part supported by the Swedish Medical Research Council (Project No B68-11*X*-144-04B).

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The Crystal and Molecular Structure of the 2-Oxide of 4-Methyl-3-(*p*-bromophenyl)-1,2,5-oxadiazole

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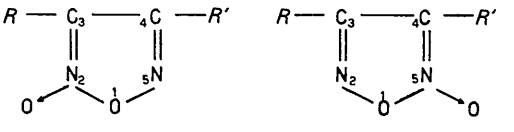
(*Received* 12 *March* 1968)

The 2-oxide of 4-methyl-3-(*p*-bromophenyl)-1,2,5-oxadiazole, BrC_6H_4–$(C_2N_2O_2)$–CH_3, is the isomer of lower melting point (88–89 °C), obtained by oxidation of methyl(*p*-bromophenyl)glyoxime. It crystallizes in the monoclinic system, space group $P2_1/n$, with four molecules in a cell having: $a_0 = 12{\cdot}720$, $b_0 = 10{\cdot}362$, $c_0 = 7{\cdot}415$ Å; $\beta = 97°\,54'$. A crystal structure analysis has been made, based on all the X-ray reflexions accessible to Cu $K\alpha$ radiation, measured with an automatic diffractometer. The molecule has the *N*-oxide structure (furoxan) and it is only approximately planar. A contact occurs between the bromine atoms and the extranuclear oxygen atoms of neighbouring molecules and this may explain the departure from strict planarity. An intramolecular contact takes place between the extranuclear oxygen atom of the furoxan group and a carbon atom of the phenyl ring; it may explain the chemical behaviour of this compound as compared with that of the higher melting isomer.

Following Wieland & Semper (1908), the term 'furoxan' is now generally accepted for those compounds which can be considered as oxidation products of α-dioximes and which are characterized by a $-C_2N_2O_2-$ nucleus. With the aryl-alkyl furoxans in particular, the existence of isomers with different chemical behaviour led to speculations about their structural formulae (*e.g.* Kaufman & Picard, 1959).

Recent neutron magnetic resonance and kinetics studies (Mallory & Cammarata, 1966) favour a positional isomerism of the following type.



I II

In order to solve this problem, we have undertaken the X-ray crystal structure analysis of the pair of