stack structure, the observed electrical conductivity is very low ($\sigma = 3 \times 10^{-6}$ S m^{-1}).

Financial support from the Danish Natural Science Research Council and the EEC ESPRIT programme (BRA3121) is gratefully acknowledged.

References

CHRISTENSEN, J. B., JOHANNSEN, I. & BECHGAARD, K. (1991). *J. Org. Chem.* Submitted.

FLANDROIS, S. & CHASSEAU, D. (1977). *Acta Cryst.* **B33**, 2744–2750.

JOHNSON, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

LONGO, J. & RICHARDSON, M. F. (1982). *Acta Cryst.* **B38**, 2724–2726.

NAKASUJI, K., SASAKI, M., KOTANI, T., MURATA, I. ENOKI, T., IMAEDA, K., INOKUCHI, H., KAWAMOTO, A. & TANAKA, J. (1987). *J. Am. Chem. Soc.* **109**, 6970–6975.

SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

SHELDRICK, G. M. (1990). *Acta Cryst.* **A46**, 467–473.

SPEK, A. L. (1990). *Acta Cryst.* **A46**, C-31.

THORUP, N., RINDORF, G., JACOBSEN, C. S., BECHGAARD, K., JOHANNSEN, I. & MORTENSEN, K. (1985). *Mol. Cryst. Liq. Cryst.* **120**, 349–352.

Acta Cryst. (1992). C**48**, 533–536

Molecular Co-Crystals of Carboxylic Acids. 3.* Structures of the 1:1 Adducts of 2,4,6-Trinitrobenzoic Acid with 4-Aminobenzoic Acid and 3-Hydroxypyridine

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(*Received* 22 *May* 1991; *accepted* 3 *September* 1991)

Abstract. (1) $C_7H_8NO_2^+.C_7H_2N_3O_8^-.H_2O$, $M_r = 412.3$, orthorhombic, *Pbcn*, $a = 29.528$ (4), $b = 11.306$ (2), $c = 10.603$ (1) Å, $V = 3539.9$ (8) Å^3, $Z = 8$, $D_m = 1.55$, $D_x = 1.546$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 0.15$ mm^{-1}, $F(000) = 1696$, $T = 295$ K, $R = 0.039$ for 958 observed reflections. (2) $C_5H_6NO^+.C_7H_2N_3O_8^-$, $M_r = 352.2$, monoclinic, $P2_1/c$, $a = 7.276$ (3), $b = 8.310$ (1), $c = 24.130$ (7) Å, $\beta = 92.48$ (2)°, $V = 1457.6$ (7) Å^3, $Z = 4$, $D_m = 1.60$, $D_x = 1.604$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 0.15$ mm^{-1}, $F(000) = 720$, $T = 295$ K, $R = 0.032$ for 1368 observed reflections. Compound (1) may be prepared by both solid-state and solution reactions. Crystals were obtained from water. Extensive hydrogen bonding between amino groups, carboxylic acids and waters exists. The two acids are uniquely hydrogen bonded across one carboxylic acid oxygen pair, with no interactions between the other two oxygens. Compound (2) was prepared in aqueous solution and crystallized from water. In this adduct, hydrogen bonding exists between the deprotonated carboxylic acid groups and the protonated pyridine nitrogens.

Introduction. 4-Aminobenzoic acid (4-ABA) is recognized as an important acid for molecular adduct formation. Prior to 1989 only two molecular co-crystals with 4-ABA were known, 4-nitropyridine *N*-oxide (Lechat, 1984) and 1,3-dimethyl-2-imidazolidinone (Ueda, Onishi & Nagai, 1986). Both the carboxylic acid and amino groups on 4-ABA have potential for hydrogen-bonding interactions. This property, together with the linearity of the molecule, was used in the synthesis of co-crystals with other carboxylic acids, particularly nitrobenzoic acids (Etter, Frankenbach & Bernstein, 1989; Etter & Frankenbach, 1989). Adduct formation may also result from a solid-state reaction, simply by grinding two acids together. In the structure of the 4-ABA–3,5-dinitrobenzoic acid adduct (Etter, Frankenbach & Bernstein, 1989) the carboxylic acids form hydrogen-bonded cyclic dimers while the amino and nitro groups also interact. 2,4,6-Trinitrobenzoic acid (TNBA) is an acid not previously reported in molecular adduct formation, possibly because it readily decarboxylates when boiled in water, forming 1,3,5-trinitrobenzene (TNB) (Coffey, 1977). This was observed in attempted co-crystal preparation of TNBA with indole-3-acetic acid (IAA), giving

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[*] Part 2: Lynch, Smith, Byriel & Kennard (1991*a*).

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0108-2701/92/030533-04$03.00

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters* (Å^2 × 10^3)

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

	x	*y*	*z*	U_{eq}
Compound (1)				
C(1*A*)	0.6598 (2)	0.5610 (5)	0.2391 (5)	39 (3)
C(11*A*)	0.6300 (2)	0.4638 (5)	0.2962 (6)	52 (4)
O(11*A*)	0.6283 (1)	0.3712 (3)	0.2322 (4)	57 (2)
O(12*A*)	0.6115 (2)	0.4820 (4)	0.4003 (4)	85 (3)
C(2*A*)	0.7070 (2)	0.5566 (5)	0.2435 (5)	40 (4)
N(2*A*)	0.7297 (2)	0.4579 (4)	0.3117 (5)	60 (4)
O(21*A*)	0.7080 (2)	0.4020 (4)	0.3855 (5)	97 (4)
O(22*A*)	0.7696 (2)	0.4402 (4)	0.2871 (4)	78 (3)
C(3*A*)	0.7348 (2)	0.6377 (5)	0.1867 (5)	47 (4)
C(4*A*)	0.7145 (2)	0.7277 (5)	0.1205 (5)	42 (4)
N(4*A*)	0.7430 (2)	0.8124 (5)	0.0506 (5)	53 (3)
O(41*A*)	0.7245 (2)	0.8893 (4)	−0.0093 (5)	83 (3)
O(42*A*)	0.7835 (2)	0.8002 (4)	0.0569 (4)	83 (3)
C(5*A*)	0.6688 (2)	0.7401 (5)	0.1119 (5)	41 (3)
C(6*A*)	0.6415 (2)	0.6564 (4)	0.1706 (5)	36 (3)
N(6*A*)	0.5928 (2)	0.6679 (5)	0.1548 (5)	52 (3)
O(61*A*)	0.5687 (1)	0.5855 (4)	0.1794 (5)	74 (3)
O(62*A*)	0.5789 (1)	0.7622 (4)	0.1167 (5)	79 (3)
C(1*B*)	0.4174 (2)	−0.0075 (5)	0.1257 (4)	44 (3)
C(11*B*)	0.4136 (2)	0.1139 (5)	0.1785 (6)	57 (4)
O(11*B*)	0.3725 (2)	0.1585 (4)	0.1719 (4)	66 (3)
O(12*B*)	0.4451 (2)	0.1672 (4)	0.2227 (5)	90 (3)
C(2*B*)	0.4595 (2)	−0.0582 (6)	0.1139 (6)	56 (4)
C(3*B*)	0.4650 (2)	−0.1694 (6)	0.0648 (6)	57 (4)
C(4*B*)	0.4277 (2)	−0.2291 (5)	0.0238 (5)	44 (4)
N(4*B*)	0.4333 (2)	−0.3467 (4)	−0.0330 (5)	56 (3)
C(5*B*)	0.3856 (2)	−0.1822 (5)	0.0338 (6)	53 (4)
C(6*B*)	0.3801 (2)	−0.0696 (5)	0.0855 (6)	54 (4)
O(*w*)	0.4824 (2)	0.6106 (5)	0.6290 (6)	152 (5)
Compound (2)				
C(1*A*)	0.0339 (3)	0.2617 (3)	0.0385 (1)	36 (1)
C(11*A*)	0.1169 (3)	0.2495 (3)	0.0978 (1)	40 (2)
O(11*A*)	0.1634 (3)	0.3786 (2)	0.1197 (1)	55 (1)
O(12*A*)	0.1270 (3)	0.1111 (2)	0.1169 (1)	51 (1)
C(2*A*)	−0.1416 (3)	0.3217 (3)	0.0268 (1)	37 (1)
O(21*A*)	−0.2383 (3)	0.3149 (3)	0.1164 (1)	68 (1)
O(22*A*)	−0.3477 (3)	0.4997 (3)	0.0621 (1)	67 (1)
N(2*A*)	−0.2499 (3)	0.3831 (3)	0.0720 (1)	46 (1)
C(3*A*)	−0.2226 (4)	0.3291 (3)	−0.0261 (1)	44 (2)
C(4*A*)	−0.1228 (4)	0.2726 (3)	−0.0686 (1)	47 (2)
N(4*A*)	−0.2049 (5)	0.2748 (3)	−0.1258 (1)	62 (2)
O(41*A*)	−0.3706 (4)	0.2880 (3)	−0.1307 (1)	79 (2)
O(42*A*)	−0.1011 (4)	0.2638 (3)	−0.1636 (1)	86 (2)
C(5*A*)	0.0531 (5)	0.2173 (3)	−0.0608 (1)	49 (2)
C(6*A*)	0.1276 (4)	0.2143 (3)	−0.0075 (1)	41 (1)
N(6*A*)	0.3239 (3)	0.1684 (3)	−0.0020 (1)	55 (2)
O(61*A*)	0.4105 (3)	0.2114 (3)	0.0396 (1)	68 (1)
O(62*A*)	0.3898 (4)	0.0971 (3)	−0.0402 (1)	91 (2)
N(1*B*)	0.3247 (3)	0.4406 (3)	0.2192 (1)	49 (1)
C(2*B*)	0.5031 (4)	0.4716 (3)	0.2259 (1)	46 (2)
C(3*B*)	0.5739 (4)	0.5228 (3)	0.2768 (1)	41 (2)
O(31*B*)	0.7553 (3)	0.5552 (3)	0.2811 (1)	56 (1)
C(4*B*)	0.4551 (4)	0.5398 (3)	0.3194 (1)	48 (2)
C(5*B*)	0.2715 (4)	0.5079 (4)	0.3102 (1)	57 (2)
C(6*B*)	0.2070 (5)	0.4572 (4)	0.2594 (1)	55 (2)

TNB–IAA (Lynch, Smith, Byriel & Kennard, 1991*b*). However, in the structures reported here, the 1:1 adducts of 2,4,6-trinitrobenzoic acid with 4-aminobenzoic acid (1) and with 3-hydroxypyridine (2), decarboxylation did not occur.

Table 2. *Bond distances* (Å) *and angles* (°)

Compound (1)			
C(11*A*)—C(1*A*)	1.520 (7)	C(2*A*)—C(1*A*)	1.393 (7)
C(6*A*)—C(1*A*)	1.390 (7)	O(11*A*)—C(11*A*)	1.230 (7)
O(12*A*)—C(11*A*)	1.199 (8)	N(2*A*)—C(2*A*)	1.472 (7)
C(3*A*)—C(2*A*)	1.359 (8)	O(21*A*)—N(2*A*)	1.168 (8)
O(22*A*)—N(2*A*)	1.220 (8)	C(4*A*)—C(3*A*)	1.357 (8)
N(4*A*)—C(4*A*)	1.457 (7)	C(5*A*)—C(4*A*)	1.358 (8)
O(41*A*)—N(4*A*)	1.191 (7)	O(42*A*)—N(4*A*)	1.205 (7)
C(6*A*)—C(5*A*)	1.377 (7)	N(6*A*)—C(6*A*)	1.452 (7)
O(61*A*)—N(6*A*)	1.198 (7)	O(62*A*)—N(6*A*)	1.205 (7)
C(11*B*)—C(1*B*)	1.476 (8)	C(2*B*)—C(1*B*)	1.373 (8)
C(6*B*)—C(1*B*)	1.367 (8)	O(11*B*)—C(11*B*)	1.315 (8)
O(12*B*)—C(11*B*)	1.195 (8)	C(3*B*)—C(2*B*)	1.360 (9)
C(4*B*)—C(3*B*)	1.357 (8)	N(4*B*)—C(4*B*)	1.456 (7)
C(5*B*)—C(4*B*)	1.355 (7)	C(6*B*)—C(5*B*)	1.385 (8)
C(2*A*)—C(1*A*)—C(11*A*)	122.7 (5)	C(6*A*)—C(1*A*)—C(11*A*)	121.5 (5)
C(6*A*)—C(1*A*)—C(2*A*)	115.6 (5)	O(11*A*)—C(11*A*)—C(1*A*)	116.2 (5)
O(12*A*)—C(11*A*)—C(1*A*)	118.0 (5)	O(12*A*)—C(11*A*)—O(11*A*)	125.7 (5)
N(2*A*)—C(2*A*)—C(1*A*)	119.9 (5)	C(3*A*)—C(2*A*)—C(1*A*)	124.6 (5)
C(3*A*)—C(2*A*)—N(2*A*)	115.5 (5)	O(21*A*)—N(2*A*)—C(2*A*)	117.2 (6)
O(22*A*)—N(2*A*)—C(2*A*)	118.1 (5)	O(22*A*)—N(2*A*)—O(21*A*)	124.7 (6)
C(4*A*)—C(3*A*)—C(2*A*)	116.4 (5)	N(4*A*)—C(4*A*)—C(3*A*)	118.2 (5)
C(5*A*)—C(4*A*)—C(3*A*)	123.3 (5)	C(5*A*)—C(4*A*)—N(4*A*)	118.4 (5)
O(41*A*)—N(4*A*)—C(4*A*)	117.3 (5)	O(42*A*)—N(4*A*)—C(4*A*)	118.3 (5)
O(42*A*)—N(4*A*)—O(41*A*)	124.4 (5)	C(6*A*)—C(5*A*)—C(4*A*)	118.9 (5)
C(5*A*)—C(6*A*)—C(1*A*)	121.2 (5)	N(6*A*)—C(6*A*)—C(1*A*)	120.6 (5)
N(6*A*)—C(6*A*)—C(5*A*)	118.1 (5)	O(61*A*)—N(6*A*)—C(6*A*)	119.7 (5)
O(62*A*)—N(6*A*)—C(6*A*)	116.9 (5)	O(62*A*)—N(6*A*)—O(61*A*)	123.4 (5)
C(2*B*)—C(1*B*)—C(11*B*)	119.3 (5)	C(6*B*)—C(1*B*)—C(11*B*)	121.5 (5)
C(6*B*)—C(1*B*)—C(2*B*)	119.2 (5)	O(11*B*)—C(11*B*)—C(1*B*)	114.2 (5)
O(12*B*)—C(11*B*)—C(1*B*)	122.9 (6)	O(12*B*)—C(11*B*)—O(11*B*)	122.9 (5)
C(3*B*)—C(2*B*)—C(1*B*)	121.7 (5)	C(4*B*)—C(3*B*)—C(2*B*)	118.3 (5)
N(4*B*)—C(4*B*)—C(3*B*)	118.8 (5)	C(5*B*)—C(4*B*)—C(3*B*)	121.8 (5)
C(5*B*)—C(4*B*)—N(4*B*)	119.4 (5)	C(6*B*)—C(5*B*)—C(4*B*)	119.7 (5)
C(5*B*)—C(6*B*)—C(1*B*)	119.3 (5)		
Compound (2)			
C(11*A*)—C(1*A*)	1.532 (3)	C(2*A*)—C(1*A*)	1.388 (4)
C(6*A*)—C(1*A*)	1.385 (4)	O(11*A*)—C(11*A*)	1.237 (3)
O(12*A*)—C(11*A*)	1.240 (3)	N(2*A*)—C(2*A*)	1.466 (3)
C(3*A*)—C(2*A*)	1.383 (3)	N(2*A*)—O(21*A*)	1.211 (3)
N(2*A*)—O(22*A*)	1.220 (3)	C(4*A*)—C(3*A*)	1.366 (4)
N(4*A*)—C(4*A*)	1.479 (3)	C(5*A*)—C(4*A*)	1.366 (4)
O(41*A*)—N(4*A*)	1.211 (4)	O(42*A*)—N(4*A*)	1.212 (4)
C(6*A*)—C(5*A*)	1.374 (4)	N(6*A*)—C(6*A*)	1.479 (4)
O(61*A*)—N(6*A*)	1.216 (3)	O(62*A*)—N(6*A*)	1.212 (3)
C(2*B*)—N(1*B*)	1.326 (4)	C(6*B*)—N(1*B*)	1.329 (4)
C(3*B*)—C(2*B*)	1.380 (4)	O(31*B*)—C(3*B*)	1.346 (3)
C(4*B*)—C(3*B*)	1.378 (4)	C(5*B*)—C(4*B*)	1.370 (4)
C(6*B*)—C(5*B*)	1.360 (4)		
C(2*A*)—C(1*A*)—C(11*A*)	122.4 (2)	C(6*A*)—C(1*A*)—C(11*A*)	122.8 (2)
C(6*A*)—C(1*A*)—C(2*A*)	114.8 (2)	O(11*A*)—C(11*A*)—C(1*A*)	155.5 (2)
O(12*A*)—C(11*A*)—C(1*A*)	115.1 (2)	O(12*A*)—C(11*A*)—O(11*A*)	129.4 (2)
N(2*A*)—C(2*A*)—C(1*A*)	119.5 (2)	C(3*A*)—C(2*A*)—C(1*A*)	123.7 (3)
C(3*A*)—C(2*A*)—N(2*A*)	116.8 (2)	O(21*A*)—N(2*A*)—C(2*A*)	118.5 (2)
O(22*A*)—N(2*A*)—C(2*A*)	117.2 (2)	O(22*A*)—N(2*A*)—O(21*A*)	124.3 (2)
C(4*A*)—C(3*A*)—C(2*A*)	117.3 (3)	N(4*A*)—C(4*A*)—C(3*A*)	119.3 (3)
C(5*A*)—C(4*A*)—C(3*A*)	122.6 (2)	C(5*A*)—C(4*A*)—N(4*A*)	118.1 (3)
O(41*A*)—N(4*A*)—C(4*A*)	117.0 (3)	O(42*A*)—N(4*A*)—C(4*A*)	117.4 (3)
O(42*A*)—N(4*A*)—O(41*A*)	125.6 (3)	C(6*A*)—C(5*A*)—C(4*A*)	117.7 (3)
C(5*A*)—C(6*A*)—C(1*A*)	123.9 (3)	N(6*A*)—C(6*A*)—C(1*A*)	120.5 (2)
N(6*A*)—C(6*A*)—C(5*A*)	115.4 (3)	O(61*A*)—N(6*A*)—C(6*A*)	117.6 (2)
O(62*A*)—N(6*A*)—C(6*A*)	118.0 (2)	O(62*A*)—N(6*A*)—O(61*A*)	124.3 (3)
C(6*B*)—N(1*B*)—C(2*B*)	123.3 (3)	C(3*B*)—C(2*B*)—N(1*B*)	119.6 (3)
O(31*B*)—C(3*B*)—C(2*B*)	117.2 (2)	C(4*B*)—C(3*B*)—C(2*B*)	118.2 (3)
C(4*B*)—C(3*B*)—O(31*B*)	124.6 (2)	C(5*B*)—C(4*B*)—C(3*B*)	120.0 (3)
C(6*B*)—C(5*B*)—C(4*B*)	120.0 (3)	C(5*B*)—C(6*B*)—N(1*B*)	118.8 (3)

Experimental. Compound (1) was prepared in a solid-state reaction by grinding together equimolar amounts of 2,4,6-trinitrobenzoic acid and 4-aminobenzoic acid in an agate mortar. A colour change from off-white to orange accompanied this reaction. Crystallization from water yielded dull-yellow crystal plates. Compound (2) was prepared by dissolving 3-hydroxypyridine in ammonia then evaporating to dryness. This product was then redissolved in water, and an equimolar quantity of 2,4,6-trinitrobenzoic acid added. Crystallization yielded light-brown prisms. Density was measured by flotation ($CHCl_3$/$CHBr_3$). A single triangular plate (0.16 × 0.05 × 0.24 mm) (1) and a rectangular prism (0.10 × 0.20 × 0.24 mm) (2) were used to collect data at 295 K on an Enraf–Nonius CAD-4 four-circle diffractometer using graphite-monochromatized Mo *Kα* Xradiation ($\lambda = 0.71073$ Å). Cell parameters were obtained using angle data from 25 reflections with $2\theta < 50°$. Data collection details: $2\theta/\omega$ collection mode, variable scanning rate, $2\theta_{\max} = 50°$, collection range (1) h 0–12, k 0–35, l 0–13, (2) h 0–8, k 0–9, l −28–28; total unique data 3112 (1), 2558 h, k, l (2); unobserved data 2010 (1), 1118 (2). Standards variation: (1) 0,20,0, $50\bar{2}$, $\bar{5}04$ −13% (allowed for by scaling), (2) $04\bar{8}$, $0,\bar{1},\bar{16}$, $2,0,\bar{10}$ +2.4%; 958 (1) and 1368 (2) reflections with $I > 2.5\sigma(I)$ used in structure refinement. Data were corrected for Lorentz and polarization effects but not for absorption. The structures were solved by direct methods using *SHELXS*86 (Sheldrick, 1986). Blocked-matrix least squares (F's) with anisotropic thermal parameters for all non-hydrogens gave for (1) $R = 0.039$ and $wR = 0.042$ $\{w = 0.95/[\sigma^2(F_o) + 1.2 \times 10^{-3}(F_o)^2]\}$ and for (2) $R = 0.032$ and $wR = 0.037$ $\{w = 1.445/[\sigma^2(F_o) + 1.5 \times 10^{-3}(F_o)^2]\}$ (*SHELX*76; Sheldrick, 1976). Hydrogens were located by difference methods and their positional and thermal parameters refined. Maximum (Δ/σ) values in the last cycle were 0.01 (1) and 0.02 (2) for all non-hydrogen atoms. Maximum and minimum difference peaks were 0.16, −0.31 (1) and 0.19, −0.17 e Å^{-3} (2) respectively. Atomic scattering factors were from *International Tables for X-ray Crystallography* (1974, Vol. IV). Atomic positional and thermal parameters are listed in Table 1 while bond distances and angles are given in Table 2.* Atom-numbering schemes for the molecules are shown in Figs. 1 and 3, and Figs. 2 and 4 show the unit-cell packing arrangements.

Discussion. The structure of (1) comprises a 1:1 adduct of TNBA and 4-ABA, together with a water molecule, involved in a hydrogen-bonded network. The proton from the carboxylic acid group of TNBA is delocalized onto the amino group of 4-ABA. Except for the deprotonated carboxylic acid group on TNBA, both 4-ABA and TNBA molecules are planar [torsion angle C(2*A*)—C(1*A*)—C(11*A*)—O(11*A*) = −73.8 (6)°]. The two acids are uniquely hydrogen bonded across one oxygen pair [O(11*A*)···O(11*B*) 2.59 Å, $1 - x$, y, $\frac{1}{2} - z$], with no interactions between the other two oxygens. This is similar to the

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54587 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

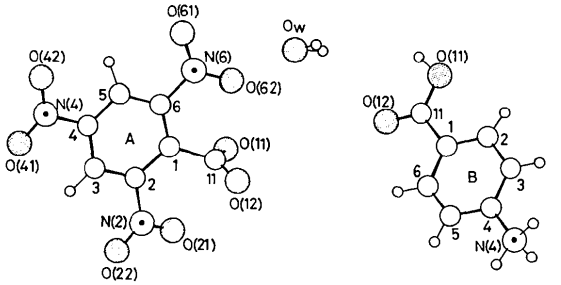

Fig. 1. Molecular configuration and atom-numbering scheme for the adduct pair in (1). Unless otherwise indicated, atoms are carbons.

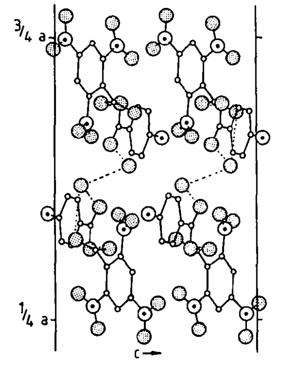

Fig. 2. Packing of (1) in the unit cell viewed down **a**.

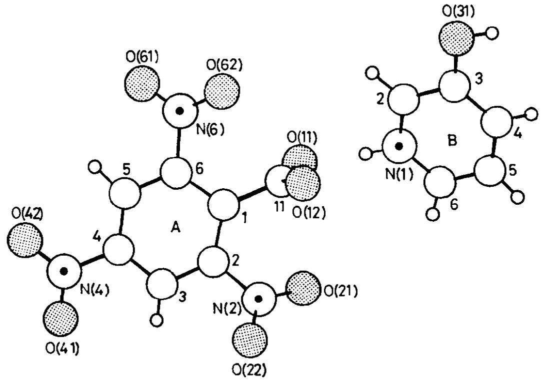

Fig. 3. Molecular configuration and atom-numbering scheme for the adduct pair in (2).

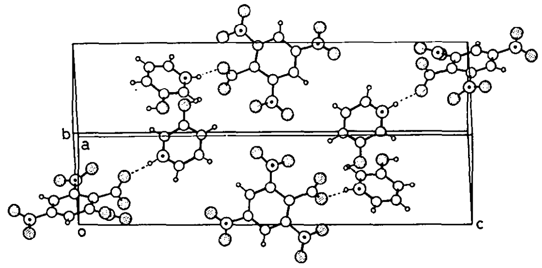

Fig. 4. Perspective view of the packing of (2) in the unit cell.

hydrogen bonding found in the tryptophan–oxalic acid adduct (Bakke & Mostad, 1980). The benzene rings of each acid in (1) are stacked in the c cell direction. The protonated amino group on 4-ABA forms possible hydrogen bonds to a water molecule $\mathrm{N}(4B)\cdots\mathrm{O}w$ (2.74 Å, $x-1+y$, z) and both deprotonated carboxylic acid oxygens [$\mathrm{N}(4B)\cdots\mathrm{O}(11A)$ 2.71 Å, x, $-y$, $1-z$; $\mathrm{N}(4B)\cdots\mathrm{O}(12A)$ 2.69 Å, $1-x$, y, $1\frac{1}{2}-z$], while the water molecules hydrogen bond with each other [$\mathrm{O}w\cdots\mathrm{O}w'$ 2.68 Å, $1-x$, y, $1\frac{1}{2}-z$], and with carboxylic oxygens [$\mathrm{O}w\cdots\mathrm{O}(12B)$ 2.91 Å, x, $1-y$, $\frac{1}{2}+z$].

Structure (2) is a 1:1 TNBA and 3-HP adduct, with the carboxylic acid proton of TNBA delocalized on the pyridine nitrogen of 3-HP. As for (1), the molecules are planar, except for the carboxylic acid group of the acid [comparative torsion angle −72.9 (3)°]. Hydrogen bonding exists between the carboxylic acid group and the pyridine nitrogen [$\mathrm{O}(11A)\cdots\mathrm{N}(1B)$ 2.68 Å, x, y, z]. No significant interactions exist between the hydroxy group and the acid. One set of o-nitro groups forms a dimerized pair across the centre of symmetry. The benzene rings of each compound are stacked in the b cell dimension. Extensive hydrogen bonding and zwitterion formation in both adducts may be the reason for the stability of the TNBA molecules towards decarboxylation.

The authors wish to thank the Australian Research Council, the University of Queensland and the Queensland University of Technology for financial assistance.

References

Bakke, O. & Mostad, A. (1980). *Acta Chem. Scand.* **B34**, 559–570.

Coffey, S. (1977). *Rodd's Chemistry of Carbon Compounds*, Vol. 3, p. 48. Amsterdam: Elsevier.

Etter, M. C. & Frankenbach, G. M. (1989). *Chem. Mater.* **1**, 10–12.

Etter, M. C., Frankenbach, G. M. & Bernstein, J. (1989). *Tetrahedron Lett.* **30**, 3617–3620.

Lechat, J. (1984). *Acta Cryst.* **A40**, C-264.

Lynch, D. E., Smith, G., Byriel, K. A. & Kennard, C. H. L. (1991*a*). *Aust. J. Chem.* **44**, 1017–1022.

Lynch, D. E., Smith, G., Byriel, K. A. & Kennard, C. H. L. (1991*b*). *Aust. J. Chem.* **44**, 809–817.

Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Sheldrick, G. M. (1986). *SHELXS86*. Program for the solution of crystal structures. Univ. of Göttingen, Germany.

Ueda, H., Onishi, H. & Nagai, T. (1986). *Acta Cryst.* **C42**, 462–464.

Acta Cryst. (1992). **C48**, 536–538

Structure of Methyl 4-Chloro-*N*-(2-tolyl)benzimidate

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(*Received* 2 *May* 1991; *accepted* 16 *August* 1991)

Abstract. $\mathrm{C_{15}H_{14}ClNO}$, $M_r = 259.74$, monoclinic, $P2_1/c$, $a = 11.078$ (3), $b = 13.076$ (5), $c = 9.828$ (3) Å, $\beta = 111.71$ (1)°, $V = 1322.7$ (8) Å^3, $Z = 4$, $D_x = 1.304$ g cm^{-3}, $\lambda(\mathrm{Mo}\ K\alpha) = 0.71069$ Å, $\mu = 2.73$ cm^{-1}, $F(000) = 544$, $T = 300$ K, final $R = 0.063$ for 1497 unique reflections with $F < 2\sigma(F)$. The conformation corresponds to that of the unsubstituted compound. The two phenyl rings make an angle of 73.3 (1)°.

Introduction. Four stereoisomers of N-substituted imidates may exist. They are characterized as *ZsZ*, *ZsE*, *EsZ* or *EsE*. Lumbroso & Bertin (1970) reported the structure *EsZ* based on dipole measure-

0108-2701/92/030536-03$03.00