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

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(*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 ($\sin\theta/\lambda > 0{\cdot}46$ 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,

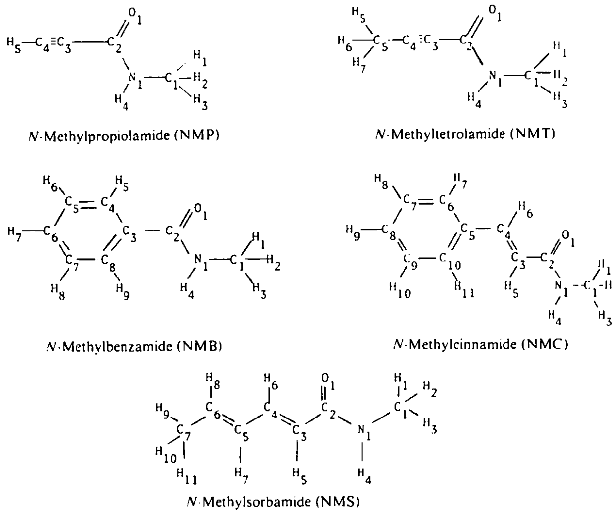

Fig. 1. Chemical formulae and labelling of atoms.

1971). *E* maps computed with the models which had the highest figures of merit, revealed the molecular skeletons.

The individual atomic parameters of the C, N, O atoms of all five molecules were first refined isotropically, and then anisotropically, in a full-matrix least-squares program. Next, all H atoms, except those of the methyl groups, were inserted in chemically reasonable positions, and refined isotropically. The methyl H atoms were then clearly located on electron-density difference maps. Finally, all the parameters were refined until convergence. No parameter shift was greater than $0{\cdot}3\sigma$. The scattering factors used were taken from *International Tables for X-ray Crystallography* (1962). The details and the results of the refinement are presented in Table 3.

The final atomic coordinates, and their e.s.d.'s are listed in Table 4. The observed bond lengths and angles and their e.s.d.'s are compiled in Table 5.*

2.1. *Molecular shape of the N-methylamide group*

The amide groups CCON in the five structures are each planar to within 0·005 Å (Table 6). The methyl C atom attached to N deviates, on average, by 0·006 Å from the plane of the amide system (Table 6).

The average torsion angle φ(H—C—N—C) about the N—CH_3 bond, derived from the values of the three individual torsion angles (φ_1,φ_2,φ_3) for the three methyl H atoms by taking the average φ_1, $\varphi_2 - 120$ and $\varphi_3 - 240°$, are listed in Table 7. According to an experimental and theoretical analysis of the conformational properties of the N—CH_3 group of *N*-methylamides (Hagler, Leiserowitz & Tuval, 1976), the conformation in which one of the C—H bonds is *anti* to the C(carbonyl)—N bond is dominant, but not unique. Some of the torsion angles deviate by as much as 30° from this conformation (*e.g.* *N*-methylformamide, or *N*-methylsorbamide), and only *N*-methylformamide, in its crystal complex with oxalic acid (Leiserowitz & Nader, 1978) exhibits a conformation in which the C(carbonyl) —N bond is eclipsed by a methyl C—H bond.

Table 1. *Crystal data*

	NMP	NMT	NMB	NMC	NMS
Formula	C_4H_5NO	C_5H_7NO	C_8H_9NO	$C_{10}H_{11}NO$	$C_7H_{11}NO$
M_r	83	97	135	161	125
m.p. (°C)	86	60–62	82	110	139
Crystallization	Slow evaporation of 1 : 1 mixture of hexane and chloroform	Slow evaporation of 1 : 1 mixture of methanol and water	Slow evaporation of benzene solution	Slow evaporation of benzene solution	Slow evaporation of 1 : 1 mixture of methanol and water
Space group	*Pbca*	$P2_1/c$	*Pbca*	*Aba*2	$Pna2_1$
$a, \sigma(a)$ (Å)	13·361 (2)	7·354 (1)	16·734 (2)	11·289 (1)	24·224 (3)
$b, \sigma(b)$	8·567 (1)	9·225 (1)	9·615 (1)	17·175 (2)	4·923 (1)
$c, \sigma(c)$	8·267 (1)	8·429 (1) $\beta = 96{\cdot}02$ (3)°	9·246 (1)	9·528 (1)	6·416 (1)
Radiation, λ(Mo $K\alpha_1$) = 0·70926 Å λ(Cu $K\alpha_1$) = 1·54051 Å	Mo $K\alpha_1$	Mo $K\alpha_1$	Cu $K\alpha_1$	Mo $K\alpha_1$	Mo $K\alpha_1$
Z	8	4	8	8	4
D_c (g cm^{-3})	1·16	1·14	1·20	1·16	1·08
V (Å^3)	946·3	571·9	1487·6	1847·4	765·1
μ (cm^{-1})	1	1	7	1	1

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* Lists of thermal parameters, intermolecular distances and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33114 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Intensity measurement and processing*

Data were collected at room temperature (~25°C).

	NMP	NMT	NMB	NMC	NMS
Diffractometer	Siemens	Nonius	Siemens	Siemens	Siemens
Radiation	Mo $K\alpha$	Mo $K\alpha$	Cu $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
Monochromatization	Zr,Y balanced filters	Graphite-crystal monochromator	Ni filter	Zr,Y balanced filters	
Crystal dimensions (mm × 10^{-1})	3 × 4 × 4	3 × 5 × 4	2 × 4 × 1	2 × 2 × 7	2 × 2 × 7
Crystal mount axis in reciprocal coordinates [*hkl*]	[010]	[001]	[010]	[001]	[010]
Scanning mode	$\theta/2\theta$ step scan (0·01° step)				
Step-scan time for intensity and background profiles (s)	0·4, 0·2	0·5, 0·2	0·4, 0·4	0·4, 0·2	0·8, 0·4
Maximum θ angle (°)	27·5	28·5	70·0	27·5	27·0
Reflection interval for four monitor reflections	60	100	100	50	50
Variation in the computed absorption factor *A* (Coppens, Leiserowitz & Rabinovich, 1965)	0·98–0·99	0·98–0·99	0·87–0·94	0·97–0·99	0·97–0·99
Number of reflections measured	2113	2328	3401	3162	2892
Number of unique reflections	1100	1316	1412	1418	917
Number of 'unobserved' reflections for which $F_o^2 < 2\sigma(F_o^2)$	303	434	310	831	395
Reliability factor R'*	0·03	0·05	0·02	0·05	0·06

* $R' = \Sigma_{i,j}(F_{i,j} - \bar{F}_j)^2/\Sigma_{i,j}F^2_{i,j}$, where $\bar{F}_j = \Sigma_i\, w_{ij}F_{ij}/\Sigma_i\, w_{ij}$ is the weighted average of the *j*th group of *i* symmetry-equivalent reflections, F_{ij} is the individual value of each reflection in the group and w_{ij} is the corresponding weight.

Table 3. *Crystal structure refinement*

	NMP	NMT	NMB	NMC	NMS
Minimized quantity	$\Sigma\, w(F_o^2 - \lvert F_c\rvert^2)^2$				
Number of parameters refined	75	92	127	149	125
Number of reflections used in last cycle	800	990	1170	665	547
Number of reflections given zero weight believed to have extinction errors	22	6	20	6	6
R (including 'unobserved' reflections)	0·045	0·057	0·045	0·076	0·061
$r[=\Sigma\, w(F_o^2 - \lvert F_c\rvert^2)^2/\Sigma\, wF_o^4]$	0·007	0·012	0·007	0·004	0·007

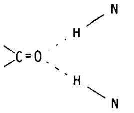
3. Crystal packing of secondary amides and the N—H···O bond

3.1. *Introduction*

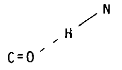
This discussion covers the following topics: (i) the preferred N—H···OC geometry in which the carbonyl O atom participates in two N—H···O bonds, and in a single N—H···O bond; (ii) the basic hydrogen-bonding motifs in *trans* secondary amides; (iii) a description and analysis of the hydrogen-bonding packing motifs of *N*-methylamides as determined by the requirements of the N—H···O bond as well as by the nature of the residue *R*; (iv) the IR N—H stretching frequency and the angular geometry of the N—H···O=C bond in *N*-methylamides; (v) a comparison of N—H···O distances in primary and secondary amides.

3.2. *The preferred geometry of the* N—H···O *bond*

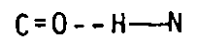
An analysis of the molecular packing modes of primary amides *R*—CONH$_2$ (Leiserowitz & Schmidt, 1969) has shown that the N—H···O=C system tends to adopt, the *R* group permitting, the motif (1), which is coplanar and contains two linear N—H···O bonds symmetrically disposed about the carbonyl C=O bond with C=O···N angles ≃120°.



(1)



(2*a*)



(2*b*)

While these results indicate that the geometry of the N—H···O motif (1) is most favourable when the

Table 4. *Fractional atomic coordinates* (× 10⁴ *for* C, N, O *and* × 10³ *for* H) *and their estimated standard deviations*

	x	*y*	*z*		*x*	*y*	*z*
(*a*) *N*-Methylpropiolamide (NMP)							
C(1)	5631 (1)	3122 (2)	−16 (2)	C(2)	4129 (1)	1545 (2)	216 (1)
C(3)	3319 (1)	1051 (2)	1279 (2)	C(4)	2669 (1)	576 (2)	2078 (2)
N(1)	4734 (1)	2613 (2)	826 (1)	O(1)	4223 (1)	969 (1)	−1144 (1)
H(1)	543 (2)	370 (3)	−96 (3)	H(2)	605 (2)	379 (3)	69 (2)
H(3)	599 (1)	226 (3)	−45 (3)	H(4)	457 (1)	298 (2)	175 (2)
H(5)	213 (1)	14 (2)	276 (2)				
(*b*) *N*-Methyltetrolamide (NMT)							
C(1)	3247 (3)	−29 (2)	3187 (3)	C(2)	6130 (2)	−35 (1)	2026 (2)
C(3)	7518 (2)	853 (1)	1390 (2)	C(4)	8681 (2)	1549 (2)	876 (2)
C(5)	10078 (3)	2435 (2)	248 (3)	N(1)	4743 (2)	690 (1)	2525 (2)
O(1)	6271 (2)	−1354 (1)	2091 (2)	H(1)	251 (4)	−58 (4)	255 (4)
H(2)	367 (3)	−84 (3)	386 (3)	H(3)	270 (4)	64 (3)	375 (4)
H(4)	472 (2)	157 (2)	249 (2)	H(5)	1098 (4)	187 (3)	−29 (3)
H(6)	963 (4)	317 (3)	−37 (4)	H(7)	1072 (4)	296 (3)	104 (4)
(*c*) *N*-Methylbenzamide (NMB)							
C(1)	4010 (1)	9005 (2)	1566 (3)	C(2)	5071 (1)	8353 (2)	3235 (2)
C(3)	5803 (1)	8764 (1)	4052 (1)	C(4)	6227 (1)	9966 (2)	3776 (2)
C(5)	6916 (1)	10260 (2)	4544 (2)	C(6)	7180 (1)	9364 (2)	5599 (2)
C(7)	6756 (1)	8170 (2)	5894 (2)	C(8)	6075 (1)	7868 (2)	5125 (2)
N(1)	4720 (1)	9312 (1)	2419 (2)	O(1)	4808 (1)	7154 (1)	3314 (1)
H(1)	376 (1)	989 (3)	125 (2)	H(2)	413 (1)	837 (2)	78 (2)
H(3)	361 (1)	844 (2)	219 (2)	H(4)	491 (1)	1017 (2)	238 (2)
H(5)	603 (1)	1059 (2)	303 (2)	H(6)	721 (1)	1115 (2)	431 (2)
H(7)	765 (1)	956 (2)	612 (2)	H(8)	698 (1)	753 (2)	665 (2)
H(9)	577 (1)	698 (2)	530 (2)				
(*d*) *N*-Methylcinnamide (NMC)							
C(1)	4143 (7)	−887 (5)	5483 (9)	C(2)	2576 (4)	28 (3)	6150 (0)
C(3)	1593 (5)	528 (4)	5617 (7)	C(4)	938 (4)	982 (3)	6444 (8)
C(5)	−40 (5)	1490 (3)	5987 (7)	C(6)	−419 (6)	2092 (4)	6853 (9)
C(7)	−1318 (7)	2604 (4)	6429 (9)	C(8)	−1857 (6)	2508 (4)	5150 (9)
C(9)	−1516 (6)	1904 (4)	4304 (9)	C(10)	−598 (5)	1405 (4)	4696 (7)
N(1)	3210 (4)	−326 (2)	5159 (6)	O(1)	2812 (3)	−46 (2)	7419 (5)
H(1)	457 (4)	−73 (3)	627 (8)	H(2)	392 (5)	−142 (3)	568 (6)
H(3)	473 (5)	−88 (3)	487 (6)	H(4)	295 (4)	−22 (3)	426 (5)
H(5)	146 (4)	54 (3)	463 (5)	H(6)	120 (4)	97 (3)	750 (6)
H(7)	0 (5)	214 (3)	778 (5)	H(8)	−154 (4)	303 (3)	719 (5)
H(9)	−252 (4)	292 (3)	487 (5)	H(10)	−34 (5)	100 (2)	409 (5)
H(11)	−192 (5)	180 (3)	339 (6)				
(*e*) *N*-Methylsorbamide (NMS)							
C(1)	2482 (2)	4048 (9)	−139 (9)	C(2)	3456 (1)	2757 (8)	−114 (9)
C(3)	4026 (2)	3763 (9)	−146 (9)	C(4)	4461 (2)	2203 (8)	0 (0)
C(5)	5027 (2)	3066 (9)	−84 (9)	C(6)	5459 (2)	1472 (9)	−182 (9)
C(7)	6047 (3)	2224 (9)	−187 (9)	N(1)	3063 (1)	4649 (7)	−117 (9)
O(1)	3345 (1)	326 (5)	−114 (9)	H(1)	243 (2)	236 (9)	−77 (9)
H(2)	237 (2)	402 (9)	137 (7)	H(3)	226 (2)	536 (8)	−78 (7)
H(4)	315 (1)	627 (7)	9 (9)	H(5)	406 (1)	548 (7)	19 (9)
H(6)	440 (1)	44 (6)	−57 (6)	H(7)	511 (1)	491 (8)	−56 (7)
H(8)	541 (2)	−26 (9)	−49 (9)	H(9)	609 (2)	413 (9)	−57 (9)
H(10)	625 (3)	225 (9)	−119 (9)	H(11)	627 (3)	144 (9)	122 (9)

carbonyl O atom participates in *two* hydrogen bonds, the question arises whether this N—H···O geometry is still preferred if the system contains only *one* N—H···O bond. This question is answered in part by the crystal structure of, and polarized IR data on, cyanuric acid, as discussed by a number of authors (Leiserowitz & Schmidt, 1969; Coppens & Vos, 1971). Its hydrogen-bonding network (Fig. 2) comprises two

Table 5. *Bond lengths* (Å), *bond angles* (°) *and their estimated standard deviations*

(*a*) *N*-Methylpropiolamide

C(1)–N(1)	1·453 (2)	C(3)–C(4)	1·164 (2)
C(2)–O(1)	1·234 (2)	C(1)–H(3)	0·95 (2)
C(1)–H(1)	0·96 (2)	C(2)–N(1)	1·321 (2)
N(1)–H(4)	0·86 (2)	C(1)–H(2)	1·00 (2)
C(2)–C(3)	1·457 (2)	C(4)–H(5)	0·99 (2)

N(1)–C(1)–H(1)	108·4 (13)	N(1)–C(1)–H(2)	111·0 (13)
N(1)–C(1)–H(3)	111·3 (13)	H(1)–C(1)–H(2)	109·5 (19)
H(1)–C(1)–H(3)	103·5 (19)	H(2)–C(1)–H(3)	112·7 (18)
C(3)–C(2)–N(1)	115·2 (1)	C(3)–C(2)–O(1)	120·6 (1)
N(1)–C(2)–O(1)	124·2 (1)	C(2)–C(3)–C(4)	176·1 (2)
C(3)–C(4)–H(5)	178·0 (11)	C(1)–N(1)–C(2)	122·0 (1)
C(1)–N(1)–H(4)	122·0 (11)	C(2)–N(1)–H(4)	116·0 (11)

(*b*) *N*-Methyltetrolamide

C(1)–N(1)	1·446 (3)	C(1)–H(3)	0·90 (3)
C(2)–O(1)	1·222 (2)	C(5)–H(7)	0·92 (3)
C(1)–H(2)	0·97 (2)	C(2)–N(1)	1·325 (2)
C(5)–H(5)	0·99 (3)	C(4)–C(5)	1·455 (3)
N(1)–H(4)	0·81 (2)	C(1)–H(1)	0·88 (3)
C(2)–C(3)	1·454 (2)	C(5)–H(6)	0·90 (3)
C(3)–C(4)	1·187 (2)		

N(1)–C(1)–H(1)	118·2 (23)	N(1)–C(1)–H(2)	111·7 (14)
N(1)–C(1)–H(3)	107·0 (20)	H(1)–C(1)–H(2)	93·1 (25)
H(1)–C(1)–H(3)	115·7 (28)	H(2)–C(1)–H(3)	110·4 (24)
C(3)–C(2)–N(1)	115·2 (1)	C(3)–C(2)–O(1)	121·2 (1)
N(1)–C(2)–O(1)	123·6 (1)	C(2)–C(3)–C(4)	178·3 (2)
C(3)–C(4)–C(5)	178·5 (2)	C(4)–C(5)–H(5)	113·5 (16)
C(4)–C(5)–H(6)	113·7 (18)	C(4)–C(5)–H(7)	111·3 (23)
H(5)–C(5)–H(6)	111·0 (25)	H(5)–C(5)–H(7)	107·4 (26)
H(6)–C(5)–H(7)	98·8 (26)	C(1)–N(1)–C(2)	122·2 (1)
C(1)–N(1)–H(4)	117·3 (12)	C(2)–N(1)–H(4)	120·4 (12)

(*c*) *N*-Methylbenzamide

C(1)–N(1)	1·456 (3)	C(1)–H(3)	1·04 (2)
C(2)–O(1)	1·236 (2)	C(4)–H(5)	0·97 (2)
C(4)–C(5)	1·382 (3)	C(7)–H(8)	1·01 (2)
C(7)–C(8)	1·374 (3)	C(2)–N(1)	1·328 (2)
C(1)–H(2)	0·97 (2)	C(3)–C(4)	1·381 (2)
C(6)–H(7)	0·94 (2)	C(6)–C(7)	1·376 (3)
N(1)–H(4)	0·89 (2)	C(1)–H(1)	0·99 (2)
C(2)–C(3)	1·493 (2)	C(5)–H(6)	1·01 (2)
C(3)–C(8)	1·390 (2)	C(8)–H(9)	1·01 (2)
C(5)–C(6)	1·374 (3)		

N(1)–C(1)–H(1)	109·7 (12)	N(1)–C(1)–H(2)	111·1 (11)
N(1)–C(1)–H(3)	109·7 (11)	H(1)–C(1)–H(2)	114·0 (16)
H(1)–C(1)–H(3)	109·3 (16)	H(2)–C(1)–H(3)	102·7 (16)
C(3)–C(2)–N(1)	117·8 (1)	C(3)–C(2)–O(1)	120·6 (1)
N(1)–C(2)–O(1)	121·5 (1)	C(2)–C(3)–C(4)	123·4 (1)
C(2)–C(3)–C(8)	117·8 (1)	C(4)–C(3)–C(8)	118·9 (1)
C(3)–C(4)–C(5)	120·3 (2)	C(3)–C(4)–H(5)	118·5 (11)
C(5)–C(4)–H(5)	121·2 (11)	C(4)–C(5)–C(6)	120·3 (2)
C(4)–C(5)–H(6)	117·9 (11)	C(6)–C(5)–H(6)	121·8 (11)
C(5)–C(6)–C(7)	119·8 (2)	C(5)–C(6)–H(7)	120·2 (12)
C(7)–C(6)–H(7)	120·0 (11)	C(6)–C(7)–C(8)	120·1 (2)
C(6)–C(7)–H(8)	117·5 (11)	C(8)–C(7)–H(8)	122·3 (11)
C(3)–C(8)–C(7)	120·6 (2)	C(3)–C(8)–H(9)	118·4 (11)
C(7)–C(8)–H(9)	121·0 (11)	C(1)–N(1)–C(2)	121·9 (2)
C(1)–N(1)–H(4)	117·5 (11)	C(2)–N(1)–H(4)	120·6 (11)

(*d*) *N*-Methylcinnamide

C(1)–N(1)	1·461 (9)	C(1)–H(1)	0·93 (7)
C(2)–O(1)	1·244 (5)	C(4)–H(6)	1·05 (5)
C(5)–C(10)	1·390 (9)	C(8)–H(9)	1·07 (5)
C(7)–C(8)	1·372 (13)	N(1)–H(4)	0·93 (5)
C(1)–H(2)	0·97 (5)	C(2)–N(1)	1·331 (6)
C(3)–H(5)	0·95 (5)	C(4)–C(5)	1·472 (8)
C(7)–H(8)	1·05 (5)	C(6)–C(7)	1·403 (11)
C(10)–H(10)	0·95 (4)	C(9)–C(10)	1·397 (9)
C(2)–C(3)	1·492 (7)	C(1)–H(3)	0·89 (5)
C(3)–C(4)	1·333 (9)	C(6)–H(7)	1·01 (5)
C(5)–C(6)	1·390 (10)	C(9)–H(11)	1·00 (6)
C(8)–C(9)	1·369 (11)		

N(1)–C(1)–H(1)	110·7 (35)	N(1)–C(1)–H(2)	118·8 (34)
N(1)–C(1)–H(3)	113·1 (35)	H(1)–C(1)–H(2)	104·9 (52)
H(1)–C(1)–H(3)	97·7 (50)	H(2)–C(1)–H(3)	109·2 (48)
C(3)–C(2)–N(1)	114·9 (4)	C(3)–C(2)–O(1)	123·2 (4)
N(1)–C(2)–O(1)	121·8 (4)	C(2)–C(3)–C(4)	123·3 (6)
C(2)–C(3)–H(5)	117·7 (27)	C(4)–C(3)–H(5)	118·9 (28)
C(3)–C(4)–C(5)	126·0 (7)	C(3)–C(4)–H(6)	113·4 (25)
C(5)–C(4)–H(6)	120·5 (25)	C(4)–C(5)–C(6)	119·7 (6)
C(4)–C(5)–C(10)	122·6 (6)	C(6)–C(5)–C(10)	117·7 (6)
C(5)–C(6)–C(7)	121·2 (7)	C(5)–C(6)–H(7)	115·8 (32)
C(7)–C(6)–H(7)	122·9 (32)	C(6)–C(7)–C(8)	120·1
C(6)–C(7)–H(8)	114·0 (29)	C(8)–C(7)–H(8)	125·9 (28)
C(7)–C(8)–C(9)	119·3 (7)	C(7)–C(8)–H(9)	117·0 (28)
C(9)–C(8)–H(9)	123·7 (28)	C(8)–C(9)–C(10)	121·1 (8)
C(8)–C(9)–H(11)	121·4 (30)	C(10)–C(9)–H(11)	117·5 (30)
C(5)–C(10)–C(9)	120·5 (6)	C(5)–C(10)–H(10)	118·6 (29)
C(9)–C(10)–H(10)	120·9 (29)	C(1)–N(1)–C(2)	122·6 (6)
C(1)–N(1)–H(4)	123·7 (28)	C(2)–N(1)–H(4)	113·5 (28)

(*e*) *N*-Methylsorbamide

C(1)–N(1)	1·438 (5)	C(1)–H(1)	0·93 (5)
C(2)–O(1)	1·227 (5)	C(5)–H(7)	0·98 (4)
C(5)–C(6)	1·310 (7)	C(7)–H(9)	0·97 (5)
C(1)–H(3)	0·94 (4)	C(2)–N(1)	1·331 (5)
C(4)–H(6)	0·96 (3)	C(4)–C(5)	1·437 (6)
C(7)–H(11)	1·12 (7)	C(1)–H(2)	1·00 (5)
N(1)–H(4)	0·84 (4)	C(3)–H(5)	0·88 (4)
C(2)–C(3)	1·467 (5)	C(6)–H(8)	0·88 (4)
C(3)–C(4)	1·307 (6)	C(7)–H(10)	0·81 (8)
C(6)–C(7)	1·471 (8)		

N(1)–C(1)–H(1)	109·1 (25)	N(1)–C(1)–H(2)	104·5 (30)
N(1)–C(1)–H(3)	115·7 (26)	H(1)–C(1)–H(2)	111·4 (45)
H(1)–C(1)–H(3)	109·9 (42)	H(2)–C(1)–H(3)	106·0 (41)
C(3)–C(2)–N(1)	115·9 (3)	C(3)–C(2)–O(1)	122·4 (3)
N(1)–C(2)–O(1)	121·7 (3)	C(2)–C(3)–C(4)	124·0 (4)
C(2)–C(3)–H(5)	113·8 (19)	C(4)–C(3)–H(5)	118·7 (20)
C(3)–C(4)–C(5)	126·4 (4)	C(3)–C(4)–H(6)	112·2 (16)
C(5)–C(4)–H(6)	114·1 (15)	C(4)–C(5)–C(6)	126·0
C(4)–C(5)–H(7)	119·0 (18)	C(6)–C(5)–H(7)	112·0 (19)
C(5)–C(6)–C(7)	128·5 (6)	C(5)–C(6)–H(8)	118·2 (26)
C(7)–C(6)–H(8)	112·6 (26)	C(6)–C(7)–H(9)	110·1 (28)
C(6)–C(7)–H(10)	125·7 (58)	C(6)–C(7)–H(11)	112·4 (35)
H(9)–C(7)–H(10)	73·7 (79)	H(9)–C(7)–H(11)	118·9 (53)
H(10)–C(7)–H(11)	111·1 (66)	C(1)–N(1)–C(2)	123·7 (4)
C(1)–N(1)–H(4)	116·2 (21)	C(2)–N(1)–H(4)	119·4 (21)

Table 6. *Deviations from best planes*

Compound	Plane*	Equation of best plane	$\left[\left(\frac{\Sigma\Delta^2}{n-1}\right)^{1/2} \times 10^3\right]^\dagger$	Deviations ($\times 10^2$ Å) of other atoms from best plane
NMP	I	$7{\cdot}8009x - 6{\cdot}1603y + 3{\cdot}1157z - 2{\cdot}3390 = 0$	2	H(4) −7, C(1) 12, C(4) 4
NMT	I	$2{\cdot}9531x + 0{\cdot}6542y + 7{\cdot}3000z - 3{\cdot}2875 = 0$	1	H(4) 3, C(1) 0, C(4) 1, C(5) 2
NMB	I	$9{\cdot}5209x - 2{\cdot}5917y - 7{\cdot}1836z - 0{\cdot}3414 = 0$	2	H(4) −2, C(1) 2
	II	$9{\cdot}2321x - 4{\cdot}7079y - 6{\cdot}2428z + 1{\cdot}2869 = 0$	12	C(1) 23, N(1) −25, O(1) 29
NMC	I	$6{\cdot}9885x + 13{\cdot}4650y - 0{\cdot}4384z - 1{\cdot}5758 = 0$	5	H(4) 1, C(1) 11
	II	$7{\cdot}5697x + 10{\cdot}4433y - 4{\cdot}0494z + 0{\cdot}8889 = 0$	14	C(2) 38, C(3) 37, N(1) 89, O(1) −3
	III	$7{\cdot}2898x + 12{\cdot}8963y - 1{\cdot}3195z - 1{\cdot}1017 = 0$	1	C(1) 5, N(1) 14, O(1) −9
NMS	I	$0{\cdot}2145x + 0{\cdot}1910y + 6{\cdot}4161z - 0{\cdot}0017 = 0$	4	H(4) 13, C(1) −3
	IV	$0{\cdot}2457x + 0{\cdot}0917y + 6{\cdot}4150z - 0{\cdot}0639 = 0$	40	C(1) −5, N(1) −2, O(1) −5

* Atom groups forming the best planes are designated: (I) the amide group CCON, (II) the phenyl ring $C{-}C_6H_5$, (III) the vinyl system $-C{=}C-$, (IV) the carbon chain $C{-}C{=}C{-}C{=}C{-}C$.

† $\Sigma\Delta^2$ is the sum of the squares of the deviations (Å) from the best plane of the n atoms forming this plane.

Table 7. *Torsion angles* φ [H—C(*methyl*)—N—C] *and their estimated standard deviations*

Molecule	φ (°)
N-Methylpropiolamide	169 (2)
N-Methyltetrolamide	164 (4)
N-Methylbenzamide	167 (2)
N-Methylcinnamide	156 (3)
N-Methylsorbamide	147 (3)

different N—H···O bonds, a cyclic hydrogen-bonded N—H···O pair, in which the angle C=O···N ≃120° as shown in (2*a*), and a collinear N—H···O=C bond as shown in (2*b*). Their respective N—H···O distances (Å) and corresponding N—H stretching frequencies ν_s (cm^{-1}) are 2·805 and 3060; 2·784 and 3210. These results seem to be in contradiction to the linear correlation between $\Delta\nu_s$ and N···O distance (R) given by Nakamoto, Margoshes & Rundle (1955) in which the slope $\Delta R/\Delta\nu_s \simeq 8 \times 10^{-4}$ (Å cm). These results suggest that: (i) $\Delta\nu_s$ is dependent not only on the N···O distance but also on the angular geometry of the N—H···OC bond, (ii) motif (2*a*) is energetically preferred over that of (2*b*). This latter suggestion appears to be in keeping with a study of the packing modes of carboxylic acids (Leiserowitz, 1976) in which it was deduced that the linear O—H···O hydrogen bond with an O(H)···O=C angle ≃120° is more favourable than a collinear O—H···O=C system.

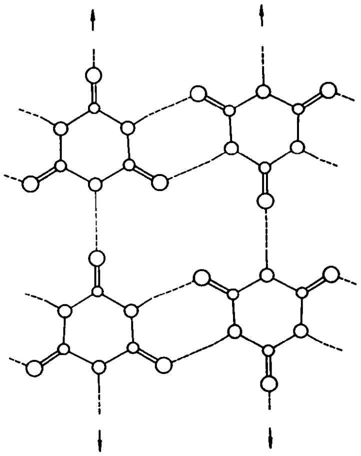
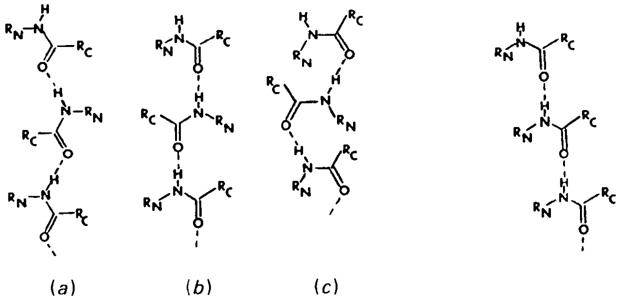


Fig. 2. Cyanuric acid (Verschoor & Keulen, 1971). Hydrogen-bonded layer.

3.3. *Basic hydrogen-bonding motifs of secondary amides*

According to crystal structures of acyclic *N*-mono-substituted *trans*-amides $R_C{-}CONHR_N$, two hydrogen-bonding motifs, (3) and (4), are generally observed.



(3) Glide, or 2_1-axis, motif

(4) Translation motif

Motif (3) comprises hydrogen-bonded ribbons in which the molecules are related by a glide or a 2_1 axis. The angular geometry of the N—H···O=C system might vary as it depends upon the tilt of the molecules with respect to the glide plane (or 2_1 axis). This results in three, more or less distinct, modes, (3*a*), (3*b*) and (3*c*). In both (3*a*) and (3*c*) the C=O···N angle may vary from 130–155°. In (3*b*) the N–H···O=C system tends to be collinear; the C=O···N angle varies from 180–155°. The molecules in motif (4) are related by translation and so its N–H···O=C system tends to be collinear. Of these four motifs (3*c*) appears to be the least satisfactory because of the obviously short contacts between the residues R_C and R_N. On the basis of the arguments given above that the favoured N–H···O=C geometry is exhibited by motif (2*a*) as against (2*b*), motif (3*a*), in a planar arrangement with a C=O···N angle ≃120°, is preferred over that of (3*b*) or (4).

Table 8 lists the hydrogen-bonding modes and N–H···O=C geometries of some secondary monoamides, *N*-methylamides excluded. The molecules appear in the hydrogen-bonding modes (3*a*), (3*c*) and (4). According to this short list it appears that if a monoamide molecule contains R_C and R_N residues which differ radically in size (*i.e.* acetanilide, *p*-bromoacetanilide, *p*-chloroacetanilide and *N*-propyltripropylacetamide) the molecules tend to interlink *via* the glide, or 2_1 axis, motif (3), exemplified by acetanilide (Brown, 1966) in Fig. 3. In motif (3*a*) contact between like bulky groups is avoided; were the molecules to hydrogen bond by translation as in motif (4) the contact distances $R_C \cdots R_C$ and $R_N \cdots R_N$ would be forced to be the same along the 5 Å axis. Examples of hydrogen-bonded molecules related by translation and glide are shown in Figs. 4 and 5 respectively.

N-Bromoacetamide is a unique example in the list of a molecule that packs in motif (3*c*), unlike the other molecules interconnected by a glide, or 2_1 axis, in motif (3*a*).

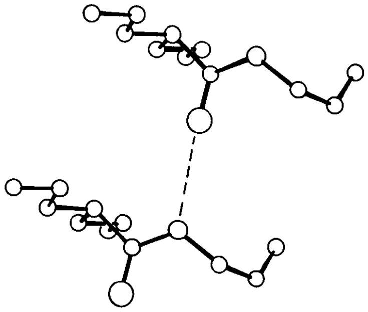


Fig. 4. *N*-Propyldipropylacetamide (Cohen-Addad & Grand, 1974*a*). Hydrogen-bonded molecules related by translation.

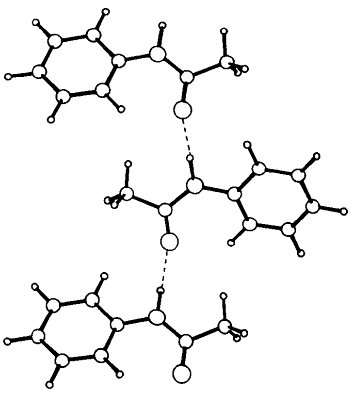


Fig. 3. Acetanilide (Brown, 1966). Hydrogen-bonding arrangement containing molecules related by a twofold screw axis.

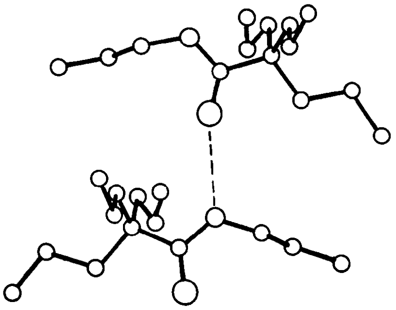
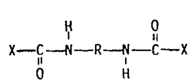


Fig. 5. *N*-Propyltripropylacetamide (Cohen-Addad & Grand, 1974*b*). Hydrogen-bonded molecules related by a glide.

Table 8. N–H···O *geometry in N-monosubstituted amides*

Compound	Hydrogen-bonding motif*	Distance (Å) N···O	Angle (°) C=O···N	C–N···O	Reference
N-Bromoacetamide	Glide motif (3*c*)	2·784	149·2	121·7	Dubey (1971)
N-Propyldipropylacetamide	Translation motif (4)	2·865	177·0	118·4	Cohen-Addad & Grand (1974*a*)
N-Propyltripropylacetamide	Glide motif (3*a*)	2·949	162·0	126·8	Cohen-Addad & Grand (1974*b*)
Acetanilide	Twofold screw-axis motif (3*a*)	2·943	139·1	122·0	Brown (1966)
p-Bromoacetanilide	Glide motif (3*a*)	2·87	158·0	126·0	Andreetti, Cavalca, Domiano & Musatti (1968)
p-Chloroacetanilide	Glide motif (3*a*)	2·83			Subramanian (1966)

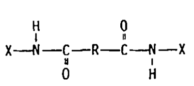
* See §3.3 for description of motifs (3*a*), (3*c*) and (4).



$$X{-}\underset{O}{\underset{\|}{C}}{-}\overset{H}{\overset{|}{N}}{-}R{-}\underset{H}{\underset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}X$$

X	R	Reference
CH_3	$(CH_2)_6$	Bailey (1955)
C_2H_5	$(CH_2)_6$	Jensen (1962)

(5*a*)



$$X{-}\overset{H}{\overset{|}{N}}{-}\underset{O}{\underset{\|}{C}}{-}R{-}\overset{O}{\overset{\|}{C}}{-}\underset{H}{\underset{|}{N}}{-}X$$

X	R	Reference
C_2H_5	$(CH_2)_4$	Benedetti, Ciajolo & Corradini (1973)
$Cl{-}C_2H_4$	$(CH_2)_3$	Benedetti, Ciajolo & Corradini (1973)

(5*b*)

Secondary diamides of the types shown in (5*a*) and (5*b*), in which *R* is a hydrocarbon chain, tend to form hydrogen bonds by translation, as this motif is independent of the length of the chain *R*. The motif is found in the reported crystal structures of the molecules listed in (5), exemplified by *N*,*N*′-diethyladipamide in Fig. 6, as well as all, but for one exception, of the undetermined crystal structures of secondary glutaramides, whose cell constants are listed in Table 9. The exception [$X = C_6H_5{-}CH(CH_3)$] forms a hydrogen-bonded motif along a glide of 9·5 Å. It is evident from Fig. 7 that a hydrogen-bonded arrangement generated by a glide (or 2_1 axis) is only possible in secondary diamides if a particular geometric relation exists between the length of the chain $C{-}R{-}C$ and that of the substituent *X*.

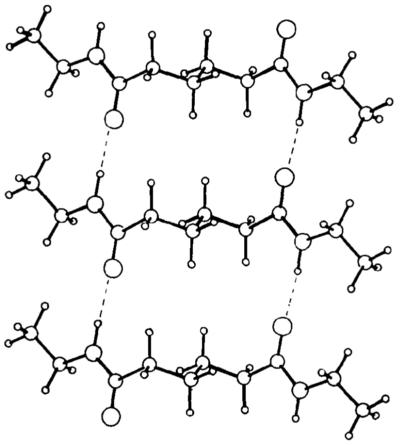
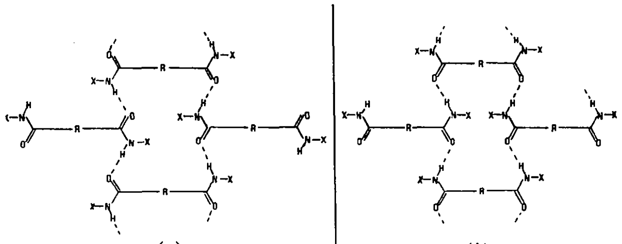


Fig. 6. *N*,*N*′-Diethyladipamide (Benedetti, Ciajolo & Corradini, 1973). Hydrogen-bond motif along the 5 Å translation axis.



(*a*) (*b*)

Fig. 7. Diamides hydrogen-bonded by a glide (or 2_1 axis). (*a*) Centrosymmetric molecule. (*b*) Twofold molecular symmetry.

3.4. *Description of the hydrogen-bonding modes of* $RCONHCH_3$

The packing modes of R_CCONHR_N discussed in the foregoing section as a function of various R_C and R_N groups do not provide insight as to the preferred N—H···O bond motif. We shall examine this point in the *N*-methylamides $RCONHCH_3$, and also the question as to what extent the N—H···O geometry is determined by the size and composition of the residue *R*.

Classifying the available crystal structures of eight *N*-methylamides, two distinct groups are formed: (i) *N*-methylacetamide (Katz & Post, 1960), *N*-methylpropiolamide, *N*-methyltetrolamide, *N*-methylbenzamide and *N*-methylcinnamide which pack in the glide, or 2_1-axis, motif (3), (ii) *N*-methyl-α-chloroacetamide (Koyama, Shimanouchi & Iitaka, 1971), *N*-methyldipropylacetamide (Grand & Cohen-Addad, 1973), and *N*-methylsorbamide which exhibit the translation motif (4).

3.4.1. *Glide and twofold screw axis hydrogen-bonded motifs*

3.4.1.1. *N-Methylacetamide*. The hydrogen-bonded molecules (Fig. 8) pack in the glide motif (3*a*) along a 9·6 Å axis. They are coplanar by virtue of a crystallographic mirror plane. The N···O distance is 2·83 Å, the C=O···O angle is 141·5° and the C—N···O angle is 119·0° (Table 10).

3.4.1.2. *N-Methylpropiolamide*. The N—H···O system is generated by a glide of 8·27 Å, as shown in Fig. 9(*a*) and (*b*). This figure reveals that the N—H vector approaches the C=O bond in a direction similar to that depicted in the rarely observed motif (3*c*), the N—H bond lying close to the N—CH_3 methyl group of the

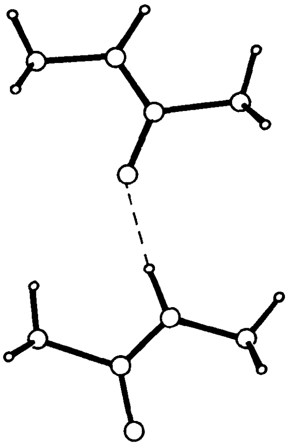
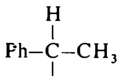
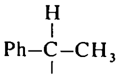
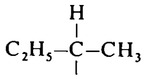
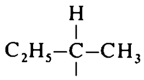


Fig. 8. The hydrogen-bonded structure of *N*-methylacetamide (Katz & Post, 1960). The hydrogen atomic positions, not reported by Katz & Post, were clearly located *via* electron density difference maps utilizing their observed structure factors.

Table 9. *Cell constants of some glutaric acid diamides* X–N(–H)–C(=O)–(CH$_2$)$_3$–C(=O)–N(–H)–X

X	R or RS*	a (Å)	b (Å)	c (Å)	β (°)	Z	Space group	D_c (g cm^{-3})	Hydrogen-bonding mode symmetry element, axis
 $\mathrm{Ph{-}\overset{\overset{H}{\vert}}{\underset{\vert}{C}}{-}CH_3}$	R	19·15	5·08	21·31	112·9	4	$C2$	1·18	Translation, 5·1 Å axis
 $\mathrm{Ph{-}\overset{\overset{H}{\vert}}{\underset{\vert}{C}}{-}CH_3}$	RS	17·88	11·56	9·48	95	4	$P2_1/c$	1·15	Glide, 9·5 Å axis
 $\mathrm{C_2H_5{-}\overset{\overset{H}{\vert}}{\underset{\vert}{C}}{-}CH_3}$	R	14·49	11·10	4·91	92	2	$P2_1$	1·02	Translation, 4·9 Å axis
 $\mathrm{C_2H_5{-}\overset{\overset{H}{\vert}}{\underset{\vert}{C}}{-}CH_3}$	RS	27·85	11·11	4·90	91	4	$P2_1/a$	1·01	Translation, 4·9 Å axis
CH$_3$CH$_2$CH$_2$–		14·35	5·19	17·66	98·5	4	$A2/a$	1·12	Translation, 5·2 Å axis

* R represents a pure enantiomeric composition. RS represents a racemic composition (RR and SS diamides in equimolar quantities).

Table 10. *Hydrogen-bonding geometry and* N–H *stretching frequencies* (cm^{-1}) *of N-methylamides*

Distances are in Å, angles in degrees.

N-Methyl derivatives of:	Acetamide	Propiolamide	Tetrolamide	*α-Chloro-acetamide	Dipropyl-acetamide	Benzamide	Sorbamide	Cinnamide
Mode of generating hydrogen bond	Glide of 9·6 Å	Glide of 8·3 Å	2_1 axis of 9·2 Å	Translation of 5·1 Å	Translation of 4·9 Å	2_1 axis of 9·6 Å	Translation of 4·9 Å	Glide of 9·5 Å
N···O distance	2·833	2·866	2·856	2·830	2·818	2·925	2·873	2·892
N···O=C angle	141·5	130·6	159·2	154·8	179·5	139·6	179·0	144·1
C–N···O angle	119·0	118·8	137·2	146·9	119·1	131·3	120·7	110·6
Deviations of N–H from amide plane to which it is hydrogen-bonded	0, 0	1·42, 1·0	0·21, 0·1	0·47, 0·3	0·01, 0·2	1·71, 1·3	0·02, 0·1	1·21, 0·8
$\nu_{\mathrm{N-H}}$, in dilute CCl$_4$	3475	3450	3440				3440	3440
$\nu_{\mathrm{N-H}}$, crystalline film	3300	3240	3300				3260	3260
$\Delta\nu_{\mathrm{N-H}}$	175	210	140				180	180
Reference	(1), (2)	(3)	(3)	(4)	(5)	(3)	(3)	(3)

References: (1) Katz & Post (1960) for structure determination. (2) Mizushima *et al.* (1950) for IR measurements. (3) This work. (4) Koyama, Shimanouchi & Iitaka (1971). (5) Grand & Cohen-Addad (1973).

* Average values taken from two molecules per asymmetric unit.

amide system to which it is hydrogen-bonded. The hydrogen-bonded molecules are not coplanar (Table 10 and Fig. 9*b*); the N atom lies 1·4 Å, and its attached H 1·0 Å, from the amide plane to which N–H is hydrogen-bonded. The N–H···O bond is linear (Fig. 9*b*). The observed N···O distance in *N*-methylpropiolamide is 2·87 Å, the C=O···N angle is 130·6° and the C–N···O angle is 118·8° (Table 10).

The molecular packing of *N*-methylpropiolamide contains an additional stabilizing interaction between the acetylene H atom and the carbonyl O atom (Fig. 9). The C(H)···O distance is 3·2 Å (H···O 2·2 Å) and the C–H···O bond linear. The ≡C–H···O–C< system is approximately coplanar and the C=O···H(C≡) angle is 120°. The existence of the acetylenic C–H···O interaction in the solid is further supported by IR data. The IR spectrum of *N*-methylpropiolamide in very dilute CCl$_4$ shows two peaks in the range 3000–3500 cm^{-1}, one at 3300, which corresponds to the value for the free H–C(≡C) stretching frequency (Bellamy, 1958; Calabrese, McPhail & Sim, 1966) and the second at 3450 cm^{-1} for the free N–H

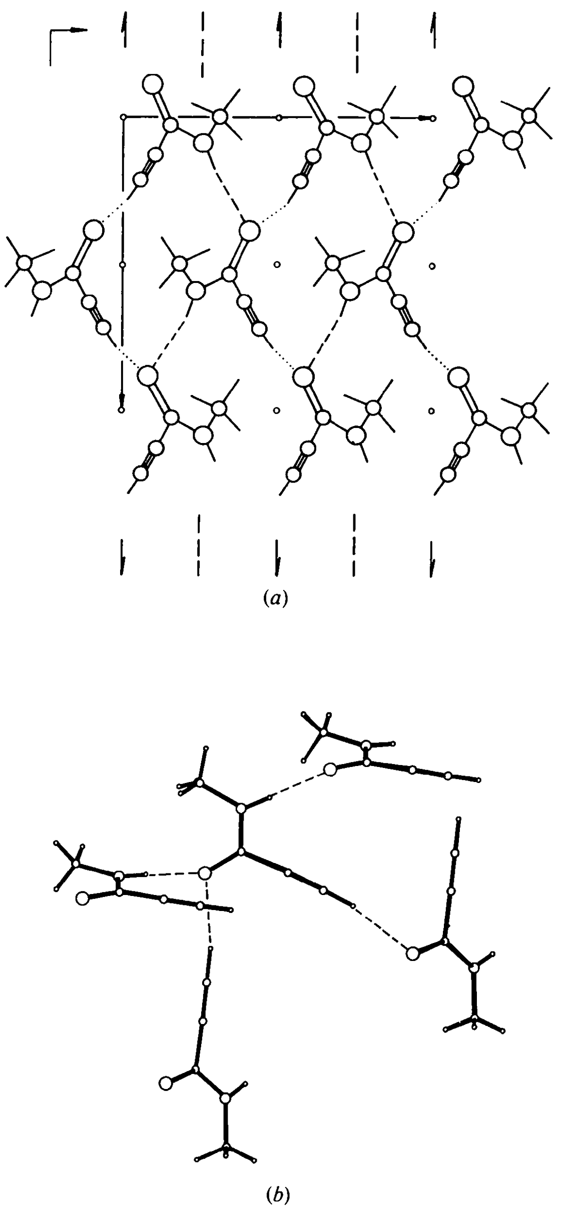


Fig. 9. *N*-Methylpropiolamide. (*a*) Packing arrangement viewed along **a**. (*b*) N–H···O and C–H···O interactions seen perpendicular to the plane of the central molecule.

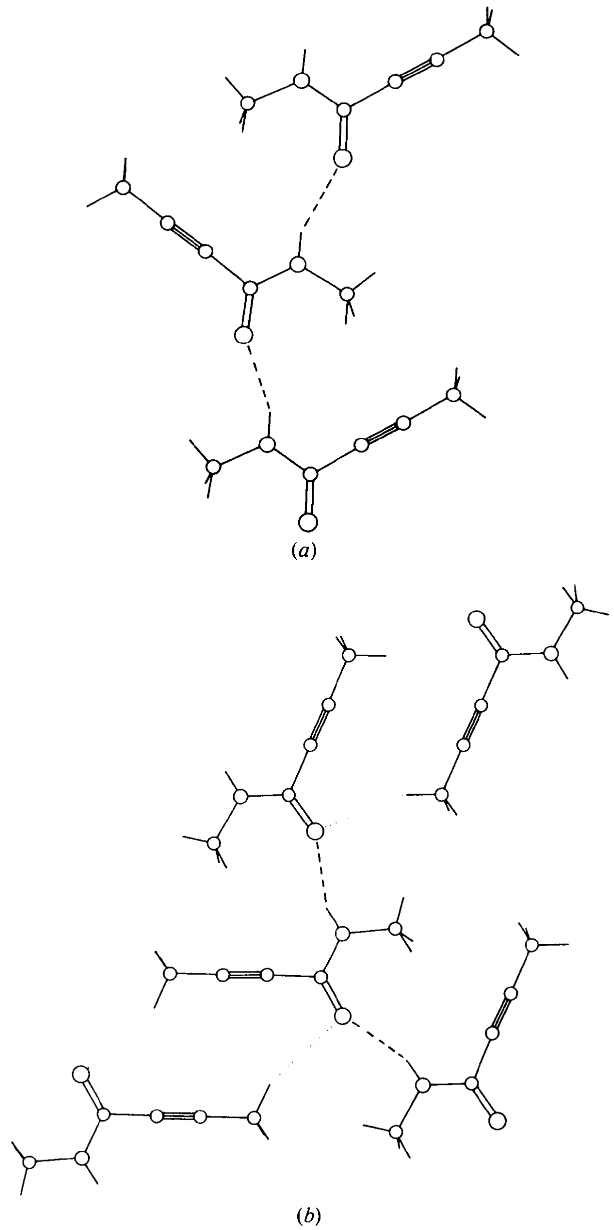


Fig. 10. *N*-Methyltetrolamide. (*a*) Hydrogen-bonded array along a twofold screw axis. (*b*) Layer structure.

Table 11. *Stretching frequency* (cm^{-1}) *shift in acetylenic* CH ··· O *'hydrogen-bonded' systems*

Compound	$\nu_{\equiv CH\ free}$	$\nu_{\equiv CH\ bonded}$	$\Delta\nu$	H···O (Å)	Reference
Bromomethylacetylene	3311	3209*	102		Allerhand & Schleyer (1963)
Butylacetylene	3315	3233*	82		
Benzoylacetylene	3305	3233†	73		Brand, Eglinton & Morman (1960)
o-Chlorobenzoylacetylene	3304	3235†	69	2·2	Ferguson & Islam (1966)
Propargyl 2-bromo-3-nitrobenzoate $NO_2-C_6H_3Br-C(=O)-O-CH_2-C\equiv C-H$	3313	3266†	47	2·4	Calabrese, McPhail & Sim (1966)

* $\nu_{\equiv CH\ bonded}$ is the frequency of the compound in dimethyl sulphoxide-d_6.
† $\nu_{\equiv CH\ bonded}$ is the frequency of the compound in the crystal.

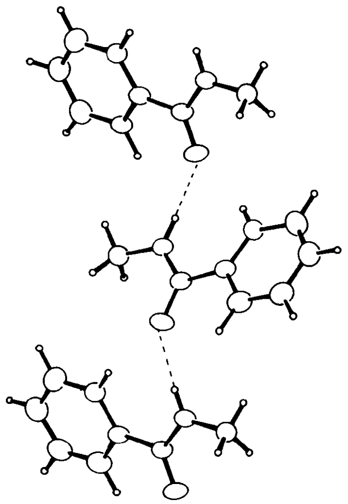


Fig. 11. N-Methylbenzamide. Hydrogen-bonded chains generated by a twofold screw axis.

stretching frequency in *trans* secondary amides (Bellamy, 1958). In the IR spectrum of crystalline N-methylpropiolamide the peak due to the acetylenic H atom appears at 3190 cm^{-1}. This shift of 110 cm^{-1} corresponds to the frequency decrease when the H atom is no longer free, and compares well with the shift in frequency in acetylenic C–H···O hydrogen-bonded systems summarized in Table 11.

3.4.1.3. *N-Methyltetrolamide*. The molecules form N–H···O bonds along a 2_1 axis of 9·2 Å. The observed hydrogen-bonding motif (Fig. 10) resembles motif (3*b*) whose N–H···O=C bond tends to be collinear. The N(H)···O=C angle is 159·2°, the C–N···O angle is 137·2° and the N···O bond length is 2·86 Å (Table 10). The structure incorporates approximately coplanar centrosymmetric dimers (Fig. 10*b*) in which one of the methyl C–H bonds of the $\equiv C-CH_3$ group lies in the plane of the dimer and straddles the $C\equiv C$ and C=O bonds of the neighbouring paired molecule. The $\equiv C-CH_3$ methyl group is part of the cylindrically symmetric acetylenic system, so the methyl group can adopt any angular conformation. Thus, the observation that the C–H bond lies in the plane of the molecular pair suggests that it is held therein by intrapair forces. The C–H···O and C–H···$C\equiv C$ (centre) distances within the pair are 2·7 and 3·0 Å respectively. A very similar motif also appears in the crystal structure of α-tetrolic acid (Benghiat & Leiserowitz, 1972), suggesting that the pair motif in N-methyltetrolamide is stabilized by weak bifurcated C–H···O and C–H···($C\equiv C$) interactions.

3.4.1.4. *N-Methylbenzamide and N-methylcinnamide*. These two molecules exhibit the effect of bulky phenyl and styryl groups on the N–H···O bond motif. The hydrogen-bonded molecules in N-methylbenzamide are related to each other by a 2_1 axis of 9·61 Å in an arrangement (Fig. 11) similar to motif (3*a*). The amide groups of the hydrogen-bonded molecules are not coplanar; the N atom lies 1·7 Å, and the attached H atom 1·3 Å, away from the amide plane to which N–H is hydrogen-bonded. The N···O distance is 2·93 Å, the C=O···N angle is 139·6° and the C–N···O angle is 131·3° (Table 10). The pronounced non-planarity of the N–H···O=C system and the relatively long N···O distance of 2·93 Å in N-methylbenzamide deviate distinctly from the corresponding values of other N-methylamides (Table 10). These 'distortions' are most likely induced by the necessity to avoid too short intermolecular contacts between the N-methyl group and the phenyl ring along the hydrogen-bond chain.

A feature in N-methylbenzamide worthy of mention is the 14° angle of twist of the benzene ring with respect to the amide group as compared with the 24·6° angle of twist observed in benzamide (Blake & Small, 1972), 28·7° in *m*-methylbenzamide (Orii, Nakamura, Takaki,

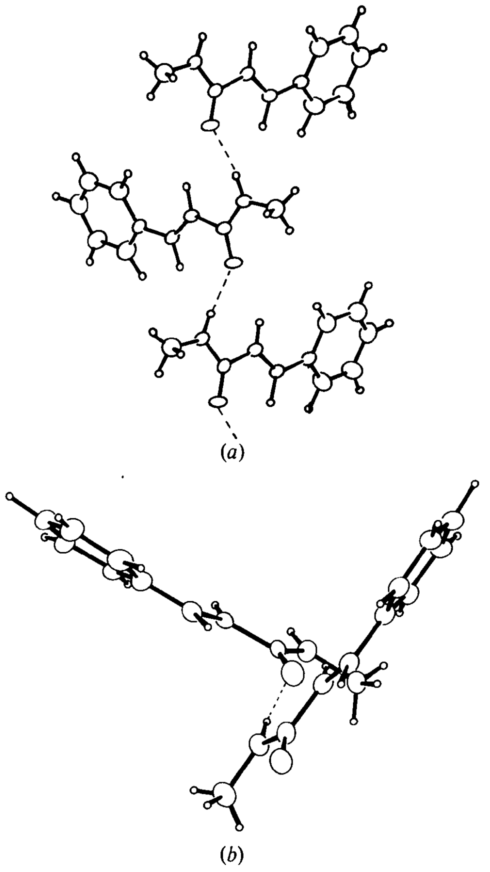
Table 12. *Angles of twist* (°) *in the benzamide and cinnamide series and the symmetry mode of generating the hydrogen bond*

Compound	Symmetry mode	Dihedral angle between the planes of groups* *A* and *B*	*A* and *C*	*B* and *C*	References
Terephthalamide	Translation	23			Cobbledick & Small (1972)
Benzamide	Translation	24·6			Blake & Small (1972)
m-Methylbenzamide	Translation	28·7			Orii *et al.* (1963)
N-Methylbenzamide	Twofold screw axis	14			This work
Hippuric acid	Twofold screw axis	14			Ringertz (1971)
Cinnamide	Translation		14	10	Osaki & Schmidt (unpublished)
p-Chlorocinnamide	Twofold screw axis		14	−6	Rabinovich (1969)
N-Methylcinnamide	Glide		18·5	4·8	This work

* *A* = Ph; *B* = –C(=O)–N–; *C* = –C=C–.

Sasada & Kakudo, 1963) and 23° in terephthalamide (Cobbledick & Small, 1972) (Table 12). According to Blake & Small (1972), this torsion angle in benzamide overcomes a too short intramolecular contact between the ring H and the H attached to the N. Because this intramolecular contact also exists in *N*-methylbenzamide the question arises as to why the twist angle in *N*-methylbenzamide is at least 10° less than in the other derivatives. The answer is provided by their different hydrogen-bonding patterns. The hydrogen-bonded molecules of *N*-methylbenzamide are related by a 2_1 axis; thus, the bulky phenyl groups do not interfere with each other along the 2_1 axis, rather the phenyl group makes intermolecular contact with the comparatively small $N-CH_3$ group. Consequently, the intramolecular H(*ortho*)···H(amide) interaction induces a twist of only 14°. This is further supported by the crystal structure of hippuric acid (Ringertz, 1971). Its phenylamide moieties (C_6H_5-CONH) are hydrogen-bonded along a 2_1 axis; the angle between the phenyl and amide planes is 14° (Table 12). In contrast to *N*-methylbenzamide (and hippuric acid), benzamide derivatives hydrogen-bonded along a 5 Å axis contain phenyl groups which would be in too close a contact but for the 23° twist of the phenyl group out of the plane of the amide system. This argument is supported by a previous interpretation (Leiserowitz & Schmidt, 1969) of the differences between the hydrogen-bond arrangement in benzamide and picolinamide (Takano, Sasada & Kakudo, 1966) both of which belong to the translation type. The lower angle of twist of 19° in the latter, possibly due to an (amide)N—H···N(aromatic) interaction which opposes further rotation, causes significant differences between the benzamide and picolinamide structures: the translation axis has expanded from 5·01 to 5·19 Å and the interpair N···O distance has risen from 2·91 to 3·01 Å.

N-Methylcinnamide appears in motif (3*a*). The molecules are H-bonded *via* a glide plane with an axial length of 9·5 Å (Fig. 12*a*). The motif is not planar (Fig. 12*b*). A planar system would necessitate an angle of


(*a*)

(*b*)

Fig. 12. *N*-Methylcinnamide. (*a*) Chain of hydrogen-bonded molecules generated by a glide. (*b*) A view displaying the non-planarity of the hydrogen-bonded system.

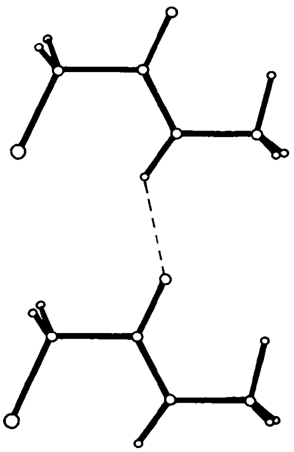


Fig. 13. *N*-Methyl-α-chloroacetamide (Koyama, Shimanouchi & Iitaka, 1971). The hydrogen-bond array. The hydrogen positions, not reported by Koyama, Shimanouchi & Iitaka, had been clearly located *via* electron density difference maps utilizing their observed structure factors.

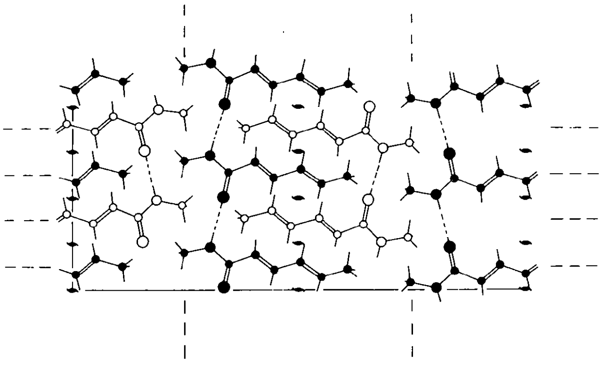


Fig. 14. *N*-Methylsorbamide. Packing seen along **c**.

90° between the glide and amide group planes. In *N*-methylcinnamide this angle is 47·8°, thus yielding a hydrogen-bonded system in which the N atom is 1·2 Å, and its attached H 0·8 Å, away from the plane of the amide group towards which the N—H vector points (Table 10). The N—H···O distance is 2·89 Å, the C=O···N angle is 144·1° and the C—N···O angle is 110·6° (Table 10).

In *N*-methylcinnamide the observed angle of twist of the phenyl ring with respect to the vinyl group is 18·5°. This angle is 14° both in cinnamide (Osaki & Schmidt, unpublished) and *p*-chlorocinnamide (Rabinovich, 1969); thus we conclude that the 18·5° angle of twist in *N*-methylcinnamide comprises an angle of 14° due to the intramolecular H(*ortho*)···H(ethylenic) repulsion and an additional twist of 4·5°, probably due to intermolecular forces.

3.4.2. *Translation hydrogen-bonding motif* (4)

3.4.2.1. *N-Methyl-α-chloroacetamide*. The crystal contains two molecules in the asymmetric unit, each of which forms a layer structure. The molecular packing modes in these two layers are almost identical. Within each layer the molecules are bound through N—H···O contacts along a translation axis of 5·1 Å, as in motif (4). The average hydrogen-bond distances and angles are N—H···O 2·83 Å, C=O···N 154° and C—N···O 147° (Table 10). These angles reflect the observation that the N—H···O=C system is distinctly not collinear (Fig. 13).

3.4.2.2. *N-Methylsorbamide*. The molecules are hydrogen-bonded along a translation axis of 4·92 Å (Fig. 14) as in motif (4). The C—N···O angle is 119·1° and the N···O distance is 2·82 Å (Table 10).

3.4.2.3. *N-Methyldipropylacetamide*. The molecules form hydrogen-bonded ribbons along a translation axis of 4·85 Å (Fig. 15). The propyl side chains of the molecule, which extend symmetrically on either side of the plane of the amide group, make van der Waals contacts along the 4·9 Å axis. The >C=O···H—N system is planar, and incorporates a collinear N—H···O=C bond of length 2·82 Å (Table 10).

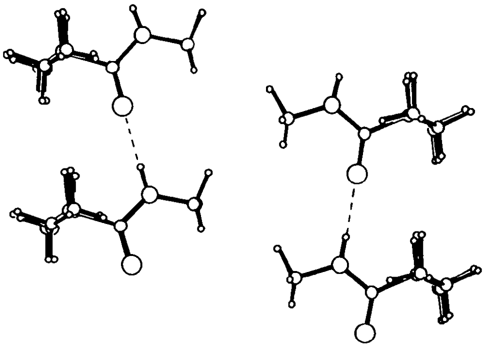


Fig. 15. *N*-Methyldipropylacetamide (Grand & Cohen-Addad, 1973). Hydrogen-bonding layer.

3.5. *Analysis of the hydrogen-bonding modes of* $R\mathrm{CONHCH_3}$

The hydrogen-bonding motifs of *N*-methylamides $R\mathrm{CONHCH_3}$ are analysed in terms of the nature of the residue *R* and various N—H···O=C geometries; in particular, the 'idealized' hydrogen-bonding geometry in which the system N—H···O=C< is planar, the N—H···O bond is linear and the O=C···(H)N angle is ≃120°.

Molecules which contain bulky *R* groups tend to form the hydrogen-bonding motif (3*a*) *via* a 2_1 axis, or glide, to permit the bulky groups to be sufficiently well separated. Insertion into the 5 Å translation mode (4) would incur prohibitively short contacts. *N*-Methylbenzamide and *N*-methylcinnamide fall into this class; they both pack in motif (3*a*) (Figs. 11 and 12). Their hydrogen-bonded systems are not 'ideal' (Table 10). Obviously neither molecule can pack in the 'idealized' form of motif (3*a*) since their *R* groups are too large to permit a planar hydrogen-bonded array in which the N—H···O bond is linear and the C=O···N angle is ≃120°. The insertion of *N*-methylbenzamide or *N*-methylcinnamide into the translation motif (4) would necessitate a change in molecular shape. For *N*-methylbenzamide this would require, as in benzamide itself, a twist angle between the amide and phenyl groups of 25° to permit a reasonable N···O bond distance of 2·95 Å and no prohibitively short contacts between the neighbouring phenyl groups; the observed angle of twist is 14°.

The translation motif (4), in which N—H···O=C tends to be collinear, has an advantage over the glide, or 2_1 axis, motif (3*a*) for molecules with hydrocarbon chains; motif (4) would embody a close-packed arrangement whereas in motif (3*a*) the hydrocarbon chains would be separated from each other resulting in a lack of intermolecular contacts along the hydrogen-bonding axis. Both *N*-methylsorbamide and *N*-methyldipropylacetamide appear to substantiate this line of reasoning. In both crystal structures their hydrocarbon chains make van der Waals contacts with one another along the hydrogen-bonding 5 Å axis. Were either molecule to pack in the glide motif (3*a*) the hydrocarbon chain would make contact only with the N—$\mathrm{CH_3}$ methyl group along the hydrogen-bonding axis. That *N*-methylsorbamide and *N*-propyldipropylacetamide may pack in the glide motif (3*a*) is indisputable since similar molecules, such as *N*-methylcinnamide and *N*-methyltripropylacetamide (Cohen-Addad & Grand, 1974*b*), pack in the glide motif (3*a*). The insertion of *N*-methylsorbamide, or *N*-methyldipropylacetamide, into the 'idealized' arrangement of motif (3*a*) would induce too close a contact between residue *R* and the N—CH$_3$ methyl group, as demonstrated in Fig. 16 for *N*-methylsorbamide.

N-Methyl-α-chloroacetamide, which appears in the translation motif (4), exemplifies how the geometry of the N—H···O=C bond may be distorted by the *R* residue. The molecule forms a distinctly nonlinear N—H···O bond (Fig. 13) in contrast to a number of other amides which pack in the translation mode (4). Were *N*-methyl-α-chloroacetamide to adopt a collinear N—H···O=C bond, the packing arrangement would incorporate too close a Cl···O contact, ≃2·6 Å; the observed Cl···O distance is 3·7 Å. Insertion into a coplanar form of the glide motif (3*a*) with a linear N—H···O bond as depicted in Fig. 17 would introduce too short a Cl···O distance, ≃2·5 Å, even allowing for a wide variation of the C=O···N angle.

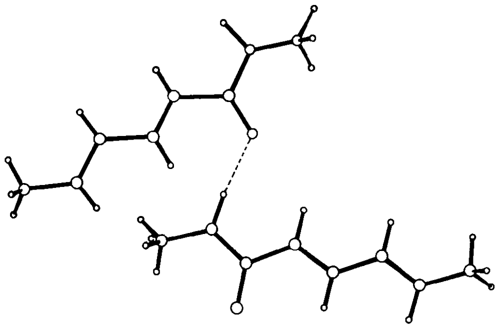


Fig. 16. *N*-Methylsorbamide. Hydrogen-bonded molecules inserted into the 'idealized' form of motif (3*a*).

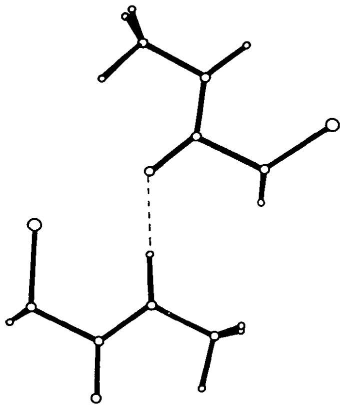


Fig. 17. *N*-Methyl-α-chloroacetamide inserted into the 'idealized' form of motif (3*a*).

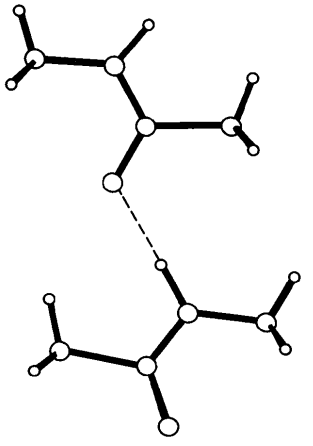
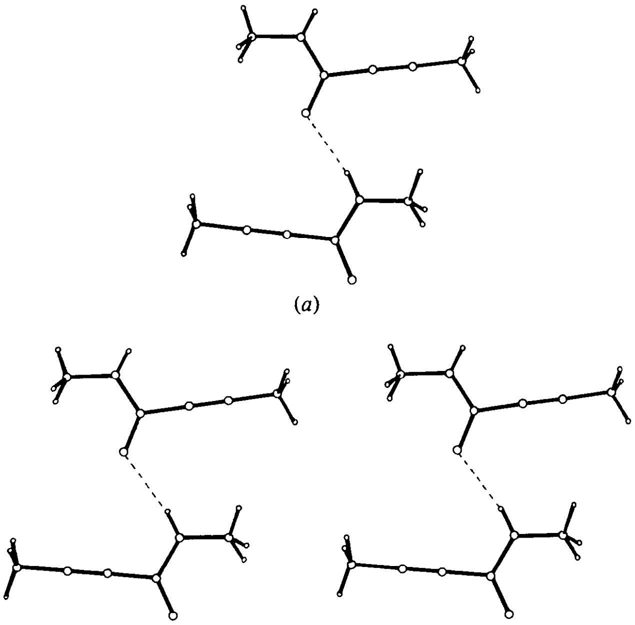


Fig. 18. *N*-Methylacetamide inserted into the 'idealized' form of motif (3*a*).

Table 13. *Energies* (kcal mol^{-1}) *of the experimental and hypothetical hydrogen-bonded motifs in N-methyltetrolamide*

Hydrogen-bond motif		Lattice energy
(1) Experimental		
One-dimensional hydrogen array (Fig. 10*a*)		−10·5
Two-dimensional layer structure (Fig. 10*b*)		−15·7
(2) Hypothetical		
(*a*) 'Idealized' motif (3*a*) with a C=O···N angle of 120°	array (Fig. 19*a*)	−12·6
	layer (Fig. 19*b*)	−14·1
(*b*) 'Idealized' motif (3*a*) with a C=O···N angle of 140°	array	−11·9
	layer	−13·4
(*c*) Translation motif (4) with a collinear N—H···O=C bond	array (Fig. 20*a*)	−11·9
	layer (Fig. 20*b*)	−13·5



(*a*)

(*b*)

Fig. 19. (*a*) *N*-Methyltetrolamide inserted into the 'idealized' form of the hydrogen-bonding motif (3*a*). (*b*) Hypothetical layer structure containing the 'idealized' hydrogen-bonding motif in (*a*).

N-Methylacetamide, which contains the small CH_3 residue, is the only reported structure that approaches the 'idealized' form of motif (3*a*). The hydrogen-bonded array is planar, the N—H···O system linear, and the C=O···N angle is 141·5°. The 'idealized' arrangement is precluded, for this would lead to a short contact of ∼2·1 Å between the H atoms of the N—CH_3 and C—CH_3 methyl groups (Fig. 18). It is possible to insert *N*-methylacetamide into the translation motif (4), with a collinear N—H···O=C bond, without inducing any short contacts, yet *N*-methylacetamide does not pack in this mode, suggesting a preference for motif (3*a*).

The hypothesis that *R*$CONHCH_3$ should tend to pack in the 'idealized' form of motif (3*a*), provided *R* is sufficiently small, is not borne out by the crystal structure of *N*-methyltetrolamide. The observed hydrogen-bonding arrangement (Fig. 10*a*), which resembles the 2_1-axis motif (3*b*), in which the N—H···O=C system is collinear, appears to be a comparatively open structure. This raises the question whether the observed hydrogen-bonding array is induced by the necessity to satisfy certain favourable intermolecular contacts and, moreover, whether the 'idealized' motif (3*a*) is precluded since it would not permit as favourable a packing arrangement as that observed. *N*-Methyltetrolamide forms a layer structure (Fig. 10*b*), which contains C—H···O and C—H···C≡C contacts that also appear in the crystal structure of the α modification of tetrolic acid (see § 3.4.1.3). We therefore suggest that it is these contacts which have played a significant role in determining the molecular arrangement of the hydrogen-bonded array. In order to substantiate these arguments, lattice energies were computed of *N*-methyltetrolamide in its observed, and some hypothetical, hydrogen-bonded arrangements. The computations were confined to (i) a comparison of observed and hypothetical one-dimensional hydrogen-bonded arrays (Figs. 10*a*, 19*a*, 20*a*), and (ii) a comparison of the observed layer structure (Fig. 10*b*) with hypothetical layers (Figs. 19*b* and 20*b*), constructed from the hypothetical one-dimensional hydrogen-bonded arrays. The force field used, of the Lennard–Jones type, was derived by Hagler, Huler & Lifson (1974) through a least-squares fit to experimental crystal structures, heats of sublimation of amide crystals and dipole moments of some amide molecules. The hydrogen bond was represented by partial charges placed on the amide atoms H, C, N and O and by nonbonded parameters between these atoms.

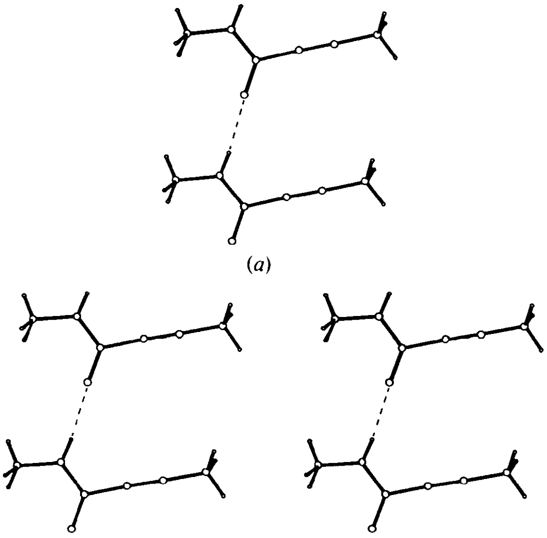


Fig. 20. *N*-Methyltetrolamide. (*a*) Hypothetical hydrogen-bonded array generated by translation. (*b*) Postulated layer structure incorporating hydrogen-bond motif of (*a*).

The results of these lattice-energy computations are listed in Table 13. The observed hydrogen-bonded array (Fig. 10*a*) is less stable, by at least 1·4 kcal mol^{-1}, than any of the hypothetical arrangements (Figs. 19*a*, 20*a*), obviously because of the lack of intermolecular contacts which is evident in Fig. 10(*a*). The most stable hydrogen-bonded array, with an energy of −12·6 kcal mol^{-1}, is the hypothetical arrangement shown in Fig. 19(*a*) which embodies the 'idealized' form of the glide motif (3*a*). The hypothetical array which contains molecules related by translation (Fig. 20*a*) has an energy of −11·9 kcal mol^{-1}.

In contrast to the hydrogen-bonded chains, the observed two-dimensional layer structure (Fig. 10*b*) is more stable than any of the postulated layer structures (Figs. 19*b*, 20*b*) by 1·7 kcal mol^{-1}, which emphasizes the importance of interactions between hydrogen-bonded chains in determining the molecular arrangement in the hydrogen-bond motif. However, these calculations can only support, but not prove, that the 'idealized' motif (3*a*) is overridden by the need to satisfy C—H···O and C—H···C≡C interactions.

That weak, but specific, interactions, such as C—H···O, may determine the mode of hydrogen-bonding is nicely exemplified by the crystal structure of *N*-methylpropiolamide which contains both a N—H···O bond and an acetylenic C—H···O contact of 3·2 Å. The N—H···O chain generated by a glide along the *c* axis (Fig. 9*a*) resembles the rarely observed glide motif (3*c*). *N*-Methylpropiolamide probably adopts its N—H···O motif to accommodate the acetylenic C—H···O interaction. By comparison, the analogous propiolic acid (Leiserowitz & Olovsson, 1978) does not form an acetylenic C—H···O(carbonyl) contact. The observed N—H···O=C geometry is 'ideal' insofar as the N—H···O bond is approximately linear and the C=O···N angle is 131°. However the N—H bond is not coplanar with the amide group to which it is hydrogen-bonded (Table 10). A hypothetical, planar N—H···O=C< system with the 'idealized' geometry is ruled out since it would induce short $CH_3\cdots H{-}N$ contacts. Although *N*-methylpropiolamide can easily be accommodated in the 'idealized' form of motif (3*a*), or even into the translation motif (4), it would not be possible to incorporate $C{-}H\cdots O$ contacts in which the $C{-}H\cdots O$ bond is linear, the $O{=}C\cdots(H)C$ angle $\simeq 120°$ and the $C{-}H\cdots O{=}C<$ system coplanar, for such an arrangement would contain a short $CH_3\cdots H{-}C\equiv$ contact.

3.6. N—H···O *geometry in N-methylamides and IR* N—H *stretching frequency*

The N—H stretching frequency (ν_{N-H}) of free molecules of amides in very dilute solutions of non-polar solvents is higher than that of the bonded molecules in the solid state. This shift of ν_{N-H} caused by the N—H···O bond in the crystal serves as a yardstick to measure the relative strengths of N—H···O bonds.

The inverse linear correlation between $\Delta\nu_{N-H}$ and the N···O distance (Nakamoto, Margoshes & Rundle, 1955) does not appear to stand up to close scrutiny, as is evident from the results on cyanuric acid discussed in § 3.2. To shed further light on the N—H···O bond strength as a function of its geometry, values of $\Delta\nu_{N-H}$ of *N*-methylpropiolamide, *N*-methyltetrolamide, *N*-methylcinnamide and *N*-methylsorbamide were obtained from IR measurements of ν_{N-H} in CCl_4 for the free molecules, and from thin crystalline films between plates of NaCl for the bound molecules in the solid (Table 10). We first compare only *N*-methylamides with similar *R* groups and similar conformations of the $N{-}CH_3$ methyl groups to be more assured that differences in $\Delta\nu_{N-H}$ are due only to differences in N—H···O=C geometry. The torsion angles of C—N—C(methyl)—H for the four molecules are 169, 164, 156 and 147° respectively (Table 7). Consequently we compare *N*-methylpropiolamide with *N*-methyltetrolamide, and *N*-methylcinnamide with *N*-methylsorbamide.

Values of $\Delta\nu_{N-H}$ of 210 and 140 cm^{-1} for *N*-methylpropiolamide and *N*-methyltetrolamide indicate a stronger N—H···O bond in the former, despite equal distances of 2·87 and 2·86 Å (Table 10). Nevertheless, these results appear to be in accordance with the more 'favourable' N—H···O=C angular geometry in *N*-methylpropiolamide (C=O···N 131 and C—N···O 119 *vs* C=O···N 159 and C—N···O 137°, Table 10) on the assumption that motif (2*a*) is energetically more favourable than (2*b*).

The values of $\Delta\nu_{N-H}$ in *N*-methylsorbamide and in *N*-methylcinnamide are equal (180 cm^{-1}) which fits in with their almost equal N—H···O distances (2·87, 2·89 Å). The angular geometries of N—H···O=C in both crystal structures (Table 10) are far from the 'idealized' values, hence we have made no comparison.

A comparison between all four *N*-methylamides, as well as that of *N*-methylacetamide (Table 10), does not yield a clear-cut relation between $\Delta\nu_{N-H}$ and the N—H···O=C geometry.

3.7. *The* N—H···O *distance in primary and secondary amides*

The average N—H···O distance for secondary *trans* amides is 2·85 Å (Tables 8 and 10). These amide groups are linked by single N—H···O bonds. Secondary *cis* amides may be interlinked by N—H···O

Table 14. N—H···O *distances* (Å) *in secondary amides with a cis* O=C—N—H *conformation*

The hydrogen-bonds are formed either into a cyclic pair or along a twofold screw axis.

Compound	Hydrogen-bonding mode	NH···O distance	Reference
Diketopiperazine	Cyclic pair	2·85	Degeilh & Marsh (1959)
cyclo-(L-Ala-L-Ala)	Cyclic pair	2·89 (mean)	Sletten (1970)
Cyanuric acid	Cyclic pair	2·80	Verschoor & Keulen (1971)
Uric acid	Cyclic pair	2·83	Ringertz (1966)
	2_1 axis of 6·3 Å	2·81	
Homophthalimide	Cyclic pair	2·86	Ammon & Wheeler (1974)
5-Ethyl-6-methyluracil	Cyclic pair	2·80 (mean)	Reeke & Marsh (1966)
Uracil	Cyclic pair	2·87	Stewart & Jensen (1967)
Succinimide	Cyclic pairs	2·87	Mason (1961)
5-Fluorouracil	Cyclic pair	2·80 (mean)	Fallon (1973)
cyclo-(L-Ala-D-Ala)	2_1 axis of 6·2 Å	2·89	Sletten (1970)
α-Pyridone	2_1 axis of 5·7 Å	2·77	Penfold (1953)
2-Oxazolidinone	2_1 axis of 5·7 Å	2·86	Turley (1972)
Parabanic acid	(Pseudo)2_1 axis of 5·0 Å	2·86 (mean)	Davies & Blum (1955)
6-Azauracil	Two perpendicular 2_1 axes of 5·0 and 4·9 Å	2·85 (mean)	Singh & Hodgson (1974)
Glutarimide	2_1 axis of 7·4 Å	2·94	Petersen (1971)

bonds in two distinct motifs. The amide groups may form cyclic hydrogen-bonded pairs, and so are linked by double N—H···O bonds, or they may be interlinked by a 2_1 axis, and are thus connected by single N—H···O bonds. This latter motif is not uncommon. The length of this 2_1 axis varies from 4·9 Å (not necessarily the lower limit) to an upper limit of approximately 7·4 Å according to Table 14. The trace of the hydrogen-bonded chain along the 2_1 axis is helical with a radius inversely proportional to the length of the 2_1 axis. This helical arrangement is demonstrated by the packing arrangement of 6-azauracil (Singh & Hodgson, 1974) shown in Fig. 21. According to Table 14 the average N—H···O distances in cyclic pairs and in chains generated by a 2_1 axis are 2·84 and 2·85 Å respectively. These results demonstrate that the length of the N—H···O bond in secondary amides does not seem to depend on the mode of hydrogen bonding nor on the *cis* or *trans* configuration of the amide group.

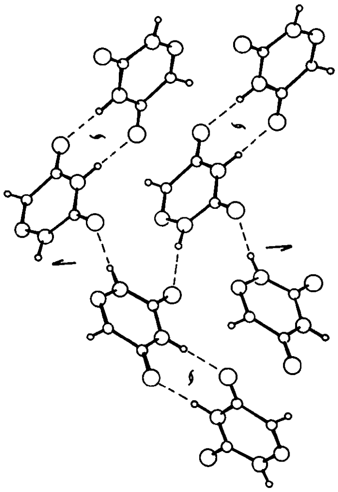


Fig. 21. 6-Azauracil (Singh & Hodgson, 1974). Helical N—H···O bonded chains along two perpendicular 2_1 axes.

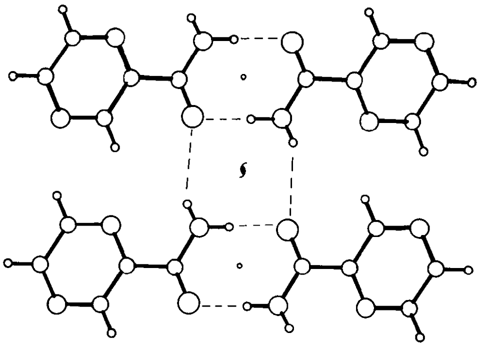
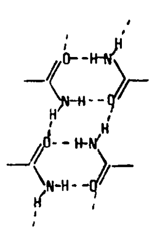


Fig. 22. β-Pyrazinecarboxamide (Rø & Sørum, 1972*a*). Hydrogen-bonding arrangement.

The average N—H···O distance of 2·94 Å in primary amides (Leiserowitz & Schmidt, 1969) is distinctly longer than in secondary amides. This longer hydrogen bond might be partially due to overcrowding within the hydrogen-bonding system in primary amides (6) in which cyclic hydrogen-bonded pairs are further linked by interpair N—H···O bonds.



(6)

However, this argument is weakened by the following observation. In the crystal structure of the β (Fig. 22) and δ modifications of pyrazinecarboxamide $C_4N_2H_3$—$CONH_2$ (Rø & Sørum, 1972*a*,*b*) the interpair N—H···O distances linking the cyclic amide pairs are 3·24 and 3·48 Å in the β and δ modifications respectively, distances appreciably longer than the average N—H···O bond of 2·94 Å. The intrapair N—H···O bonds forming the cyclic pairs are 2·92 and 2·90 Å in the β and δ forms respectively. That these two distances are only a little shorter than 2·94 Å, despite the fact that their cyclic amide pairs are well separated, appears to indicate that the overcrowded hydrogen-bond motif (6) cannot be the major factor responsible for the relatively long N—H···O bonds in primary amides. Another factor which may be responsible for the significant difference in N···O length between primary and secondary amides is a possible difference in the charge distribution in their N—H bonds.

Summary

The results and analysis on the crystal packing of *N*-methylamides demonstrates that the residue *R* plays an important role in determining the intermolecular arrangement of the hydrogen-bonded system. Regarding the preferred hydrogen-bonding geometry the N—H···O bond tends to be linear, the N—H···O=C< system coplanar but evidence is marginal for a preferred C=O···H(N) angle in the range of 130–180°.

We are indebted to A. T. Hagler for his interest and the use of his computer programs on lattice-energy calculations. We thank Mrs K. Reich and Y. Halfon for technical help and Miss L. Heller for the preparation of chemical compounds. Partial support from a MINERVA grant is acknowledged.

References

Allerhand, A. & Schleyer, P. V. R. (1963). *J. Am. Chem. Soc.* **85**, 1715–1723.

Ammon, H. L. & Wheeler, G. L. (1974). *Acta Cryst.* B**30**, 1146–1154.

Andreetti, G. D., Cavalca, L., Domiano, P. & Musatti, A. (1968). *Acta Cryst.* B**24**, 1195–1198.

Bailey, M. (1955). *Acta Cryst.* **8**, 575–578.

Bellamy, L. J. (1958). *Infra Red Spectra of Complex Molecules*. New York: John Wiley.

Benedetti, E., Ciajolo, M. R. & Corradini, P. (1973). *Eur. Polym. J.* **9**, 101–109.

Benedetti, E., Ciajolo, M. R. & Corradini, P. (1974). *Eur. Polym. J.* **10**, 1201–1205.

Benghiat, V. & Leiserowitz, L. (1972). *J. Chem. Soc. Perkin Trans.* 2, pp. 1763–1768.

Blake, C. C. F. & Small, R. W. H. (1972). *Acta Cryst.* B**28**, 2201–2206.

Brand, J. C. D., Eglinton, G. & Morman, J. F. (1960). *J. Chem. Soc.* pp. 2526–2533.

Brown, C. J. (1966). *Acta Cryst.* **21**, 442–445.

Calabrese, J. C., McPhail, A. T. & Sim, G. A. (1966). *J. Chem. Soc. B*, pp. 1235–1241.

Cobbledick, R. E. & Small, R. W. H. (1972). *Acta Cryst.* B**28**, 2893–2896.

Cohen-Addad, C. & Grand, A. (1974*a*). *Acta Cryst.* B**30**, 186–192.

Cohen-Addad, C. & Grand, A. (1974*b*). *Acta Cryst.* B**30**, 1342–1346.

Coppens, P., Leiserowitz, L. & Rabinovich, D. (1965). *Acta Cryst.* **18**, 1035–1038.

Coppens, P. & Vos, A. (1971). *Acta Cryst.* B**27**, 146–158.

Davies, D. R. & Blum, J. J. (1955). *Acta Cryst.* **8**, 129–136.

Degeilh, B. & Marsh, R. E. (1959). *Acta Cryst.* **12**, 1007–1014.

Dubey, R. J. (1971). *Acta Cryst.* B**27**, 23–25.

Fallon, L. III (1973). *Acta Cryst.* B**29**, 2549–2559.

Ferguson, G. & Islam, K. M. S. (1966). *J. Chem. Soc. B*, pp. 593–600.

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* A**27**, 368–375.

Germain, G. & Woolfson, M. M. (1968). *Acta Cryst.* B**24**, 91–96.

Grand, A. & Cohen-Addad, C. (1973). *Acta Cryst.* B**29**, 1149–1151.

Hagler, A. T., Huler, E. & Lifson, S. (1974). *J. Am. Chem. Soc.* **96**, 5319–5327.

Hagler, A. T., Leiserowitz, L. & Tuval, M. (1976). *J. Am. Chem. Soc.* **98**, 4600–4612.

International Tables for X-ray Crystallography (1962). Vol. III, p. 202. Birmingham: Kynoch Press.

Jensen, L. H. (1962). *Acta Cryst.* **15**, 433–440.

Katz, J. L. & Post, B. (1960). *Acta Cryst.* **13**, 624–628.

Koyama, Y., Shimanouchi, T. & Iitaka, Y. (1971). *Acta Cryst.* B**27**, 940–946.

Leiserowitz, L. (1976). *Acta Cryst.* B**32**, 775–802.

Leiserowitz, L. & Nader, F. (1978). To be published.

Leiserowitz, L. & Olovsson, I. (1978). *Acta Cryst.* B**34**. To be published.

Leiserowitz, L. & Schmidt, G. M. J. (1969). *J. Chem. Soc. A*, pp. 2372–2382.

Mason, R. (1961). *Acta Cryst.* **14**, 720–724.

Mizushima, S., Simanouti, T., Nagakura, S., Kuratani, K., Tsuboi, M., Baba, H. & Fujioka, O. (1950). *J. Am. Chem. Soc.* **72**, 3490–3494.

Nakamoto, K., Margoshes, M. & Rundle, R. E. (1955). *J. Am. Chem. Soc.* **77**, 6480–6486.

Orii, S., Nakamura, T., Takaki, Y., Sasada, Y. & Kakudo, M. (1963). *Bull. Chem. Soc. Jpn*, **36**, 788–793.

Penfold, B. R. (1953). *Acta Cryst.* **6**, 591–600.

Petersen, C. S. (1971). *Acta Chem. Scand.* **25**, 379–389.

Rabinovich, D. (1969). *J. Chem. Soc. A*, pp. 2361–2366.

Reeke, G. N. Jr & Marsh, R. E. (1966). *Acta Cryst.* **20**, 703–708.

Ringertz, H. (1966). *Acta Cryst.* **20**, 397–403.

Ringertz, H. (1971). *Acta Cryst.* B**27**, 285–291.

Rø, C. & Sørum, H. (1972*a*). *Acta Cryst.* B**28**, 991–998.

Rø, C. & Sørum, H. (1972*b*). *Acta Cryst.* B**28**, 1677–1684.

Singh, P. & Hodgson, H. J. (1974). *Acta Cryst.* B**30**, 1430–1435.

Sletten, E. (1970). *J. Am. Chem. Soc.* **92**, 172–177.

Stewart, R. F. & Jensen, L. H. (1967). *Acta Cryst.* **23**, 1102–1105.

Subramanian, E. (1966). *Z. Kristallogr.* **123**, 222–234.

Takano, T., Sasada, Y. & Kakudo, M. (1966). *Acta Cryst.* **21**, 514–522.

Turley, J. W. (1972). *Acta Cryst.* B**28**, 140–143.

Verschoor, G. C. & Keulen, E. (1971). *Acta Cryst.* B**27**, 134–145.