

The Unique Occurrence of an Organic Tri-heteromolecular Adduct: The Crystal Structure of the (3 : 1 : 1) 4-Aminobenzoic Acid—2,4,6-Trinitrobenzoic Acid—1,3,5-Trinitrobenzene Cocrystal

Daniel E. Lynch,^a Graham Smith*^b Karl A. Byriel^b and Colin H. L. Kennard^b

^a School of Chemistry, Queensland University of Technology, PO Box 2434, Brisbane, Qld., 4001, Australia

^b Department of Chemistry, The University of Queensland, Qld., 4072, Australia

Crystals obtained from a solid-state reaction of 4-aminobenzoic acid and 2,4,6-trinitrobenzoic acid are shown by X-ray crystallography to consist of a (3 : 1 : 1) tri-heteromolecular adduct between 4-aminobenzoic acid, 2,4,6-trinitrobenzoic acid and 1,3,5-trinitrobenzene.

Etter and coworkers have prepared and characterized a series of cocrystals including those with 4-aminobenzoic acid (4-ABA) and various nitro-substituted benzoic acids.^{1,2} A feature of this series is the [R₂²(8)] heterodimer³ formed between the carboxylic acid groups of the two species. 4-ABA shows a tendency to cocrystallize because of the presence of both donor and acceptor sites available for hydrogen bonding. This property is evident in other 4-aminobenzoic cocrystals.⁴⁻⁶ The amino group is also available for protonation by strong acids such as 2,4,6-trinitrobenzoic acid (TNBA). However, TNBA readily decarboxylates when boiled in water,⁷ and the product of the decomposition, 1,3,5-trinitrobenzene (TNB) has been found in a cocrystal structure with indole-3-acetic acid.⁵

A complex of 4-ABA and TNBA was prepared in a solid state reaction by grinding together equimolar amounts of the two acids. This was accompanied by a colour change from off-white to bright yellow. Crystals could only be obtained by

recrystallization from water. The resultant product was predominantly a (1 : 1) (4-ABA–TNBA) adduct whose structure was determined. Also present were bright-red crystals thought to be an adduct of 4-ABA and TNB, a previously reported but uncharacterized reaction product.⁹ However, a crystal selected from this crop was subsequently found to be a unique triheteromolecular adduct, reported here.[†] This struc-

[†] *Crystal data* for (4-ABA–TNBA–TNB) (3:1:1) (*T* = 296 K, Enraf-Nonius CAD-4 diffractometer): C₃₄H₁₃N₉O₂₀, *M* = 867.0, triclinic, space group *P*1, *a* = 8.05(1), *b* = 13.50(2), *c* = 17.73(2) Å, α = 98.38(8), β = 96.67(8), γ = 95.05(8)°, *U* = 1882(4) Å³, *F*(000) = 880; *Z* = 2, *D*_c = 1.529 g cm⁻³, μ (Mo–K α) = 0.86 cm⁻¹, specimen 0.12 × 0.12 × 0.24 mm, 6613 unique reflections, 1394 with *I* > 2.5 σ (*I*) used in refinement, 2 θ _{max} = 50°; *R* = 0.063, *R*_w = 0.064, *s* = 1.21. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

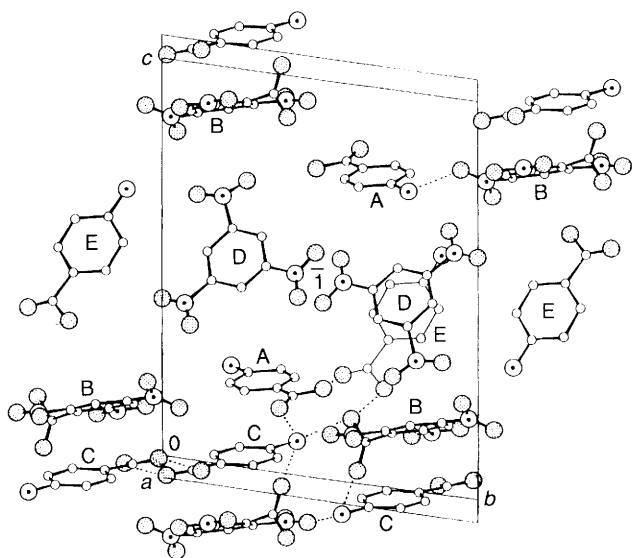


Fig. 1 Unit cell packing of (4-ABA-TNBA-TNB) (3:1:1). Dotted lines indicate possible hydrogen bonds. These distances (Å) are: O(11A)···N(4C), 2.91(1), $(-1-x, -y, 2-z)$; O(12A)···O(11E), 2.61(1), $(-2+x, -1+y, z)$; N(4A)···O(41B), 2.92(1), O(11B)···N(4C), 2.74(1); O(12B)···N(4C), 2.77(1), $(1-x, 1-y, 2-z)$; O(12B)···O(12E), 2.60(1); O(11C)···O(12C), 2.61(1), $(2-x, -y, 2-z)$.

ture shows a captured intermediate stage between the acid form (4-ABA-TNBA) and the decarboxylated form (4-ABA-TNB).

Fig. 1 shows the (3:1:1) molecular ratio of (4-ABA-TNBA-TNB) with one 4-ABA molecule and the TNB

molecule stacked down the *a* direction of the cell while the other two 4-ABA molecules and the TNBA molecules are stacked down the *c* cell direction. The three independent 4-ABA molecules are indicated by A, C and E, the TNBA molecule is B and the TNB molecule is D. All molecules, except D, are involved in an extensive hydrogen bonding network involving both carboxy oxygens and amino nitrogens (see Fig. 1). Owing to a lack of intense data, not all the hydrogens could be located, but it is evident that the amino group of molecule C is protonated. Molecule C forms $[R_2^2(8)]$ hydrogen bonded cyclic dimers³ across an inversion centre in the cell (O···O, 2.61(1) Å), but these are unusual in being non-coplanar.

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

Received, 12th September 1991; Com. 1104739F

References

- 1 M. C. Etter and G. M. Frankenbach, *Chem. Mater.*, 1989, **1**, 10.
- 2 M. C. Etter, G. M. Frankenbach and J. Bernstein, *Tetrahedron Lett.*, 1989, **30**, 3617.
- 3 M. C. Etter, *Acc. Chem. Res.*, 1990, **23**, 120.
- 4 H. Ueda, H. Onishi and T. Nagai, *Acta Crystallogr., Sect. C*, 1986, **42**, 462.
- 5 D. E. Lynch, G. Smith, K. A. Byriel and C. H. L. Kennard, *Aust. J. Chem.*, 1991, **44**, 809.
- 6 D. E. Lynch, G. Smith, K. A. Byriel and C. H. L. Kennard, *Z. Kristallogr.*, in the press.
- 7 S. Coffey, in *Rodd's Chemistry of Carbon Compounds*, Elsevier, Amsterdam, 1977, vol. III, p. 48.
- 8 D. E. Lynch, G. Smith, K. A. Byriel and C. H. L. Kennard, *Acta Crystallogr.*, accepted for publication.
- 9 P. G. Stecher, in *The Merck Index*, Merck and Co. Inc., Rahway, NJ, 8th edn., 1968, p. 53.