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Supramolecular Structure of 2,4,6-Trinitrophenol

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The compound 2,4,6-trinitrophenol with the molecular formula $C_6H_3N_3O_7$, crystallizes with two crystallographically independent but chemically identical molecules in the asymmetric unit. The dihedral angle formed by the two benzene rings is about 67.49º. The crystal structure displays four intramolecular hydrogen bonds between the hydrogen atoms from the phenolic alcohols and the oxygen or nitrogen atoms from the nitro groups. In the crystal structure, the intermolecular O-H···O and C-H···O hydrogen bonding interactions link molecules into infinite three-dimensional supramolecular network structure.

Key Words: 2,4,6-Trinitrophenol, Supramolecular structure.

INTRODUCTION

Nitro compounds, especially aromatic nitro compounds have been widely studied owing to their potential application in, for example, pathology[1], materials science[2] and nonlinear optical (NLO) materials[3]. 2,4,6-Trinitrophenol, commonly known as picric acid (TNP), is a nonlinear optical crystal with molecular formula $C_6H_3N_3O_7$. 2,4,6-Trinitrophenol is also a well-known material used in dyeing industry[4]. Herein, we report the supramolecular structure of 2,4,6-trinitrophenol.

EXPERIMENTAL

The reagents and solvents were analytical grade reagents used without further purification. C, H and N analyses were carried out with a GmbH VariuoEL V3.00 automatic elemental analyzer. X-Ray single crystal structure was determined on a Bruker Smart APEX CCD area detector. Melting points was measured by the use of a microscopic melting point apparatus made in Beijing Taike Instrument Limited Company and the thermometer was uncorrected.

General procedure: To an acetone solution (30 mL) of 2,2'-[ethylenedioxybis(nitriloethylidyne)]diphenol (54.0 mg, 0.164 mmol) was added an acetone solution (20 mL) of copper picrate tetrahydrate (96.0 mg, 0.162 mmol). The colour of the mixed solution turned to brilliant yellow immediately. Then the mixture was placed in a hexane atmosphere, after 2 months, several yellow primatical crystals of the title compound suitable for X-ray diffraction analysis were obtained unexpectedly. Yield, 25.9 %. m.p. 401-402 K. Anal. calcd. (%) for $C_6H_3N_3O_7$: C, 31.45; H, 1.32; N, 18.34. Found (%): C, 31.32; H, 1.34; N, 18.27.

TABLE-1
CRYSTAL DATA AND REFINEMENT PARAMETERS FOR THE TITLE COMPOUND

Empirical formula	$C_6H_3N_3O_7$
Formula weight	229.11
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	Pca2(1)
Cell dimensions	a = 9.2596(12) Å, b = 19.138(2) Å, c = 9.7075(14) Å, α = 90º, β = 90º, γ = 90º
Volume	1720.3(4) $Å^3$
Z	8
Density (calculated)	1.769 mg/m^3
Absorption coefficient	0.166 mm^{-1}
$F_{(000)}$	928
Index ranges	$-10 \le h \le 11$, $-14 \le k \le 22$, $-11 \le l \le 11$
Reflections collected/unique	7969 / 3008 [R(int) = 0.0420]
Data/restraints/parameters	3008 / 1 / 289
Goodness of fit indicator	1.027
R [$I > 2\sigma(I)$]	$R_1 = 0.0532$, $wR_2 = 0.1355$
Largest diff. peak and hole	0.463 and -0.221 e $Å^{-3}$

X-Ray structure determination: The single crystal of the 2,4,6-trinitrophenol, with approximate dimensions of 0.38 mm × 0.27 mm × 0.12 mm was placed on a Bruker Smart 1000 diffractmeter equipped with Apex CCD area detector. The diffraction data were collected using a graphite monochromated MoK_α radition (λ = 0.71073 Å) at 298(2) K.

TABLE-2
SELECTED BOND LENGTHS (Å) AND ANGLES (º) FOR THE TITLE COMPOUND

Bond	Lengths	Bond	Lengths	Bond	Lengths
N(1)-O(3)	1.187(6)	N(4)-O(10)	1.209(7)	N(5)-O(11)	1.213(6)
N(1)-O(2)	1.204(7)	N(4)-O(9)	1.223(7)	N(5)-O(12)	1.213(7)
N(1)-C(2)	1.473(7)	N(4)-C(8)	1.464(8)	N(5)-C(10)	1.460(6)
N(2)-O(5)	1.210(6)	N(3)-O(6)	1.206(6)	N(6)-O(14)	1.173(6)
N(2)-O(4)	1.232(6)	N(3)-O(7)	1.241(6)	N(6)-O(13)	1.181(7)
N(2)-C(4)	1.474(7)	N(3)-C(6)	1.448(6)	N(6)-C(12)	1.477(8)
O(8)-C(7)	1.368(7)	–	–	–	–
Bond	**Angles**	**Bond**	**Angles**	**Bond**	**Angles**
O(3)-N(1)-O(2)	120.4(5)	O(10)-N(4)-C(8)	118.5(6)	C(5)-C(4)-N(2)	119.3(5)
O(3)-N(1)-C(2)	118.6(5)	O(9)-N(4)-C(8)	118.5(6)	C(3)-C(4)-N(2)	118.7(5)
O(2)-N(1)-C(2)	120.9(5)	O(11)-N(5)-O(12)	124.0(5)	C(9)-C(8)-N(4)	117.3(6)
O(5)-N(2)-O(4)	125.0(5)	O(11)-N(5)-C(10)	117.8(5)	C(9)-C(10)-N(5)	119.7(5)
O(5)-N(2)-C(4)	117.6(5)	O(12)-N(5)-C(10)	118.2(5)	C(11)-C(10)-N(5)	118.0(5)
O(4)-N(2)-C(4)	117.2(5)	O(14)-N(6)-O(13)	120.9(7)	C(11)-C(12)-N(6)	115.6(5)
O(6)-N(3)-O(7)	122.4(5)	O(14)-N(6)-C(12)	120.6(6)	O(8)-C(7)-C(12)	119.5(5)
O(6)-N(3)-C(6)	118.1(5)	O(13)-N(6)-C(12)	118.4(5)	C(12)-C(11)-C(10)	117.9(5)
O(7)-N(3)-C(6)	119.5(4)	O(1)-C(1)-C(2)	120.5(4)	C(7)-C(12)-N(6)	122.2(5)
O(10)-N(4)-O(9)	122.9(6)	O(1)-C(1)-C(6)	123.2(5)	C(7)-C(8)-N(4)	120.7(5)
C(5)-C(6)-C(1)	122.5(5)	O(8)-C(7)-C(8)	123.2(5)	C(11)-C(12)-C(7)	122.2(5)
C(5)-C(6)-N(3)	117.9(5)	C(3)-C(2)-N(1)	117.2(5)	C(1)-C(6)-N(3)	119.6(5)
C(1)-C(2)-N(1)	121.1(5)	–	–	–	–

The structure was solved by using the program SHELXS-97[5] and Fourier difference techniques and refined by full-matrix least-squares method on F^2 using SHELXL-97[6]. Details of the data collection and refinements of title compound are given in Table-1. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added theoretically.

RESULTS AND DISCUSSION

X-Ray crystallographic analysis revealed the crystal structure of 2,4,6-trinitrophenol and the structure is shown in Fig. 1. Selected bond distances and angles are listed in Table-2. The crystal structure of the title compound is built up by only the $C_6H_3N_3O_7$ molecules, in which all bond lengths are in normal ranges. There are two crystallographically independent but chemically identical molecules (A and B) in the asymmetric unit. In both molecules, the phenolic alcohol and nitro groups are essentially coplanar with the attached benzene ring. The two benzene rings form a dihedral angle of *ca.* 67.49º.

In the crystal structure, there are four strong intramolecular O-H···O and O-H···N hydrogen bonds (O(1)-H(1)···O(2), O(1)-H(1)···N(1)in molecule A and O(8)-H(8)···O(14), O(8)-H(8)···N(6) in molecule B) between the phenolic hydroxyl

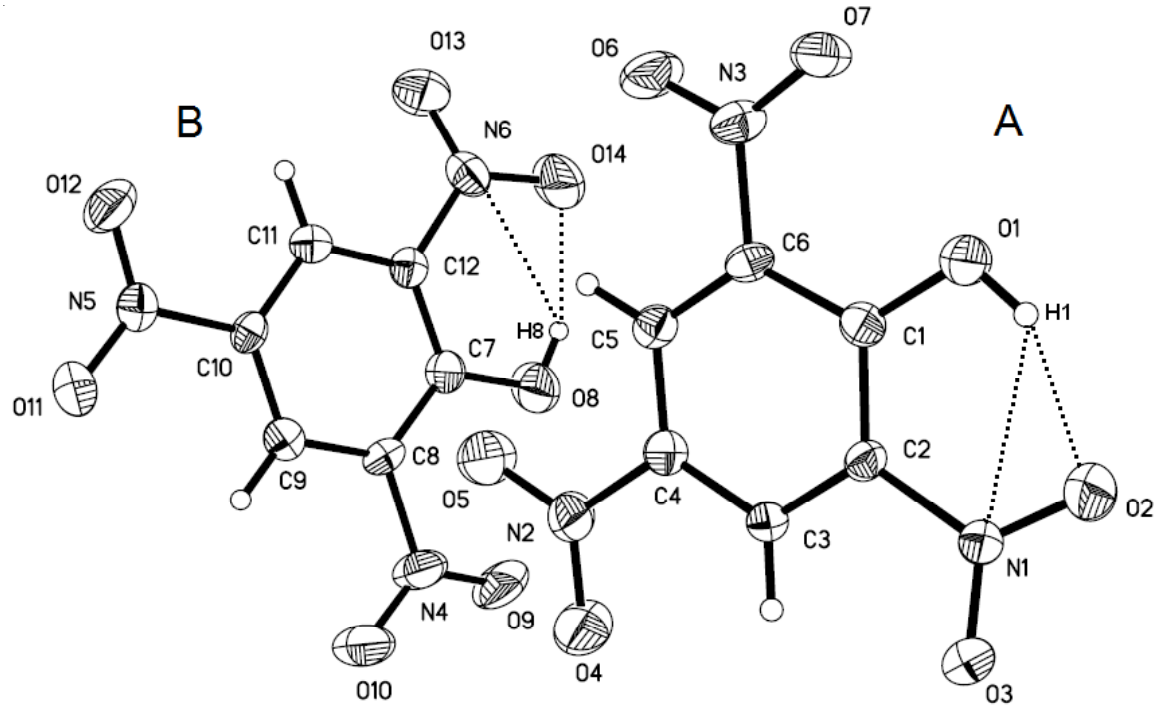

Fig. 1. Molecule structure of the title compound with atom numbering showing the intramolecular hydrogen bonds

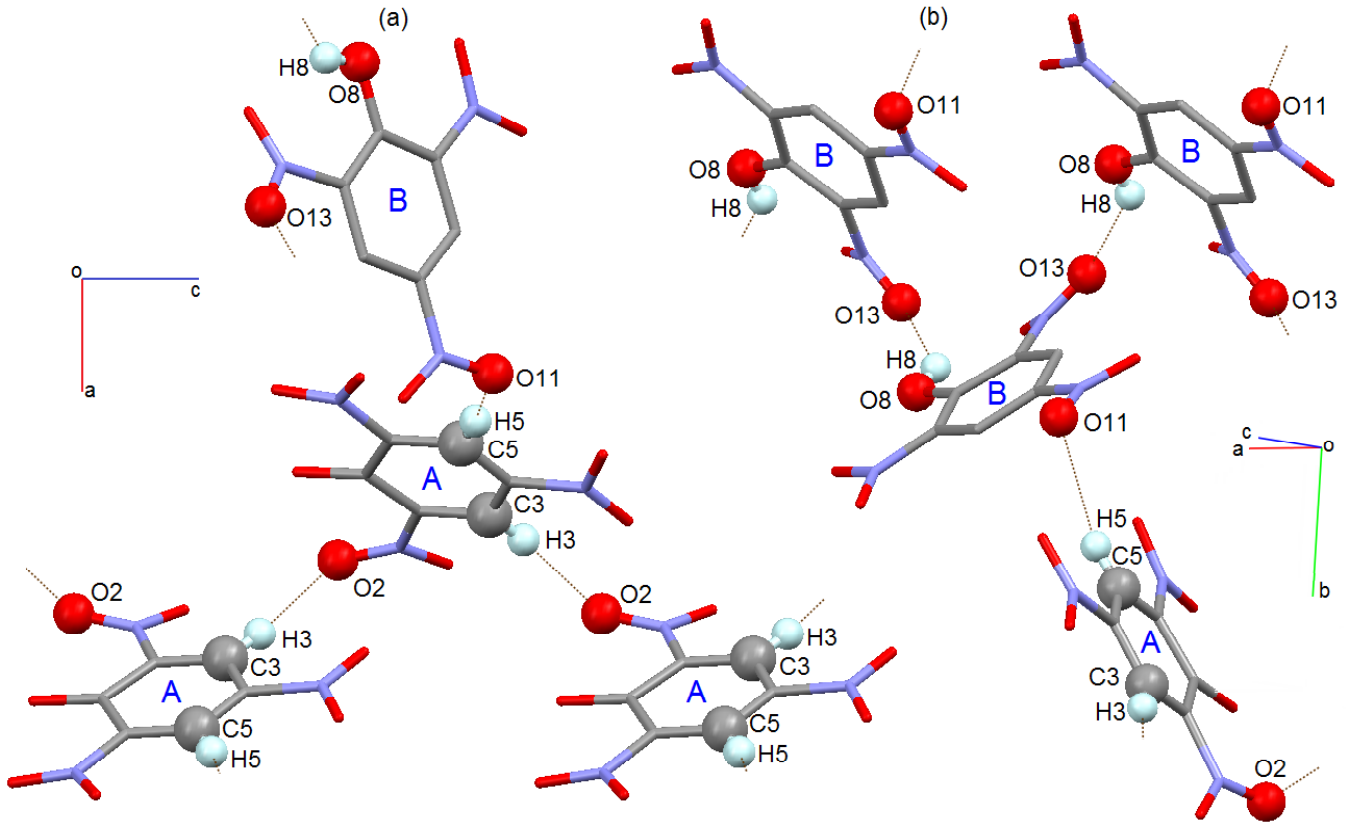

Fig. 2. View of the 2D supramolecular layer within the title compound (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity)

groups (-OH) and the nitro oxygen (O) and nitro nitrogen (N) atoms (Table-3), which generate six-membered S(6) ring motifs (Fig. 1). In addition, every molecule A links two other molecules A *via* intermolecular C(3)-H(3)···O(2) hydrogen-bonding and one molecules B *via* intermolecular C(5)-H(5)···O(11) hydrogen-bonding interactions into an infinite 2D-layer supramolecular structure on the ac crystallographic plane (Fig. 2a). Whereas, every molecule B links two other molecules B *via* intermolecular O(8)-H(8)···O(13) hydrogen-bonding and one molecules A *via* intermolecular C(5)-H(5)···O(11) hydrogen-bonding interactions into the other infinite 2D-layer supramolecular structure on the ab crystallographic plane (Fig. 2b). Thus, the crystal packing of the compound shows a self-assembling infinite three-dimensional supramolecular network structure.

TABLE-3
HYDROGEN-BONDING DATA [Å, º]

D-H···A	d(D-H)	d(H···A)	d(D···A)	∠D-H···A
O(1)-H(1)···O(2)	0.820	1.88	2.599(6)	146
O(1)-H(1)···N(1)	0.820	2.346	2.839(2)	118
O(8)-H(8)···O(14)	0.820	1.925	2.622(9)	142
O(8)-H(8)···N(6)	0.820	2.370	2.841(3)	118
O(8)-H(8)···O(13)	0.820	2.601	3.252(3)	138
C(3)-H(3)···O(2)	0.930	2.450	3.373(7)	173
C(5)-H(5)···O(11)	0.930	2.628	3.540(7)	167

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