

tassium ion. Thus, it is to be expected that rubidium ion would not exchange unless swelling of the crystals occurred in the presence of rubidium ion. This point is being investigated and will be reported on subsequently.

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**The crystal and molecular structure of 2-bromo-*N*-salicylideneaniline.** By A. H. BURR and A. D. HOBSON\*,  
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$C_6H_4(OH)CH=NC_6H_4Br$  crystallizes in the orthorhombic space group  $P2_12_12_1$  with lattice constants  $a=12.30(4)$ ,  $b=7.09(2)$  and  $c=13.44(4)$  Å. The crystals are photochromic; the mechanism of the photo-reversible change has been attributed to the shift of the hydroxylic hydrogen atom to the nitrogen atom of one molecule. The molecular configuration verifies the existence of intramolecular hydrogen bonding and the packing is of the same type as in other *N*-salicylideneanilines whose structures are known.

### Introduction

It has been shown by earlier workers (Cohen, Hirshberg & Schmidt, 1959) that when the pale yellow crystals of anil are irradiated with near ultraviolet wavelengths an induced absorption band is produced. This corresponds to a deepening in colour of the anil crystals to orange-red. The original colour may be restored by keeping the crystals in the dark for some time, by heating them (thermal bleaching) or by exposing them to visible light (optical bleaching).

Various theories have been proposed to explain the photochromic mechanism in anils but all of the more recent ones (Cohen *et al.*, 1959; Cohen & Schmidt, 1962; Wettermark & Dogliotti, 1964; Anderson & Wettermark, 1965; Dudek & Dudek, 1966; Ledbetter, 1966; Becker & Richey, 1967) stress the importance of an enol-keto tautomerism caused by the intramolecular movement of the hydroxylic hydrogen atom to the azomethine nitrogen atom promoted by the activating radiation. The structural requirements for this mechanism in 2-bromo-*N*-salicylideneaniline were investigated by X-ray analysis.

### Experimental

2-Bromo-*N*-salicylideneaniline was prepared by condensing salicylaldehyde with *o*-bromoaniline. Recrystallization from absolute ethanol produced pale yellow crystals melting at 86°C and having a measured density of  $1.56 \pm 0.01$  g.cm<sup>-3</sup>.

Larger crystals were tabular in habit, exhibiting form {110}. X-ray examination confirmed that the compound was orthorhombic;  $a=12.30(4)$ ,  $b=7.09(2)$ ,  $c=13.44(4)$  Å. Further, systematic absences of reflexions  $h00$ ,  $0k0$  and  $00l$  for  $h$ ,  $k$  or  $l$  odd were noted, indicating space group  $P2_12_12_1$ . Hence, the assumption that the unit cell contains 4 molecules (occupying general positions) gives a calculated density of 1.60 g.cm<sup>-3</sup>.

A crystal was selected for intensity measurements and shaped into an approximate cube of side 90μ. It was mounted on a Weissenberg goniometer and zero-layer photographs were obtained with the crystal rotating first about the  $y$  axis and then about the  $x$  axis. The multiple-film technique (involving 2 packs of 4 films each) was used, with Cu  $K\alpha$  radiation. Observed intensities of 324 reflexions were acquired by visual estimation using a prepared intensity scale. Intensity values were corrected for Lorentz and polarization factors; absorption corrections were neglected on the grounds that the use of such a small crystal had made their application unnecessary. The observed intensities were put on an approximately absolute scale by employing a scaling factor derived by the Wilson (1942) method.

### Structure determination

The presence of the relatively heavy bromine atoms facilitated the interpretation of two-dimensional Patterson vector maps which were computed from the observed intensities. From projections along [100] and [010] coordinates were deduced for the bromine general position and thence a preliminary set of structure factors was calculated, based on the bromine position only. From these structure factors

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an improved scale factor and overall temperature factor were obtained by the Thewlis (1952) method.

The phased structure factors were then used in the computation of (100) and (010) electron density maps. From these maps all atomic positions except those of the hydrogen atoms were found and refined isotropically by the method of least squares until the residual index  $R$  had steadied at 0.147.

Table 1. *Atomic coordinates\**

The fractional coordinates are multiplied by  $10^4$ .

	$x$	$y$	$z$
Br	1283	5123	4251
O	8588	3563	6137
N	9392	6661	5538
C(1)	8812	6222	7205
C(2)	8510	4371	7029
C(3)	8045	2993	7791
C(4)	8026	3845	8716
C(5)	8103	6317	8966
C(6)	8686	6744	8194
C(7)	9240	7310	6446
C(8)	9683	7872	4841
C(9)	9282	9823	4646
C(10)	9558	0898	3960
C(11)	0422	0547	3267
C(12)	0808	8720	3350
C(13)	0517	7532	4110

\* The mean standard deviation for the bromine atom was 0.008 Å and for the other atoms (excluding hydrogen) was 0.05 Å.

### Discussion

Since only two-dimensional data were used the e.s.d.'s of the positional parameters were much higher than would be the case in a three-dimensional structure determination. In view of this it was felt that the inclusion of anisotropic temperature factors and hydrogen atoms in the refinement would be unjustified.

The main interest of this structure lay in the comparative intramolecular and intermolecular O...N distances. After computation of the interatomic spacings in the two cases it was found that the intramolecular distance ( $2.62 \pm 0.08$  Å) was less than the shortest intermolecular O...N distance ( $4.99 \pm 0.08$  Å), thus supporting the thesis that the movement of the hydroxylic hydrogen atom during the photochromic change is intramolecular rather than intermolecular.

The structure was also compared with the isomorphous chloro derivative (Bregman, Leiserowitz & Osaki, 1964) to examine any possible effect of the change of halogen atom. Apart from minor differences (such as the expected lengthening of the halogen-aryl contact) no significant change could be detected as far as the existing e.s.d.'s allowed.

No further work on this compound is envisaged.

This work was presented in a thesis by one of us (ADH) for the Master's degree of the University of Wales.

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**Space groups of L-tyrosine and L-tryptophane – a corrigendum.** By B. KHAWAS and G. S. R. KRISHNA MURTI, *Division of Agricultural Physics, Indian Agricultural Research Institute, New Delhi 12, India.*

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It has been kindly pointed out to us by Dr Gerald Strahs (New York Medical College, New York) that the centric space groups  $Pnam$  and  $Pmmm$  assigned to L-tyrosine and L-tryptophane (Khawas & Krishna Murti, 1969) demand the presence of DL-tyrosine and DL-tryptophane in the crystals and that the contradiction for L-tryptophane can be removed by assigning the acentric space group  $P222$  instead of  $Pmmm$ . No acentric space group can be assigned to

L-tyrosine satisfying the apparent systematic extinctions of X-ray reflexion. Presumably the extinctions are accidental.

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