

Structures of *N*-Acetylbenzamide, *N*-Propionylbenzamide and *N*-Butyrylbenzamide and Analysis of Imide Hydrogen-Bond Patterns

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Abstract. *N*-Acetylbenzamide, $C_9H_9NO_2$ (I), $M_r = 163.18$, orthorhombic, *Pbca*, $a = 8.990$ (2), $b = 9.208$ (3), $c = 19.619$ (3) Å, $V = 1624$ (1) Å³, $Z = 8$, $D_x = 1.335$ (1) g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.89$ cm⁻¹, $F(000) = 688$, $T = 295$ K, $R = 0.031$ for 865 observed reflections. *N*-Propionylbenzamide, $C_{10}H_{11}NO_2$ (II), $M_r = 177.20$, monoclinic, $P2_1/c$, $a = 10.485$ (2), $b = 23.236$ (4), $c = 8.132$ (2) Å, $\beta = 108.43$ (2)°, $V = 1880$ (1) Å³, $Z = 8$, $D_x = 1.252$ (1) g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.82$ cm⁻¹, $F(000) = 752$, $T = 297$ K, $R = 0.044$ for 1407 observed reflections. *N*-Butyrylbenzamide, $C_{11}H_{13}NO_2$ (III), $M_r = 191.23$, monoclinic, $P2_1/n$, $a = 8.270$ (4), $b = 12.660$ (3), $c = 10.459$ (3) Å, $\beta = 108.16$ (3)°, $V = 1040$ (1) Å³, $Z = 4$, $D_x = 1.221$ (1) g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.79$ cm⁻¹, $F(000) = 408$, $T = 298$ K, $R = 0.038$ for 1060 observed reflections. Compound (I) crystallizes in the *Z,Z(trans-trans)* conformation in chains linked by N—H···O hydrogen bonds. (I): N···O = 2.910 (2) Å, NH···O = 170 (3)°. Compounds (II) and (III) crystallize in the *E,Z(cis-trans)* conformation and are linked by N—H···O hydrogen bonds forming eight-membered ring dimers. (II): N···O = 3.019 (4) Å, NH···O = 167 (3)° and N···O = 2.982 (4) Å, NH···O = 170 (3)°; (III): N···O = 2.990 (2) Å, NH···O = 165 (2)°.

Introduction. As part of a comprehensive study of the structures and hydrogen-bond patterns of simple acyclic imides and their cocrystals, we have prepared three homologous *N*-acylbenzamides. Their crystal structures and comparative hydrogen-bond patterns are presented here. It is shown that the —NH protons are always used in hydrogen bonding, that at least one of the two carbonyl O atoms is used as an acceptor site in hydrogen bonding and that both hydrogen-bond chains and dimers are observed in these structures. The factors contributing to the specific hydrogen-bond patterns that are formed include conformational energy differences, differential steric demands of the alkyl substituents and differential hydrogen-bond strengths. It is not pos-

sible to predict *a priori* how these factors will balance one another or which of several possible hydrogen-bond patterns will form, although several common features recur in all of the patterns.

Experimental. Compound (I) was synthesized as described by Baburao, Costello, Petterson & Sander (1968). Colorless plates obtained from ethanol. Crystal of dimensions 0.50 × 0.25 × 0.10 mm used for data collection. Enraf-Nonius CAD-4 diffractometer, Mo $K\alpha$ radiation, graphite monochromator; lattice parameters obtained from least-squares refinement using 25 reflections in the range $21 < 2\theta < 36^\circ$; space group determined from systematic absences ($0kl: k \neq 2n; h0l: l \neq 2n; hk0: h \neq 2n$). ω - 2θ scan technique, scan speed 1.0–20.0° min⁻¹, $2\theta_{\max} = 51.9^\circ$; $0 \leq h \leq 10$, $0 \leq k \leq 11$, $-23 \leq l \leq 24$; 1821 unique reflections measured, equivalent reflections averaged ($R_{\text{int}} = 0.032$). Three standard reflections showed no significant loss in intensity during data collection. Absorption corrections were not applied. Lorentz, polarization and secondary-extinction corrections were made. Structure solved by direct methods with *MITHRIL* (Gilmore, 1984) and *DIRDIF* (Beurskens, 1984). All non-H atoms refined anisotropically; atom H1 refined isotropically; H2, H2', H2'' refined isotropically as a group; other H atoms included in structure-factor calculation placed in idealized positions ($d_{C-H} = 0.95$ Å) with assigned isotropic $B = 1.2 \times B$ of bonded atoms; $\sum w(|F_o| - |F_c|)^2$ minimized where $w = 4F_o^2/\sigma^2(F_o^2)$. $R = 0.031$, $wR = 0.038$, $S = 1.16$ for 865 unique observed reflections [$I > 3\sigma(I)$], 121 parameters, $(\Delta/\sigma)_{\max} < 0.01$, $\Delta\rho$ from -0.12 to 0.19 e Å⁻³. All calculations using *TEXSAN* (Molecular Structure Corporation, 1985) with scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). Atomic parameters are listed in Table 1† and selected interatomic distances and angles given in Table 2.

† Lists of structure factors, anisotropic thermal parameters, least-squares planes and deviations, intermolecular distances (to 3.5 Å) and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53260 (57 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2) with e.s.d.'s in parentheses
$$B_{eq} = (1/3) \sum_i \sum_j B_{ij} a_i^* a_j^* a_i \cdot a_j$$

| | x | y | z | B_{eq} |
|-----------------------------|-------------|-------------|--------------|----------|
| <i>N-Acetylbenzamide</i> | | | | |
| O1 | 0.6445 (2) | -0.1267 (2) | -0.08559 (8) | 4.78 (7) |
| O2 | 0.8614 (2) | -0.1514 (1) | 0.01384 (7) | 4.06 (6) |
| N1 | 0.7200 (2) | 0.0471 (2) | -0.01021 (8) | 3.40 (7) |
| C1 | 0.6501 (2) | -0.0004 (2) | -0.06940 (9) | 3.33 (8) |
| C2 | 0.5810 (3) | 0.1177 (3) | -0.1097 (1) | 4.9 (1) |
| C3 | 0.8105 (2) | -0.0343 (2) | 0.03142 (8) | 3.00 (7) |
| C4 | 0.8454 (2) | 0.0266 (2) | 0.10015 (8) | 2.93 (7) |
| C5 | 0.7568 (2) | 0.1305 (2) | 0.13176 (8) | 3.26 (7) |
| C6 | 0.7919 (2) | 0.1774 (2) | 0.1968 (1) | 3.9 (1) |
| C7 | 0.9145 (3) | 0.1225 (2) | 0.2302 (1) | 4.17 (9) |
| C8 | 1.0029 (3) | 0.0195 (3) | 0.1988 (1) | 4.2 (1) |
| C9 | 0.9686 (2) | -0.0291 (2) | 0.1340 (1) | 3.55 (8) |
| H1 | 0.708 (2) | 0.132 (3) | -0.001 (1) | 3.4 (4) |
| <i>N-Propionylbenzamide</i> | | | | |
| O1 | 0.6324 (3) | -0.3620 (1) | 0.8584 (3) | 5.8 (1) |
| O2 | 0.4380 (3) | -0.2154 (1) | 0.6293 (4) | 8.0 (1) |
| N1 | 0.6045 (3) | -0.2674 (1) | 0.8145 (4) | 4.8 (2) |
| C1 | 0.3963 (4) | -0.3987 (2) | 0.6260 (5) | 6.7 (2) |
| C2 | 0.4238 (4) | -0.3352 (1) | 0.6569 (5) | 5.4 (2) |
| C3 | 0.5592 (4) | -0.3235 (1) | 0.7824 (5) | 4.2 (2) |
| C4 | 0.5437 (4) | -0.2163 (2) | 0.7452 (5) | 5.0 (2) |
| C5 | 0.6143 (3) | -0.1623 (1) | 0.8212 (5) | 4.3 (2) |
| C6 | 0.7166 (4) | -0.1595 (1) | 0.9759 (5) | 4.8 (2) |
| C7 | 0.7728 (4) | -0.1072 (2) | 1.0397 (5) | 5.7 (2) |
| C8 | 0.7278 (4) | -0.0574 (2) | 0.9507 (6) | 6.1 (2) |
| C9 | 0.6268 (4) | -0.0596 (2) | 0.7954 (6) | 6.3 (2) |
| C10 | 0.5700 (4) | -0.1116 (2) | 0.7296 (5) | 5.4 (2) |
| H1N | 0.677 (3) | -0.266 (1) | 0.884 (4) | 4.3 (9) |
| O11 | 0.8640 (3) | -0.2796 (1) | 1.1096 (4) | 7.4 (1) |
| O12 | 1.0411 (2) | -0.4264 (1) | 1.3554 (3) | 5.6 (1) |
| N11 | 0.8919 (3) | -0.3744 (1) | 1.1441 (4) | 4.5 (1) |
| C11 | 1.0998 (4) | -0.2442 (2) | 1.3467 (5) | 7.3 (2) |
| C12 | 1.0605 (4) | -0.3071 (1) | 1.3314 (5) | 5.5 (2) |
| C13 | 0.9337 (4) | -0.3184 (2) | 1.1897 (5) | 4.8 (2) |
| C14 | 0.9478 (3) | -0.4256 (1) | 1.2217 (4) | 4.2 (2) |
| C15 | 0.8855 (3) | -0.4794 (1) | 1.1324 (5) | 3.8 (2) |
| C16 | 0.8065 (4) | -0.4818 (1) | 0.9616 (5) | 4.8 (2) |
| C17 | 0.7575 (4) | -0.5339 (2) | 0.8868 (5) | 6.0 (2) |
| C18 | 0.7861 (4) | -0.5835 (2) | 0.9816 (6) | 6.3 (2) |
| C19 | 0.8642 (4) | -0.5812 (2) | 1.1532 (6) | 6.1 (2) |
| C20 | 0.9129 (4) | -0.5295 (2) | 1.2273 (5) | 5.2 (2) |
| H11N | 0.813 (4) | -0.375 (1) | 1.060 (4) | 6 (1) |
| <i>N-Butyrylbenzamide</i> | | | | |
| O1 | 0.4708 (2) | 0.3772 (1) | 1.0362 (2) | 5.58 (8) |
| O2 | -0.0346 (2) | 0.4227 (1) | 0.8401 (2) | 5.26 (7) |
| N1 | 0.2418 (2) | 0.4704 (1) | 0.9252 (2) | 3.72 (7) |
| C1 | 0.2327 (4) | 0.0764 (2) | 0.9423 (3) | 6.8 (1) |
| C2 | 0.3333 (3) | 0.1769 (2) | 0.9845 (2) | 4.7 (1) |
| C3 | 0.2244 (2) | 0.2742 (1) | 0.9389 (2) | 3.71 (9) |
| C4 | 0.3207 (2) | 0.3748 (1) | 0.9716 (2) | 3.61 (8) |
| C5 | 0.0715 (2) | 0.4920 (2) | 0.8632 (2) | 3.40 (8) |
| C6 | 0.0246 (2) | 0.6038 (1) | 0.8282 (2) | 3.23 (8) |
| C7 | -0.1445 (2) | 0.6240 (2) | 0.7532 (2) | 4.2 (1) |
| C8 | -0.1997 (3) | 0.7244 (2) | 0.7170 (2) | 5.0 (1) |
| C9 | -0.0904 (3) | 0.8077 (2) | 0.7547 (2) | 5.0 (1) |
| C10 | 0.0760 (3) | 0.7897 (2) | 0.8294 (3) | 4.8 (1) |
| C11 | 0.1339 (2) | 0.6888 (2) | 0.8658 (2) | 4.0 (1) |
| H1N | 0.311 (3) | 0.523 (1) | 0.938 (2) | 4.6 (5) |

Table 2. Selected intramolecular distances (\AA) and angles ($^\circ$) with e.s.d.'s in parentheses

| | | | |
|-----------------------------|-----------|--------------|-----------|
| <i>N-Acetylbenzamide</i> | | | |
| O1—C1 | 1.207 (2) | C4—C9 | 1.389 (3) |
| O2—C3 | 1.221 (2) | C4—C5 | 1.391 (3) |
| N1—H1 | 0.812 | C5—C6 | 1.384 (3) |
| N1—C3 | 1.375 (2) | C6—C7 | 1.378 (3) |
| N1—C1 | 1.391 (2) | C7—C8 | 1.382 (3) |
| C1—C2 | 1.481 (3) | C8—C9 | 1.383 (3) |
| C3—C4 | 1.494 (2) | | |
| H1—N1—C3 | 118.68 | C9—C4—C5 | 119.8 (2) |
| H1—N1—C1 | 114.94 | C9—C4—C3 | 117.4 (2) |
| C3—N1—C1 | 126.3 (2) | C5—C4—C3 | 122.7 (2) |
| O1—C1—N1 | 122.8 (2) | C6—C5—C4 | 119.7 (2) |
| O1—C1—C2 | 123.3 (2) | C7—C6—C5 | 120.4 (2) |
| N1—C1—C2 | 113.9 (2) | C6—C7—C8 | 120.0 (2) |
| C1—C2—N1 | 122.4 (2) | C7—C8—C9 | 120.2 (2) |
| O2—C3—C4 | 120.5 (2) | C8—C9—C4 | 119.9 (2) |
| N1—C3—C4 | 117.1 (2) | | |
| <i>N-Propionylbenzamide</i> | | | |
| O1—C3 | 1.213 (4) | O11—C13 | 1.212 (4) |
| O2—C4 | 1.207 (4) | O12—C14 | 1.211 (4) |
| N1—H1N | 0.79 (3) | N11—H11N | 0.89 (3) |
| N1—C4 | 1.381 (4) | N11—C14 | 1.386 (4) |
| N1—C3 | 1.384 (4) | N11—C13 | 1.387 (4) |
| C1—C2 | 1.508 (5) | C11—C12 | 1.515 (5) |
| C2—C3 | 1.488 (5) | C12—C13 | 1.482 (5) |
| C4—C5 | 1.487 (4) | C14—C15 | 1.490 (4) |
| C5—C6 | 1.373 (4) | C15—C16 | 1.376 (4) |
| C5—C10 | 1.393 (4) | C15—C20 | 1.376 (4) |
| C6—C7 | 1.378 (5) | C16—C17 | 1.379 (5) |
| C7—C8 | 1.368 (5) | C17—C18 | 1.366 (5) |
| C8—C9 | 1.369 (5) | C18—C19 | 1.378 (5) |
| C9—C10 | 1.378 (5) | C19—C20 | 1.367 (5) |
| H1N—N1—C4 | 119 (2) | H11N—N11—C14 | 119 (2) |
| H1N—N1—C3 | 111 (2) | H11N—N11—C13 | 111 (2) |
| C4—N1—C3 | 130.2 (3) | C14—N11—C13 | 129.1 (3) |
| C3—C2—C1 | 112.6 (3) | C13—C12—C11 | 112.8 (3) |
| O1—C3—N1 | 118.3 (3) | O11—C13—N11 | 117.9 (3) |
| O1—C3—C2 | 121.8 (3) | O11—C13—C12 | 121.9 (3) |
| N1—C3—C2 | 119.9 (3) | N11—C13—C12 | 120.2 (3) |
| O2—C4—N1 | 121.6 (3) | O12—C14—N11 | 121.9 (3) |
| O2—C4—C5 | 121.6 (3) | O12—C14—C15 | 121.9 (3) |
| N1—C4—C5 | 116.7 (3) | N11—C14—C15 | 116.2 (3) |
| C6—C5—C10 | 118.8 (3) | C16—C15—C20 | 119.0 (3) |
| C6—C5—C4 | 124.3 (3) | C16—C15—C14 | 123.9 (3) |
| C10—C5—C4 | 116.9 (3) | C20—C15—C14 | 117.1 (3) |
| C5—C6—C7 | 120.3 (3) | C15—C16—C17 | 120.2 (3) |
| C8—C7—C6 | 120.8 (4) | C18—C17—C16 | 120.4 (4) |
| C7—C8—C9 | 119.5 (4) | C17—C18—C19 | 119.5 (4) |
| C8—C9—C10 | 120.3 (4) | C20—C19—C18 | 120.0 (4) |
| C9—C10—C5 | 120.2 (4) | C19—C20—C15 | 120.8 (4) |
| <i>N-Butyrylbenzamide</i> | | | |
| O1—C4 | 1.215 (2) | C5—C6 | 1.483 (3) |
| O2—C5 | 1.211 (2) | C6—C11 | 1.381 (3) |
| N1—H1N | 0.86 (2) | C6—C7 | 1.398 (3) |
| N1—C5 | 1.382 (2) | C7—C8 | 1.363 (3) |
| N1—C4 | 1.390 (2) | C8—C9 | 1.365 (3) |
| C1—C2 | 1.509 (3) | C9—C10 | 1.374 (3) |
| C2—C3 | 1.514 (3) | C10—C11 | 1.375 (3) |
| C3—C4 | 1.483 (2) | | |
| H1N—N1—C5 | 117 (1) | N1—C5—C6 | 117.0 (2) |
| H1N—N1—C4 | 113 (1) | C11—C6—C7 | 117.9 (2) |
| C5—N1—C4 | 129.4 (2) | C11—C6—C5 | 125.2 (2) |
| C1—C2—C3 | 112.0 (2) | C7—C6—C5 | 116.9 (2) |
| C4—C3—C2 | 113.7 (2) | C8—C7—C6 | 121.1 (2) |
| O1—C4—N1 | 117.4 (2) | C7—C8—C9 | 120.4 (2) |
| O1—C4—C3 | 122.2 (2) | C8—C9—C10 | 119.5 (2) |
| N1—C4—C3 | 120.5 (2) | C9—C10—C11 | 120.8 (2) |
| O2—C5—N1 | 121.3 (2) | C10—C11—C6 | 120.3 (2) |
| O2—C5—C6 | 121.7 (2) | | |

Compound (II) was synthesized by refluxing benzamide and propionyl chloride in acetonitrile for 6 h. Yellow crystals obtained from ethanol. Crystal of dimensions $0.45 \times 0.35 \times 0.20$ mm used for data collection. Enraf-Nonius CAD-4 diffractometer, Mo $K\alpha$ radiation, graphite monochromator; lattice parameters obtained from least-squares refinement using 25 reflections in the range $20 < 2\theta < 34^\circ$; space group determined from systematic absences ($h0l$: $l \neq 2n$; $0k0$: $k \neq 2n$). ω - 2θ scan technique, scan speed 4.0 - $20.0^\circ \text{ min}^{-1}$, $2\theta_{\text{max}} = 48^\circ$; $-11 \leq h \leq 11$, $0 \leq k \leq$

26 , $-9 \leq l \leq 2$; 3037 unique reflections measured, equivalent reflections averaged ($R_{\text{int}} = 0.024$). Three standard reflections showed no significant loss in intensity during data collection. Absorption corrections were not applied. Lorentz, polarization and secondary-extinction corrections were made. Struc-

Table 3. *Hydrogen-bond lengths and angles*

| D—H...A | Symmetry | d(D...A) (Å) | angle (DH...A) (°) |
|---|-----------------------------------|------------------------|--------------------|
| (I) <i>N</i> -Acetylbenzamide N1—H1...O2 | $\frac{1}{2}-x, \frac{1}{2}+y, z$ | 2.910 (2) | 170 (3) |
| (II) <i>N</i> -Propionylbenzamide* N1—H1N...O11 N11—H11N...O1 | | 3.019 (4) 2.982 (4) | 167 (3) 170 (3) |
| (III) <i>N</i> -Butyrylbenzamide N1—H1N...O1 | $-x, -y, -z$ | 2.990 (2) | 165 (2) |

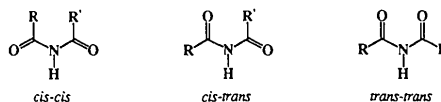
* The two molecules in the asymmetric unit form a dimer with a pseudo inversion center. Hydrogen bonds occur between these two units.

ture solved by direct methods with *MITHRIL* (Gilmore, 1984) and *DIRDIF* (Beurskens, 1984). All non-H atoms refined anisotropically; atoms H1N and H11N refined isotropically; other H atoms included in structure-factor calculation placed in idealized positions ($d_{C-H} = 0.95 \text{ \AA}$) with assigned isotropic $B = 1.2 \times B$ of bonded atoms; $\sum w(|F_o| - |F_c|)^2$ minimized where $w = 4F_o^2/\sigma^2(F_o^2)$. $R = 0.044$, $wR = 0.054$, $S = 1.32$ for 1407 unique observed reflections [$I > 3\sigma(I)$], 244 parameters, $(\Delta/\sigma)_{\max} = 0.59$, $\Delta\rho$ from -0.13 to 0.16 e \AA^{-3} . All calculations using *TEXSAN* (Molecular Structure Corporation, 1985) with scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). Atomic parameters are listed in Table 1 and selected interatomic distances and angles given in Table 2.

Compound (III) was synthesized by refluxing benzamide and butyryl chloride in acetonitrile for 3 h. Colorless prisms obtained from toluene. Crystal of dimensions $0.60 \times 0.50 \times 0.20 \text{ mm}$ used for data collection. Enraf-Nonius CAD-4 diffractometer, Mo $K\alpha$ radiation, graphite monochromator; lattice parameters obtained from least-squares refinement using 25 reflections in the range $18 < 2\theta < 42^\circ$; space group determined from systematic absences ($h0l: h + l \neq 2n; 0k0: k \neq 2n$). $\omega-2\theta$ scan technique, scan speed $10.0-20.0^\circ \text{ min}^{-1}$, $2\theta_{\max} = 47.9^\circ$; $0 \leq h \leq 9$, $-14 \leq k \leq 14$, $-11 \leq l \leq 10$; 1724 unique reflections measured, equivalent reflections averaged ($R_{\text{int}} = 0.034$). Three standard reflections showed no significant loss in intensity during data collection; empirical absorption correction applied using *DIFABS* (Walker & Stuart, 1983), transmission range = $0.89-1.10$. Lorentz, polarization and secondary-extinction corrections were made. Structure solved by direct methods with *MITHRIL* (Gilmore, 1984) and *DIRDIF* (Beurskens, 1984). All non-H atoms refined anisotropically; atom H1N refined isotropically; other H atoms included in structure-factor calculation placed in idealized positions ($d_{C-H} = 0.95 \text{ \AA}$) with assigned isotropic $B = 1.2 \times B$ of bonded atom; $\sum w(|F_o| - |F_c|)^2$ minimized where $w = 4F_o^2/\sigma^2(F_o^2)$. $R = 0.038$, $wR = 0.048$, $S = 1.33$ for 1060 unique observed reflections [$I > 3\sigma(I)$], 132 parameters, $(\Delta/\sigma)_{\max} < 0.01$, $\Delta\rho$ from -0.17 to 0.15 e \AA^{-3} . All calculations

using *TEXSAN* (Molecular Structure Corporation, 1985) with scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). Atomic parameters are listed in Table 1 and selected interatomic distances and angles given in Table 2. Hydrogen-bond lengths and angles for (I)–(III) are given in Table 3.

Discussion. Symmetrical acyclic imides ($R = R'$) may exist in three possible planar conformations, *cis-cis*, *cis-trans*, and *trans-trans*, differentiated by the relative positions of the carbonyl groups with respect to the central NH bond.



The *cis-cis* conformation is the highest-energy form due to repulsive 1,5 intramolecular nonbonding interactions between R and R' , and is not observed in solution (Noe & Raban, 1975) or in the solid state. The *trans-trans* conformation is destabilized by about 4 kJ mol^{-1} relative to the *cis-trans* conformation by electrostatic repulsion between the two relatively close O atoms (Radom & Riggs, 1980). In unsymmetrical imides ($R \neq R'$), two *cis-trans* isomers are possible. Previously reported X-ray crystal structures of acyclic imides (uncomplexed and with no hydrogen-bonding functional groups present in the R groups) show that the *trans-trans* conformation is found in five out of the six known structures (Matias, Jeffrey & Ruble, 1988; Kuroda, Taira, Uno & Osaki, 1975; Uechi, Watanabe & Osaki, 1966; Hvostlef, Tracy & Nash, 1986; Bates, Janda & Wright, 1985; Mizrahi & Niven, 1983). Diacetamide, the simplest imide, crystallizes in two polymorphs, one of which is *cis-trans* (Matias, Jeffrey & Ruble, 1988) and the other *trans-trans* (Kuroda, Taira, Uno & Osaki 1975). Thus, from previous studies we expect to see both *cis-trans* and *trans-trans* conformations for imides in the solid state even though the *trans-trans* form is a higher-energy conformer.

N-Acetylbenzamide, (I), Fig. 1, adopts the *trans-trans* conformation. *N*-Propionylbenzamide, (II), and *N*-butyrylbenzamide, (III), Figs. 2 and 3, respectively, crystallize in the *cis-trans* conformation. The two molecules present in the asymmetric unit of (II) and the molecules of (III) adopt the *cis-trans* conformation with the acyl carbonyls *cis* and the benzoyl carbonyls *trans* with respect to each NH bond.

Deviations of the OCNCO moiety from planarity are seen in all three structures due to repulsive 1,5 interactions between the two O atoms in (I) and repulsive 1,6 interactions between the *trans* carbonyl O atoms and the $\alpha\text{C-H}$ protons in (II) and (III). These distortions lead to an increase in the O1...O2

separation in (I) from an ideal distance of about 2.4 Å, assuming normal bond lengths and 120° bond angles, to 2.768 (2) Å. The O2...C2 and O12...C12 separations in (II) and the O2...C3 separation in (III) are also long [2.800 (4), 2.790 (4) and 2.974 (3) Å, respectively].

The six previously reported X-ray crystal structures of simple acyclic imides show that *cis-trans*

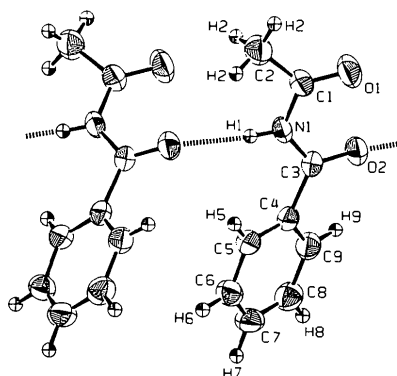


Fig. 1. The molecular geometry and hydrogen-bonding scheme of (I), *N*-acetylbenzamide. Molecules of (I) are observed in the *trans-trans* conformation and are hydrogen bonded in chains linked by NH...O hydrogen bonds between H1 and O2 atoms of glide-related molecules. In this structure, the benzoyl carbonyl group is used in hydrogen bonding, while the acyl carbonyl group is not hydrogen bonded. Thermal ellipsoids are depicted at 50% probability. Dashed lines indicate hydrogen bonds.

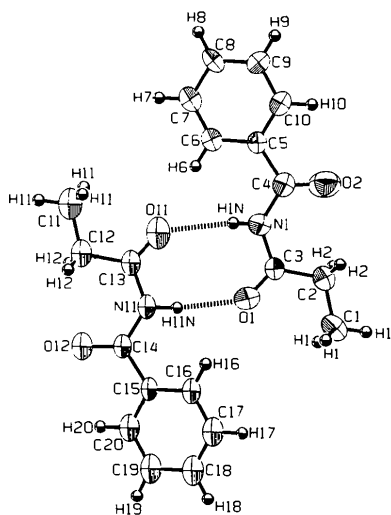


Fig. 2. The molecular geometry and hydrogen-bonding scheme of (II), *N*-propionylbenzamide. There are two molecules per asymmetric unit, both of which adopt the *cis-trans* conformation. The molecules in the asymmetric unit form dimers with a pseudo inversion center linked by NH...O hydrogen bonds between the acyl carbonyl group and the NH group of its neighbor. The benzoyl carbonyl group is not hydrogen bonded. The dimers lie in planes parallel to the (202) faces. Thermal ellipsoids are depicted at 50% probability. Dashed lines indicate hydrogen bonds.

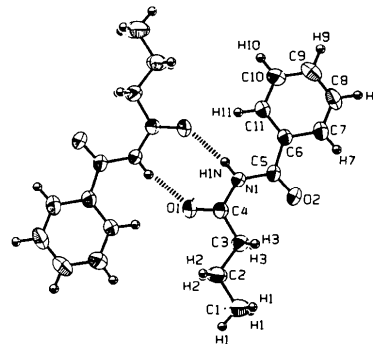
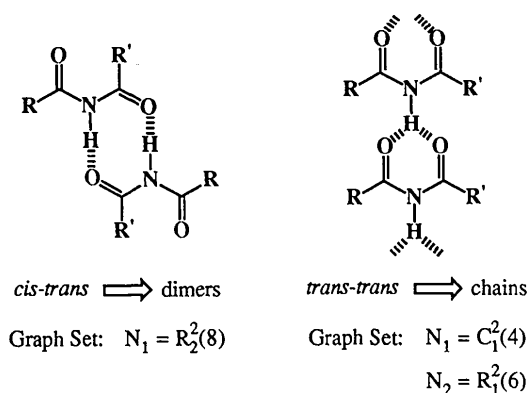


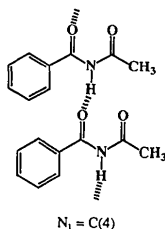
Fig. 3. The molecular geometry and hydrogen-bonding scheme of (III), *N*-butyrylbenzamide. Molecules of (III) are observed in the *cis-trans* conformation and form dimers linked by NH...O hydrogen bonds between the acyl carbonyl group and the NH group of its neighbor. The benzoyl carbonyl group is not hydrogen bonded. The dimers lie in planes parallel to the (103) faces. Thermal ellipsoids are depicted at 50% probability. Dashed lines indicate hydrogen bonds.

conformers always occur in a dimeric hydrogen-bond pattern and that all *trans-trans* conformers, except bis(2,2-dimethylpropionyl)amine (Hvoslef, Tracy & Nash, 1986), occur in chains with bifurcated hydrogen bonds. Imides have two potential hydrogen-bond acceptors (C=O) and one hydrogen-bond donor (NH). The *cis-trans* conformers use only one of the hydrogen-bond acceptors in forming hydrogen-bonded dimers. The *trans-trans* conformers can use both hydrogen-bond acceptors in forming chains linked by bifurcated NH...O hydrogen bonds. The formation of bifurcated hydrogen bonds is believed to contribute to the stabilization of the *trans-trans* conformation in the solid state (Mizrahi & Niven, 1983). The differences in these two types of hydrogen-bond patterns are seen using graph set notation, a method recently developed for analyzing and comparing hydrogen-bond patterns (Etter, MacDonald & Bernstein, 1990). [This notation indicates the cyclic (*R*) nature of the *cis-trans* dimer, with two proton donors and two proton acceptors (sub- and superscripts) used in the pattern. Ring size is indicated in parentheses. For the *trans-trans* pattern, one proton donor participates in two graphs. One is a chain with a repeat pattern of four; the other is a six-membered ring. Both graphs use one donor and two acceptors.]

The crystal structure of (I) shows a hydrogen-bond pattern that has not previously been seen. Molecules of (I) crystallize in the *trans-trans* conformation, but form $C_1^1(4)$ hydrogen-bond patterns only. This motif is a subset of the graph set observed for all other *trans-trans* conformers [$C_1^2(4)$]. The hydrogen-bond chains are oriented along the *b* axis and involve NH...O hydrogen bonds from the —NH of one molecule to the benzoyl O atom of the next glide-related molecule [NH...O = 2.107, N(H)...O =



2.910 (2) Å]. The acetyl carbonyl group is *not* hydrogen bonded [NH \cdots O = 3.069, N(H) \cdots O = 3.563 (2) Å]. As in the hydrogen-bond patterns of the other imides, (I) uses the *syn* lone pair of electrons in forming its $C_1^1(4)$ hydrogen-bonding pattern (with one donor and one acceptor indicated by default values of one for sub- and superscripts).



In structure (II), the *cis-trans* conformation and the expected $R_2^2(8)$ hydrogen-bonding pattern are observed. Dimers with pseudo inversion centers are formed by hydrogen bonds between the *cis* propionyl O atom of one molecule in the asymmetric unit and the NH group of the other. The carbonyl O atom of the *trans* benzoyl group is not hydrogen bonded. Compound (III), which is also observed in the *cis-trans* conformation, crystallizes in an $R_2^2(8)$ pattern with centrosymmetric dimers formed by hydrogen bonds between the *cis* butyryl O atom and the NH of an inversion-related molecule. As in (II), the carbonyl O of the *trans* benzoyl group is not hydrogen bonded.

The unit-cell packing patterns of (I)–(III) are shown in Fig. 4. In (I), the mean molecular plane of one imide makes a dihedral angle of about 85° with the glide-related molecules in the hydrogen-bonded chain. The hydrogen-bonded chains in (I) are oriented antiparallel to one another. In (II) and (III), the dimers lie in planes parallel to $(\bar{2}02)$ and $(\bar{1}03)$, respectively.

These structures illustrate the difficulties inherent in predicting *a priori* how crystal packing forces, hydrogen bonding and conformational preferences will balance one another in determining hydrogen-

bond patterns. Certain features are common to these three structures and to the six structures from the literature:

1. The —NH protons and at least one carbonyl O atom are used in hydrogen bonding.
2. Only the *syn* lone pairs of electrons of the carbonyl groups are used in hydrogen bonding.
3. *cis-trans* imides (three crystal structures) pack in hydrogen-bond patterns with $R_2^2(8)$ graph sets.
4. *trans-trans* imides (six crystal structures) form hydrogen-bond chains.
5. The most common graph set for imide chains is $N_1 = C_1^1(4)$ [$R_1^1(6)$]. One example of a chain with graph set $C_1^1(4)$ has also been observed.

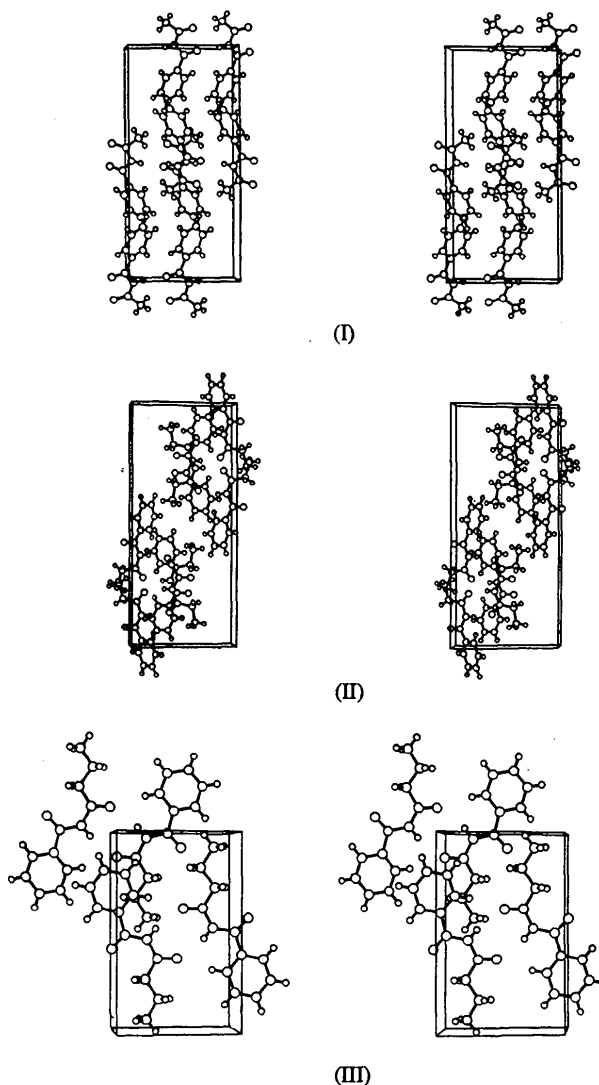


Fig. 4. Stereoscopic views of the unit cells of *N*-acetylbenzamide (I), *N*-propionylbenzamide (II) and *N*-butrylbenzamide (III), viewed along [100], [100] and [001], respectively. (I) **b** horizontal, **a** vertical, **c** towards the viewer; (II), (III) **a** horizontal, **b** vertical, **c** towards the viewer.

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1,2,3,3,8-Pentamethyl-5-trifluoromethyl-2,3-dihydro-1H-pyrrolo[2,3-g]quinolin-7(8H)-one

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Abstract. $C_{17}H_{19}F_3N_2O$, $M_r = 324.34$, monoclinic, $P2_1/a$, $a = 10.694$ (3), $b = 12.216$ (3), $c = 12.356$ (4) Å, $\beta = 94.24$ (3)°, $V = 1609.8$ (8) Å³, $Z = 4$, $D_x = 1.338$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 1.02$ cm⁻¹, $F(000) = 680$, $T = 296$ K, $R = 0.044$ for 1781 observed reflections. The quinolone ring is planar and the dihydropyrrole ring adopts an envelope conformation with a mean absolute torsion angle of 25°.

Introduction. The title compound (I), a laser dye (Schimitschek, Trias, Hammond, Henry & Atkins, 1976), has been found to give simultaneous dual super-radiant emission in benzene- and toluene-like solvents under nitrogen laser excitation: one emission around 438 nm and another around 469 nm (Sastikumar & Masilamani, 1990). This interesting photophysical property has also been observed in alkylaminocoumarin derivatives and it is attributed to both normal and twisted intramolecular charge transfer (TICT) states of the molecule in the excited state (Masilamani, Chandrasekar, Sivaram, Sivasankar & Natarajan, 1986; Masilamani, Sastikumar, Natarajan & Natarajan, 1987; Ramalingam, Palanisamy, Masilamani & Sivaram,

1989). In the TICT state the plane of the alkylamino (donor) group is said to be perpendicular to the plane of the acceptor moiety. The concept that the twisting of the donor group produces the anomalous band has been supported by the observation that the inhibition of twisting through the use of a rigid amino group results in only one band (Masilamani, 1987). But the dual emission by the title compound contradicts this hypothesis as the donor group here is part of the five-membered ring which cannot allow a 90° twist in the $\dot{N}-C(sp^2)$ bond of the alkylamino group. The structural study of this compound suggests another possible model for the dual emission.

Experimental. Compound from Exciton (USA), yellow cubic crystals from methanol; Rigaku AFC5R diffractometer, graphite-monochromated Mo $K\alpha$ radiation; crystal dimensions 0.2 × 0.2 × 0.2 mm; cell dimensions from 20 angles in the range $15 \leq 2\theta \leq 20^\circ$, $2\theta_{\max} = 50^\circ$. Intensities measured in the range $h = 0$ to 13, $k = 0$ to 15 and $l = -15$ to 15, $\omega-2\theta$ scan; three standard reflections (202, $\bar{1}\bar{1}3$, 20 $\bar{1}$) monitored every 150 measurements showed no significant change. 2417 unique reflections ($R_{\text{int}} = 0.023$) of