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References

BRISSON, J. & BRISSE, F. (1982). *Acta Cryst.* B**38**, 2663–2667.
CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.
HARKEMA, S., VAN HUMMEL, G. J. & GAYMANS, R. J. (1980). *Acta Cryst.* B**36**, 3182–3184.
MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1978). *MULTAN*78. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.
PALMER, A. & BRISSE, F. (1980). *Acta Cryst.* B**36**, 1447–1452.
PINEAULT, C. (1982). MSc Thesis, Univ. de Montréal.
PINEAULT, C. & BRISSE, F. (1983). *Acta Cryst.* C**39**, 1434–1437.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

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Structure of *N*-Ethylmaleimide, $C_6H_7NO_2$

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Abstract. $M_r = 125{\cdot}12$, monoclinic, $P2_1/c$, $a = 11{\cdot}875$ (7), $b = 6{\cdot}681$ (5), $c = 8{\cdot}393$ (3) Å, $\beta = 103{\cdot}73$ (4)°, $V = 646{\cdot}84$ Å^3, $Z = 4$, $D_x = 1{\cdot}286$ Mg m^{-3}, Ni-filtered Cu $K\bar{\alpha}$ radiation, $\lambda = 1{\cdot}5418$ Å, m.p. = 318·7 K, $F(000) = 264$, $\mu = 0{\cdot}830$ mm^{-1}, room temperature, final $R = 0{\cdot}067$ for 761 reflections with $I > 3\sigma(I)$. Thermal diffuse scattering is strongly associated with the intense low-angle reflections. The molecules are held in the crystalline lattice solely by van der Waals interactions, thus accounting for the high vapor pressure.

Introduction. *N*-Ethylmaleimide (NEM) reacts quickly and specifically with thiol groups. It is used to determine numbers of sulfhydryl groups in peptides and proteins, and the effects of sulfhydryl-group modifications on proteins (Means & Feeney, 1971).

Experimental. NEM was obtained in crystalline form, 99+% pure, from Mann Research Laboratories, Inc. To prevent sublimation of the crystal (m.p. 318·7 K), it was mounted inside a glass capillary tube with smaller crystals, and the tube sealed. Irregular rectangular prism, 1·2 × 0·4 × 0·3 mm, Enraf–Nonius CAD-4 diffractometer, cell measurement with reflections in the range $\theta = 8$–52°, $\omega/2\theta$ scan of width 1·5° and variable speed, absorption correction by the empirical method of North, Phillips & Mathews (1968) with a maximum correction of 1·271 and a minimum correction of 1·003, maximum $(\sin\theta)/\lambda = 0{\cdot}5614$ Å^{-1}, range in $h = -13$ to 13, $k = 0$ to 7, $l = -9$ to 9, average decay of standard reflections 2·0%, 2177 reflections measured, 951 unique reflections, $R_{merge} = 3{\cdot}34\%$, 190 unobserved reflections with $I < 3\sigma(I)$. Data reduction, calculation of Fourier maps and least-squares refinement performed with the programs of the XRAY70 system of Stewart, Kundell & Baldwin (1970).* Structure solved by direct methods using *MULTAN*77 (Main, Lessinger, Woolfson, Germain & Declercq, 1977). The non-hydrogen atoms were all located readily on the *E* map. Full-matrix least-squares refinement on $|F|$ was performed with $w = [\sigma^2(I)]^{-1}$ [from $\sigma^2(I)$ as defined in Fujinaga & James (1980)]. H atoms were located at an intermediate stage of refinement from a $\Delta\rho$ map. In the final cycles of refinement positional parameters for all atoms, anisotropic thermal-vibration parameters for non-hydrogen atoms, isotropic thermal-vibration parameters for H atoms and the structure factor scale factor were varied; $R_w = 0{\cdot}067$. Maximum and average Δ/σ in final cycle 0·46 and 0·04 respectively. Max. and min. peaks on final $\Delta\rho$ map 0·23 and −0·22 e Å^{-3}. Atomic scattering factors for non-hydrogen atoms from Cromer & Mann (1968), for H from Mason & Robertson (1966). No correction for secondary extinction was required.

Discussion. Positional and equivalent isotropic thermal-vibration parameters are given in Table 1 for non-hydrogen atoms, and a view of the molecule is given in Fig. 1.†

* C. G. Broughton's map-display and molecule-manipulation program *M*3, which runs on an MMS-X interactive graphics system of Barry, Molnar & Rosenberger (1976), was invaluable in interpretation of Fourier maps, assignment of initial atomic coordinates and composition of figures.

† Lists of structure factors, anisotropic thermal parameters for non-hydrogen atoms, and coordinates and isotropic thermal parameters for H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38683 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Atomic coordinates and thermal parameters*

	x	*y*	*z*	B_{eq}(Å^2)*
N(1)	0·2368 (2)	0·4111 (3)	0·5589 (2)	5·7 (1)
O(1)	0·3248 (2)	0·1300 (3)	0·4863 (3)	8·2 (1)
O(2)	0·1114 (2)	0·6128 (3)	0·6550 (3)	7·3 (1)
C(1)	0·2512 (2)	0·2053 (4)	0·5431 (3)	6·6 (1)
C(2)	0·1565 (3)	0·1090 (4)	0·6047 (3)	6·7 (1)
C(3)	0·0947 (3)	0·2496 (5)	0·6530 (3)	6·4 (1)
C(4)	0·1435 (2)	0·4481 (3)	0·6257 (3)	5·7 (1)
C(5)	0·3105 (3)	0·5624 (4)	0·5112 (4)	6·3 (1)
C(6)	0·4090 (3)	0·6235 (6)	0·6466 (5)	8·1 (2)

* $B_{eq} = \frac{4}{3}\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

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

N(1)–C(1)	1·396 (3)	C(1)–C(2)	1·489 (5)
N(1)–C(4)	1·378 (4)	C(2)–C(3)	1·315 (5)
N(1)–C(5)	1·453 (4)	C(3)–C(4)	1·486 (4)
O(1)–C(1)	1·202 (4)	C(5)–C(6)	1·481 (4)
O(2)–C(4)	1·209 (3)		
C(1)–N(1)–C(4)	110·2 (2)	C(1)–C(2)–C(3)	108·8 (2)
C(1)–N(1)–C(5)	124·2 (2)	C(2)–C(3)–C(4)	108·9 (3)
C(4)–N(1)–C(5)	125·6 (2)	N(1)–C(4)–C(3)	106·4 (2)
O(1)–C(1)–N(1)	124·6 (3)	N(1)–C(4)–O(2)	124·7 (2)
O(1)–C(1)–C(2)	129·6 (2)	C(3)–C(4)–O(2)	128·9 (3)
N(1)–C(1)–C(2)	105·7 (2)	N(1)–C(5)–C(6)	113·4 (3)

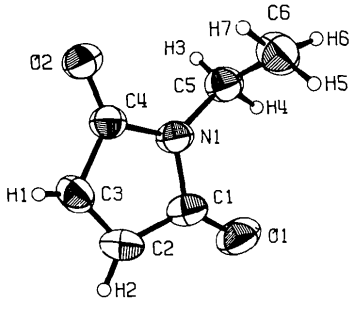

Fig. 1. View of the molecule of NEM. Thermal ellipsoids are drawn at 35% probability for non-hydrogen atoms, and H atoms are represented by spheres of arbitrary radius.

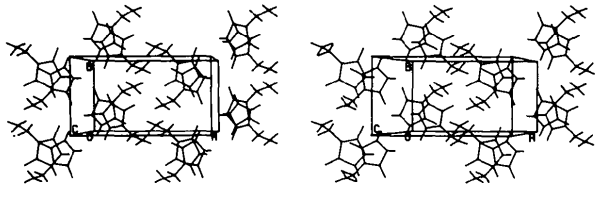

Fig. 2. Stereoscopic view of the contents of the unit cell.

A selected list of bond lengths and interbond angles in NEM is given in Table 2. These parameters have been compared with those of related molecules, including 2-bromo-3-(2-indolyl)-*N*-methylmaleimide–dioxane (Ueda, Mihara & Matsuo, 1977), 3,4,5,6-tetrahydro-3,6-dithiaphthalimide (Kirfel, Will & Fickentscher, 1975) and *N*-(4-methoxyphenyl)-3,6-dithiacyclohexene-1,2-dicarboximide (Dobrowolska & Bukowska-Strzyżewska, 1980). The comparison shows that both bond lengths and interbond angles are not unusual for this maleimide moiety. The maleimide ring is planar; the r.m.s. deviation of the five ring atoms from the plane is 0·003 Å.

The ring portion of the molecule shows very high bilateral symmetry with respect to bond lengths and angles, through a line bisecting N(1) and the C(2)–C(3) bond. This symmetry is observed also in the similar values for the torsional angles C(1)–N(1)–C(5)–C(6) [−92·1 (4)°] and C(4)–N(1)–C(5)–C(6) [87·8 (3)°]. This can be contrasted with the analogous angles in *N*-(4-methoxyphenyl)-3,6-dithiacyclohexene-1,2-dicarboximide (Dobrowolska & Bukowska-Strzyżewska, 1980) of −56·5 and 137·5°.

The final $\Delta\rho$ map showed a few significant peaks of residual electron density. The largest features on the map probably result from anisotropic motion of the N and O atoms perpendicular to the plane of the ring, which has not been satisfactorily accounted for by the six-parameter anisotropic thermal-motion model. The largest axis of the anisotropic thermal ellipsoids of the atoms in the molecule is perpendicular to the plane of the ring, and the residual difference electron density may indicate additional molecular libration in this direction.

All of the intermolecular contacts between non-hydrogen atoms are greater than 3·24 Å, and the crystal is maintained solely by van der Waals forces. NEM melts at 318·7, maleimide at 366 and maleamate at 425 K. The low melting point of NEM, and the high anisotropic thermal motion and molecular libration can be attributed to decreased potential for hydrogen bonding. Hydrophobic interactions appear to be the main determinant of the packing configuration, which is the stacking of the rings (Fig. 2). The relative rotation of the adjacent molecules along the *c* axis places O(1) of one molecule near the center of the ring of the next molecule, reducing electron-repulsion effects. The direction of the anisotropic thermal motion of the atoms closest to O(1) is also shifted somewhat from being perpendicular to the molecular plane (Fig. 1).

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References

BARRY, C. D., MOLNAR, C. E. & ROSENBERGER, F. U. (1976). Technical Memorandum No. 229. Computer Systems Laboratory, Washington Univ., St Louis, MO.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.
DOBROWOLSKA, W. & BUKOWSKA-STRZYŻEWSKA, M. (1980). *Acta Cryst.* B**36**, 890–893.
FUJINAGA, M. & JAMES, M. N. G. (1980). *Acta Cryst.* B**36**, 3196–3199.
KIRFEL, A., WILL, G. & FICKENTSCHER, K. (1975). *Acta Cryst.* B**31**, 1973–1975.
MAIN, P., LESSINGER, L., WOOLFSON, M. M., GERMAIN, G. & DECLERCQ, J.-P. (1977). *MULTAN77. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.
MASON, R. & ROBERTSON, G. B. (1966). *Advances in Structure Research by Diffraction Methods,* Vol. 2, edited by R. BRILL & R. MASON, p. 57. New York: Interscience.
MEANS, G. E. & FEENEY, R. E. (1971). *Chemical Modification of Proteins,* pp. 110–114. San Francisco: Holden-Day, Inc.
NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The XRAY70 system. Computer Science Center, Univ. of Maryland, College Park, MD.
UEDA, I., MIHARA, S. & MATSUO, T. (1977). *Acta Cryst.* B**33**, 3216–3218.

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Conformation of the O^6-Alkyl Group in Nucleosides: Structure of 4-Methoxy-1-(β-D-ribofuranosyl)pyrazolo[3,4-*d*]pyrimidine, $C_{11}H_{14}N_4O_5$

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Abstract. $M_r = 282{\cdot}3$, monoclinic, $P2_1$, $a = 13{\cdot}015$ (2), $b = 7{\cdot}741$ (1), $c = 6{\cdot}791$ (1) Å, $\beta = 112{\cdot}59$ (1)°, $V = 631{\cdot}7$ (3) Å^3, $Z = 2$, $D_m = 1{\cdot}48$, $D_x = 1{\cdot}484$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å, $\mu = 10{\cdot}3$ cm^{-1}, $T = 294$ K, $F(000) = 296$; the final $R = 0{\cdot}028$ for 1288 reflections ($\geq 2\sigma$). The molecule has the *anti* conformation ($\chi = 71{\cdot}6°$). The ribose has the C(3′)*endo*–C(2′)*exo* ($^3T_2$) pucker with the following pseudorotation parameters: $P = 6{\cdot}3$ (2)° and $\tau_m = 38{\cdot}2$ (2)°. The conformation across C(4′)–C(5′) is *trans*, instead of the preferred g^+. The orientation of the O^6-alkyl group is 'distal' to the five-membered ring and in spite of the partial shielding of N(1) by the alkyl group, N(1) receives a hydrogen bond from the hydroxyl oxygen O(5′). There is no stacking of the bases in the crystal structure. Molecules related by twofold screw axes are connected to each other by an O(5′)–H(O5′)···N(1) hydrogen bond and form an infinite chain. Molecules related by the **c** translation are on top of each other at 6·6 Å and are linked by an O(2′)–H(O2′)···O(5′) hydrogen bond. An interesting C–H···O hydrogen bond to the ring oxygen O(1′) from C(7)–H is present in the crystal structure.

Introduction. Pyrazolo[3,4-*d*]pyrimidine is an analog of purine in which the atoms N(7) and C(8) are interchanged with respect to the purine. Antibiotics such as tubercidin can be viewed as 4-amino-6-aza nucleosides of the above ring system (Suhadolnik, 1970). Several 4-aminopyrazolo[3,4-*d*]pyrimidine derivatives have shown growth-inhibitory activities in tumor cell lines (Hong, De, Tritsch & Chheda, 1976; Sutcliffe, Zee-cheng, Cheng & Robins, 1962) as well as in other biological systems (Krenitsky, Elion, Strelitz & Hitchings, 1967). The pyrazolo[3,4-*d*]pyrimidine ring has provided a very important drug, commonly known as allopurinol, which serves as an excellent inhibitor of xanthine oxidase in man and thereby effectively relieves hyperuricemia condition in gout as well as in certain cancers. It also protects and potentiates the antitumor activity of drugs such as 6-mercaptopurine by preventing the oxidation of the latter by xanthine oxidase to 6-thiouric acid (Rundles & Wyngaarden, 1969; Rundles, 1966).

Of the several nucleosides prepared in our laboratory, the title compound (I) (4-*O*-methylallopurinol riboside) was the most potent against L-1210 mouse leukemia cells *in vitro* (I_{50}, 10^{-5} *M*). In view of the antitumor activity and also because it is a 4-*O*-methylallopurinol riboside we have carried out a detailed X-ray crystallographic analysis of its molecular structure and conformation (Srikrishnan, Parthasarathy, De & Chheda, 1978). This compound can be regarded as a purine derivative, 6-*O*-methyl-7-aza-8-deazainosine. As a result, the atom numbering in the molecules for the crystallographic work follows that of purine and is different from that for the pyrazolopyrimidine ring system and is given in Fig. 1. For ease of comparison of the X-ray results with other similar compounds, the numbering is similar to those followed in other purine nucleosides; however the standard chemical nomenclature is used elsewhere in the paper.

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