respectively. The plane through C(7) and cyano group atoms C(8) and N is

$$0.849X' - 0.468Y' + 0.247Z' = -0.594.$$

In the benzyl ring the mean valence angle 119·9° and the mean bond length 1·41 Å are in agreement with the corresponding data found in the literature. No angle in the benzyl ring differs significantly from the mean of 119·9°, nor C—C bond length from the mean of 1·41 Å. The lengths of C(1)—C(2) and C(7)—C(8) do not differ significantly.

The distortion in the angle Br—C(1)—C(2), 114·9 (1·37)°, from the tetrahedral value of 109·6° is due to an interaction between Br and N. There are no short interatomic contacts, which show that the structure is held by only van der Waals forces, which in turn are responsible for the high thermal vibrations of the atoms and the decomposition observed when the substance is exposed to the atmosphere.

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Study of Photochromic Sydnones.
II. Structure of 4-Bromo-3-(3-pyridyl)sydnone

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Abstract

The structure and absolute configuration of $C_7H_4BrN_3O_2$ have been determined by the heavy-atom method; refinement led to $R = 0.029$ for 766 observed reflexions. The unit cell is orthorhombic, space group $P2_12_12_1$, with $a = 7.175$ (2), $b = 17.018$ (8), $c = 6.875$ (3) Å, $V = 839.5$ (6) Å^3, $Z = 4$. A significant intermolecular contact between Br and O(6), 2·979 (4) Å, was found. The pyridyl rings of neighbouring molecules are stacked one over the other making a dihedral angle of 16·3°.

Introduction

The title compound changes its colour irreversibly under the influence of UV light ($\lambda < 400$ nm). The original white colour was re-established after dissolution in ethanol and recrystallization (Nešpůrek & Šorm, 1977). This anomalous behaviour was observed only with sydnone halogen derivatives. Therefore we con-sider it useful to estimate the role of the halogen substituent in the structure.

Experimental

Single crystals were synthesized by the method of Puranik & Suschitzky (1967) and grown by freezing from ethanol. The crystal used was ground to a sphere with $r = 0.15$ mm.

Crystal data

$C_7H_4BrN_3O_2$, orthorhombic, $P2_12_12_1$, $a = 7.175$ (2), $b = 17.018$ (8), $c = 6.875$ (3) Å, $V = 839.5$ (6) Å^3, $Z = 4$, $D_m = 1.84$ (3), $D_x = 1.92$ Mg m^{-3}; FW 242, m.p. 407–409 K, $F(000) = 472$, $\lambda(\text{Mo }K\alpha) = 0.71069$ Å, $\mu(\text{Mo }K\alpha) = 5.15$ mm^{-1}; the density was determined by flotation in a Clerici solution; systematic absences: $h00$ for h odd; $0k0$ for k odd; $00l$ for l odd. The dimensions of the cell were determined by refining 16 reflexions measured with an automated diffractometer (Mo $K\alpha$, graphite monochromator) at room temperature.

The intensities were measured with the same Syntex $P2_1$ diffractometer by the $\omega-2\theta$ method. The minimum scan rate was $1\cdot0°$ min^{-1}. Other measurement conditions were the same as in Hašek, Hlavatá & Huml (1977). Up to $\sin\theta/\lambda = 0\cdot595$ Å^{-1}, 894 independent reflexions were measured, 766 of which were taken as observed $(I_o > 1\cdot96\sigma_I$, where σ_I was calculated from counting statistics). During the measurements (45 kV, 20 mA, 33 h) no significant changes of the diffracted intensities were observed, though the crystal darkened completely.

Structure determination and refinement

The structure was solved by the heavy-atom method and refined by a block-diagonal least-squares procedure with a modified NRC 10 program (Ahmed, Hall, Pippy & Huber, 1966). The function minimized was $\sum w(|F_o| - |F_c|)^2$, with $w^{-1} = \sigma_F^2 + (0\cdot022F_o)^2$. Unobserved reflexions were excluded from the refinement. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974) except for H (Stewart, Davidson & Simpson, 1965). Anomalous-dispersion corrections were included for Br and O. A correction for secondary extinction was not performed because of the small, negative isotropic extinction coefficient (Stout & Jensen, 1968). No absorption correction was made.

All non-hydrogen atoms were refined anisotropically, H atoms isotropically. In the last cycle all shifts dropped below $0\cdot15$ of their e.s.d.'s. The agreement coefficients are:

$$R = \sum||F_o| - |F_c||/\sum|F_o| = 0\cdot029,$$

$$R_w = [\sum w(|F_o| - |F_c|)^2/\sum (w|F_o|^2)]^{1/2} = 0\cdot017,$$

$$S = [\sum w(|F_o| - |F_c|)^2/(m-n)]^{1/2} = 1\cdot05,$$

where $n = 132$ refined parameters, and $m = 766$ reflexions. For final parameters see Tables 1 and 2. The other possible enantiomorph $(R_w = 0\cdot030)$ was eliminated by the Hamilton (1965) test.*

The six highest maxima $(0\cdot28$ to $0\cdot56$ e Å^{-3}) on the final difference map were located at $0\cdot8$ to $1\cdot2$ Å from the Br atom, and two maxima of $0\cdot32$ e Å^{-3} were $0\cdot8$ Å from N(2) and $1\cdot9$ Å from Br.

Structure description and discussion

The numbering scheme and bond distances are given in Fig. 1. The thermal motion of the molecule was studied

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* Lists of structure factors, anisotropic thermal parameters and a list of the 13 highest maxima in the final difference Fourier synthesis have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34027 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional coordinates* $(\times10^4)$ *and equivalent $\bar{B}$ values with e.s.d.'s in parentheses*

$\bar{B} = (4/3)(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2)$ where β_{ij} is defined by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{23}kl + \beta_{13}hl)]$ for non-hydrogen atoms.

	x	y	z	$\bar{B}$ (Å^2)
O(1)	2888 (5)	5827 (2)	6244 (5)	3·5 (2)
N(2)	2956 (7)	6412 (3)	4860 (6)	3·3 (2)
N(3)	1370 (6)	6340 (2)	3939 (6)	2·7 (2)
C(4)	275 (8)	5756 (3)	4586 (8)	2·8 (2)
C(5)	1224 (8)	5403 (3)	6144 (8)	3·1 (2)
O(6)	899 (6)	4871 (3)	7258 (6)	4·3 (2)
C(7)	1062 (8)	6859 (3)	2310 (8)	2·7 (2)
C(8)	842 (9)	6539 (3)	462 (9)	3·7 (3)
N(9)	596 (7)	6972 (3)	−1123 (7)	4·2 (2)
C(10)	602 (9)	7757 (4)	−848 (9)	4·6 (3)
C(11)	822 (9)	8110 (3)	903 (9)	4·8 (3)
C(12)	1075 (9)	7662 (3)	2538 (9)	3·7 (3)
Br(13)	−2104 (1)	5535 (0)	3701 (1)	3·5 (0)

Table 2. *Fractional coordinates* $(\times10^3)$ *and isotropic temperature factors for the H atoms, with e.s.d.'s in parentheses*

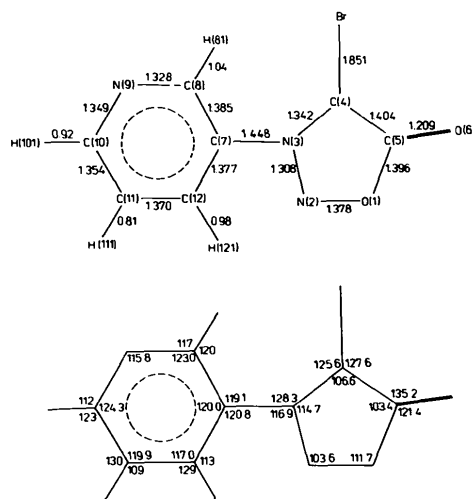|	x	y	z	B_{iso} (Å^2)
H(81)	82 (10)	593 (3)	29 (10)	7 (2)
H(101)	48 (7)	803 (3)	−200 (6)	3 (1)
H(111)	101 (9)	857 (3)	117 (8)	6 (2)
H(121)	110 (6)	782 (2)	390 (5)	2 (1)

Fig. 1. The numbering scheme of 4-bromo-3-(3-pyridyl)sydnone with bond distances and angles. E.s.d.'s of bond distances vary between 0·005 and 0·009 Å and of C—H bonds from 0·03 to 0·09 Å. Bond-angle e.s.d.'s are 0·3–0·5° for non-hydrogen atoms and 2·4–4·5° for angles involving H atoms.

by the TLS method (Schomaker & Trueblood, 1968). Only part of the molecule, consisting of the sydnone ring, Br and O(6), can be approximated by a rigid body $[\text{r.m.s.} = \{\sum_{ik}[U_{ik}(\text{exp.}) - U_{ik}(\text{calc.})]^2/n\}^{1/2} = 0\cdot0019$; e.s.d. $= \{\sum_{ik}[U_{ik}(\text{exp.}) - U_{ik}(\text{calc.})]^2/(n-s)\}^{1/2} =$

0·0023; $(r.m.s.)' = \{\sum_{ik} \sigma^2[U_{ik}(exp.)]/n\}^{1/2} = 0·0026$, where n is the number of vibration tensor components and s the number of derived quantities (20 for the TLS approximation)]. Bond-length corrections (Cruickshank, 1956) were not applied, because they lie within one e.s.d.

Differences between bond distances in the sydnone ring in this structure and in the previous one (Hašek, Obrda, Huml, Nešpůrek, Šorm & Chojnacki, 1978) checked by statistical tests were not significant. The C(4)–Br length, 1·851 (6) Å, is equal to the value in *International Tables for X-ray Crystallography* (1974).

A close intermolecular contact exists between O(6) and Br^i (Table 3). Its value of 2·979 (4) Å is about 0·37 Å shorter than the sum of the van der Waals radii (Fig. 2). The angle $C(4^i)$–Br$^i\cdots$O(6) is 178·3 (2)°. This intermolecular contact can be described as a charge-transfer interaction, similar to that in *N*-(*p*-bromophenyl)sydnone (Bärnighausen, Jellinek, Munnik & Vos, 1963), and 3-*p*-bromophenyl-1-nitroso-2-pyrazoline (Sabesan & Venkatesan, 1971). The interaction is stronger in our case; the Br$^i\cdots$O(6) distance is about 0·2 Å shorter than the similar length in the structures mentioned above.

Our IR measurements of the title compound in tetrahydrofuran solution show a single band at 178·0 mm^{-1}, which corresponds to C=O stretching. In contrast, solid-state samples show a complicated structure of the same band with three dominating maxima at 171·0, 174·5 and 177·0 mm^{-1}, which reflect the existence of interactions in the crystal.

There is also a contact, 2·939 (6) Å, between O(6) and N(2^{ii}) which is approximately equal to the sum of the van der Waals radii. Pairs of molecules are alternately linked by O(6)$\cdots$Br^i and O(6)$\cdots$N(2^{ii}) contacts. Molecules in pairs are symmetry-related by a 2_1 axis parallel to **c**.

The sydnone ring in this structure is more planar $(\chi^2 = 3·9)$ than in 3-phenyl-4-(3-methyl-1-buten-2-yl)-sydnone $(\chi^2 = 195·6)$. A detailed description of the weighted mean planes through the sydnone and pyridyl rings is given in Table 4. The angle of 59·8° between the two planes compares with 54·9° in the previous structure.

The pyridyl rings of neighbouring molecules are stacked one over the other making a dihedral angle of 16·3°. The distance between the centres of neighbouring pyridyl rings is 3·768 Å. This packing causes a higher value of the packing coefficient (Kitaigorodsky, 1970), $k = 0·80$ for 4-bromo-3-(3-pyridyl)sydnone, $k = 0·70$ for 3-phenyl-4-(3-methyl-1-buten-2-yl)sydnone. The mutual intermolecular distances of atoms in pyridyl rings are given in Table 3. It follows that this structure is consistent with the intermolecular interpretation of sydnone photochromism (Mitsui & Ebara, 1973).

Table 3. *Intermolecular distances between atoms of adjacent pyridyl rings and their e.s.d.'s* (Å)

C(7)–C(10^{iii})	3·469 (9)	N(9)–C(11^{iv})	3·432 (9)
C(8)–C(10^{iii})	3·630 (9)	–C(11^{iii})	3·755 (9)
–C(11^{iii})	3·742 (9)	–C(12^{iv})	3·443 (8)
–C(11^{iv})	3·770 (9)	C(10)–C(10^{iii})	3·872 (9)
		–C(10^{iv})	3·872 (9)
		–C(12^{iv})	3·523 (9)

Symmetry code

(i)	$-x-\frac{1}{2},\quad 1-y,\quad z+\frac{1}{2}$	(iii)	$x+\frac{1}{2},\quad \frac{1}{2}-y,\quad -z$
(ii)	$\frac{1}{2}-x,\quad 1-y,\quad z+\frac{1}{2}$	(iv)	$x-\frac{1}{2},\quad \frac{1}{2}-y,\quad -z$

Fig. 2. The structure of 4-bromo-3-(3-pyridyl)sydnone viewed along **c**.

Table 4. *Weighted mean planes*

The equations are related to the orthonormal system of coordinates. Deviations and their e.s.d.'s are in Å.

Plane (1): sydnone ring [O(1),N(2),N(3),C(4),C(5)]
$0·4280x - 0·6360y - 0·6420z + 8·1770 = 0, \chi^2 = 3·92$

Plane (2): pyridyl ring [C(7),C(8),N(9),C(10),C(11),C(12)]
$0·9899x + 0·0182y - 0·1409z - 0·7502 = 0, \chi^2 = 2·80$

	Deviation from plane (1)	Deviation from plane (2)
O(1)	0·002 (4)	0·877 (4)
N(2)	0·000 (5)	1·078 (5)
N(3)	–0·003 (4)	0·038 (4)
C(4)	0·007 (5)	–0·820 (6)
C(5)	–0·007 (5)	–0·308 (6)
O(6)	–0·022 (4)	–0·664 (5)
C(7)	0·064 (5)	0·006 (6)
C(8)	1·155 (6)	–0·002 (5)
N(9)	1·309 (5)	0·001 (6)
C(10)	0·341 (6)	–0·002 (7)
C(11)	–0·747 (7)	–0·002 (7)
C(12)	–0·907 (6)	0·006 (7)
Br	–0·093 (1)	–2·431 (1)

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The Molecular and Crystal Structure of the Alkaloid Cinchonine

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Abstract

The crystal structure of the alkaloid cinchonine, $C_{19}H_{22}N_2O$, has been solved by direct methods and refined by full-matrix least-squares computations to $R = 0.053$ for 1935 reflexions measured on a diffractometer. The monoclinic unit cell, space group $P2_1$ with $a = 10.763$ (3), $b = 7.177$ (2), $c = 11.090$ (3) Å, $\beta = 107.92$ (2)° contains two molecules. The molecules form hydrogen-bonded chains along twofold screw axes. The conformation of the free cinchonine base is the same as that found for the (cinchoninium)$^{2+}$ cation; the differences in the bond lengths and angles are discussed.

Introduction

The molecular structure and absolute configuration of diprotonated cinchonine was determined as the result of the X-ray structure analysis of cinchoninium tetra-chlorocadmate(II) dihydrate (Oleksyn, Stadnicka & Hodorowicz, 1978). It seemed interesting, therefore, to establish the structure of the free cinchonine base
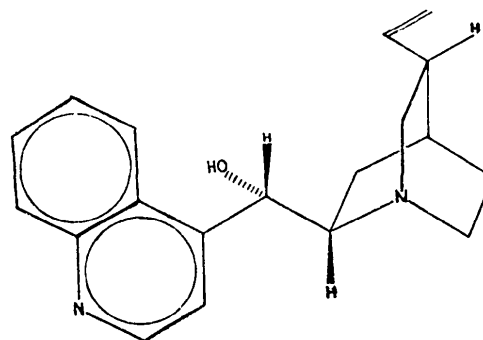
in order to study the effect of protonation on the geometry of the molecule.

Crystal data for crystalline cinchonine were first determined by Paretzkin (1956).