$C_{22}H_{15}Br_2NO$

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Trinitromethane

HOLGER SCHÖDEL, RÜDIGER DIENELT
AND HANS BOCK*

*Department of Chemistry,
Johann Wolfgang Goethe University,
Marie Curie Strasse 11, D-60439 Frankfurt/Main,
Germany*

Abstract

The structure of cubic trinitromethane, CHN_3O_6, 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 $HC(NO_2)_3$ 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 $\omega(H—C—N—NO_2)$ 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 C_3 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 $HC(NO_2)_3$ 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 $[C(NO_2)_3]^-$. 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 $HCNO_2$ fragment. The molecular C_3 symmetry is verified by normal temperature ellipsoids of the NO_2 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, $(O_2N)_3CH···O(CH_2CH_2)_2O···HC(NO_2)_3$, 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 inito* 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 $[O_2N=C(NO_2)—N(O)OH]_n$ in close analogy to the recently crystallized and structurally characterized *aci*-diphenylnitromethane dimer $[(H_5C_6)_2C=N(OHO)_2N=C(C_6H_5)_2]$ (Bock *et al.*, 1993).
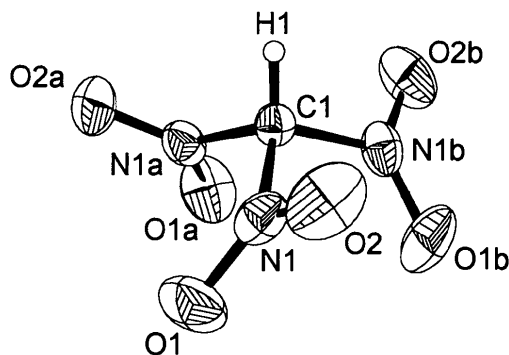
Fig. 1. Plot of displacement ellipsoids drawn at the 50% probability level together with numbering scheme for trinitromethane.
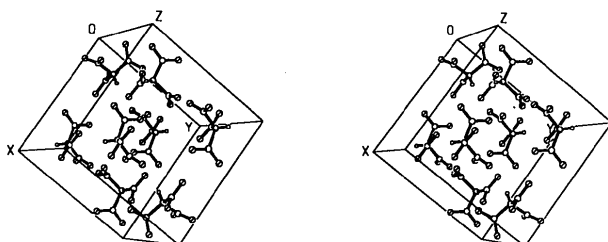

Fig. 2. Stereodiagram of the molecular packing in the unit cell viewed perpendicular to one N—C—N fragment.

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 (Macbeth, 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

CHN₃O₆   Mo $K\alpha$ radiation
$M_r = 151.05$ $\lambda = 0.71073$ Å
Cubic   Cell parameters from 48
$Pa\bar{3}$ reflections
$a = 10.358$ (1) Å $\theta = 17.5$–21°
$V = 1111.3$ Å³ $\mu = 0.19$ mm^{-1}

$Z = 8$ $T = 200$ K
$D_x = 1.806$ Mg m^{-3} Rectangular block
                        $0.3 \times 0.2 \times 0.2$ mm
                        Colourless

Data collection

Siemens AED-2 diffractometer $R_{int} = 0.0525$
ω–θ scans $\theta_{max} = 27.5°$
Absorption correction: $h = 0 \rightarrow 13$
                        $k = 0 \rightarrow 13$
none $l = 0 \rightarrow 13$
1461 measured reflections   4 standard reflections
431 independent reflections   frequency: 30 min
351 observed reflections   intensity variation: none
   $[I > 2\sigma(I)]$

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 $P = [\max(F_o^2,0) + 2F_c^2]/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.18$ e Å^{-3}
$\Delta\rho_{min} = -0.18$ e Å^{-3}
Extinction correction:
   $F^* = F_c/[k(1.0 + 0.001\chi \times F_c^2\lambda^3/\sin2\theta)^{1/4}]$
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* (Å²)

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	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)	x	x	0.024 (1)

Table 2. *Selected geometric parameters* (Å, °)

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).

A list of structure factors has been deposited with the IUCr (Reference: SE1040). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

Krishna C. Joshi, Rakesh Bohra,* Renuka Jain and Seema Arora

Department of Chemistry, University of Rajasthan, Jaipur-302004, India

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Abstract

The reaction of isatin with benzamidine hydrochloride in methanol yields the title compound, benzamidium (2-acetamidobenzoyl)formate (C_7H_9-$N_2^+.C_{10}H_8NO_4^-$). 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 K_2CO_3 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 (Lenhert, Lukehart, Sotiropoulos & Srinivasan, 1984; Beatrice, Kurt, Dieler & Gerhard, 1991), the molecular structure of this compound appeared to be of considerable interest.

(I)
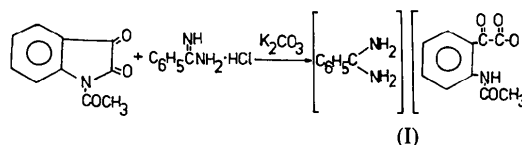
The IR spectrum (KBr pellet) of the compound showed the following absorptions: 3400–3240 (broad, NH, NH$_2$), 1700 (CO), 1450 (C—N), 1320 (C⋯N) cm^{-1}. The following ^{1}H NMR parameters confirm the structure of the compound: δ 2.18 (*s*, 3H, CH$_3$), 3.48 (broad, 4H, NH$_2$), 6.86–8.38 (*m*, 9H, Ar), 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.

(II)