

binding of tRNA and proper sequence of amino acids in the polypeptide chain.

Further work will be needed to choose between these possibilities. There is, of course, no present proof that MH acts in an identical fashion in higher plants.

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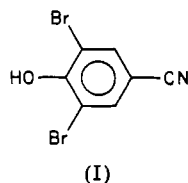
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## Crystal and Molecular Structure of Herbicides. 4. Bromoxynil

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The crystal and molecular structure of bromoxynil [3,5-dibromo-4-hydroxybenzonitrile,  $C_7H_3NBr_2O$ , triclinic,  $P\bar{1}$ ,  $a = 9.154(3)$  Å,  $b = 11.752(3)$  Å,  $c = 8.345(4)$  Å,  $\alpha = 109.03(3)^\circ$ ,  $\beta = 105.62(4)^\circ$ ,  $\gamma = 95.87(5)^\circ$ ,  $Z = 4$ , Mo  $K\alpha$  radiation,  $\rho_{\text{calcd}} = 2.301$  g  $\text{cm}^{-3}$ ,  $\mu = 106.8$   $\text{cm}^{-1}$  (correction made)] has been determined by three-dimensional X-ray analysis. The structure was solved by direct methods and refined to a final  $R = 0.065$  for 1606 observed reflections [ $|F_o| > 3\sigma(F_o)$ ]. Bromoxynil crystallizes with two nearly identical molecules in the asymmetric unit.

Bromoxynil (I) is a known inhibitor of the Hill reaction



(photosynthetic electron transport) as it will cause 50% inhibition at a concentration of 18  $\mu\text{M}$ . As a result, the

plant's energy supply is disrupted, eventually leading to death (Corbett, 1974).

One would like to have a good understanding of the exact mechanism(s) being followed in the course of a herbicide's interaction so that the compound will selectively eliminate unnecessary plants yet will not harm crops or man. It is usually assumed that Hill reaction inhibitors operate by binding to some site or sites in the chloroplast. If this is correct, and it is difficult to see how some other mechanism could operate, one would ideally require information about the nature of the site. We have embarked on a series of molecular structure determinations of herbicides (Baughman et al., 1978, 1980a,b) to better infer important structural features of this site. The distance and angle information afforded by X-ray crystallography can supply this information.

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Table I. Final Fractional Unit Cell Positional Parameters for Bromoxynil

	molecule A			molecule B		
	x	y	z	x	y	z
Br(1)	0.5373 (2) <sup>a</sup>	-0.2575 (1)	0.1046 (2)	-0.2523 (2)	0.5307 (1)	0.8496 (2)
Br(2)	0.4608 (2)	0.2318 (1)	0.3812 (2)	0.2789 (2)	0.4672 (1)	0.6340 (2)
O	0.401 (1)	-0.0497 (8)	0.277 (1)	0.047 (1)	0.5980 (7)	0.769 (1)
N	1.018 (1)	0.163 (1)	0.092 (2)	-0.142 (1)	-0.008 (1)	0.598 (2)
C(1)	0.784 (1)	0.078 (1)	0.165 (2)	-0.064 (1)	0.227 (1)	0.668 (2)
C(2)	0.740 (1)	-0.047 (1)	0.128 (2)	-0.158 (1)	0.303 (1)	0.735 (2)
C(3)	0.604 (1)	-0.089 (1)	0.158 (2)	-0.123 (1)	0.426 (1)	0.766 (2)
C(4)	0.525 (1)	-0.005 (1)	0.242 (2)	0.006 (1)	0.478 (1)	0.737 (2)
C(5)	0.574 (1)	0.118 (1)	0.278 (2)	0.099 (1)	0.397 (1)	0.667 (2)
C(6)	0.703 (1)	0.162 (1)	0.240 (2)	0.064 (1)	0.273 (1)	0.632 (2)
C(7)	0.915 (1)	0.123 (1)	0.123 (2)	-0.107 (1)	0.095 (1)	0.627 (2)
H(1)	0.800	-0.104	0.082	-0.245	0.270	0.759
H(2)	0.734	0.247	0.265	0.126	0.220	0.584

<sup>a</sup> In this and succeeding tables estimated standard deviations are given in parentheses for the least significant figures. Since the hydrogens were not refined, no standard deviations are given. Estimated standard deviations in later tables include the errors in the lattice constants.

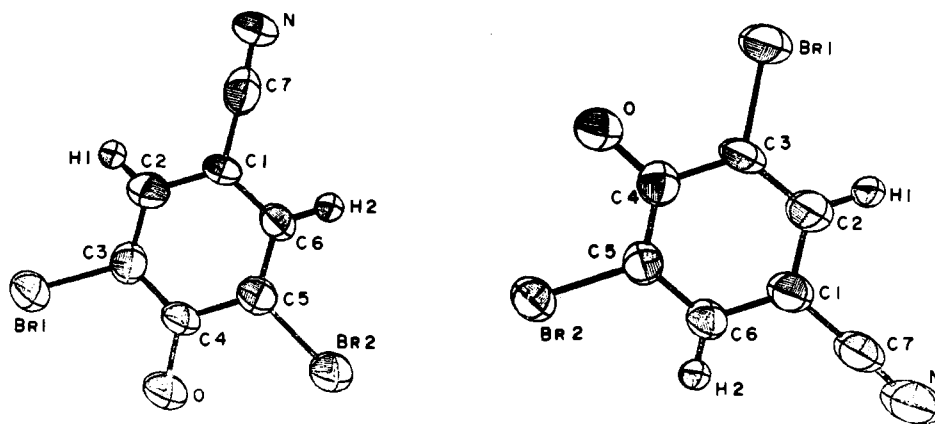


Figure 1. The two symmetry-independent bromoxynil molecules showing 50% probability ellipsoids; 30% for hydrogens. Molecule A is shown on the right; molecule B is shown on the left.

## EXPERIMENTAL SECTION

**Crystal Data.** At 27 °C using Mo K $\alpha$  radiation ( $\lambda = 0.71002$  Å), a rectangular prismatic crystal with dimensions  $0.30 \times 0.30 \times 0.20$  mm yielded the following information: triclinic,  $a = 9.154$  (3) Å,  $b = 11.752$  (3) Å,  $c = 8.345$  (4) Å,  $\alpha = 109.03$  (3)°,  $\beta = 105.62$  (4)°,  $\gamma = 95.87$  (5)°,  $Z = 4$ , space group  $P\bar{1}$ ,  $\mu = 106.8$  cm<sup>-1</sup> (correction made).

**Intensity Data, Structure Determination, and Refinement.** Four octants of data within a  $2\theta$  sphere of 45° were collected at room temperature (27 °C) with graphite monochromated Mo K $\alpha$  X radiation on an automated four-circle diffractometer designed and built in the Ames Laboratory and previously described by Rohrbaugh and Jacobson (1974). A total of 2723 reflections were recorded in the  $hkl$ ,  $h\bar{k}l$ ,  $h\bar{k}\bar{l}$ , and  $h\bar{k}l$  octants. Examination of the data revealed no systematic absences. Since there are four molecules per unit cell and a center of symmetry was predicted by a Howells et al. (1950) test, the space group was assigned as  $P\bar{1}$ . Equivalent data, corrected for Lorentz and polarization effects, were averaged, yielding 1606 observed [ $|F_o| > 3\sigma(F_o)$ ] intensities (Lawton and Jacobson, 1968). Since  $\mu = 106.8$  cm<sup>-1</sup>, an absorption correction was applied; maximum and minimum transmission factors were 0.12 and 0.041, respectively.

The structure was solved by using the program MULTAN (Main et al., 1971) to locate the four bromine atoms. This was followed by successive structure factor (Lapp and Jacobson, 1979) and electron density map (Powell and Jacobson, 1980) calculations. Refinement by full-matrix least-squares techniques (Lapp and Jacobson, 1979) minimizing the function  $\sum[\omega(|F_o| - |F_c|)^2]$ , where  $\omega = 1/\sigma_F^2$ ,

yielded a final  $R = 0.065$  using anisotropic thermal parameters for all nonhydrogen atoms. Ring hydrogens were placed at 0.95 Å from each respective carbon. As the hydroxyl hydrogens were not seen in a difference map, they were not used in the refinement. A final difference map showed no residual electron density greater than 0.5 electron.

## DESCRIPTION OF STRUCTURE

The presence of four molecules in the space group  $P\bar{1}$  requires two symmetry-independent molecules in the asymmetric unit. Coordinates for the two molecules are given in Table I (see paragraph at end of paper regarding supplementary material for more information). This in turn allows evaluation of the effects of packing forces on molecular structure since the environment around these two molecules is not quite the same. Distances and angles are noted in Tables II and III, respectively (Busing et al., 1964). No significant differences between the structures are observed as both the A and B molecules have essentially identical bond lengths and angles. Nearly all distances (Table II) are confirmed to agree with literature values (Sutton, 1958). Each C(1)-C(7) distance is essentially identical with the comparable C-C distances (1.44 and 1.43 Å) reported respectively for tetracyanobenzene (Niimura et al., 1968) and 9-cyanoanthracene (Rabaud and Clastre, 1959).

Both molecules are planar to within standard deviations, the maximum displacement of any atom being 0.09 Å, the average, 0.025 Å. The two molecules whose coordinates are given in Table I are nearly coplanar. Maximum and

Table II. Selected Distances (Angstroms) for Bromoxynil

bonding distance	A	B
C(1)-C(2)	1.38 (2)	1.39 (2)
C(2)-C(3)	1.41 (2)	1.37 (2)
C(3)-C(4)	1.40 (2)	1.39 (2)
C(4)-C(5)	1.37 (2)	1.43 (1)
C(5)-C(6)	1.40 (2)	1.37 (2)
C(6)-C(1)	1.39 (2)	1.38 (2)
C(1)-C(7)	1.44 (2)	1.46 (2)
C(3)-Br(1)	1.88 (1)	1.89 (1)
C(4)-O	1.35 (1)	1.33 (1)
C(5)-Br(2)	1.90 (1)	1.89 (1)
C(7)=N	1.14 (2)	1.15 (2)

Table III. Bond Angles (Degrees) for Bromoxynil

angle	A	B
C(1)-C(2)-C(3)	119 (1)	119 (1)
C(2)-C(3)-C(4)	120 (1)	122 (1)
C(3)-C(4)-C(5)	119 (1)	117 (1)
C(4)-C(5)-C(6)	122 (1)	122 (1)
C(5)-C(6)-C(1)	118 (1)	118 (1)
C(6)-C(1)-C(2)	122 (1)	122 (1)
C(7)-C(1)-C(2)	120 (1)	119 (1)
C(7)-C(1)-C(6)	118 (1)	120 (1)
Br(1)-C(3)-C(2)	120.2 (8)	120.2 (9)
Br(1)-C(3)-C(4)	119.4 (8)	118.1 (9)
O-C(4)-C(3)	118 (1)	124 (1)
O-C(4)-C(5)	124 (1)	119.0 (9)
Br(2)-C(5)-C(4)	119.0 (8)	117.3 (8)
Br(2)-C(5)-C(6)	118.6 (9)	120.7 (8)
N=C(7)-C(1)	177 (1)	178 (1)

average deviations from a least-squares plane containing all 26 atoms are 0.29 and 0.085 Å, respectively. Figure 1 gives a computer drawing (Johnson, 1971) of both molecules.

As there are no intermolecular distances less than those predicted by van der Waals contacts, the slight bond length and angle, disparities (Tables II and III) within each ring are likely a result of substituent effects rather than of distortions induced by intermolecular interactions. Unexpected bond length and angle anomalies and intermolecular forces strong enough to result in an active species other than the single molecule seem to be ruled out. Therefore, the distances and angles provided here should be good for theoretical comparisons of the herbicidal activity of bromoxynil.

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**Supplementary Material Available:** A listing of the observed and calculated structure factor amplitudes (4 pages). Ordering information is given on any current masthead page.

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