

anionic layer in the formation of a herringbone cationic structure. In the design of crystals containing 2-amino-5-nitropyridinium polar arrangements, the parameters which govern the non-centrosymmetry are the dimensions and charge of associated counter-anions (Table 1) which are able to dilute the organic cations in the expected structure: large individual anions or chained or layered polymeric aggregates can be useful tools to induce acentric crystalline frameworks. Advantages of such organic salts compared to molecular salts include relatively easy crystal growth and crystal transparency.

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#### References

- BAGIEU-BEUCHER, M., MASSE, R. & TRANQUI, D. (1991). *Z. Anorg. Allg. Chem.* **606**, 59–71.
- CENSE, J. M. (1989). *Tetrahedron Comput. Methodol.* **2**(1), 65–71.
- COLAPIETRO, M., DOMENICANO, A., MARCIANTE, C. & PORTALONE, G. (1982). *Z. Naturforsch. Teil B*, **37**, 1309–1311.
- COTTON, A., FRENZ, B. A. & HUNTER, D. (1975). *Acta Cryst.* **B31**, 302–304.
- CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.2B. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- DEWAR, M. J. S. (1950). *J. Chem. Soc.* pp. 2329–2334.
- Enraf-Nonius (1977). *Structure Determination Package*. Enraf-Nonius, Delft, The Netherlands.
- FISCHER, R. X. (1985). *J. Appl. Cryst.* **18**, 258–262.
- GUNTER, P., BOSSHARD, C., SUTTER, K., AREND, H., CHAPUIS, G., TWIEG, R. J. & DOBROWSKI, D. (1987). *Appl. Phys. Lett.* **50**(9), 486–488.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
- KOTLER, Z., HIERLE, R., JOSSE, D., ZYSS, J. & MASSE, R. (1992). *J. Opt. Soc. Am.* **9**(4), 534–547.
- KURTZ, S. K. & PERRY, T. T. (1968). *J. Appl. Phys.* **39**, 3798–3813.
- MAIN, P., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (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.
- MASSE, R. & ZYSS (1991). *J. Mol. Eng.* **1**, 141–151.
- NICOUD, J. F. (1988). *Mol. Cryst. Liq. Cryst.* **156**, 257–268.
- PECAUT, J. & MASSE, R. (1993). *Acta Cryst.* **B49**, 277–282.
- TOMARU, S., MATSUMOTO, S., KURIHARA, T., SUZUKI, H., Ooba, N. & KAINO, T. (1991). *Appl. Phys. Lett.* **58**(23), 2583–2585.
- ZYSS, J., MASSE, R., BAGIEU-BEUCHER, M. & LEVY, J. P. (1992). *Adv. Mater.* Submitted.

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## Crystal Structures and Polymorphism in Aliphatic *p*-Amidobenzoic Acids

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#### Abstract

(I) *p*-Propanamidobenzoic acid acetic acid solvate,  $C_{10}H_{11}NO_3 \cdot \frac{1}{2}C_2H_4O_2$ ,  $M_r = 223.23$ , monoclinic,  $P2_1/n$ ,  $a = 5.135$  (1),  $b = 24.556$  (5),  $c = 9.496$  (2) Å,  $\beta = 105.33$  (3)°,  $V = 1155$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.28$  g cm<sup>-3</sup>,  $\lambda(Mo K\alpha) = 0.71069$  Å,  $\mu = 0.095$  mm<sup>-1</sup>,  $F(000) = 472$ ,  $T = 295$  K,  $R = 0.062$  for 1108 observed reflections. (II) *p*-Butanamidobenzoic acid,  $C_{11}H_{13}NO_3$ ,  $M_r = 207.23$ , triclinic,  $P\bar{1}$ ,  $a = 5.120$  (6),  $b = 6.595$  (2),  $c = 15.786$  (3) Å,  $\alpha = 100.98$  (2),  $\beta = 94.48$  (5),  $\gamma = 98.15$  (5)°,  $V = 515$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.34$  g cm<sup>-3</sup>,  $\lambda(Mo K\alpha) = 0.71069$  Å,  $\mu = 0.091$  mm<sup>-1</sup>,  $F(000) = 220$ ,  $T = 295$  K,  $R = 0.078$  for 1229 observed reflections. (III) *p*-

Pentanamidobenzoic acid,  $C_{12}H_{15}NO_3$ ,  $M_r = 221.26$ , monoclinic,  $P2_1/c$ ,  $a = 5.081$  (4),  $b = 24.066$  (6),  $c = 9.662$  (4) Å,  $\beta = 82.06$  (6)°,  $V = 1170$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.26$  g cm<sup>-3</sup>,  $\lambda(Mo K\alpha) = 0.71069$  Å,  $\mu = 0.084$  mm<sup>-1</sup>,  $F(000) = 472$ ,  $T = 295$  K,  $R = 0.057$  for 1673 observed reflections. (IV) *p*-Nonanamidobenzoic acid,  $C_{16}H_{23}NO_3$ ,  $M_r = 277.36$ , triclinic,  $P\bar{1}$ ,  $a = 5.176$  (1),  $b = 6.731$  (5),  $c = 22.127$  (17) Å,  $\alpha = 92.79$  (6),  $\beta = 91.13$  (4),  $\gamma = 100.04$  (4)°,  $V = 758$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.22$  g cm<sup>-3</sup>,  $\lambda(Mo K\alpha) = 0.71069$  Å,  $\mu = 0.078$  mm<sup>-1</sup>,  $F(000) = 300$ ,  $T = 295$  K,  $R = 0.119$  for 1178 observed reflections. The effect of varying alkyl chain length upon the hydrogen-bonding pattern for a series of aliphatic amidobenzoic acids has been investigated. (II) and (IV) are isostructural. Acid dimers are formed, with the dimers further

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hydrogen bonded through the amide groups to form ribbons. The ribbons form 'blocks' through short inter-ribbon C—H...O contacts. These 'blocks' are stacked along *c* and connected by van der Waals forces. X-ray powder-pattern analysis demonstrates that for powdered materials this structure can accommodate a range of chain lengths. Structures (I) and (III) are also similar. Acid dimers are hydrogen bonded through the amide group to form 'corrugated' sheets, which are stacked along the *a* axis, held together by van der Waals forces. This packing arrangement is restricted to specific alkyl chain lengths.

### Introduction

As part of a general study on the stability of organic peracids and peracid salts (Kariuki & Jones, 1992), and in particular the role of hydrogen bonding in controlling the crystal structure of peracid and acid amides (Feeder & Jones, 1992), we report here the structures for four *p*-amidobenzoic acids.

### Experimental

Samples of (I)–(IV) were provided by Solvay Interlox plc. White transparent plate-like crystals of (II) and (IV) were crystallized from ethanol solution. The white transparent rod-like crystals of (III) were also obtained from ethanol, and the yellow transparent rod-like crystals of (I) from glacial acetic acid. Lattice parameters were refined using 25 reflections. An Enraf–Nonius CAD-4 four-circle diffractometer in the  $\omega/2\theta$  mode with graphite-monochromated radiation was used and all measurements were made at 295 K. Standard reflections (see Table 1) were recen-tered every 100 reflections and scanned every hour to check for crystal movement and stability. The structures of (I) and (III) were solved by direct methods using *SHELXS84* (Sheldrick, 1984), and (II) and (IV) by direct methods using *SHELXS86* (Sheldrick, 1986). All four were refined (on *F*) by full-matrix least-squares analysis using *SHELX76* (Sheldrick, 1976). [In (I) structure solution revealed the presence of included solvent (acetic acid) which was refined with fixed half-occupancies for the heavy atoms, the H atoms were not located.] The ring, alkyl and amino H atoms were fixed geometrically and refined with isotropic thermal parameters. The carboxylic H-atom coordinates, which were obtained for (III) from the difference Fourier synthesis map, could not be obtained for (I), (II) and (IV). All non-H atoms were refined with anisotropic thermal parameters. No absorption correction or weighting was applied. High *R* values were found for (II) and (IV), mainly it is believed because of the poor quality of the few crystals which could be obtained. The particularly

Table 1. Summary of data collection and refinement parameters

	(I)	(II)	(III)	(IV)
Independent molecules	1	1	1	1
$2\theta$ range for cell ( $^\circ$ )	16–28	18–26	16–26	16–28
$2\theta$ range for full data ( $^\circ$ )	3–50	3–60	3–60	3–56
Range <i>h, k, l</i>	–6,6; 0,29; 0,11	–7,7; –9,9; 0,22	–7,7; 0,33; 0,13	–6,6; –8,8; 0,29
Standard reflections	021; 162	133; 107	192; 263	104; 113
Crystal size (mm)	0.3 × 0.1 × 0.1	0.4 × 0.3 × 0.1	0.4 × 0.1 × 0.1	0.4 × 0.2 × 0.1
Measured reflections	2025	2996	3368	3719
Observed reflections ( <i>F</i> > 3 $\sigma$ <i>F</i> )	1108	1229	1663	1178
No. of parameters refined	159	136	185	190
<i>R</i>	0.062	0.078	0.057	0.119
Max. shift/e.s.d.	0.006	0.009	0.164	0.001
Max. height (e $\text{Å}^{-3}$ )	+0.21	+0.33	+0.19	+0.36
Min. height (e $\text{Å}^{-3}$ )	–0.22	–0.27	–0.21	–0.35

high *R* value for (IV) could also be as a result of heavy-atom disorder at the end of the alkyl chain which was not modelled. Data collection and refinement parameters are summarized in Table 1. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).

### Discussion

Atomic fractional parameters are given in Table 2,\* bond lengths and angles in Tables 3 and 4, and the atomic numbering schemes shown in Figs. 1(a)–1(d).

The bond distances and angles found for (I), (II), (III) and (IV) are very similar to those found for *p*-acetamidobenzoic acid (Kashino, Matsushita, Iwamoto, Yamaguchi & Haisa, 1986). Also the average bond lengths and angles associated with the alkyl chains of the amido groups are similar to those reported for 6-(6-aminohexanamido)hexanoic acid monohydrate (Kasai, Yamanaka, Miki, Tanaka, Post & Morawetz, 1981). The lengths of the C(7)—O(71) and C(7)—O(72) bonds are almost identical for (I), (II) and (IV), suggesting a disordered model for the carboxylic acid groups, also observed in *p*-acetamidobenzoic acid (Kashino, Matsushita, Iwamoto, Yamaguchi & Haisa, 1986). No such disorder is seen for the carboxyl group of (III).

The molecular geometries of (II) and (IV) are very similar. The benzene rings *A*(II) and *A*(IV) are planar to within 0.008 and 0.023 Å, respectively. The C(1) N(1) C(8) O(8) C(9) atoms forming the amide groups *B*(II) and *B*(IV) are also planar to within 0.031 and 0.025 Å. The dihedral angles are *A*(II)*B*(II) 38.0 and *A*(IV)*B*(IV) 39.3°. The COO group makes

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55900 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HU0416]

Table 2. Fractional atomic coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters ( $\times 10^3$ ) for non-H atoms with *e.s.d.*'s in parentheses

$$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}$ ( $\text{\AA}^2$ )
(I) <i>p</i> -Propanamidobenzoic acid acetic acid solvate				
N(1)	652 (7)	7145 (2)	1642 (4)	41
O(8)	-2087 (7)	7384 (1)	-560 (3)	57
O(71)	7098 (7)	5341 (2)	-921 (4)	66
O(72)	9364 (7)	5331 (2)	1438 (4)	64
C(1)	2191 (9)	6726 (2)	1254 (5)	39
C(2)	1709 (10)	6498 (2)	-126 (5)	48
C(3)	3405 (10)	6098 (2)	-402 (5)	50
C(4)	5593 (10)	5919 (2)	700 (5)	46
C(5)	6029 (10)	6142 (2)	2077 (5)	52
C(6)	4345 (10)	6541 (2)	2364 (5)	48
C(7)	7468 (10)	5504 (2)	393 (6)	52
C(8)	-1327 (9)	7447 (2)	763 (5)	44
C(9)	-2480 (11)	7878 (2)	1557 (6)	64
C(10)	-4700 (15)	8201 (3)	631 (7)	92
C(1aa)*	1510 (24)	5009 (6)	5035 (14)	147
O(1aa)	2499 (33)	5410 (5)	5318 (17)	143
O(2aa)	2382 (30)	4578 (5)	4515 (15)	142

(II) <i>p</i> -Butanamidobenzoic acid				
N(1)	5045 (8)	-3417 (6)	7657 (3)	45
O(8)	744 (7)	-3923 (6)	7948 (3)	59
O(71)	2875 (7)	2903 (6)	5189 (3)	55
O(72)	6997 (8)	4261 (6)	5756 (3)	54
C(1)	4916 (10)	-1841 (7)	7155 (3)	40
C(2)	7107 (10)	-310 (8)	7247 (4)	45
C(3)	7126 (10)	1247 (8)	6771 (4)	44
C(4)	4923 (10)	1225 (7)	6199 (3)	38
C(5)	2746 (10)	-318 (8)	6097 (3)	45
C(6)	2737 (10)	-1878 (8)	6578 (3)	43
C(7)	4952 (10)	2927 (7)	5680 (3)	40
C(8)	2987 (10)	-4332 (8)	7993 (3)	41
C(9)	3657 (12)	-6106 (9)	8443 (4)	58
C(10)	1959 (14)	-6482 (10)	9140 (4)	73
C(11)	2725 (17)	-8297 (11)	9540 (5)	101

(III) <i>p</i> -Pentanamidobenzoic acid				
N(1)	762 (5)	2825 (1)	8347 (2)	41
O(8)	1422 (5)	2523 (1)	10488 (2)	65
O(71)	-7794 (5)	4651 (1)	10743 (3)	59
O(72)	-8196 (5)	4671 (1)	8477 (3)	63
C(1)	-1153 (6)	3243 (1)	8698 (3)	40
C(2)	-1833 (7)	3451 (1)	10040 (3)	50
C(3)	-3744 (6)	3861 (1)	10281 (3)	49
C(4)	-5013 (6)	4070 (1)	9211 (3)	43
C(5)	-4290 (7)	3867 (2)	7869 (3)	53
C(6)	-2393 (6)	3458 (1)	7616 (3)	50
C(7)	-7124 (6)	4490 (1)	9531 (4)	46
C(8)	1941 (6)	2503 (1)	9222 (3)	44
C(9)	4009 (6)	2101 (1)	8512 (4)	52
C(10)	3588 (6)	1515 (1)	9099 (4)	53
C(11)	1086 (7)	1248 (2)	8747 (4)	62
C(12)	694 (10)	660 (2)	9305 (5)	95

(IV) <i>p</i> -Nonanamidobenzoic acid				
N(1)	3978 (17)	68 (16)	3181 (6)	46
O(8)	-439 (14)	-595 (15)	2964 (5)	62
O(71)	2821 (16)	7789 (14)	4878 (5)	59
O(72)	6716 (16)	8851 (14)	4485 (5)	55
C(1)	4076 (20)	1880 (19)	3525 (6)	37
C(2)	6267 (21)	3409 (17)	3469 (7)	40
C(3)	6449 (22)	5213 (20)	3788 (7)	40
C(4)	4523 (22)	5578 (20)	4184 (7)	40
C(5)	2384 (22)	4007 (20)	4258 (7)	45
C(6)	2159 (22)	2187 (22)	3942 (7)	51
C(7)	4698 (24)	7494 (21)	4521 (7)	47
C(8)	1770 (23)	-1105 (21)	2920 (7)	46
C(9)	2143 (24)	-3060 (21)	2610 (8)	55
C(10)	-148 (23)	-3993 (21)	2195 (7)	49
C(11)	59 (25)	-6091 (21)	1949 (7)	45
C(12)	-2485 (26)	-7105 (26)	1604 (8)	66
C(13)	-2417 (27)	-9146 (23)	1338 (9)	68
C(14)	-4956 (30)	-10160 (25)	1020 (9)	75
C(15)	-4908 (35)	-12159 (29)	718 (11)	97
C(16)	-7448 (35)	-13251 (31)	410 (10)	98

\* aa denotes acetic acid.

Table 3. Bond lengths ( $\text{\AA}$ )

	(I)	(II)	(III)	(IV)
C(1)—C(2)	1.386 (8)	1.377 (9)	1.389 (6)	1.404 (17)
C(2)—C(3)	1.382 (9)	1.382 (9)	1.381 (6)	1.362 (20)
C(3)—C(4)	1.388 (8)	1.385 (8)	1.386 (6)	1.386 (19)
C(4)—C(5)	1.380 (8)	1.376 (9)	1.388 (6)	1.409 (18)
C(5)—C(6)	1.381 (9)	1.389 (9)	1.375 (6)	1.366 (20)
C(6)—C(1)	1.387 (8)	1.378 (9)	1.393 (6)	1.402 (19)
C(7)—C(4)	1.483 (9)	1.510 (9)	1.475 (6)	1.447 (20)
C(7)—O(71)	1.277 (8)	1.263 (8)	1.236 (6)	1.299 (17)
C(7)—O(72)	1.266 (8)	1.250 (8)	1.295 (4)	1.269 (17)
O(72)—H(72)	*	*	0.898 (58)	*
C(1)—N(1)	1.404 (8)	1.428 (8)	1.407 (6)	1.399 (18)
C(8)—N(1)	1.354 (8)	1.336 (8)	1.347 (6)	1.370 (17)
C(8)—O(8)	1.223 (7)	1.216 (8)	1.216 (5)	1.254 (16)
C(8)—C(9)	1.508 (9)	1.544 (9)	1.521 (6)	1.499 (20)
C(9)—C(10)	1.474 (9)	1.490 (10)	1.523 (6)	1.512 (20)
C(10)—C(11)	—	1.539 (11)	1.504 (7)	1.510 (20)
C(11)—C(12)	—	—	1.518 (7)	1.543 (20)
C(12)—C(13)	—	—	—	1.475 (22)
C(13)—C(14)	—	—	—	1.513 (21)
C(14)—C(15)	—	—	—	1.477 (25)
C(15)—C(16)	—	—	—	1.522 (24)
C(1aa)—C(1aa')	1.535 (25)	—	—	—
C(1aa)—O(1aa)	1.106 (17)	—	—	—
C(1aa)—O(2aa)	1.298 (18)	—	—	—

Symmetry operator: (i)  $-x, 1-y, 1-z$ .

\* H(72) not located.

† aa denotes acetic acid.

Table 4. Bond angles ( $^\circ$ )

	(I)	(II)	(III)	(IV)
C(8)—N(1)—C(1)	128.6 (4)	124.7 (5)	127.8 (4)	126.1 (11)
C(2)—C(1)—N(1)	124.9 (5)	117.2 (5)	123.9 (4)	117.9 (12)
C(6)—C(1)—N(1)	115.6 (5)	121.8 (6)	117.0 (4)	122.9 (13)
C(6)—C(1)—C(2)	119.5 (6)	121.0 (6)	119.1 (4)	119.1 (13)
C(3)—C(2)—C(1)	120.1 (6)	120.1 (6)	119.6 (4)	120.4 (13)
C(2)—C(3)—C(4)	120.4 (6)	118.9 (6)	121.4 (4)	121.3 (13)
C(5)—C(4)—C(7)	120.5 (6)	120.2 (6)	121.9 (3)	120.4 (14)
C(3)—C(4)—C(7)	120.5 (6)	118.7 (5)	119.5 (3)	121.6 (13)
C(3)—C(4)—C(5)	119.0 (6)	121.1 (6)	118.6 (3)	118.0 (14)
C(6)—C(5)—C(4)	121.0 (6)	119.8 (6)	120.4 (4)	121.7 (14)
C(5)—C(6)—C(1)	119.8 (6)	119.1 (6)	120.8 (4)	119.4 (14)
O(71)—C(7)—C(4)	118.1 (6)	117.1 (5)	120.7 (4)	119.6 (13)
O(72)—C(7)—C(4)	118.8 (6)	119.0 (6)	116.0 (4)	120.1 (13)
O(72)—C(7)—O(71)	123.0 (6)	123.9 (6)	123.3 (4)	120.2 (14)
H(72)—O(72)—C(7)	*	*	117.2 (36)	*
O(8)—C(8)—N(1)	123.2 (6)	126.1 (6)	123.7 (4)	121.3 (13)
O(9)—C(8)—N(1)	114.0 (5)	113.4 (5)	115.0 (4)	116.0 (12)
C(9)—C(8)—O(8)	122.8 (5)	120.4 (6)	121.3 (4)	122.6 (13)
C(10)—C(9)—C(8)	115.0 (5)	114.1 (6)	111.6 (4)	113.0 (12)
C(9)—C(10)—C(11)	—	110.6 (7)	112.9 (4)	112.9 (12)
C(12)—C(11)—C(10)	—	—	113.0 (4)	111.2 (13)
C(13)—C(12)—C(11)	—	—	—	114.6 (14)
C(14)—C(13)—C(12)	—	—	—	114.2 (14)
C(15)—C(14)—C(13)	—	—	—	115.5 (16)
C(16)—C(15)—C(14)	—	—	—	117.0 (18)
O(1aa)—C(1aa)—O(2aa)	129.5 (18)	—	—	—
C(1aa)—C(1aa)—O(1aa)	115.4 (18)	—	—	—
C(1aa)—C(1aa)—O(2aa)	114.0 (18)	—	—	—

Symmetry operator: (i)  $-x, 1-y, 1-z$ .

\* H(72) not located.

† aa denotes acetic acid.

angles of  $2.8^\circ$  with *A*(II),  $3.5^\circ$  with *A*(IV),  $35.2^\circ$  with *B*(II), and  $36.2^\circ$  with *B*(IV).

Figs. 2(a) and 2(b) are *PLUTO* (Motherwell & Clegg, 1978) plots showing the packing arrangements for (II) and (IV) demonstrating that the intermolecular hydrogen bonding is identical to that found for *p*-acetamidobenzoic acid (Kashino, Matsushita, Iwamoto, Yamaguchi & Haisa, 1986). All three structures are isostructural. There are two types of hydrogen bond. The first is formed between two

carboxyl groups producing a centrosymmetric ring dimer [(II)  $O\cdots O=C = 2.602$ ; (IV)  $O\cdots O=C = 2.578 \text{ \AA}$ ]. This is a very common motif in carboxylic acids (Kashino & Haisa, 1980). Dimers related by translation along the *a* axis are further hydrogen bonded by linear amide–amide contacts. [(II)  $N-H\cdots O=C$  1.946;  $N\cdots O=C$  3.058  $\text{\AA}$ ; (IV)  $N-H\cdots O=C$  1.994;  $N\cdots O=C$  3.044  $\text{\AA}$ ]. Combination of the two produces a ribbon-type arrangement. The dihedral angle *AB* is typical of this mode of hydrogen bonding in aromatic amides (Haisa, Kashino, Ueno, Shinozaki & Matsuzaki, 1980), especially when the amido group is large (Cohen-Addad, 1973). The ribbons are then held together through short inter-ribbon  $C-H\cdots O$  contacts as shown for (II) in

Fig. 2(c). This side-by-side arrangement is very common amongst *p*-substituted benzoic acids, e.g. *p*-toluic acid (Takwale & Pant, 1971) and *p*-chlorobenzoic acid (Colapietro & Domenicano, 1982). In this way blocks of molecules are formed. From Fig. 2(c) it is clear that the local environments of both O atoms of the carboxyl group are very similar, explaining why the group is almost totally disordered in these structures. This phenomenon has been fully discussed by Leiserowitz (1976). The blocks are then stacked along *c* and held together by van der Waals interactions.

This general structure would appear to be capable of accommodating any chain length (with adjustment to the *c*-axis dimension). Evidence for this

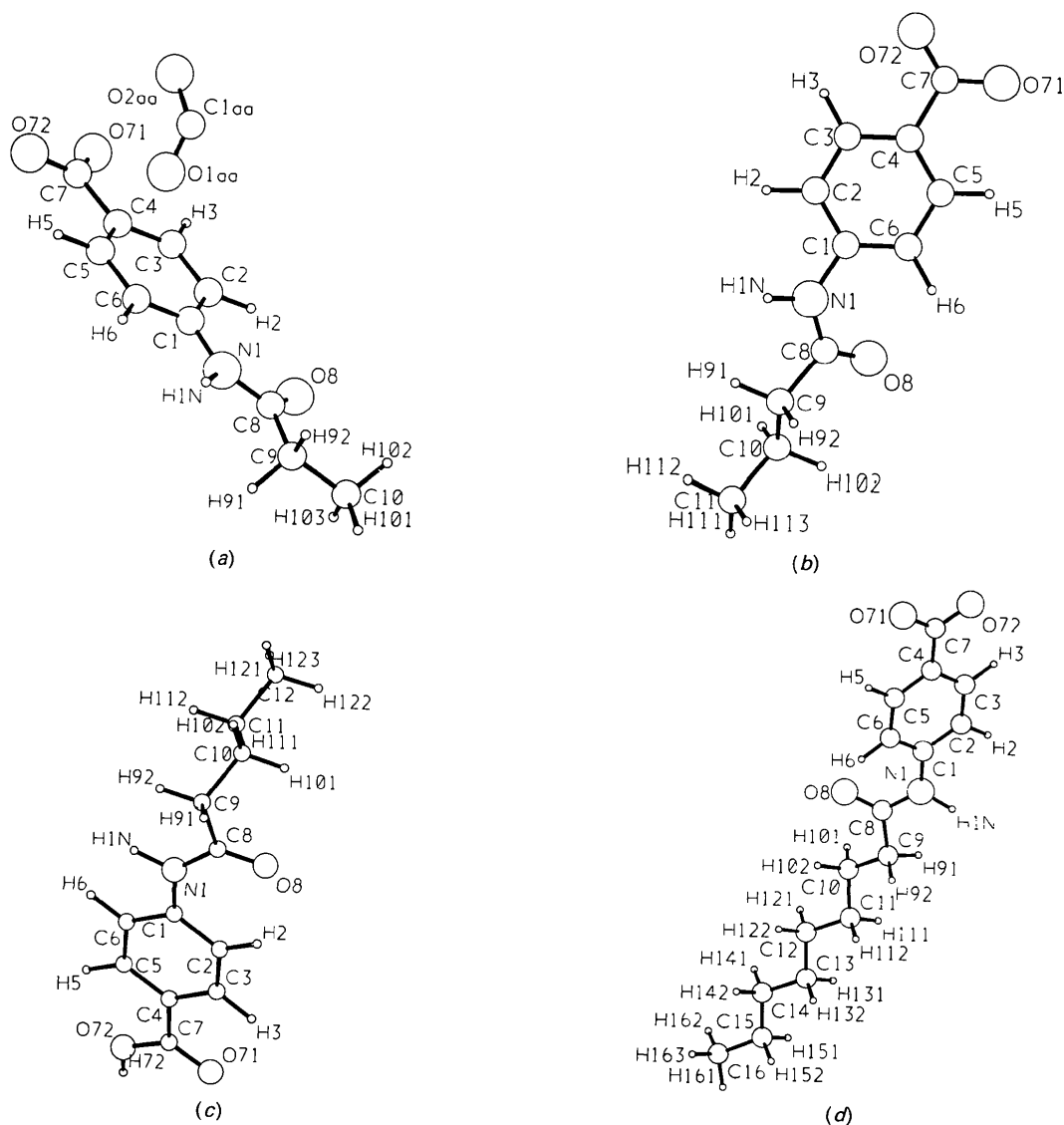


Fig. 1. (a) Atom-numbering scheme for (I). (b) Atom-numbering scheme for (II). (c) Atom-numbering scheme for (III). (d) Atom-numbering scheme for (IV).

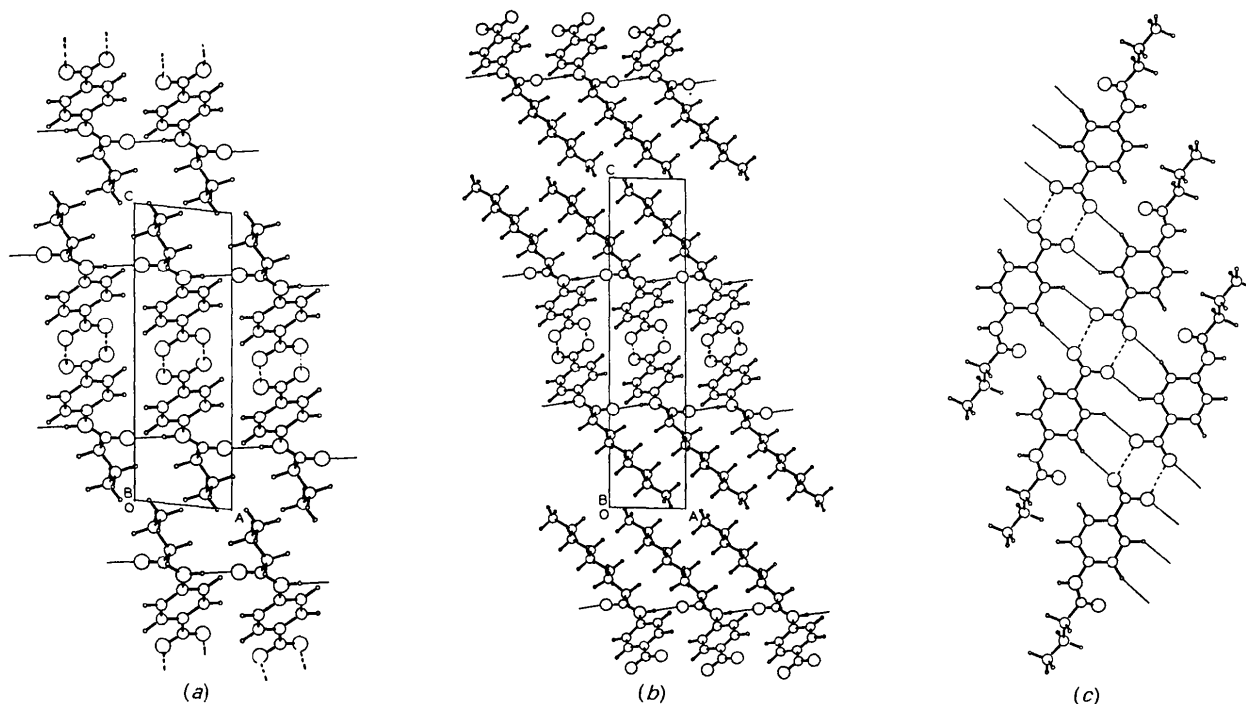


Fig. 2. (a), (b) Packing diagrams for the structures of (II) and (IV) (viewed down the  $b$  axis) illustrating the stacking of the blocks along the  $c$  axis. Also demonstrated is the independence of the chain length from the hydrogen-bonding pattern. (c) The side-by-side arrangement of dimers present in the structure of (II), illustrating some short  $C-H\cdots O$  connections (view perpendicular to the plane of the benzene ring). A similar arrangement occurs in the structure of (IV).

comes from studying the X-ray powder patterns, before recrystallization, of a selection of other members of this homologous series. This shows that the profiles for each powder are similar, and match closely the simulated powder pattern from the structures of *p*-acetamidobenzoic acid, of (II) and of (IV).

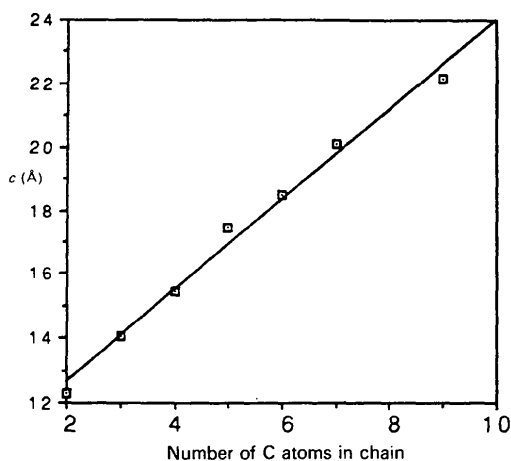


Fig. 3. Plot demonstrating the linear relationship between the  $c$ -axis dimension (measured from the X-ray powder pattern) and the number of carbon atoms in the chain for the translation structure.

Location of the (001) reflection then allows an approximate value for the ' $c$ -axis' length to be calculated for various chain lengths. Fig. 3 demonstrates that the relationship between chain length and the size of  $c$  is linear. This is not the case for  $n$ -aliphatic acids, which only show linear relationships for the long spacing within the groups containing even and odd numbers of carbon atoms in the chain (Swern, Witnauer, Eddy & Parker, 1955). It is noteworthy, however, that suitable crystals for full structural analysis for all of the values of  $n$  for these acid amides have not been obtained.

The molecular geometries of (I) and (III) are similar. The benzene rings  $A(I)$  and  $A(III)$  are planar to within 0.009 and 0.008 Å, as are the  $C(1) N(1) C(8) O(8) C(9)$  atoms forming the amide groups  $B(I)$  and  $B(III)$  to within 0.013 and 0.015 Å. The dihedral angles are  $A(I)B(I)$  8.3° and  $A(III)B(III)$  12.0°. The COO group of (I) makes an angle of 4.9° with  $A(I)$ , and 6.4° with  $B(I)$ . The COOH group for (III) is planar to within 0.014 Å and makes the dihedral angles of 4.8° with  $A(III)$  and 11.4° with  $B(III)$ .

Figs. 4(a) and 4(b) are *PLUTO* (Motherwell & Clegg, 1978) plots showing the packing arrangements and the intermolecular hydrogen bonding for (I) and (III). There are two types of hydrogen bond. The centrosymmetric carboxylic ring dimers are again

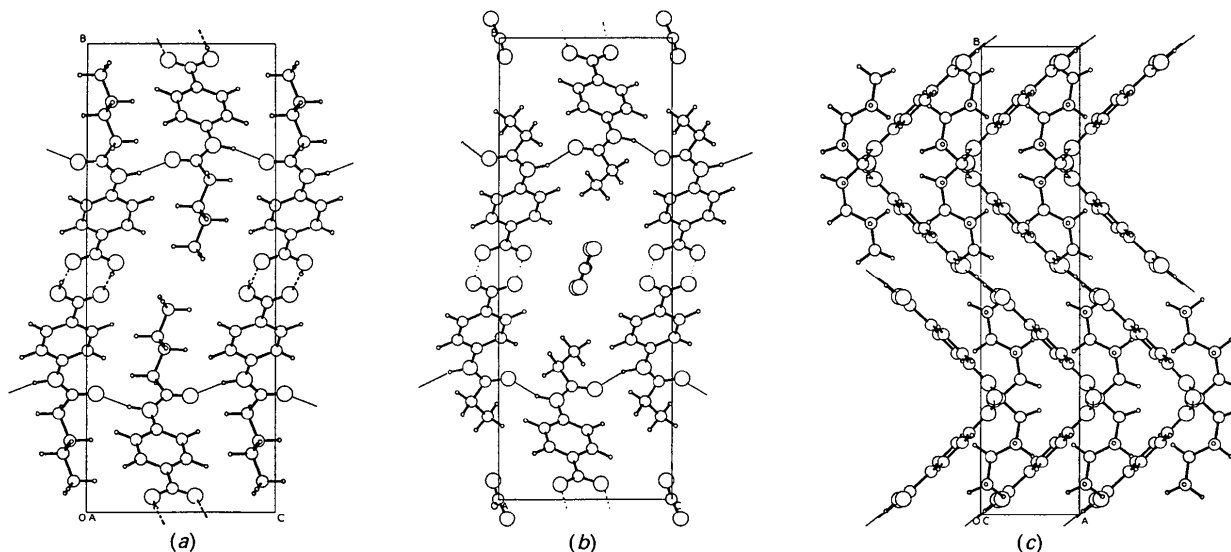


Fig. 4. (a) Packing diagram for the structure of (III) demonstrating the sheet-like arrangement as viewed down the *a* axis. (b) Packing diagram for the structure of (I) demonstrating the sheet-like arrangement as viewed down the *a* axis. (c) Packing diagram for the structure of (III) as viewed down the *c* axis, illustrating the 'corrugated' nature of the sheets.

observed [(I)  $O \cdots O=C$  2.594; (III)  $O-H \cdots O=C$  1.770;  $O \cdots O=C$  2.639 Å] as are the linear amide-amide contacts, but this time they are between dimers related by a twofold screw axis, [(I)  $N-H \cdots O=C$  1.845;  $N \cdots O=C$  2.849 Å; (III)  $N-H \cdots O=C$  1.821;  $N \cdots O=C$  2.862 Å]. The dihedral angle *AB* is similar to other aromatic amides exhibiting this mode of hydrogen bonding (Haisa, Kashino, Ueno, Shinozaki & Matsuzaki, 1980).

In both the structures (I) and (III) the hydrogen bonding produces 'corrugated' sheets. In (III) the sheets are stacked along the *a* axis, held together through van der Waals forces as can be seen in Fig. 4(c). The local intersheet environments of the two O atoms O(71) and O(72) are different, and so the carboxyl group is ordered. This pattern of hydrogen bonding is feasible only for a limited chain length since the distance between sheets is fixed so that longer chain lengths may not be accommodated. In addition shorter chain lengths leave tubular voids through the structure. This second possibility would be allowed if such voids could be filled by a 'guest'. This is exactly the situation for the structure of (I) where the voids are filled with disordered acetic acid. The guest is not hydrogen bonded to the host lattice. The local environments of the O(71) and O(72) atoms are now almost identical, and a disordered model of the carboxyl group is seen.

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#### References

- COHEN-ADDAD, C. (1973). *Acta Cryst.* **B29**, 157–161.  
 COLAPIETRO, M. & DOMENICANO, A. (1982). *Acta Cryst.* **B38**, 1953–1957.  
 FEEDER, N. & JONES, W. (1992). *Mol. Cryst. Liq. Cryst.* **211**, 111–124.  
 HAISA, M., KASHINO, S., UENO, T., SHINOZAKI, N. & MATSUZAKI, Y. (1980). *Acta Cryst.* **B36**, 2306–2311.  
 KARIUKI, B. M. & JONES, W. (1992). *Mol. Cryst. Liq. Cryst.* **211**, 233–256.  
 KASAI, N., YAMANAKA, T., MIKI, K., TANAKA, N., POST, B. & MORAWETZ, M. (1981). *Acta Cryst.* **B37**, 1628–1631.  
 KASHINO, S. & HAISA, M. (1980). *Acta Cryst.* **B36**, 346–353.  
 KASHINO, S., MATSUSHITA, T., IWAMOTO, T., YAMAGUCHI, K. & HAISA, M. (1986). *Acta Cryst.* **C42**, 457–462.  
 LEISEROWITZ, L. (1976). *Acta Cryst.* **B32**, 775–802.  
 MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.  
 SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination, Univ. of Cambridge, England.  
 SHELDRICK, G. M. (1984). *SHELXS84*. Program for the solution of crystal structures. Univ. of Göttingen, Germany.  
 SHELDRICK, G. M. (1986). *SHELXS86*. Program for the solution of crystal structures. Univ. of Göttingen, Germany.  
 SWERN, D., WITNAUER, L. P., EDDY, C. R. & PARKER, W. E. (1955). *J. Am. Chem. Soc.* **77**, 5537–5541.  
 TAKWALE, M. G. & PANT, L. M. (1971). *Acta Cryst.* **B27**, 1152–1158.