base of benzothiazole is added. The C(2) atom is sp^3-hybridized in this compound (Miler-Srenger, 1969).

We wish to thank Dr Samat for providing the crystalline sample.

References

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.

Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **18**, 104–109.

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

Merlino, S. (1971). *Acta Cryst.* B**27**, 2491–2492.

Miler-Srenger, E. (1969). *Bull. Soc. Chim. Fr.* p. 3970.

Miler-Srenger, E. (1974). *Acta Cryst.* B**30**, 1911–1914.

Miler-Srenger, E. & Robert, F. (1978). *Acta Cryst.* B**34**, 585–588.

Pletcher, J., Sax, M., Sengupta, S., Chu, J. & Yoo, C. S. (1972). *Acta Cryst.* B**28**, 2928–2935.

Rienzo, F. di, Domenicano, A., Portalone, G. & Vaciago, A. (1976). Proceedings of the Yugoslav Centre of Crystallography, Suppl. to Vol. 11, pp. A102–104.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Acta Cryst. (1978). B**34**, 1226–1230

The Crystal and Molecular Structure of 2-Acetamido-2,3-dideoxy-5,6-*O*-isopropylidene-D-*threo*-hex-2-enono-1,4-lactone, $C_{11}H_{15}NO_5$

By Živa Ružić-Toroš

'Rudjer Bošković' Institute, PO Box 1016, 41001 *Zagreb, Yugoslavia*

and I. Leban

Chemistry Department, University of Ljubljana, Murnikova 6, 61000 *Ljubljana, Yugoslavia*

(*Received* 18 *August* 1977; *accepted* 26 *October* 1977)

2-Acetamido-2,3-dideoxy-5,6-*O*-isopropylidene-D-*threo*-hex-2-enono-1,4-lactone is monoclinic with a = 5·218 (1), b = 22·703 (3), c = 10·138 (1) Å, β = 100·32 (1)°, Z = 4, space group $P2_1$. The structure was solved by *MULTAN* and refined to an R of 0·048. The lactone group and ring in both independent molecules are planar within experimental error. The dioxolane rings are puckered. Two asymmetric molecules are connected by N–H···O (3·006 and 2·935 Å) hydrogen bonds forming dimers in the crystal lattice.

Experimental

The compound crystallizes as colourless prismatic rods. The unit-cell dimensions (Table 1) were determined from oscillation photographs with Cu $K\alpha$ radiation. The precise values were then deduced from zero-layer rotation patterns of single crystals (around **a** and **b**) taken in the asymmetric (Straumanis) position and indexed by means of corresponding Weissenberg photographs (Popović, 1974).

Table 1. *Crystallographic and physical data*

2-Acetamido-2,3-dideoxy-5,6-*O*-isopropylidene-D-*threo*-2-enono-1,4-lactone, $C_{11}H_{15}NO_5$

FW	241·24	Z	4
Space group	$P2_1$	U	1181·56 Å^3
a	5·218 (1) Å	D_c	1·357 g cm^{-3}
b	22·703 (3)	μ(Cu $K\alpha$)	6·80 cm^{-1}
c	10·138 (1)	Crystal shape	Prismatic
β	100·32 (1)°		

The space group was determined from Weissenberg photographs. The diffraction symmetry and space-group extinctions indicated $P2_1$ or $P2_1/m$; since the molecule is optically active the space group is necessarily $P2_1$. The intensities were collected on an automatic Enraf–Nonius CAD-4 four-circle diffractometer with Ni-filtered Cu $K\alpha$ radiation (ω–2θ mode, variable scan rate, $0 < 2\theta < 180°$). 3427 intensities were collected and the symmetrically related reflexions were averaged to 2478 independent reflexions. 489 of these were unobserved ($I \leq 2\sigma$). The data were corrected for variations in the intensities of reference reflexions, and for Lorentz and polarization effects.

Table 2. *Final positional parameters* ($\times 10^4$) *for non-hydrogen atoms*

Molecule *A*	*x*	*y*	*z*	Molecule *B*	*x*	*y*	*z*
C(1)	4729 (12)	3835 (3)	5645 (6)	C(1)	6230 (12)	5094 (3)	−525 (6)
C(2)	6812 (12)	4133 (3)	5099 (6)	C(2)	4258 (11)	4762 (3)	35 (6)
C(3)	7440 (12)	3803 (3)	4108 (6)	C(3)	4271 (12)	4941 (3)	1290 (6)
C(4)	5802 (12)	3266 (3)	3976 (6)	C(4)	6339 (12)	5406 (3)	1630 (6)
C(5)	4142 (11)	3176 (3)	2601 (5)	C(5)	5224 (12)	5990 (3)	1958 (6)
C(6)	5863 (13)	3077 (3)	1537 (6)	C(6)	3964 (13)	5962 (3)	3219 (7)
C(7)	3439 (13)	2239 (3)	1630 (6)	C(7)	6442 (11)	6800 (3)	3273 (6)
C(8)	1103 (15)	1958 (4)	794 (8)	C(8)	8785 (13)	7060 (3)	4147 (7)
C(9)	5355 (17)	1800 (4)	2371 (9)	C(9)	4612 (15)	7262 (3)	2516 (7)
C(10)	9736 (13)	4980 (3)	5299 (6)	C(10)	832 (12)	4015 (3)	−404 (6)
C(11)	10602 (16)	5521 (3)	6159 (7)	C(11)	−317 (14)	3548 (3)	−1400 (7)
O(1)	3684 (9)	3982 (0)	6558 (4)	O(1)	6806 (10)	5056 (2)	−1621 (4)
O(4)	4102 (8)	3338 (2)	4958 (4)	O(4)	7429 (8)	5472 (2)	415 (4)
O(5)	2625 (8)	2652 (2)	2557 (4)	O(5)	7296 (8)	6404 (2)	2331 (4)
O(6)	4647 (9)	2606 (2)	760 (4)	O(6)	5101 (9)	6432 (2)	4044 (4)
O(10)	10645 (9)	4840 (2)	4323 (4)	O(10)	106 (9)	4104 (2)	662 (4)
N	7785 (10)	4658 (2)	5686 (5)	N	2817 (10)	4337 (2)	−773 (5)

Structure determination and refinement

THe structure was solved by *MULTAN* (Declercq, Germain, Main & Woolfson, 1973). Overall temperature and scale factors were determined (Wilson, 1942) and normalized structure factors were derived. The *E* map with the highest combined figure of merit calculated from 300 reflexions with $|E| \geq 1{\cdot}5$ revealed the positions of 32 non-hydrogen atoms. The positions of two remaining non-hydrogen atoms were located from a resulting Fourier synthesis. The refinement of the structure was carried out by a full-matrix least-squares procedure minimizing $\Sigma w||F_o| - |F_c||^2$ with $w = 1/\sigma^2_{F_o}$. Heavy-atom coordinates, isotropic thermal parameters and a scale factor were refined to an *R* of 0·102. The positions of the H atoms were determined from a difference Fourier synthesis after a few cycles of anisotropic refinement ($R = 0{\cdot}070$). The H atoms on the C(11) terminal methyl group were too disordered to be located in the difference map. In the last cycle, one scale factor, the atomic coordinates and the anisotropic thermal parameters for the non-hydrogen atoms were varied. For H atoms the coordinates were taken from difference Fourier maps and the isotropic thermal parameters were those of the bonded atoms. The final agreement indices were $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0{\cdot}048$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma F_o]^{1/2} = 0{\cdot}058$.*

Scattering factors given by Cromer & Mann (1968) and (for H) by Stewart, Davidson & Simpson (1965) were used.

Table 3. *Positional parameters* ($\times 10^3$) *and isotropic thermal parameters* ($\times 10^2$) *for the hydrogen atoms*

	x	*y*	*z*	*U* (Å^2)
Molecule *A*				
H(3)	887	386	352	4·6
H(4)	699	297	420	4·0
H(5)	279	348	237	3·5
H(6,1)	780	300	200	4·4
H(6,2)	570	342	102	4·4
H(8,1)	000	227	62	6·1
H(8,2)	40	160	125	6·1
H(8,3)	150	180	−8	6·1
H(9,1)	433	160	290	6·7
H(9,2)	564	148	180	6·7
H(9,3)	670	208	280	6·7
H(N)	720	486	630	4·4
Molecule *B*				
H(3)	326	480	190	4·1
H(4)	795	527	238	3·8
H(5)	406	616	120	3·9
H(6,1)	409	559	366	4·9
H(6,2)	220	604	300	4·9
H(8,1)	983	677	463	5·3
H(8,2)	986	739	355	5·3
H(8,3)	800	720	475	5·3
H(9,1)	550	750	200	5·5
H(9,2)	397	748	325	5·5
H(9,3)	310	708	190	5·5
H(N)	310	428	−153	4·0

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33155 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

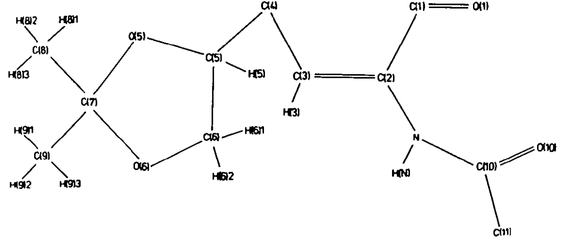

Fig. 1. The numbering of the atoms.

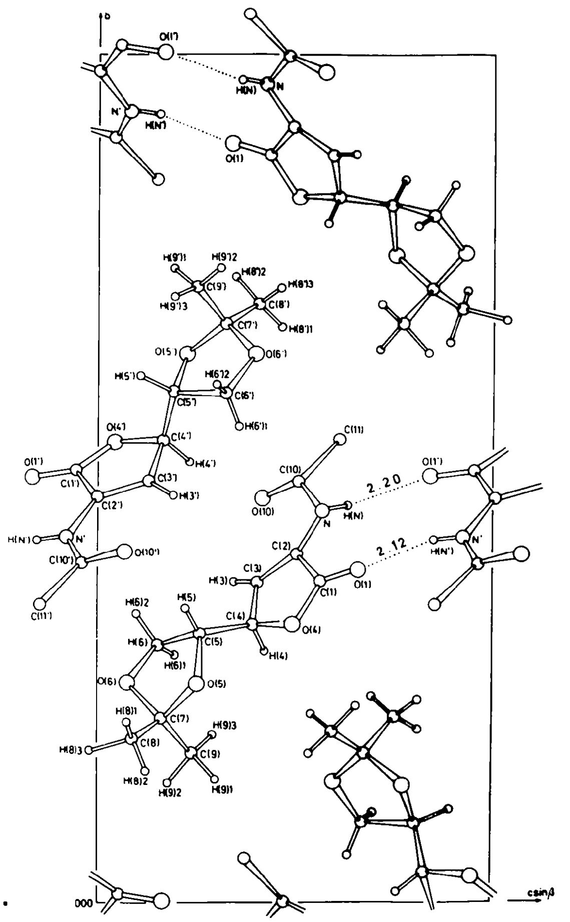

Fig. 2. A view of the crystal structure along **a** showing the packing arrangement and hydrogen bonds. A right-hand coordinate system has been chosen so that the positive direction of the *a* axis is away from the reader.

The calculations were carried out on the Univac 1110 computer at the University Computing Centre in Zagreb with the XRAY 72 system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). Positional and (for H) thermal parameters are listed in Tables 2 and 3.

Description and discussion of the structure

The numbering of the atoms is shown in Fig. 1. Molecular packing and the hydrogen-bond scheme are in Fig. 2. Interatomic distances and angles are listed in Table 4, and displacements of the atoms from the least-squares planes through the lactone groups, lactone rings and dioxolane rings are in Table 5. Dihedral angles defining the conformation about C(4)—C(5) and the dioxolane rings are given in Table 6.

The differences in bond lengths between the two independent molecules are within three standard deviations.

The C—C bond lengths [except for C(1)—C(2) and C(3)—C(4), molecule *A*] vary from 1·497 to 1·539 Å and are in agreement with the value for a C—C single bond. The C=C distances of 1·340 (9) (molecule *A*) and 1·334 (8) Å (molecule *B*) are comparable with those found in L-ascorbic acid (Hvoslef, 1968) and with the value for C=C [1·337 (7) Å] given in *International Tables for X-ray Crystallography* (1968). The C—C single bonds in the lactone rings [1·470 (9) (molecule *A*) and 1·469 (9) Å (molecule *B*)] are shortened because of the influence of C=O and C=C double bonds. The C—O bonds in the lactone rings are asymmetric: 1·334 (8), 1·457 (8) Å (molecule *A*) and 1·351 (7), 1·455 (8) Å (molecule *B*). This asymmetry has been observed in all lactones, *e.g.* in L-ascorbic acid (Hvoslef, 1968), γ-D-gulonolactone (Berman, Rosenstein & Southwick, 1971), D-glucono-1,5-lactone (Hackert & Jacobson, 1971) and 2-acetamido-2,3-dideoxy-D-*threo*-hex-2-enono-1,4-lactone (Ružić-Toroš & Kojić-Prodić, 1976).

The mean length of the C—O bonds in the dioxolane rings is 1·427 Å, individual differences all being $<3\sigma$ from this value. The values for all kinds of bond lengths in dioxolane rings are in good agreement with those in methyl 3,4-isopropylidene-β-L-*erythro*-pentapyranosid-2-ulose (Palmer & Palmer, 1976).

The C=O bond lengths are in the range 1·204 (8)–1·224 (8) Å. All values are usual for C=O double bonds.

The internal angles in the lactone rings are in the range 104·6 (5)–109·2 (5)°. Their mean value for each molecule (108°) is equal to the calculated angle in a regular pentagon. The influence of the five-membered-ring geometry on the values of the bond angles next to the double bonds (C—C—C, O—C—C) is obvious. The same distortions are observed in L-ascorbic acid (Hvoslef, 1968), 2-acetamido-2,3-dideoxy-D-*threo*-hex-2-enono-1,4-lactone (Ružić-Toroš & Kojić-Prodić, 1976) and 2-acetamido-2,3-dideoxy-D-*erythro*-hex-2-enono-1,4-lactone (Ružić-Toroš & Lazarini, 1978).

The atoms defining the lactone group are planar with a maximum deviation of 0·027 Å for O(4) (molecule *A*) (0·006 Å in molecule *B*) (Table 5). C(3) belonging to the lactone ring is displaced 0·002 Å (molecule *A*) and 0·008 Å (molecule *B*) out of the least-squares plane through the lactone group. The lactone group and ring in both molecules are planar within experimental error. Displacements from the least-squares planes are less for molecule *B*.

The conformation of the molecules can be numerically described by the torsion angles (Table 6). The orientation of the lactone ring relative to the dioxolane ring is described by the torsion angle about C(4)—C(5). The torsion angles about C(5)—O(5) and C(6)—O(6) and the best planes show the puckering of the dioxolane rings. C(7) in the dioxolane ring is displaced −0·414 Å (molecule *A*) and 0·492 Å

Table 4. *Bond distances* (Å) *and angles* (°)

	Molecule *A*	Molecule *B*
C(1)–C(2)	1·470 (9)	1·469 (9)
C(1)–O(1)	1·204 (8)	1·205 (8)
C(1)–O(4)	1·334 (8)	1·351 (7)
C(2)–C(3)	1·340 (9)	1·334 (8)
C(2)–N	1·386 (8)	1·394 (7)
C(3)–C(4)	1·482 (9)	1·505 (9)
C(3)–H(3)	1·04	0·93
C(4)–C(5)	1·517 (7)	1·510 (9)
C(4)–O(4)	1·457 (8)	1·455 (8)
C(4)–H(4)	0·92	1·07
C(5)–C(6)	1·538 (9)	1·539 (10)
C(5)–O(5)	1·426 (8)	1·430 (7)
C(5)–H(5)	0·99	0·97
C(6)–O(6)	1·410 (9)	1·418 (8)
C(6)–H(6,1)	1·05	0·95
C(6)–H(6,2)	0·93	0·92
C(7)–C(8)	1·497 (10)	1·497 (9)
C(7)–C(9)	1·513 (11)	1·530 (9)
C(7)–O(5)	1·445 (9)	1·440 (8)
C(7)–O(6)	1·438 (9)	1·412 (8)
C(8)–H(8,1)	0·91	0·93
C(8)–H(8,2)	1·03	1·16
C(8)–H(8,3)	1·01	0·85
C(9)–H(9,1)	0·94	0·93
C(9)–H(9,2)	0·96	1·00
C(9)–H(9,3)	0·99	1·00
C(10)–C(11)	1·527 (10)	1·512 (8)
C(10)–O(10)	1·213 (8)	1·224 (8)
C(10)–N	1·367 (9)	1·374 (8)
N–H(N)	0·87	0·82

	Molecule *A*	Molecule *B*
C(2)–C(1)–O(1)	129·0 (5)	128·9 (5)
C(2)–C(1)–O(4)	108·8 (5)	108·8 (5)
O(1)–C(1)–O(4)	122·2 (6)	122·3 (6)
C(1)–C(2)–C(3)	108·7 (5)	109·2 (5)
C(1)–C(2)–N	118·2 (5)	117·9 (5)
C(3)–C(2)–N	133·0 (6)	132·9 (6)
C(2)–C(3)–C(4)	108·2 (6)	108·2 (5)
C(3)–C(4)–C(5)	114·8 (5)	112·2 (5)
C(3)–C(4)–O(4)	104·9 (5)	104·6 (4)
C(5)–C(4)–O(4)	109·0 (5)	108·6 (5)
C(4)–C(5)–C(6)	110·8 (5)	112·6 (5)
C(4)–C(5)–O(5)	111·3 (5)	109·4 (5)
C(6)–C(5)–O(5)	104·3 (5)	102·9 (5)
C(5)–C(6)–O(6)	104·0 (5)	105·3 (5)
C(8)–C(7)–C(9)	113·5 (6)	113·3 (6)
C(8)–C(7)–O(5)	109·9 (6)	108·8 (5)
C(8)–C(7)–O(6)	107·5 (5)	109·8 (5)
C(9)–C(7)–O(5)	110·5 (6)	109·6 (5)
C(9)–C(7)–O(6)	111·3 (6)	110·9 (5)
O(5)–C(7)–O(6)	103·6 (5)	103·9 (5)
C(11)–C(10)–O(10)	123·9 (6)	123·8 (6)
C(11)–C(10)–N	115·2 (6)	114·9 (5)
O(10)–C(10)–N	120·9 (6)	121·3 (5)
C(1)–O(4)–C(4)	109·2 (5)	109·2 (5)
C(5)–O(5)–C(7)	109·6 (5)	106·0 (5)
C(6)–O(6)–C(7)	107·4 (5)	108·3 (5)
C(2)–N–C(10)	124·8 (6)	124·2 (5)

Table 5. *Displacements from the least-squares planes* (Å)

Atoms included in the calculations of the least-squares planes are denoted by asterisks.

	Molecule *A*	Molecule *B*
Lactone group		
C(2)*	0·010	0·002
C(1)*	0·007	0·002
O(1)*	−0·020	−0·005
O(4)*	0·027	0·006
C(4)*	−0·024	−0·006
C(3)	−0·002	0·008
Dioxolane ring		
C(5)*	0·091	0·059
C(6)*	−0·091	−0·060
O(5)*	−0·061	−0·041
O(6)*	0·061	0·041
C(7)	−0·414	0·492

Table 6. *Torsion angles* (°) *describing the conformation about* C(4)–C(5) *and the dioxolane ring*

	Molecule *A*	Molecule *B*
C(3)–C(4)–C(5)–O(5)	−179·9 (5)	177·5 (5)
C(3)–C(4)–C(5)–H(5)	−62	−57
O(4)–C(4)–C(5)–O(5)	−65·2 (7)	−75·1 (6)
O(4)–C(4)–C(5)–C(6)	−178·0 (5)	178·6 (5)
H(4)–C(4)–C(5)–C(6)	−54	−64
H(4)–C(4)–C(5)–H(5)	177	166
O(5)–C(5)–C(6)–O(6)	17·0 (6)	11·1 (6)
C(6)–C(5)–O(5)–C(7)	4·7 (6)	−32·9 (6)
C(4)–C(5)–O(5)–C(7)	−112·7 (5)	−147·2 (5)
C(5)–C(6)–O(6)–C(7)	−34·9 (6)	13·9 (7)

Table 7. *Hydrogen bonds*

The atoms marked with a prime correspond to molecule *B*.

X–H···*Y*	*X*···*Y*	*X*–H	H···*Y*	*X*–H···*Y*	Symmetry operation
N–H(N)···O(1′)	3·006 (7)Å	0·87 Å	2·20 Å	154°	*x,y,z*; *x,y,z* + 1
N′–H(N′)···O(1)	2·935 (7)	0·82	2·12	171	*x,y,z*; *x,y,z* + 1

(molecule *B*) from the plane defined by C(5), C(6), O(5) and O(6) (Table 5). Examination of the internal molecular geometry of both symmetrically independent molecules shows that the only difference between them is puckering of the dioxolane rings. These two modes of puckering could be explained by the available space in the crystal lattice.

The dihedral angles between the lactone rings and the planes of the dioxolane rings are 7·4° for molecule *A* and 8·3° for molecule *B*.

Two symmetrically independent molecules are connected by two N—H···O hydrogen bonds [3·006 (7) and 2·935 (7) Å] forming dimers (Fig. 2 and Table 7).

The intensities were collected at the Department of Chemistry, University of Ljubljana. The authors are grateful to Professor L. Golič for the facilities placed at their disposal. They thank Dr N. Pravdić for crystals and Dr B. Kojić-Prodić for very valuable discussions.

References

Berman, H. M., Rosenstein, R. D. & Southwick, J. (1971). *Acta Cryst.* B**27**, 7–10.

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

Declercq, J. P., Germain, G., Main, P. & Woolfson, M. M. (1973). *Acta Cryst.* A**29**, 231–234.

Hackert, M. L. & Jacobson, R. A. (1971). *Acta Cryst.* B**27**, 203–209.

Hvoslef, J. (1968). *Acta Cryst.* B**24**, 23–25.

International Tables for X-ray Crystallography (1968). Vol. III, 2nd ed., p. 276. Birmingham: Kynoch Press.

Palmer, H. T. & Palmer, R. A. (1976). *Acta Cryst.* B**32**, 377–380.

Popović, S. (1974). *J. Appl. Cryst.* **7**, 291–292.

Ružić-Toroš, Ž. & Kojić-Prodić, B. (1976). *Acta Cryst.* B**32**, 2333–2336.

Ružić-Toroš, Ž. & Lazarini, F. (1978). *Acta Cryst.* B**34**, 854–858.

Stewart, J. M., Kruger, G. J., Ammon, H. L., Dickinson, C. & Hall, S. R. (1972). The XRAY system – version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Wilson, A. J. C. (1942). *Nature* (*London*), **150**, 151–152.

Acta Cryst. (1978). B**34**, 1230–1247

Molecular-Packing Modes. *N*-Methylamides

By L. Leiserowitz and M. Tuval

Department of Structural Chemistry, The Weizmann Institute of Science, Rehovot, Israel

(*Received* 5 *September* 1977; *accepted* 13 *October* 1977)

The crystal structures of *N*-methyl derivatives of propiolamide, tetrolamide, benzamide, cinnamide and sorbamide were determined. The hydrogen-bonding motifs of *N*-methylamides $RCONHCH_3$ are analysed in terms of: (i) the nature of the residue *R*; (ii) the three principal modes of generating hydrogen-bonded arrays in secondary *trans*-amides, *i.e.* translation, glide, 2_1 axis; (iii) an 'idealized' N—H···O bonding geometry in which the N—H···O bond is linear, the N—H···O=C system coplanar and the C=O···(H)N angle ≃120°. The mode of hydrogen bonding is determined primarily by the nature of the *R* group. The N—H···O bond tends to be linear and the N—H···O=C< system planar. Evidence is marginal for a preferred C=O···H(N) angle in the range of 130–180°. Comparison of N—H···O distances in *trans* and *cis* amides does not reveal any systematic differences (mean N—H···O distance 2·85 Å). In comparison, the average N—H···O distance of 2·94 Å in primary amides is distinctly longer.

1. Introduction

This study concerns the factors determining the molecular-packing modes of *N*-methylamides R—C(=O)—N(—H)—CH_3 and the geometric nature of their N—H···O bonds. Our aim has been to determine the hydrogen-bond packing of R—$CONHCH_3$ as a function of the attached residue *R*. The structure analyses presented here are of *N*-methylpropiolamide (NMP), *N*-methyltetrolamide (NMT), *N*-methylbenzamide (NMB), *N*-methylcinnamide (NMC) and *N*-methylsorbamide (NMS), whose formulae are depicted in Fig. 1.

2. Structure, solutions and results

The crystal data of the five amides (Fig. 1) are listed in Table 1. Accurate cell dimensions were derived by a least-squares procedure based on high-order reflections ($\sin \theta/\lambda > 0·46$ Å^{-1}) measured on a diffractometer.

The three-dimensional X-ray intensity data were collected on a diffractometer controlled by an IBM 1800 computer. The details of the data collection and processing are given in Table 2.

The crystal structures were solved by means of the multisolution method (Germain & Woolfson, 1968) *via* the program *MULTAN* (Germain, Main & Woolfson,