

## O-Methyl [2-(2-Methyl-5-nitro-1*H*-imidazol-1-yl)ethyl]thiocarbamate (Carnidazole) Monohydrate

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**Abstract.** C<sub>8</sub>H<sub>12</sub>N<sub>4</sub>O<sub>3</sub>S.H<sub>2</sub>O, monoclinic,  $P2_1/n$ ,  $a = 6.4455$  (9),  $b = 20.334$  (3),  $c = 9.3744$  (8) Å,  $\beta = 97.39$  (1)° (from Weissenberg photographs and single-crystal diffractometry),  $D_m = 1.423$  (by flotation),  $D_c = 1.402$  Mg m<sup>-3</sup> for  $Z = 4$ ,  $\lambda(\text{Cu } K\alpha) = 1.54178$  Å,  $\mu(\text{Cu } K\alpha) = 2.42$  mm<sup>-1</sup>. The structure was solved by direct methods. The positional and thermal parameters were refined by a block-diagonal least-squares procedure converging to a conventional  $R$  of 0.052 ( $R_w = 0.053$ ) for 1659 reflections with  $(\sin \theta/\lambda)_{\max} = 0.588$  Å<sup>-1</sup>. The nitroimidazole groups and water molecules are connected to form layers parallel to the  $bc$  plane.

**Introduction.** Carnidazole is a nitroheterocyclic compound active against both anaerobic protozoa and bacteria.

Suitable crystals were grown at room temperature by slow evaporation from an 80% water–methanol solution. Preliminary photographic data indicated a monoclinic lattice with systematic absences ( $h0l$ ,  $h + l = 2n + 1$  and  $0k0$ ,  $k = 2n + 1$ ) consistent with the space group  $P2_1/n$ . Precise cell dimensions and their associated standard deviations were obtained from a least-squares fit to the setting angles of 15 reflections.

A crystal of approximate dimensions 0.3 × 0.3 × 0.4 mm was used for the data collection with graphite-monochromated Cu  $K\alpha$  radiation on a CAD-4 automatic diffractometer. 2146 reflections were measured by  $\theta$ – $2\theta$  scans to  $2\theta_{\max} = 130^\circ$ . Of these, 1659 were considered as observed [ $I_{\text{rel}} > 2.5\sigma(I_{\text{rel}})$ ] and used in the analysis. The data were corrected for Lorentz–polarization effects but not for absorption.

The structure was solved by direct methods using the programs *SINGEN* and *PHASE* of the XRAY system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) (336  $|E|$  values  $> 1.4$ ) which gave sites for all non-hydrogen atoms. Refinement of the positional and anisotropic thermal parameters of the 17 non-hydrogen atoms by block-diagonal least-squares methods (*CRYLSQ* link of the XRAY system) resulted in  $R =$

7.8%. The 14 H atoms were then located from a difference synthesis, and they were included as a fixed-atom contribution with the isotropic temperature factors of their parent atoms. Final refinement gave  $R = 5.2\%$ . The average and maximum shift-to-error ratios for the last cycle were 0.13 and 0.53. The final difference map showed maximum densities of 0.3 e Å<sup>-3</sup>.

The scattering factors of Cromer & Mann (1968) were used for the non-hydrogen atoms, those of Stewart, Davidson & Simpson (1965) for H. Table 1

Table 1. *Positional parameters* ( $\times 10^4$ , for H  $\times 10^3$ )

|        | <i>x</i>  | <i>y</i>    | <i>z</i> |
|--------|-----------|-------------|----------|
| N(1)   | 5491 (4)  | 8316 (1)    | 3212 (3) |
| C(2)   | 5534 (6)  | 8206 (2)    | 1805 (4) |
| N(3)   | 5730 (5)  | 7564 (2)    | 1514 (4) |
| C(4)   | 5804 (6)  | 7253 (2)    | 2801 (4) |
| C(5)   | 5639 (6)  | 7699 (2)    | 3856 (4) |
| N(6)   | 5611 (5)  | 7577 (2)    | 5324 (4) |
| O(7)   | 5560 (6)  | 6989 (2)    | 5689 (4) |
| O(8)   | 5640 (5)  | 8030 (2)    | 6198 (3) |
| C(9)   | 5392 (8)  | 8724 (2)    | 685 (4)  |
| C(10)  | 5226 (5)  | 8964 (2)    | 3871 (4) |
| C(11)  | 7290 (6)  | 9236 (2)    | 4617 (4) |
| N(12)  | 8861 (4)  | 9334 (1)    | 3666 (3) |
| C(13)  | 9069 (6)  | 9878 (2)    | 2916 (4) |
| O(14)  | 10788 (4) | 9831 (1)    | 2241 (3) |
| C(15)  | 11428 (7) | 10389 (2)   | 1453 (5) |
| S(16)  | 7455 (2)  | 10518.4 (5) | 2805 (1) |
| O(17)  | 10898 (4) | 8111 (1)    | 3906 (3) |
| H(4)   | 553       | 676         | 282      |
| H(10a) | 474       | 925         | 300      |
| H(10b) | 418       | 893         | 455      |
| H(11a) | 704       | 965         | 511      |
| H(11b) | 787       | 898         | 560      |
| H(12)  | 1000      | 896         | 363      |
| H(9a)  | 579       | 919         | 84       |
| H(9b)  | 547       | 854         | –17      |
| H(9c)  | 380       | 882         | 50       |
| H(15a) | 1000      | 1056        | 77       |
| H(15b) | 1204      | 1078        | 215      |
| H(15c) | 1259      | 1028        | 79       |
| H(17a) | 1083      | 788         | 481      |
| H(17b) | 1081      | 788         | 296      |

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contains the final atomic coordinates. Fig. 1 is a perspective view of the molecule.\*

**Discussion.** The title compound crystallizes with one water molecule in the unit cell. Bond lengths and angles are listed in Table 2. Within experimental error the chemically equivalent bond lengths and angles appear

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34046 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

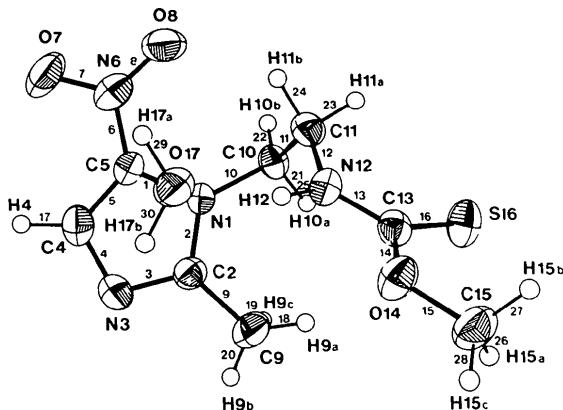


Fig. 1. An ORTEP plot (Johnson, 1976) of the title compound. The thermal ellipsoids are plotted at the 50% probability level. H atoms are represented by spheres of arbitrary radius.

Table 2. Bond distances (Å) and angles (°) with *e.s.d.*'s in parentheses

|     |           |      |           |       |           |
|-----|-----------|------|-----------|-------|-----------|
| 1   | 1.391 (4) | 11   | 1.525 (5) | 21    | 1.02      |
| 2   | 1.341 (4) | 12   | 1.447 (5) | 22    | 0.99      |
| 3   | 1.343 (5) | 13   | 1.328 (5) | 23    | 0.99      |
| 4   | 1.357 (5) | 14   | 1.348 (5) | 24    | 1.08      |
| 5   | 1.355 (5) | 15   | 1.444 (5) | 25    | 1.06      |
| 6   | 1.401 (5) | 16   | 1.661 (4) | 26    | 1.11      |
| 7   | 1.244 (5) | 17   | 1.02      | 27    | 1.08      |
| 8   | 1.232 (4) | 18   | 0.99      | 28    | 1.06      |
| 9   | 1.481 (6) | 19   | 1.04      | 29    | 1.00      |
| 10  | 1.475 (4) | 20   | 0.89      | 30    | 0.98      |
| 1-2 | 105.5 (3) | 6-7  | 116.3 (3) | 10-11 | 112.0 (3) |
| 2-3 | 112.1 (3) | 6-8  | 121.3 (3) | 11-12 | 114.0 (3) |
| 3-4 | 105.4 (3) | 7-8  | 122.3 (3) | 12-13 | 124.5 (3) |
| 4-5 | 109.9 (3) | 2-9  | 124.9 (3) | 13-14 | 109.5 (3) |
| 5-1 | 107.1 (3) | 3-9  | 123.0 (3) | 13-16 | 125.6 (3) |
| 1-6 | 125.2 (3) | 1-10 | 129.0 (3) | 14-16 | 124.9 (3) |
| 5-6 | 127.7 (3) | 2-10 | 125.4 (3) | 14-15 | 119.3 (3) |

Table 3. Dihedral angles (°)

|                       |            |                         |           |                         |            |
|-----------------------|------------|-------------------------|-----------|-------------------------|------------|
| O(7)-N(6)-C(5)-N(1)   | 173.4 (3)  | N(1)-C(10)-C(11)-N(12)  | 60.6 (4)  | C(11)-N(12)-C(13)-S(16) | -6.0 (5)   |
| O(8)-N(6)-C(5)-N(1)   | -6.7 (5)   | C(10)-C(11)-N(12)-C(13) | 87.7 (4)  | N(12)-C(13)-O(14)-C(15) | -174.9 (3) |
| C(2)-N(1)-C(10)-C(11) | -102.7 (4) | C(11)-N(12)-C(13)-O(14) | 174.6 (3) | S(16)-C(13)-O(14)-C(15) | 5.7 (4)    |

normal and agree well with values for the analogous compounds sulnidazole (Germain, Declercq, Van Meerssche & Koch, 1977) and metronidazole (Blaton, Peeters & De Ranter, 1979).

The imidazole ring is planar. The average deviation from the best plane is 0.005 Å. The nitro group rotates (4.2°) about C-N from the imidazolic plane. Dihedral angles in the side chain are given in Table 3.

The nitroimidazole groups and the water molecules are connected to form layers parallel to the *bc* plane. The water molecule forms two donor hydrogen bonds: one with O(7) of the nitro group and the other with N(3) of the imidazole group. Adjacent layers are cross-linked by a strong hydrogen bridge involving the lone pair of the O of the water molecule and the N-H function of the thiocarbamate group (Table 4). A view of the stacking of two consecutive hydrogen-bonded layers is shown in Fig. 2.

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Table 4. Details of the hydrogen bonds

| A-H...B                             | A...B       | A-H    | H...B  | ∠A-H...B |
|-------------------------------------|-------------|--------|--------|----------|
| O(17)-H(17a)...N(3) <sup>(ii)</sup> | 2.818 (4) Å | 0.98 Å | 1.84 Å | 179.6°   |
| O(17)-H(17b)...O(7) <sup>(ii)</sup> | 3.002 (4)   | 1.00   | 2.13   | 143.9    |
| N(12)-H(12)...O(17)                 | 2.806 (4)   | 1.06   | 1.82   | 151.9    |

Symmetry code

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

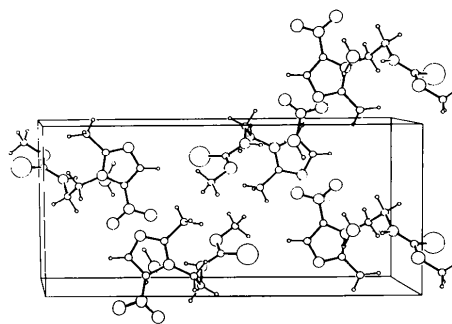


Fig. 2. Packing diagram with hydrogen bonds shown as broken lines.

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### 3,4,4 $\alpha$ ,10 $\alpha$ -Tetrahydro-7,9-dinitro-2H,5H-[1]benzopyrano[2,3-b]pyran

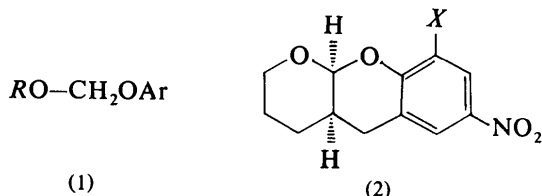
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**Abstract.** C<sub>12</sub>H<sub>12</sub>N<sub>2</sub>O<sub>6</sub>, *M<sub>r</sub>* = 280.24, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 12.777 (4), *b* = 7.954 (3), *c* = 12.448 (5) Å,  $\beta$  = 101.21 (4)°, *U* = 1241 Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.500 Mg m<sup>-3</sup>,  $\mu$ (Mo *K* $\alpha$ ) = 0.08 mm<sup>-1</sup>. The structure was refined to *R* = 0.054 for 1449 unique reflexions. The C–O lengths of the acetal group differ by 0.089 Å. One nitro group is at 43° to the plane of the benzene ring.

**Introduction.** We have shown (Jones, Kennard, Kirby & Martin, 1979, and references therein) that the differences observed between the two C–O lengths of alkyl aryl acetals (1) depend on the conformation about the acetal centre. In compounds which have a lone-pair orbital on the alkyl O atom antiperiplanar to the C–OAr bond, this bond is lengthened, and the C–OR bond shortened, compared with symmetrical acetals. This difference increases with increasing electronegativity of the OAr group, up to 0.06 Å for the 4-nitrophenyl compound (2, *X* = H) (Jones *et al.*, 1979).



Because the leaving group remains attached to the molecule, the spontaneous hydrolysis of (2, *X* = H) is

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much slower than for comparable acetals with exocyclic leaving groups (Kirby & Martin, 1978), and it has been possible to prepare the corresponding dinitro

Table 1. *Atom coordinates* ( $\times 10^4$ )

Overall isotropic temperature factor for H atoms: 0.076 (3) Å<sup>2</sup>.

|        | <i>x</i>  | <i>y</i>  | <i>z</i> |
|--------|-----------|-----------|----------|
| O(1)   | 5992 (2)  | 3309 (2)  | 2715 (1) |
| C(2)   | 5046 (3)  | 2447 (4)  | 2865 (2) |
| C(3)   | 4812 (3)  | 2737 (5)  | 3993 (3) |
| C(4)   | 5779 (3)  | 2232 (4)  | 4857 (2) |
| C(4A)  | 6761 (2)  | 3164 (3)  | 4662 (2) |
| C(5)   | 7789 (3)  | 2651 (3)  | 5435 (2) |
| C(5A)  | 8175 (2)  | 964 (3)   | 5123 (2) |
| C(6)   | 8858 (2)  | –17 (3)   | 5874 (2) |
| C(7)   | 9202 (2)  | –1556 (3) | 5565 (2) |
| C(8)   | 8874 (2)  | –2208 (3) | 4529 (2) |
| C(9)   | 8199 (2)  | –1224 (3) | 3791 (2) |
| C(9A)  | 7841 (2)  | 359 (3)   | 4057 (2) |
| O(10)  | 7158 (2)  | 1199 (2)  | 3275 (1) |
| C(10A) | 6892 (2)  | 2946 (3)  | 3486 (2) |
| N(1)   | 9943 (2)  | –2535 (3) | 6370 (2) |
| O(11)  | 10169 (2) | –2004 (3) | 7309 (2) |
| O(12)  | 10302 (2) | –3837 (3) | 6077 (2) |
| N(2)   | 7856 (2)  | –1914 (3) | 2679 (2) |
| O(21)  | 7614 (2)  | –3405 (2) | 2610 (2) |
| O(22)  | 7846 (2)  | –999 (3)  | 1898 (2) |
| H(1)   | 4379      | 2896      | 2263     |
| H(2)   | 5150      | 1116      | 2751     |
| H(3)   | 4638      | 4051      | 4088     |
| H(4)   | 4132      | 1988      | 4093     |
| H(5)   | 5909      | 895       | 4809     |
| H(6)   | 5634      | 2544      | 5660     |
| H(7)   | 6626      | 4470      | 4830     |
| H(8)   | 7643      | 2584      | 6260     |
| H(9)   | 8395      | 3583      | 5397     |
| H(10)  | 9121      | 426       | 6703     |
| H(11)  | 9133      | –3430     | 4308     |
| H(12)  | 7517      | 3823      | 3405     |