isolated by chromatography (cf. Table II).

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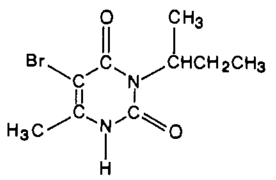
Crystal and Molecular Structure of Herbicides. 5. Bromacil (Hyvar)

Russell G. Baughman* and Pei-Jan Yu

The crystal and molecular structure of bromacil (5-bromo-3-*sec*-butyl-6-methyluracil) [monoclinic; $P2_1/n$; $a = 9.570$ (2), $b = 9.801$ (1), $c = 12.147$ (3) Å; $\beta = 106.41$ (3)°; $Z = 4$; Mo Kα radiation; $\mu = 39.65$ cm^{-1} (correction made)] has been determined by X-ray analysis. The structure was solved by the Patterson method and refined to a final $R = 0.073$ for 1004 observed reflections. Planar molecules form a dimer through NH···O intermolecular bonds. Addition of the Br and *sec*-butyl group causes a few significant bond length and angle changes in the uracil skeleton.

Bromacil (5-bromo-3-*sec*-butyl-6-methyluracil, I) is a substituted uracil herbicide. Members of this class of compounds were shown by Bucha et al. (1962) to be highly phytotoxic to a variety of plants. The mode of action of the uracils appears to be by their interference with the photosynthetic process in the plant, likely by competing with naturally occurring pyrimidines (Metcalf, 1971)



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The structural study of bromacil is part of a series (Baughman et al., 1978, 1980a,b, 1981) being carried out in order to collect a body of precise structural parameters to eventually aid in drawing interferences regarding the nature of the interaction site(s) on the chloroplast.

EXPERIMENTAL SECTION

Crystal Data. At 27 °C with graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å), a rectangular prismatic crystal with dimensions 0.36 × 0.10 × 0.16 mm yielded the following information: monoclinic; $a = 9.570$ (2), $b = 9.801$ (1), $c = 12.147$ (3) Å; $\beta = 106.41$ (3)°.

Intensity Data, Structure Determination, and Refinement. Four octants of data within a 2θ sphere of 45° were collected by the method and apparatus described by Rohrbaugh and Jacobson (1974). A total of 4095 reflections were recorded in the $\pm h,\pm k,l$ octants.

The intensity data were corrected for Lorentz and polarization effects, and since $\mu = 39.65$ cm^{-1}, an absorption correction was applied with a ϕ-scan technique (Karcher and Jacobson, 1980). The estimated variance in each intensity was calculated by

$$\sigma^2(I) = [C_T + 2C_B + (0.03C_T)^2 + (0.03C_B)^2 + (0.03C_N)^2]/A^2$$

where C_T, C_B, and C_N represent the total, background, and net counts, respectively, A is the transmission factor, and

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Table I. Final Unit Cell Positional and Isotropic Thermal Parameters and Distances from a Single Least-Squares Plane[a]

atom	x	y	z	B_{eq}[b]	D[c]
Br	1.0067 (1)[d]	0.4301 (2)	0.3122 (1)	6.7	−0.046
O1	0.5765 (8)	0.3508 (9)	0.5722 (8)	6.4	0.050
O2	0.9865 (8)	0.2086 (9)	0.4821 (8)	7.0	0.049
N1	0.7797 (9)	0.271 (1)	0.5265 (9)	5.3	−0.006
N2	0.6633 (9)	0.478 (1)	0.4479 (9)	5.5	0.047
C1	0.667 (1)	0.366 (1)	0.518 (1)	5.3	0.028
C2	0.759 (1)	0.498 (1)	0.384 (1)	5.0	−0.003
C3	0.869 (1)	0.409 (1)	0.3955 (9)	5.0	0.008
C4	0.888 (1)	0.287 (1)	0.470 (1)	5.0	0.019
C5	0.730 (1)	0.622 (2)	0.313 (1)	7.3	−0.002
C6	0.784 (1)	0.149 (2)	0.598 (1)	7.5	−0.080
C7	0.734 (2)	0.029 (2)	0.528 (2)	11.6	−1.406
C8	0.706 (2)	−0.093 (2)	0.586 (2)	12.7	−1.680
C9	0.894 (2)	0.1561 (2)	0.704 (2)	11.3	1.161
HN	0.5849	0.5481	0.4424	6.0	0.100

[a] The plane is defined by 22 atoms: the first 11 entries in this table plus the corresponding 11 related by the center of inversion $(1 - x, 1 - y, 1 - z)$. See also Figure 2. [b] $B_{eq} = {}^4/_3\sum_i\sum_j\beta_{ij}a_i \cdot a_j$. [c] D = distance from the plane to the atom coordinates as listed. Deviations of the inversion-related molecule are nearly identical in magnitude, though opposite in sign. [d] Estimated standard deviations are given in parentheses for the least significant figures. Since the hydrogens were not refined, no standard deviations are given for HN. ESD's in later tables include the errors in the lattice constants.

Table II. Selected Interatomic Distances (Angstroms)

Br—C3	1.89 (1)	C2═C3	1.34 (2)
O1═C1	1.24 (1)	C2—C5	1.47 (2)
O2═C4	1.20 (1)	C3—C4	1.47 (2)
N1—C1	1.40 (1)	C6—C7	1.44 (2)
N1—C4	1.41 (1)	C6—C9	1.42 (2)
N1—C6	1.47 (2)	C7—C8	1.45 (3)
N2—C1	1.38 (1)	O1[a]···HN[b]	1.802 (7) (2.6)[c]
N2—C2	1.37 (1)	O1[a]···N2[b]	2.80 (1) (2.9)[c]

[a] Coordinates from Table I. [b] $1 - x, 1 - y, 1 - z$. [c] Sum of van der Waals radii (Pauling, 1960).

Table III. Selected Interatomic Angles (Degrees)

C1–N1–C4	123 (1)	Br–C3–C2	121.2 (9)
C1–N1–C6	119 (1)	Br–C3–C4	115.7 (8)
C4–N1–C6	118 (1)	N1–C4–C3	114 (1)
C1–N2–C2	124 (1)	O2–C4–N1	122 (1)
N1–C1–N2	117 (1)	O2–C4–C3	124 (1)
O1–C1–N1	121 (1)	N1–C6–C7	112 (1)
O1–C1–N2	121 (1)	N1–C6–C9	113 (1)
N2–C2–C3	119 (1)	C7–C6–C9	128 (2)
N2–C2–C5	114 (1)	C6–C7–C8	118 (2)
C3–C2–C5	128 (1)	C1[a]–O1[a]···HN[b]	126.3 (8)
C2–C3–C4	123 (1)	O1[a]···HN[b]–N[b]	170.1 (5)
Torsional Angles [Signs per Klyne and Prelog (1960)]			
C1–N1–C6–C9	−104 (2)	C4–N1–C6–C7	−76 (2)
C4–N1–C6–C9	76 (2)	N1–C6–C7–C8	−168 (2)
C1–N1–C6–C7	104 (1)	C9–C6–C7–C8	45 (3)

[a] Coordinate from Table I. [b] $1 - x, 1 - y, 1 - z$.

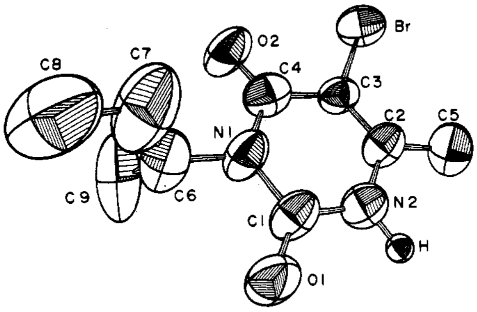

Figure 1. Bromacil molecule showing 50% probability ellipsoids, 30% for the hydrogen.

the factor 0.03 represents an estimate of nonstatistical errors. The estimated deviations in the structure factors were calculated by the finite difference method (Lawton and Jacobson, 1968). Equivalent data were averaged, yielding 1004 observed ($|F_o| > 3\sigma(F_o)$) intensities (Lawton and Jacobson, 1968). Examination of the data revealed the following systematic absences: $0k0$ when k is odd and $h0l$ when $h + l$ is odd. This implies that the space group is $P2_1/n$.

The position of the bromine atom was determined from an analysis of a standard Patterson map (Powell and Jacobson, 1980). Positions for the remaining non-hydrogen atoms were located by successive structure factor (Lapp and Jacobson, 1979) and electron density map analyses (Powell and Jacobson, 1980). The scattering factors used were those of Hanson et al. (1960) modified for the real and imaginary parts of anomalous dispersion (Templeton, 1962). The scattering factors for hydrogen were those of Stewart et al. (1965). Refinement by full-matrix least-squares techniques (Lapp and Jacobson, 1979) minimizing the function $\Sigma w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2$ yielded a final $R = \sum||F_o| - |F_c||/|F_o| = 0.073$. This R value was obtained using anisotropic thermal parameters for all non-hydrogen atoms and after the hydrogen parameters were assigned. Hydrogen positions were assigned as follows: the ring hydrogen at 1.01 Å from the nitrogen; methyl and methylene hydrogens in tetrahedral positions at 1.08 Å from the respective carbon atoms. Isotropic thermal parameters of 6.0 Å^2 were assigned to all hydrogen atoms. A final difference map (Powell and Jacobson, 1980) showed no residual electron density greater than approximately 0.5 electron/Å^3.

The final positional parameters are listed in Table I. Standard deviations were calculated from the inverse matrix of the final least-squares cycle. Bond lengths and angles are listed in Tables II and III, respectively (Busing et al., 1964). A listing of the observed and calculated structure factor amplitudes is provided as supplementary material. (See paragraph at end of paper regarding supplementary material.)

DESCRIPTION OF STRUCTURE AND DISCUSSION

The uracil portion of the bromacil molecule shown in Figures 1 and 2 (Johnson, 1971) is essentially planar (Table I) as are the parent uracil (Stewart and Jensen, 1967) and related pyrimidine (Wheatley, 1960) molecules. As with uracil, a pair of bromacil molecules is held together through an inversion center by two NH···O hydrogen bonds (Table II; Figure 2), causing the ring portions of both molecules to be essentially coplanar (Table I). However, the presence of the *sec*-butyl group on N1 in bromacil prevents formation of another hydrogen bond as is in the uracil crystal.

The addition to the uracil skeleton of bromine and a *sec*-butyl group to form bromacil causes a few significant ($\geq 3\sigma$) changes in bond lengths and angles. The C3—C4 bond length is increased from 1.43 to 1.47 Å, while C2═C3 remains the same length; C4—N1, to 1.41 from 1.371 Å; C1═O1, 1.24 from 1.215 Å; and C4═O2, 1.20 from 1.245 Å. The N1—C1—N2 angle increases to 117 from 114.0°, N2—C2═C3, 119 from 122.3°; C2═C3—C4, 123 from 118.9°; and C4—N1—C1, 123 from 126.7°. Though these changes in geometry may not be as biologically significant as the steric and charge density changes, they may prove to be subtly important in the activity of the bromacil molecule.

The presence of a center of inversion in the unit cell (Figure 2) is evidence that bromacil crystallizes as a racemic mixture, and it is likely that one enantiomorph is

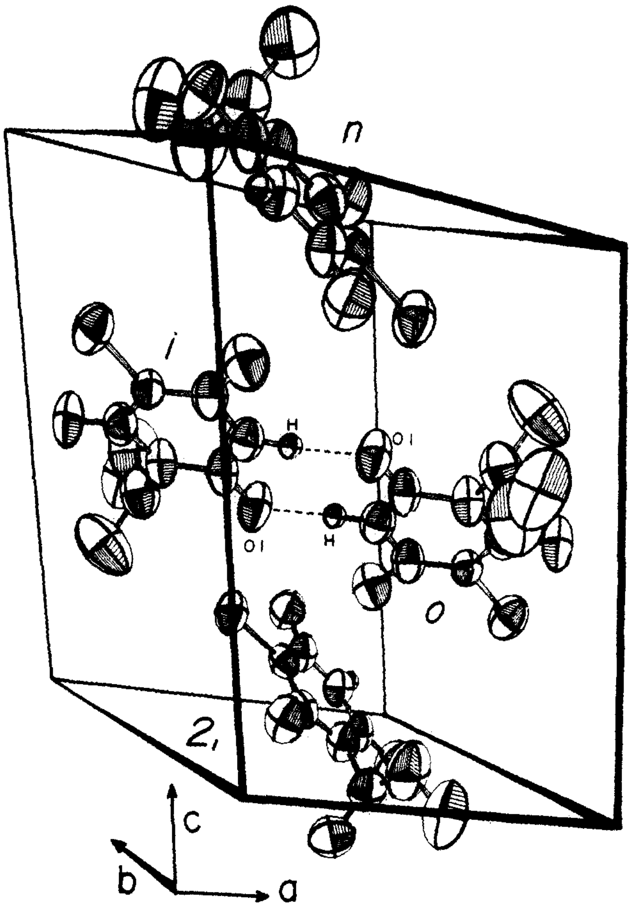

Figure 2. Unit cell of bromacil showing the four symmetry-related molecules.

more biologically active. The chirality of bromacil is due to the bonding sequence around C6, and the C6, C7, and C9 atoms in the *sec*-butyl group form a plane that is 14° from the perpendicular to the plane of the ring (Table III). So, if the rotational energy barrier about the C6—N1 bond is sufficiently high to restrict in vivo thermal interconversion of the less active into the more active enantiomorph, there may be utility in synthesizing the preferred form.

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

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