

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and least-squares-planes data have been deposited with the IUCr (Reference: AS1086). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Trinitromethane

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Abstract

The structure of cubic trinitromethane, CHN₃O₆, has been determined at 200 K. Warning: a severe explosion has been reported [Macbeth (1913). *Ber. Dtsch. Chem. Ges.* **46**, 2537–2539] during the preparation of a sodium trinitromethanide salt.

Comment

Trinitromethane is a strong hydrocarbon acid and readily forms a crystalline 2:1 adduct with dioxane, which exhibits the shortest C—H···O hydrogen bonds, with a C—O distance of only 2.94 Å (Bock, Dienelt, Schödel & Havlas, 1993), reported so far (Cambridge Structural Database, 1993; Desiraju, 1991; Taylor & Kennard, 1984). Relative to the average conformation of monomeric HC(NO₂)₃ in the gas phase as determined by electron diffraction (Sadova, Popik, Vilkov, Pankrushev & Shlyapochnikov, 1973), the only significant structural change observed in the solid hydrogen-bridged dioxane

aggregate is an increase in the mean torsion angle $\omega(\text{H—C—N—NO}_2)$ from 26 to 47°. *Ab initio* self-consistent field (SCF) calculations (Cioslowski, Mixon & Fleischmann, 1991) reproduce satisfactorily the experimental structural data and predict torsion angles of 46–48° for the molecular skeleton of approximately C₃ symmetry. This is confirmed for liquid trinitromethane by infrared and Raman spectroscopic studies (Brookes & Jonathan, 1968). The following thermodynamic values have been measured for trinitromethane (Miroshnichenko, Lebedev, Sheveleo & Gulivskajo, 1967): heat of combustion 521 kJ mol⁻¹, heat of sublimation 46 kJ mol⁻¹ and heat of evaporation 33 kJ mol⁻¹. The single-crystal structure determination of HC(NO₂)₃ reported here was undertaken after the discovery of its hydrogen-bridged adduct with dioxane, during an attempted purification by recrystallization from ether solvents (Dienelt, 1993), resulting from the strong cation solvation properties of its anion [C(NO₂)₃]⁻. This was proved for ether solution (Bock, Hauck, Näther & Havlas, 1994) and by the isolation and structural characterization of the *aci*-diphenylnitromethane dimer (Bock, Dienelt, Schödel, Havlas, Herdtweck & Herrmann, 1993).

Fig. 1 shows an enlarged plot of 50% probability displacement ellipsoids. The molecular packing in the unit cell of trinitromethane is shown in the stereoscopic view in Fig. 2. The cubic unit cell contains eight formula units and the asymmetric unit comprises the HCNO₂ fragment. The molecular C₃ symmetry is verified by normal temperature ellipsoids of the NO₂ group (Fig. 1). The shortest intermolecular distances (C···O ≥ 3.16, N···O ≥ 2.95 Å) are outside the sum of the van der Waals radii and, unexpectedly (Bock, Dienelt, Schödel & Havlas, 1994), no C—H···O hydrogen bridges are formed. In the individual molecules, the N centre is planar (Table 1: sum of angles 127.0 + 117.7 + 115.3 = 360.0°) and the nitro group is rotated out of the HCN plane by 44°. The structure parameters determined for trinitromethane remain largely unchanged on hydrogen bonding to dioxane, (O₂N)₃CH···O(CH₂CH₂)₂O···HC(NO₂)₃, where only two rotational angles are slightly larger [by 2 and 9°, respectively (Bock, Dienelt, Schödel & Havlas, 1994)]. The experimental bond lengths and angles of the title molecule are satisfactorily reproduced by an *ab initio* SCF calculation (Cioslowski, Mixon & Fleischmann, 1991), providing additional evidence for the absence of specific intermolecular interactions within the crystal lattice (Fig. 2).

A tempting target for future crystal investigations would be the isolation of *aci*-trinitromethane [O₂N=C(NO₂)—N(O)OH]_n in close analogy to the recently crystallized and structurally characterized *aci*-diphenylnitromethane dimer [(H₅C₆)₂C=N(OH)O₂—N=C(C₆H₅)₂] (Bock *et al.*, 1993).

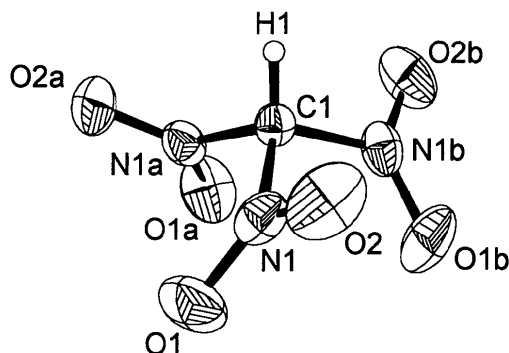


Fig. 1. Plot of displacement ellipsoids drawn at the 50% probability level together with numbering scheme for trinitromethane.

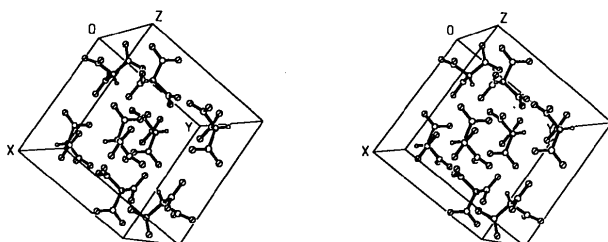


Fig. 2. Stereodiagram of the molecular packing in the unit cell viewed perpendicular to one N—C—N fragment.

Experimental

Trinitromethane (Hantzsch & Rinckenberger, 1899) is conveniently prepared by acidification of its alkali metal salts in suitable solvents (Shechter & Cates, 1961). However, as a result of the potentially explosive decomposition of low molecular weight polynitro hydrocarbons (Macheth, 1913), handling of only small amounts is advisable. On addition of 5 ml of 98% sulfuric acid to an ice-cooled stirred suspension of 3 g of $K[C(NO_2)_3]$ in 20 ml of *n*-pentane, two layers form. The heavier brown layer was extracted five times, each with 20 ml of *n*-pentane. The combined *n*-pentane solutions were slowly cooled to 193 K, the white crystalline precipitate filtered off and dried for 30 min at 273 K under 10^{-2} mbar (0.1 Pa) pressure. Trinitromethane was obtained in 85% yield (2 g, 14 mmol) with m.p. 298.5 K and characterized by IR (film): 2900 (ν_{CH}), 1600 (ν_{CNO_2}), (δ_{CH_2}), 1300 cm^{-1} (ν_{CNO_2}). It can be stored under Ar at 285 K without detectable decomposition. Single-crystal growth is accomplished by sublimation at 281 K under 10 mbar (100 Pa) pressure applying a temperature gradient of only 1–2 K, yielding mostly cubes of up to 7 mm edge length (Dienelt, 1993). Caution: the crystals, with m.p. 298.5 K, are moisture sensitive.

Crystal data

CHN_3O_6
 $M_r = 151.05$
 Cubic
 $Pa\bar{3}$
 $a = 10.358(1) \text{ \AA}$
 $V = 1111.3 \text{ \AA}^3$

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 48 reflections
 $\theta = 17.5\text{--}21^\circ$
 $\mu = 0.19 \text{ mm}^{-1}$

$Z = 8$
 $D_x = 1.806 \text{ Mg m}^{-3}$

$T = 200 \text{ K}$
 Rectangular block
 $0.3 \times 0.2 \times 0.2 \text{ mm}$
 Colourless

Data collection

Siemens AED-2 diffractometer
 ω – θ scans
 Absorption correction: none
 1461 measured reflections
 431 independent reflections
 351 observed reflections [$I > 2\sigma(I)$]

$R_{int} = 0.0525$
 $\theta_{max} = 27.5^\circ$
 $h = 0 \rightarrow 13$
 $k = 0 \rightarrow 13$
 $l = 0 \rightarrow 13$
 4 standard reflections
 frequency: 30 min
 intensity variation: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.0317$
 $wR(F^2) = 0.0772$
 $S = 1.067$
 431 reflections
 34 parameters
 All H-atom parameters refined
 $w = 1/[\sigma^2(F_o^2) + (0.0321P)^2 + 0.27P]$
 where $P = [\max(F_o^2, O) + 2F_c^2]/3$

$(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.18 \text{ e \AA}^{-3}$
 $\Delta\rho_{min} = -0.18 \text{ e \AA}^{-3}$
 Extinction correction:
 $F^* = F_c/[k(1.0 + 0.001\chi \times F_c^2 \lambda^3/\sin 2\theta)^{1/4}]$
 Extinction coefficient:
 $\chi = 0.078(6)$
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2$)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j.$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
O(1)	1.0266 (1)	0.8675 (1)	0.7821 (1)	0.057 (1)
O(2)	0.9763 (1)	0.6654 (1)	0.7875 (1)	0.053 (1)
N(1)	0.9515 (1)	0.7789 (1)	0.7912 (1)	0.033 (1)
C(1)	0.8114 (1)	<i>x</i>	<i>x</i>	0.024 (1)

Table 2. Selected geometric parameters ($\text{\AA}$, $^\circ$)

O(1)—N(1)	1.207 (2)	N(1)—C(1)	1.505 (1)
O(2)—N(1)	1.205 (2)	C(1)—H(1)	0.90 (2)
O(1)—N(1)—O(2)	127.2 (1)	N(1)—C(1)—H(1)	110.4 (1)
O(1)—N(1)—C(1)	117.5 (1)	N(1)—C(1)—N(1A)	108.6 (1)
O(2)—N(1)—C(1)	115.3 (1)		

A cooled crystal was mounted under Ar on a glass fibre rod. The systematic absences detected at $h00$ for $h = 2n + 1$ and at $0kl$ for $k = 2n + 1$ unambiguously define the space group $Pa\bar{3}$. Corrections were applied for both Lorentz and polarization effects. The structure was solved by direct methods and full-matrix least-squares refinement using *SHELXL93* (Sheldrick, 1993).

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Structure of the (2-Acetamidobenzoyl)-formate Anion as the Benzamidinium Salt

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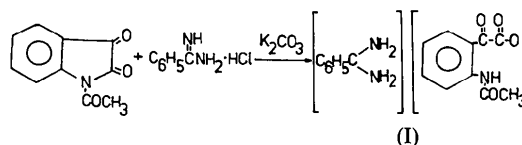
Abstract

The reaction of isatin with benzamidine hydrochloride in methanol yields the title compound, benzamidinium (2-acetamidobenzoyl)formate (C₇H₉N₂⁺·C₁₀H₈NO₄[−]). In the benzamidinium cation the configuration about the exocyclic C atoms is planar, resulting in electron delocalization in the C—N bonds. The C—O bond distances in the carboxylate

moeity in the anion are very similar (average C—O = 1.237 Å), indicating delocalization of the negative charge. Hydrogen bonds are present between the N atoms of the amidinium group and the O atoms of the carboxylate moeity of the anion. The N···O distances vary between 2.819 (5) and 2.901 (5) Å in the hydrogen bonds.

Comment

The reaction of isatin with various amino compounds to form Schiff bases has been widely studied as the products have diverse uses (Joshi, Jain & Sharma, 1986; Joshi, Dandia & Ahmed, 1989; Skiles & McNeil, 1990; Joshi, Jain & Arora, 1992; Joshi, Dandia & Ahmed, 1986). The reaction of *N*-acetyl isatin with benzamidine hydrochloride in refluxing methanolic K₂CO₃ has also been studied. The product obtained thus, (I), crystallized readily as large white needles, indicating the formation of a product other than the expected Schiff base. As a literature survey revealed that benzamidine is readily converted to a cation, resulting in ionic products (Lenhart, Lukehart, Sotiropoulos & Srinivasan, 1984; Beatrice, Kurt, Dieler & Gerhard, 1991), the molecular structure of this compound appeared to be of considerable interest.



The IR spectrum (KBr pellet) of the compound showed the following absorptions: 3400–3240 (broad, NH, NH₂), 1700 (CO), 1450 (C—N), 1320 (C···N) cm^{−1}. The following ¹H NMR parameters confirm the structure of the compound: δ 2.18 (*s*, 3H, CH₃), 3.48 (broad, 4H, NH₂), 6.86–8.38 (*m*, 9H, Ar), 11.88 (*s*, 1H, NH). The mass spectrum showed the molecular ion peak at *m/z* 327 (*M*⁺).

The title compound (I) is composed of two parts: the benzamidinium cation and the (2-acetamidobenzoyl)formate anion. The formation of this salt appears to occur through a ring-opening reaction in which a C—N bond of isatin is cleaved, followed by the addition of a water molecules resulting in the formation of (II) (an intermediate under these conditions), then a simple acid–base reaction of (II) with benzamidine rather than a Schiff base condensation.

