found in other similar structures, where they range from 93·1 (2) to 107·9 (3)° and 102·3 (5) to 102·9 (5)° respectively (Lindgren, 1978; Becker, Ruge, Skelton & White, 1979; Christoph & Beno, 1978; Bartlett, Kimura, Nakayama & Watson, 1979; Miller, Grohmann, Dannenberg & Todaro, 1981). Further the cyclopropane bond lengths in the present study are inequivalent and the ring is more scalene than in the first two references quoted above but far less so than in the next three that contain two cyclopentene rings.

A stereoview of the molecular packing is shown in Fig. 2. The molecules are linked together by O—H···O hydrogen bonds [O—H = 0·80 (2), O···O = 2·667 (5) Å, ∠O—H···O = 176 (3)°] across the $\bar{3}$ axes, the six-membered ring of such linkages thus exhibiting a perfect chair configuration. Other than a separation of 2·30 (6) Å between symmetry-related atoms H(O14), the shortest H···H intermolecular contact is 2·44 (2) Å.

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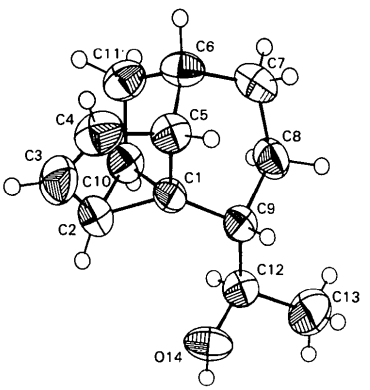


Fig. 1. View of the molecule showing thermal ellipsoids of 50% probability. H atoms are depicted as 0·1 Å radius spheres.

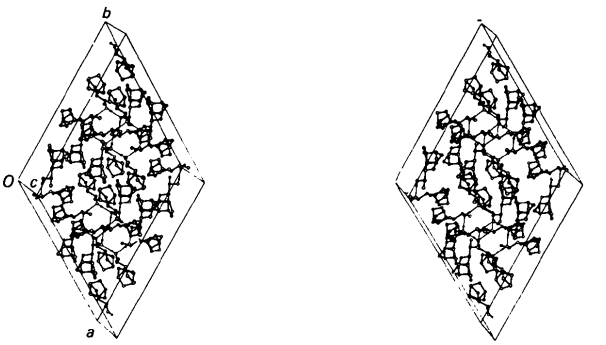


Fig. 2. Molecular packing. Hydrogen bonds are shown by thin lines and H atoms except H(O14) are omitted.

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# Structure of Azomycin (2-Nitroimidazole), $C_3H_3N_3O_2$, at 105 K

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**Abstract.** $M_r = 113·08$, monoclinic, $P2_1/c$, $a = 7·319$ (4), $b = 9·802$ (3), $c = 6·754$ (2) Å, $\beta = 115·70$ (4)°, $V = 436·6$ (4) Å$^3$ at 105 K, $Z = 4$, $D_x = 1·720$ (1), $D_m$(293 K) = 1·646 (5) Mg m$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·71069 Å, $\mu = 0·137$ mm$^{-1}$, $F(000) = 232$. Final $R = 0·040$ for 1028 unique observed reflections. The molecules are planar and connected in the **b** direction by NH···N hydrogen bonds.

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**Introduction.** The antibiotic azomycin, identified as 2-nitroimidazole by Nakamura & Umezawa (1955), has been shown to inhibit the enzyme ribonucleotide reductase of *E. coli* (Saeki, Umezawa, Tokieda-Fujishige & Hori, 1974). Structure–activity studies of inhibitors of this enzyme system have been performed recently (*cf.* Larsen, Sjöberg & Thelander, 1982). The compounds studied were hydroxyurea analogues (hydroxamic acids or hydroxyamidines). Azomycin is an example of an inhibitor with a quite different molecular structure, but it seems to react with the enzyme in the same manner as the hydroxyurea analogues (Sjöberg, unpublished results), *i.e.* by destroying the free radical of protein B2, a subunit of ribonucleotide reductase.

Table 1. *Positional parameters* ($\times 10^4$, *for* H $\times 10^3$) *and isotropic thermal parameters* (Å$^2$)

| | $x$ | $y$ | $z$ | $B_{eq}/B$ |
|---|---|---|---|---|
| N(1) | 5672 (2) | 6850 (2) | 2552 (3) | 0·91 (1)* |
| C(2) | 4659 (2) | 5697 (2) | 2492 (3) | 0·87 (1)* |
| N(3) | 5687 (2) | 4570 (2) | 2623 (2) | 0·94 (1)* |
| C(4) | 7511 (3) | 5030 (2) | 2774 (3) | 1·02 (2)* |
| C(5) | 7524 (3) | 6433 (2) | 2736 (3) | 1·07 (2)* |
| N(4) | 2625 (2) | 5707 (2) | 2279 (2) | 0·99 (2)* |
| O(1) | 1832 (2) | 6832 (1) | 2187 (3) | 1·69 (3)* |
| O(2) | 1811 (2) | 4604 (1) | 2216 (3) | 1·29 (2)* |
| H(1) | 514 (5) | 772 (3) | 242 (5) | 2·3 (3) |
| H(4) | 856 (4) | 446 (3) | 289 (4) | 1·1 (1) |
| H(5) | 851 (4) | 703 (3) | 280 (5) | 1·5 (2) |

* $B_{eq} = \frac{1}{3}\sum_i\sum_j B_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

Table 2. *Bond lengths* (Å) *and angles* (°) *for azomycin*

| | | | |
|---|---|---|---|
| N(1)–C(2) | 1·343 (3) | N(4)–O(1) | 1·235 (2) |
| C(2)–N(3) | 1·318 (3) | N(4)–O(2) | 1·226 (2) |
| N(3)–C(4) | 1·370 (3) | N(1)–H(1) | 0·93 (3) |
| C(4)–C(5) | 1·376 (3) | C(4)–H(4) | 0·93 (3) |
| C(5)–N(1) | 1·369 (3) | C(5)–H(5) | 0·92 (3) |
| C(2)–N(4) | 1·432 (2) | | |

| | | | |
|---|---|---|---|
| C(2)–N(1)–C(5) | 105·3 (2) | N(3)–C(4)–H(4) | 124 (2) |
| C(2)–N(1)–H(1) | 125 (2) | C(5)–C(4)–H(4) | 126 (2) |
| C(5)–N(1)–H(1) | 130 (2) | C(4)–C(5)–N(1) | 106·6 (2) |
| N(1)–C(2)–N(3) | 114·3 (2) | C(4)–C(5)–H(5) | 131 (2) |
| N(1)–C(2)–N(4) | 122·3 (2) | N(1)–C(5)–H(5) | 123 (2) |
| N(3)–C(2)–N(4) | 123·4 (2) | C(2)–N(4)–O(1) | 117·2 (2) |
| C(2)–N(3)–C(4) | 103·8 (2) | C(2)–N(4)–O(2) | 117·8 (2) |
| N(3)–C(4)–C(5) | 110·0 (2) | O(1)–N(4)–O(2) | 125·1 (2) |

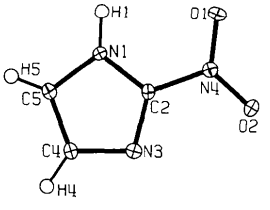


Fig. 1. *ORTEP* drawing (Johnson, 1970) of azomycin showing the conformation and the numbering scheme used. The ellipsoids enclose 50% probability. H atoms are represented by spheres of arbitrary radius.

**Experimental.** Sample of azomycin supplied by Dr J. Krogh, Roche A/S, as a gift. Crystals suitable for X-ray work obtained by slow evaporation from ethanolic solution. $D_m$ measured by flotation. Crystals grow as rectangular plates and have marked tendency to cleave into needles, with **b** as needle axis. M.p. 547–548 K (decomp.). Crystal of size 0·10 × 0·30 × 0·30 mm chosen for data collection, mounted on Enraf–Nonius CAD-4 diffractometer equipped with graphite monochromator and Nonius low-temperature device. Temperature kept at 105 (0·5) K and estimated to be correct within ±5 K. Cell dimensions determined by least squares from angular settings of 18 reflections. Intensities measured using $\theta$–$2\theta$ scan method for $\theta$ values up to 35° ($h$ 11, $k$ 15, $l$ ±10). Three standard reflections measured every 100 reflections showed no significant variations. Intensities of 2196 reflections measured, 1911 of which unique ($R_{int} = 0{\cdot}005$), 1028 reflections with $I_o \geq 2{\cdot}0\sigma(I_o)$ considered observed. No absorption corrections made. Structure solved by direct methods using *MULTAN*77 (Main, Lessinger, Woolfson, Germain & Declercq, 1977). Full-matrix least-squares refinement of positional parameters of all atoms, with anisotropic temperature factors for non-H atoms and isotropic temperature factors for H atoms. The three H atoms located in a difference map. Quantity minimized $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\{1 + [(|F_o| - 8{\cdot}5)/5{\cdot}0]^2\}$. Mean and max. $\Delta/\sigma$ in final refinement cycle 0·03 and 0·1 respectively. Final $R = 0{\cdot}040$, $wR = 0{\cdot}050$, $S = 2{\cdot}5$. $\Delta\rho$ fluctuations ±0·5 e Å$^{-3}$. Scattering factors used for H those of Stewart, Davidson & Simpson (1965), for O, N, and C those of Cromer & Mann (1968). Programs used in refinement from XRAY76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976).

**Discussion.** The final atomic parameters are listed in Table 1.* Bond lengths and angles are given in Table 2. The conformation of the molecule and the notation of the atoms are shown in Fig. 1. Like the potent inhibitors of ribonucleotide reductase earlier investigated, *i.e.* the hydroxyurea analogues (Larsen *et al.*, 1982), the azomycin molecule is nearly planar. The maximum deviation from the molecular best plane (plane I) is 0·009 (2) Å. The mean distance of the atoms of one molecule to the best plane of an adjacent molecule is 3·153 (6) Å. The imidazole ring is planar with a maximum deviation from the best plane through the ring atoms (plane II) of 0·001 (2) Å. The corresponding value for the nitro group [C(2), N(4), O(1),

* Lists of structure factors, anisotropic thermal parameters and data of best planes (I)–(III) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38962 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

and O(2), plane III] is 0·002 (2) Å; the dihedral angle between (II) and (III) is 179·2 (4)°.

The bond lengths of the imidazole ring agree very well with those found in the neutron study of imidazole at 103 K (McMullan, Epstein, Ruble & Craven, 1979), the greatest deviation [0·008 (4) Å] found in the C(4)–C(5) bond. The corresponding angles of the imidazole rings differ significantly. The observed opening of the angle at the atom to which the nitro substituent is attached, and closing of the two adjacent angles, is also observed in other nitroimidazoles (see below for references), and is probably due to the electron-withdrawing property of the nitro group. Lone-pair-induced alterations of the bond angles at N(1) and N(3) (*cf.* Simon, Schawartz & Kálmán, 1980) is also observed. In imidazole as well as in 2-nitroimidazole the N(1) ring angle is significantly greater than the N(3) angle. The same pattern is found in the room-temperature study of 2-methyl-4-nitroimidazole (Kálmán, van Meurs & Tóth, 1980), but not in protonated imidazole derivatives (Simon *et al.*, 1980) or in nitroimidazoles with a substituent in the N(1) position, *e.g.* sulnidazole (Germain, Declercq, Van Meerssche & Koch, 1977), carnidazole (Blaton, Peeters & De Ranter, 1979*a*), and metronidazole (Blaton, Peeters & De Ranter, 1979*b*). A common feature of the imidazole rings of the nitroimidazoles is that the C(2)–N(3) bond is the shortest in most cases, indicating a more or less localized double bond between these atoms. An exception is carnidazole, where no significant differences in the two C–N bonds are found. The dimensions of the nitro group are quite normal. The two N–O bond lengths differ significantly as in most of the nitroimidazole derivatives mentioned above, which are also without a molecular symmetry plane.

The packing of the azomycin molecules in the crystal is shown in Fig. 2. The molecules are arranged in layers parallel to the *ab* plane and connected by NH···N hydrogen bonds along the *b* axis [N(1)···N(3) = 2·830 (3), H(1)···N(3) = 1·91 (3) Å, ∠N(1)–H(1)···N(3) = 174 (3)° with N(3) at $1-x, y+0{\cdot}5, 0{\cdot}5-z$]. In the crystal structure of imidazole the molecules are connected by NH···N bonds of similar dimensions (McMullan *et al.*, 1979), *i.e.* 2·849 (1), 1·809 (2) Å, and 173·3 (1)°, respectively. In addition, there are probably weak contacts between the C–H groups of the imidazole ring and the O atoms of the nitro groups of neighbouring molecules, the H···O distances being in the range 2·54–2·64 (3) Å. Also, dipole–dipole forces between the molecules of adjacent layers seem to be of importance and contribute to the high melting point of the compound. The crystal structure of azomycin is an example of an efficient molecular packing, as found for other nitro-group-containing organic compounds, *cf.* Ammon & Bhattacharjee (1982).

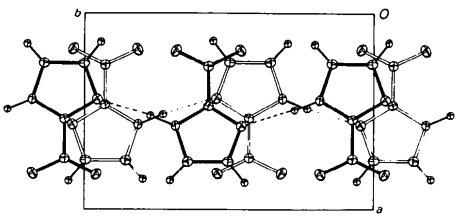


Fig. 2. The molecular packing of azomycin (Johnson, 1970) viewed along the *c* axis. Dashed lines indicate hydrogen bonds.

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