SHORT STRUCTURAL PAPERS

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2-Methyl-2-nitro-1,3-propanediol

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Abstract. $C_4H_9NO_4$; molar mass 0·13512 kg mol^{-1}; monoclinic, space group *Cc*, $a = 8{\cdot}025\,(1)$, $b = 9{\cdot}490\,(2)$, $c = 8{\cdot}960\,(3)$ Å, $\beta = 91{\cdot}57\,(3)°$; $D_m = 1{\cdot}281$, $D_c = 1{\cdot}315$ g cm^{-3} for $Z = 4$. Zr-filtered Mo $K\alpha$ radiation with automated 2θ scan for data collection. Refinement by weighted full-matrix least squares to an R of 0·054. There is no evidence for intramolecular hydrogen bonding in the crystalline state, nor is there evidence for any hydrogen bonding to the nitro groups. The intermolecular hydrogen-bonding network involves only hydroxyl groups.

Introduction. Rod and parallelepiped-shaped crystals of commercially obtained 2-methyl-2-nitro-1,3-propanediol were grown from a methanol solution containing a little dioxane. Preliminary cell dimensions were obtained from Weissenberg and precession photographs. Systematic absences were observed in *hkl* for $h + k$ odd, *h*0*l* for *l* odd, indicating possible space groups *Cc* or *C*2/*c*. The choice of the non-centrosymmetric space group *Cc* was confirmed by the structure analysis. The intensity data were measured on a Datex-automated General Electric XRD6 diffractometer. Cell dimensions were refined from 2θ measurements of 13 pairs of Friedel-related reflections.

Because the data collection for this structure determination was used to test the automated diffractometer, reflections from two asymmetric units of the space group were measured. Intensities for 4247 reflections were collected and scaled relative to the changes in the intensities of eight standard reflections, measured at regular intervals. Scaling adjustments ranged approximately 17%, most of which was attributed to volatilization of the crystal in the X-ray beam. A few very intense reflections were remeasured with the beam flux reduced and scaled such that these reflections could be included in the data reduction. Merging the symmetrically related reflections resulted in an averaged set of 1401 unique reflections, of which 224 were regarded as unobservable with $I < 1{\cdot}0\sigma(I)$ where $\sigma(I)$ was calculated from counting statistics adjusted for multiple observations.

The structure was solved with the phase-determination programs included in the crystallographic program package of the University of Maryland (XRAY 72, 1972). The phases of 145 reflections were generated from three original phases, two to define the origin and one to establish the enantiomorph. An E

Table 1. *Fractional coordinates* ($\times 10^4$; *for* H $\times 10^3$), *with estimated standard deviations in parentheses*

	x	y	z
N	1819*	2299 (3)	9525*
C(1)	2814 (5)	2358 (3)	8125 (4)
C(2)	2233 (6)	1196 (4)	7089 (5)
C(3)	2498 (5)	3819 (3)	7469 (4)
C(4)	4602 (6)	2210 (4)	8611 (5)
O(1)	2148 (6)	3155 (3)	10491 (4)
O(2)	755 (5)	1423 (3)	9659 (5)
O(3)	779 (4)	4103 (2)	7315 (4)
O(4)	4943 (5)	963 (2)	9407 (4)
H(21)	284 (4)	35 (4)	748 (3)
H(22)	297 (4)	145 (3)	618 (4)
H(23)	130 (3)	137 (2)	678 (3)
H(31)	302 (3)	376 (3)	652 (3)
H(32)	316 (3)	436 (3)	815 (4)
H(41)	481 (4)	278 (3)	921 (3)
H(42)	527 (3)	214 (3)	779 (3)
H(3)	61 (3)	412 (3)	623 (3)
H(4)	521 (4)	34 (3)	866 (4)

* Parameter fixed during refinement.

Table 2. *Interatomic distances* (Å) *and bond angles* (°)

N–O(1)	1·210 (4)	O(1)–N–O(2)	122·3 (3)
N–O(2)	1·200 (4)	O(1)–N–C(1)	117·4 (3)
C(1)–N	1·506 (4)	O(2)–N–C(1)	120·3 (3)
C(1)–C(2)	1·507 (5)	N–C(1)–C(2)	108·9 (3)
C(1)–C(3)	1·525 (4)	N–C(1)–C(3)	105·6 (3)
C(1)–C(4)	1·494 (6)	N–C(1)–C(4)	106·3 (3)
C(3)–O(3)	1·408 (6)	C(2)–C(1)–C(3)	112·5 (3)
C(4)–O(4)	1·405 (5)	C(2)–C(1)–C(4)	112·9 (3)
C(2)–H(21)	0·99 (3)	C(3)–C(1)–C(4)	110·2 (3)
C(2)–H(22)	1·05 (3)	C(1)–C(3)–O(3)	111·3 (3)
C(2)–H(23)	0·81 (2)	C(1)–C(4)–O(4)	113·5 (3)
C(3)–H(31)	0·96 (2)		
C(3)–H(32)	0·96 (3)	Hydrogen-bonding distances	
C(4)–H(41)	0·78 (3)	H(4)–O(3)	1·75 (3)
C(4)–H(42)	0·92 (2)	H(3)–O(4)	1·71 (3)
O(3)–H(3)	0·97 (3)	O(3)–O(4)	2·674 (4)
O(4)–H(4)	0·92 (3)	O(4)–O(3)	2·673 (5)

map revealed the positions of the nine nonhydrogen atoms.

The structure was refined by full-matrix least-squares methods. The coordinates of the H atoms, determined from a difference map, were included with isotropic thermal parameters in the final cycles of refinement. The final reliability indices were 0·054 and 0·036 from R and R_w, where $R = \Sigma |F_o - F_c|/\Sigma F_o$, $R_w = [\Sigma w(F_o - F_c)^2/\Sigma wF_o]^{1/2}$. The weights ($w$) were established as a function of sin θ/λ and magnitude of F such that the average $w(F_o - F_c)^2$ was independent of these quantities. The scattering factors for C, N and O were taken from *International Tables for X-ray Crystallography* (1962) and for H from Stewart, Davidson & Simpson (1965). The atomic parameters are listed in Table 1 and the bond lengths and angles in Table 2.*

Discussion. This structure determination was undertaken to investigate the possibility of intramolecular hydrogen bonding in β-nitroalcohols. It has been suggested by Urbanski (1959) that a peak shift in the 262 nm region of the ultraviolet spectra of some β-nitroalcohols in solution might be attributed to internal hydrogen bonding between hydroxyl and nitro groups, resulting in closed six-membered rings. This interpretation has been discussed by Ungnade & Kissinger (1963) and Baitinger, Schleyer, Murty & Robinson (1964). In the crystalline state, however, no intramolecular hydrogen bonding was observed in which nitro groups participated. Intermolecular hydrogen bonding between hydroxyl groups was clearly evident, with H–O distances of 1·75 (3) and 1·71 (3) Å. The nitro group is perpendicular to the approximate plane of the hydrogen-bonding network and the distances between hydroxyl H atoms and nitro O atoms are more than 2·95 Å, clearly ruling out possible hydrogen bonds. The evidence for bonded hydroxyl groups in this compound in the solid state from IR studies (Ungnade & Kissinger, 1963) may be explained by the observed hydrogen-bonding network in which each hydroxyl group is linked to two other hydroxyl groups of neighboring molecules. O(3) is the donor for the bond to O(4) at $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$ and the acceptor in the bond to O(4) at $x - \frac{1}{2}, \frac{1}{2} + y, z$. Conversely, O(4) acts both as a donor and an acceptor to O(3) of molecules situated at $\frac{1}{2} + x, y - \frac{1}{2}, z$ and $x + \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$, respectively.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32643 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.