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## Molecular Co-Crystals of Carboxylic Acids. 8.\* Structure of the 1:1 Adduct of 3,5-Dinitrobenzoic Acid with 3-Amino-1*H*,2,4-triazole

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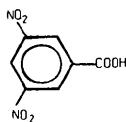
(Received 15 October 1991; accepted 2 December 1991)

**Abstract.**  $C_7H_3N_2O_6^- \cdot C_2H_5N_4^+ \cdot 2H_2O$ ,  $M_r = 332.1$ , triclinic,  $P\bar{1}$ ,  $a = 7.087$  (5),  $b = 10.330$  (6),  $c = 10.473$  (7) Å,  $\alpha = 111.76$  (3),  $\beta = 93.55$  (4),  $\gamma = 95.89$  (4)°,  $V = 704.2$  (8) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.566$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 0.15$  mm<sup>-1</sup>,  $F(000) = 344$ ,  $T = 295$  K,  $R = 0.035$  for 1656 observed reflections. The compound was prepared in toluene with crystals grown from aqueous ethanol. The two organic molecules associate to form an eight-membered hydrogen-bonded ring [NH...O, 2.88 (1) and 2.67 (1) Å], as well as being involved in a hydrogen-bonded network with two water molecules.

**Introduction.** 3-Amino-1,2,4-triazole, or amitrole (CA Registry No. 61-82-5) (3-AT), is a herbicide that is readily absorbed by roots and aerial plant parts, inducing chlorosis and causing eventual death of the plants. It reacts with most acids and bases to form salts, and it also reacts with ketones and aldehydes to



3-AT



DNBA

form derivatives of possible biological activity (Spencer, 1973). 3,5-Dinitrobenzoic acid (DNBA) has been successfully adducted with various other acids and bases (Lynch, Smith, Byriel & Kennard, 1991*a,b*), in particular with another biologically important compound, indole-3-acetic acid. The structures of DNBA (Colapietro, Domenicano, Marciante & Portalone, 1983) and 3-AT (Starova, Frank-Kamenetskaya, Makarskii & Lopirev, 1978) are known, so comparisons of structural features with those of the co-crystal adducts can be made.

**Experimental.** The title compound was prepared by refluxing equimolar amounts of 3,5-dinitrobenzoic acid and 3-aminotriazole in toluene for 20 min at 423 K. The yellow product obtained after evaporation to dryness was recrystallized from 50% aqueous ethanol, yielding yellow prisms. A crystal with dimensions 0.23 × 0.14 × 0.40 mm was used to collect data at 295 K on an Enraf-Nonius CAD-4 four-circle diffractometer using graphite-monochromated Mo  $K\alpha$  X-radiation ( $\lambda = 0.71073$  Å). Cell parameters were obtained using angle data from 25 reflections with  $2\theta < 50^\circ$ . Data collection details:  $2\theta/\omega$  collection mode, variable scanning rate;  $2\theta_{\text{max}} 50^\circ$ ; collection range  $h$  0 to 8,  $k$  -12 to 12,  $l$  -12 to 12; total data 2699; 2229 unique ( $R_{\text{int}} 0.0123$ ); 747 unobserved data; variation of three standards (136,

\* Part 7: Lynch, Smith, Byriel & Kennard (1992).

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Table 1. Atomic coordinates and equivalent isotropic thermal parameters (Å<sup>2</sup> × 10<sup>3</sup>)
$$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$$

	x	y	z	U <sub>eq</sub>
C(1A)	0.0106 (3)	0.9595 (2)	0.8098 (2)	37.0 (7)
C(11A)	-0.0114 (3)	0.8013 (2)	0.7384 (2)	38.3 (7)
O(11A)	-0.1717 (2)	0.7373 (1)	0.6834 (2)	37.8 (7)
O(12A)	0.1360 (2)	0.7449 (1)	0.7424 (2)	49.0 (8)
C(2A)	-0.1373 (3)	1.0351 (2)	0.7999 (2)	40.3 (8)
C(3A)	-0.1121 (3)	1.1785 (2)	0.8726 (2)	44.3 (8)
N(3A)	-0.2695 (3)	1.2583 (2)	0.8609 (2)	60.3 (9)
O(31A)	-0.2448 (3)	1.3842 (2)	0.9262 (3)	98.7 (9)
O(32A)	-0.4144 (3)	1.1957 (2)	0.7890 (2)	76.0 (8)
C(4A)	0.0509 (3)	1.2515 (2)	0.9555 (2)	44.0 (7)
C(5A)	0.1962 (3)	1.1736 (2)	0.9628 (2)	38.0 (7)
N(5A)	0.3721 (3)	1.2467 (2)	1.0592 (2)	48.7 (7)
O(51A)	0.4910 (3)	1.1766 (2)	1.0682 (2)	68.7 (8)
O(52A)	0.3892 (3)	1.3733 (2)	1.1086 (2)	73.0 (9)
C(6A)	0.1792 (3)	1.0303 (2)	0.8914 (2)	38.3 (7)
N(1B)	0.1696 (3)	0.2527 (2)	0.6472 (2)	53.3 (7)
N(2B)	-0.0124 (3)	0.2594 (2)	0.6002 (2)	45.3 (7)
C(3B)	-0.0413 (3)	0.3918 (2)	0.6280 (2)	41.3 (7)
N(31B)	-0.1991 (3)	0.4367 (2)	0.5993 (2)	56.7 (7)
N(4B)	0.1215 (3)	0.4718 (2)	0.6961 (2)	49.7 (8)
C(5B)	0.2463 (3)	0.3822 (2)	0.7045 (3)	54.0 (8)
O(11)	0.2752 (3)	0.9716 (2)	0.5272 (2)	61.3 (9)
O(12)	0.4634 (3)	0.7774 (2)	0.6094 (2)	61.7 (9)

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

C(11A)—C(1A)	1.510 (3)	C(2A)—C(1A)	1.390 (3)
C(6A)—C(1A)	1.387 (3)	O(11A)—C(11A)	1.242 (2)
O(12A)—C(11A)	1.254 (2)	C(3A)—C(2A)	1.378 (3)
N(3A)—C(3A)	1.479 (2)	C(4A)—C(3A)	1.367 (3)
O(31A)—N(3A)	1.212 (3)	O(32A)—N(3A)	1.203 (3)
C(5A)—C(4A)	1.386 (3)	N(5A)—C(5A)	1.465 (2)
C(6A)—C(5A)	1.377 (3)	O(51A)—N(5A)	1.206 (2)
O(52A)—N(5A)	1.208 (2)	N(31B)—C(3B)	1.313 (3)
N(4B)—C(3B)	1.337 (3)	N(2B)—C(3B)	1.330 (2)
C(5B)—N(4B)	1.366 (3)	N(1B)—C(5B)	1.288 (3)
N(2B)—N(1B)	1.369 (3)		
C(2A)—C(1A)—C(11A)	121.4 (2)	C(6A)—C(1A)—C(11A)	119.3 (2)
C(6A)—C(1A)—C(2A)	119.3 (2)	O(11A)—C(11A)—C(1A)	118.6 (2)
O(12A)—C(11A)—C(1A)	116.2 (2)	O(12A)—C(11A)—O(11A)	125.2 (2)
C(3A)—C(2A)—C(1A)	118.8 (2)	N(3A)—C(3A)—C(2A)	118.5 (2)
C(4A)—C(3A)—C(2A)	123.6 (2)	C(4A)—C(3A)—N(3A)	117.9 (2)
O(31A)—C(3A)—C(3A)	117.4 (2)	O(32A)—N(3A)—C(3A)	118.9 (2)
O(32A)—N(3A)—O(31A)	123.7 (2)	C(5A)—C(4A)—C(3A)	116.4 (2)
N(5A)—C(5A)—C(4A)	118.4 (2)	C(6A)—C(5A)—C(4A)	122.5 (2)
C(6A)—C(5A)—N(5A)	119.2 (2)	O(51A)—N(5A)—C(5A)	118.0 (2)
O(52A)—N(5A)—C(5A)	118.3 (2)	O(52A)—N(5A)—O(51A)	123.7 (2)
C(5A)—C(6A)—C(1A)	119.5 (2)	N(4B)—C(3B)—N(31B)	126.4 (2)
N(2B)—C(3B)—N(31B)	127.4 (2)	N(2B)—C(3B)—N(4B)	106.1 (2)
C(5B)—N(4B)—C(3B)	106.8 (2)	N(1B)—C(5B)—N(4B)	111.6 (2)
N(2B)—N(1B)—C(5B)	104.3 (2)	N(1B)—N(2B)—C(3B)	111.2 (2)

254, 163) -0.7%; 1656 reflections with  $I > 2.5\sigma(I)$  used in structure refinement. Data were corrected for Lorentz and polarization effects as well as for absorption (empirical); maximum and minimum transmission factors were 100.0 and 98.7% respectively. The structure was solved by direct methods using *SHELXS86* (Sheldrick, 1986). Blocked-matrix least-squares refinement (on *F*) with anisotropic thermal parameters for all non-H atoms gave  $R = 0.035$  and  $wR = 0.044$   $\{w = 1.0/[\sigma^2(F_o) + 1.2 \times 10^{-2}(F_o)^2]\}$  (*SHELX76*; Sheldrick, 1976); 256 parameters refined. H atoms were located by difference methods and their positional and thermal parameters refined. Maximum ( $\Delta/\sigma$ ) in the last cycle was 0.01 for all non-H atoms. Maximum and minimum difference peaks were 0.14 and  $-0.26 \text{ e } \text{Å}^{-3}$ . 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. The atom-numbering scheme is shown in Fig. 1.

**Discussion.** The structure of the title compound comprises a 1:1 hydrogen-bonded cyclic hetero-dimer [Graph set  $R_2^2(8)$  (Etter, 1990)] between 3,5-dinitrobenzoic acid (molecule *A*) and 3-aminotriazole (molecule *B*). These, together with two water molecules, are involved in a hydrogen-bonded network (Figs. 1 and 2). Both molecules are planar and have similar bond distances and angles to the parent structures, DNBA (Colapietro *et al.*, 1983) and 3-AT (Starova *et al.*, 1978). The eight-membered hydrogen-bonded ring [O(11A)⋯N(31B) 2.88, O(12A)⋯N(4B) 2.67 Å] is similar to that observed for the 2-aminopyrimidine-succinic acid adduct

\* Lists of structure factors, anisotropic thermal parameters, torsion angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54921 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

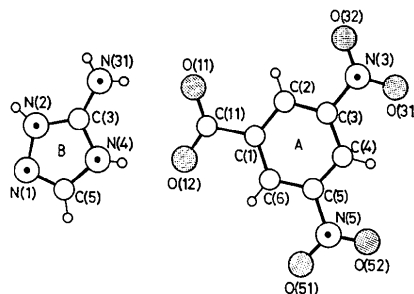


Fig. 1. Atom-numbering scheme for the individual molecules DNBA and 3-AT.

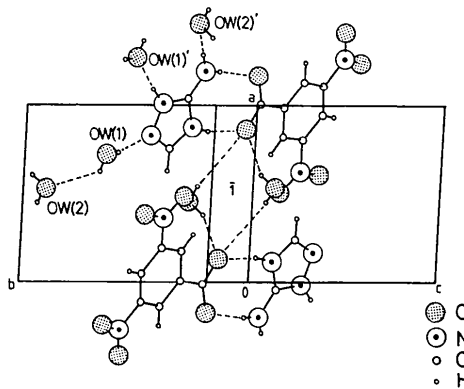


Fig. 2. Perspective view of the packing of the co-crystal in the unit cell, showing the important hydrogen-bonding interactions.

(Etter, Adsmund & Britton, 1990), except that the proton from the carboxylic acid group of DNBA is located on the adjacent ring N atom of 3-AT [N(2B)] as is the case in the 2-aminopyrimidine-oxalic acid adduct (Etter, 1991). One water molecule [OW(1)] is hydrogen-bonded to triazole N atoms N(1B) [2.71 (1) Å:  $-x, -1-y, 1-z$ ] and N(2B) [2.90 (1) Å:  $x, -1+y, z$ ], and to the second water OW(2) [2.87 (1) Å]. OW(2) forms an eight-membered hydrogen-bonded ring with O(11A) [2.77 (1) Å:  $-1+x, y, z$ ] and O(12A) [2.83 (1) Å] and is also hydrogen bonded to N(31B) [2.87 (1) Å:  $-x, 1-y, 1-z$ ].

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## Structure of *meso*-(*R,R,S,S*)-*trans*-4,5,4',5'-Tetrahydroxy-2,2'-bi(1,3-thioxolane)-Dimethylacetamide (1:2)

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**Abstract.**  $C_6H_{10}O_6S_2 \cdot 2C_4H_9NO$ ,  $M_r = 416.5$ , monoclinic,  $P2_1/c$ ,  $a = 11.782$  (2),  $b = 9.058$  (2),  $c = 9.766$  (2) Å,  $\beta = 109.30$  (1)°,  $V = 983.7$  (4) Å<sup>3</sup>,  $Z = 2$ ,  $D_m$  (by flotation) = 1.40,  $D_x = 1.405$  Mg m<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.5418$  Å,  $\mu = 2.788$  mm<sup>-1</sup>,  $F(000) = 444$ ,  $T = 293$  K,  $R = 0.0291$ ,  $wR = 0.0285$  for 1125 unique diffractometer data [ $I > 1\sigma(I)$ ]. The crystal structure and the synthesis of this heterocycle are new. The molecule  $C_6H_{10}O_6S_2$  lies on a centre of symmetry. Two solvate molecules, dimethylacetamide, are attached to it by hydrogen bonds (2.695 Å). The solvate molecules and the heterocycle molecules are arranged in the crystal on different parallel layers (100), which are linked by the hydrogen bonds. The heterocycle has an envelope conformation.

**Introduction.** Formaldehyde is used in the mineral-oil industry as an H<sub>2</sub>S scavenger. Its toxicity requires that it be substituted by a less poisonous substance, for example glyoxal. An aqueous alkaline solution of glyoxal absorbs H<sub>2</sub>S and a colourless powder deposits. Chemical analysis shows that three parts of

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glyoxal react with two parts of H<sub>2</sub>S. It was not possible to solve the structure of the product by spectroscopic methods. It was, however, possible to dissolve this colourless powder in dimethylacetamide and to grow crystals.

**Experimental.** A crystal of dimensions 0.3 × 0.3 × 0.2 mm was sealed in a Lindemann-glass capillary. 25 reflections with  $2\theta > 30^\circ$  were used for the determination of the cell parameters. One standard reflection ( $\bar{2}\bar{2}\bar{1}$ ) showed no decomposition by X-rays. 2450 reflections were collected ( $-12 < h < 12$ ;  $-9 < k < 0$ ;  $-10 < l < 10$ ), 1126 were unique,  $R_{int} = 0.013$ , and 1125 with intensities  $I > \sigma(I)$  were used for the structure analysis; Siemens *R3m/V* computer-controlled diffractometer,  $2\theta/\theta$  scan,  $2\theta$  range 2–105°; scan speed 4–15° min<sup>-1</sup>; no correction for extinction; empirical absorption correction according to the  $\psi$  method (Kopfmann & Huber, 1968; North, Phillips & Mathews, 1968),  $T_{min}, T_{max} = 0.85, 1.0$ . The phase problem was solved by direct methods (Sheldrick, 1990); all the non-H atoms were located in the first electron density synthesis (*E* map). After a few cycles