

Low-Melting 1-Methyl-2-oxo-3-(3'-*p*-bromobenzylthiocrotonyl)perhydropyrimidine

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(Received 27 March 1977; accepted 28 April 1977)

Abstract. C₁₆H₁₉N₂O₂SBr, triclinic $P\bar{1}$, $a = 17.677$ (4), $b = 8.741$ (1), $c = 5.829$ (1) Å, $\alpha = 97.29$ (1), $\beta = 99.83$ (2), $\gamma = 101.83$ (2)° (from precession photographs and single-crystal diffractometry); $Z = 2$, $D_o = 1.48$, $D_c = 1.47$ g cm⁻³ [Mammi, Del Pra, D'Angeli & Toniolo, *Ric. Sci.* (1967), **37**, 970–974]. $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu(\text{Mo } K\alpha) = 26.4$ cm⁻¹.

Introduction. Single crystals were obtained as transparent prisms elongated along *c* by slow cooling and evaporation of solutions (Mammi, Del Pra, D'Angeli & Toniolo, 1967). The intensities were collected from a crystal of approximate dimensions 0.29 × 0.11 × 0.29 mm, on a Philips PW 1100 four-circle diffractometer operating in the $\theta/2\theta$ scan mode (scan width = 1.3°, scan speed = 0.03° s⁻¹). 4984 independent reflexions up to $\theta = 30^\circ$ were measured, of which 1783 had $I > 3\sigma(I)$, $\sigma(I)$ being calculated from counting statistics. During the data collection two standard reflexions were measured every 90 min to check the stability of the crystal and the electronics. Intensities were corrected for Lorentz and polarization factors and were converted to the absolute scale by Wilson's method. Absorption and extinction corrections were applied with the program *AGNOSTC* written by Coppens, Leiserowitz & Rabinovich and modified by Hamilton, Edwards & Cahen (Coppens, 1970).

A Patterson synthesis revealed the positions of the Br and S atoms; the positions of the remaining non-hydrogen atoms were derived from a subsequent electron density map. The *R* value was 0.18. The structure was refined by full-matrix least-squares methods and the *R* value was reduced to 0.06. At this stage the H atom coordinates were calculated and then included in the refinement with isotropic temperature factors equivalent to the anisotropic factors of the atoms to which the H atoms are bonded (Hamilton, 1959); the correction for the real and imaginary parts of the anomalous dispersion was applied to Br and S only (*International Tables for X-ray Crystallography*, 1968). The final *R* value for all observed reflexions was 0.044.

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The calculations were carried out on the CYBER 76 computer of the Centro di Calcolo Interuniversitario dell'Italia Nord Orientale with the XRAY system of crystallographic programs (Stewart, Kundell & Baldwin, 1970). The scattering factors were those of Cromer & Mann (1968) for non-hydrogen atoms and from *International Tables for X-ray Crystallography* (1968) for H atoms.†

Discussion. Several reaction paths are possible in the addition of diketene to cyclic isothioureas in anhydrous conditions (Rigatti, D'Angeli, Veronese, Boccalon & Toniolo, 1969). A pair of *cis*–*trans* isomers are the principal products arising from each substrate, the *trans* isomer having a higher melting point than the *cis* (Mammi *et al.*, 1968).

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32734 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Final positional parameters and their standard deviations for non-hydrogen atoms*

	<i>x</i>	<i>y</i>	<i>z</i>
Br	0.58136 (5)	0.76374 (9)	0.8580 (1)
C(1)	0.2848 (5)	1.4043 (10)	−0.4039 (16)
C(2)	0.1675 (8)	1.2953 (13)	−0.7213 (23)
C(3)	0.1176 (7)	1.1686 (17)	−0.8582 (19)
C(4)	0.0854 (5)	1.0441 (9)	−0.7475 (14)
C(5)	0.2091 (4)	1.1371 (8)	−0.4342 (12)
C(6)	0.1186 (4)	0.8704 (8)	−0.4720 (12)
C(7)	0.1711 (3)	0.8270 (8)	−0.2813 (12)
C(8)	0.1510 (4)	0.7133 (7)	−0.1598 (12)
C(9)	0.0704 (5)	0.6005 (12)	−0.1946 (19)
C(10)	0.3065 (4)	0.8197 (8)	0.0881 (13)
C(11)	0.3708 (4)	0.7987 (8)	0.2804 (13)
C(12)	0.3849 (4)	0.8841 (8)	0.5039 (13)
C(13)	0.4461 (4)	0.8713 (8)	0.6767 (11)
C(14)	0.4939 (3)	0.7736 (7)	0.6234 (10)
C(15)	0.4809 (4)	0.6858 (7)	0.4033 (12)
C(16)	0.4197 (4)	0.6974 (8)	0.2308 (11)
N(1)	0.2184 (4)	1.2699 (7)	−0.5180 (11)
N(2)	0.1419 (3)	1.0166 (6)	−0.5456 (9)
O(1)	0.2569 (3)	1.1215 (6)	−0.2726 (11)
O(2)	0.0543 (3)	0.7847 (6)	−0.5728 (10)
S	0.2168 (1)	0.6760 (2)	0.0760 (3)

We report here the crystal and molecular structure of the low-melting isomer 1-methyl-2-oxo-3-(3'-*p*-bromobenzylthiocrotonyl)perhydropyrimidine.

The final positional and (for H) thermal parameters with their e.s.d.'s for non-hydrogen and H atoms are presented in Tables 1 and 2 respectively. A schematic drawing of the molecule with bond distances and valence angles is shown in Fig. 1.

Some least-squares-planes calculations are reported in Table 3, which indicates a molecular planarity and resonance from the ureic to the carbonyl group. In this region the bond distances and valence angles have the values expected for a conjugated system. The unusual values for the remaining distances of the pyrimidinyl ring could be explained by a statistical disorder of the

C(2) and C(3) atoms. This is supported by the very high values for their temperature factors. The vinyl group, which is planar within 0.005 Å, makes an angle of 17.8° with the above plane.

Table 3. Deviations (Å) of the atoms from some least-squares planes in the molecule, with their dihedral angles

The equations of the planes are in the form $AX + BY + CZ = D$ in orthogonal ångström space with X parallel to \mathbf{a} , Z perpendicular to \mathbf{a} in the plane of \mathbf{a} and \mathbf{c} and Y perpendicular to the plane of \mathbf{a} and \mathbf{c} . An asterisk denotes the atoms not used in the plane calculation.

$$\text{Plane 1: } 0.5233X + 0.7472Y - 0.4098Z = 7.3740$$

C(11)	0.004	C(14)	0.007
C(12)	0.0004	C(15)	-0.002
C(13)	-0.006	C(16)	-0.004
Br*	0.08	C(10)*	0.09

$$\text{Plane 2: } 0.7035X - 0.3909Y - 0.5935Z = 0.1700$$

C(5)	0.001	N(2)	0.07
O(1)	-0.01	C(6)	0.02
N(1)	-0.03	O(2)	-0.04
C(1)*	-0.17	C(2)*	0.08
C(4)*	0.09	C(7)*	0.05
C(3)*	0.48		

$$\text{Plane 3: } 0.5227X - 0.6400Y - 0.5631Z = -1.9398$$

C(6)	-0.003	C(8)	-0.006
C(7)	0.007	C(9)	0.003
O(2)*	0.26	N(2)*	-0.32
S*	-0.08	C(10)*	-0.09
C(11)*	-0.10	Br*	-0.13

Plane 1-plane 2	71.4°
Plane 1-plane 3	88.5
Plane 2-plane 3	17.8

Table 2. Fractional coordinates and thermal parameters ($\times 10^2$) for hydrogen atoms

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (Å ²)
H'(C1)	0.253	1.451	-0.289	9.8
H''(C1)	0.333	1.360	-0.395	9.8
H'''(C1)	0.317	1.373	-0.505	9.8
H'(C2)	0.130	1.378	-0.672	15.2
H''(C2)	0.205	1.362	-0.838	15.2
H'(C3)	0.070	1.195	-0.983	13.7
H''(C3)	0.154	1.110	-0.983	13.7
H'(C4)	0.035	1.078	-0.682	9.3
H''(C4)	0.062	0.930	-0.874	9.3
H(C7)	0.228	0.891	-0.236	6.2
H'(C10)	0.297	0.942	0.128	6.8
H''(C10)	0.326	0.808	-0.082	6.8
H(C12)	0.350	0.960	0.542	6.7
H(C13)	0.455	0.932	0.843	6.4
H(C15)	0.514	0.608	0.369	6.3
H(C16)	0.410	0.635	0.067	7.0
H'(C9)	0.051	0.638	-0.045	10.9
H''(C9)	0.038	0.682	-0.135	10.9
H'''(C9)	0.102	0.537	-0.301	10.9

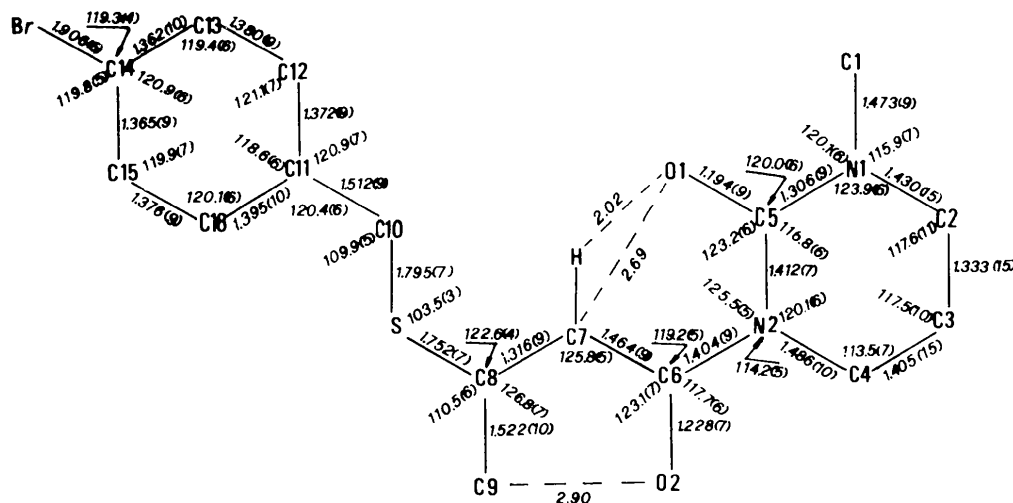


Fig. 1. Schematic drawing of the molecule with distances (Å) and angles (°).

This geometry can be explained by two particular interactions: that between C(9) and O(2) and that between the vinyl H and O(1). The former is one of repulsion, as indicated by a distance of 2.90 Å which, however, is shorter than the sum of the respective van der Waals radii. The second interaction is one of attraction and the relative positions of H, O(1) and C(7) [C...O = 2.69, H...O = 2.02 Å; ∠C-H...O = 121.2°] may suggest the formation of a C-H...O hydrogen bond.

Finally the phenyl ring makes an angle of 88.5° with the vinyl plane.

As for the crystal packing, all the intermolecular distances correspond to standard van der Waals contacts.

We thank Professor F. D'Angeli for suggesting the problem and for supplying the crystals.

References

- COPPENS, P. (1970). *Crystallographic Computing*, edited by F. R. AHMED, pp. 255–270. Copenhagen: Munksgaard.
- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A27**, 321.
- International Tables for X-ray Crystallography* (1968). Vol. III, pp. 201–212, 215. Birmingham: Kynoch Press.
- HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.
- MAMMI, M., CLEMENTE, D. A., DEL PRA, A., D'ANGELI, F., VERONESE, A. C., TONIOLO, C., RIGATTI, G., COLETTA N. & BOCCALON, G. (1968). *Chem. Commun.* pp. 741–742.
- MAMMI, M., DEL PRA, A., D'ANGELI, F. & TONIOLO, C. (1967). *Ric. Sic.* **37**, 970–974.
- RIGATTI, G., D'ANGELI, F., VERONESE, A. C., BOCCALON, G. & TONIOLO, C. (1969). *Gazz. Chim. Ital.* **99**, 1000–1016.
- STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). XRAY system. Computer Science Center, Univ. of Maryland, College Park, Maryland.

Acta Cryst. (1977). **B33**, 2977–2979

The Borine Adduct of Condylocarpine: A Case of Partially Mistaken Identity

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(Received 1 April 1977; accepted 23 May 1977)

Abstract. C₂₀H₂₅O₂N₂B, orthorhombic, $a = 10.267$ (5), $b = 16.553$ (11), $c = 10.858$ (7) Å, $Z = 4$, $P2_12_12_1$. Final R is 0.061 (1472 reflections). The structure and stereochemistry of the borine adduct of the alkaloid condylocarpine have been determined. The H atoms on B are staggered with respect to the three N–C bonds. Bond lengths and angles are in general agreement with accepted values.

Introduction. Some time ago, we were provided with crystals of a hitherto unknown compound that had been obtained by the action of mercuric acetate on the alkaloid stemmadenine (I) (Scott, 1971). The product was believed to have the molecular formula C₂₁H₂₄O₂N₂ ($M_r = 336$) and had been prepared by a mild route in a biosynthetic investigation. An X-ray analysis was undertaken to determine the structure. Cell data are as given in the *Abstract*. Systematic absences $h00$, when $h = 2n + 1$, $0k0$, when $k = 2n + 1$, and $00l$, when $l = 2n + 1$ determine the space group as $P2_12_12_1$. Data were collected on a Picker FACS-1 diffractometer (Cu $K\alpha$) and 1472 reflections out of a possible 1806 within the 2θ range 0–132° were considered observed at the 2σ level. Straightforward

application of the multiple-solution tangent-formula approach (Germain, Main & Woolfson, 1971) provided a skeleton of non-hydrogen atoms corresponding to (II). Fourier and least-squares refinement gave a structure that had one additional H atom compared with that expected for (II), $X = C$. If X were C, this would be positively charged and would thus require a corresponding negative charge. However, no evidence could be found, either by formulation of the molecule as a zwitterion or by assuming the presence of an anion in the crystal, for such a negatively charged group.

The difficulty of reconciling the apparent structure with the chemistry caused some delay in the refinement until it was realized that one of the steps following oxidation of (I) had involved treatment with borohydride, and that we were, in fact, dealing with a BH₃, not a CH₃, group on the quaternary N. In particular, the observed N–X length (~1.62 Å) was consistent with that for a B–N bond rather than for a C–N bond, and the product was thus shown to be the BH₃ adduct of the previously characterized alkaloid, condylocarpine (Sandoval, Walls, Shoolery, Wilson, Budzikiewicz & Djerassi, 1962; Biemann, Burlingame & Stauffacher, 1962). Full-matrix least-squares refinement of the