Crystal structure of 2,4,5,7-tetranitrofluorene, $C_{26}H_{12}N_8O_{16}$

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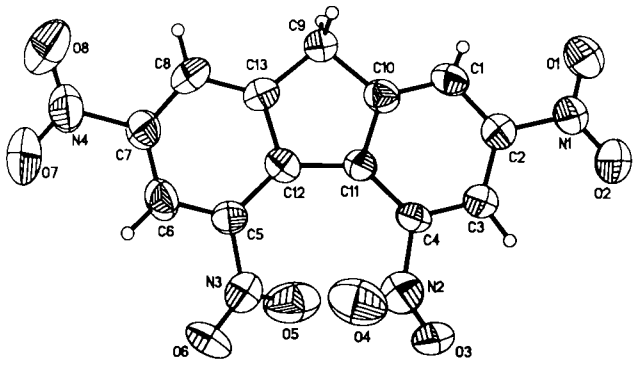

Abstract

$C_{26}H_{12}N_8O_{16}$, monoclinic, $C12/c1$ (No. 15), $a = 12.295(2)$ Å, $b = 10.657(2)$ Å, $c = 20.763(3)$ Å, $\beta = 94.308(7)°$, $V = 2712.8$ Å^3, $Z = 4$, $R_{gt}(F) = 0.105$, $wR_{ref}(F^2) = 0.353$, $T = 295$ K.

Source of material

2,4,5,7-Tetranitrofluorene (TNF) was synthesized by the following method. 2.5 g (15.0 mmol) of finely powdered fluorene were added in small portions to a mixture of 65 ml of HNO_3 ($\rho = 1.52$) and 65 ml of conc. H_2SO_4 at room temperature. The mixture was stirred and warmed in a boiling water bath for 1.5 hours. After cooling, the mixture was poured onto 400 g of ice. The precipitated powder was then filtered, using a sinter funnel, washed with large amount of water and dried. Other procedures are known from the literature [1-3]. Crystallization from acetic acid gave 4.4 g (12.7 mmol, 84%) of red needles which proved to be the pure unsolvated TNF with mp = 535 K. However, when crystallized from dry 1,4-dioxane orange prisms of the solvated product were obtained, mp = 483 K. These crystals were found to be air sensitive. However, the unsolvated crystals appeared to be quite stable over the course of the data collection.

Experimental details

The unsolvated crystal proved to be twinned, but the twins were successfully resolved using the RLATT program [4]. This allowed the structure to be solved. However, the $R_{gt}(F)$ value (0.105) is still slightly high, even though the residual electron density is less than 1 e Å^{-3}. This may be caused by incomplete resolution of overlapping reflections.

Discussion

2,4,5,7-Tetranitrofluorene (TNF) is a widely used and studied organic p-acceptor moiety [5-7]. 744 structures contain a fluorene backbone are reported in the CSD (April 2002 edition), of which 73 containing NO_2 groups [8]. However, only the 1,4-dioxane solvated form of TNF (with disordered 1,4-dioxane molecules) has thus far been reported (orthorhombic, $P2_12_12_1$, $a = 8.623(2)$ Å, $b = 11.943(2)$ Å, $c = 18.146(4)$ Å, $Z = 4$, $V = 1868.757$ Å^3) [9]. We have determined the growing conditions for both the 1,4-dioxane solvated and the unsolvated crystal forms. Direct comparison between the crystal structures of the solvated (1,4-dioxane) and the unsolvated forms is thus possible. The 1,4-dioxane solvated and the unsolvated forms of TNF crystallize in different space groups ($P2_12_12_1$, and $C2/c$, respectively). Their packing diagrams reveal no clear relationship between the molecular packing in the two crystals. A single short intermolecular contact exists between the NO_2 groups on adjacent molecules within the same layer exists in the unsolvated structure (O7···O7′ = 3.04(3) Å) compared with the complete absences thereof in the 1,4-dioxane solvated form. There are no statistically significant differences in the bond angles and bond lengths of the two forms. However, the torsion angles of the NO_2 groups differ by up to 12°.

Table 1. Data collection and handling.

Crystal:	red needle, size 0.34 × 0.40 × 0.65 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	1.45 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	41.62°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	5508, 1424
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1112
$N(param)_{refined}$:	232
Programs:	SHELXS-97 [10], SHELXTL [11], SHELXL-97 [12], SADABS [13]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(9A)	8*f*	0.8626	0.0729	0.5597	0.06(2)
H(9B)	8*f*	0.7907	-0.0373	0.5847	0.07(2)
H(1)	8*f*	0.8762	0.1033	0.6970	0.09(3)
H(6)	8*f*	0.4690	0.1589	0.4085	0.05(2)
H(8)	8*f*	0.7490	-0.0225	0.4428	0.04(2)
H(3)	8*f*	0.6502	0.3544	0.7420	0.04(2)

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Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(11)	8f	0.6631(6)	0.1986(6)	0.6084(3)	0.037(4)	0.041(4)	0.044(4)	0.002(3)	0.001(3)	0.000(3)
C(12)	8f	0.6263(6)	0.1610(6)	0.5412(3)	0.039(4)	0.041(4)	0.046(4)	-0.002(4)	-0.001(4)	0.006(3)
O(3)	8f	0.4861(5)	0.4183(6)	0.6737(3)	0.067(4)	0.088(5)	0.071(4)	0.035(4)	0.003(3)	-0.017(3)
C(13)	8f	0.7045(6)	0.0781(6)	0.5204(3)	0.046(5)	0.042(4)	0.047(5)	0.005(4)	0.009(4)	0.000(3)
C(9)	8f	0.7909(6)	0.0506(7)	0.5726(3)	0.048(5)	0.057(5)	0.047(4)	0.010(4)	0.004(4)	-0.006(4)
C(5)	8f	0.5365(6)	0.1874(6)	0.4973(4)	0.055(5)	0.039(4)	0.052(5)	0.010(4)	-0.001(4)	-0.002(4)
C(2)	8f	0.7707(6)	0.2277(7)	0.7294(4)	0.050(5)	0.056(5)	0.053(5)	0.005(4)	-0.003(4)	-0.002(4)
N(1)	8f	0.8260(6)	0.2458(8)	0.7935(3)	0.060(5)	0.083(5)	0.049(5)	0.013(4)	-0.009(4)	-0.010(4)
C(10)	8f	0.7581(6)	0.1329(7)	0.6265(3)	0.046(5)	0.047(4)	0.047(5)	0.006(4)	0.002(4)	0.006(3)
C(7)	8f	0.6073(7)	0.0637(7)	0.4184(3)	0.065(6)	0.051(5)	0.039(4)	0.007(4)	0.002(4)	0.009(4)
C(1)	8f	0.8122(6)	0.1474(7)	0.6862(4)	0.049(5)	0.051(5)	0.059(5)	0.014(4)	-0.008(4)	-0.002(4)
C(6)	8f	0.5286(7)	0.1395(7)	0.4370(4)	0.067(6)	0.058(5)	0.043(5)	0.005(5)	-0.007(4)	0.006(4)
O(2)	8f	0.7919(6)	0.3229(7)	0.8294(3)	0.090(5)	0.117(5)	0.059(4)	0.025(4)	-0.015(3)	-0.032(4)
C(8)	8f	0.6958(7)	0.0303(7)	0.4573(4)	0.062(5)	0.045(4)	0.051(5)	0.005(4)	0.022(4)	-0.001(4)
C(3)	8f	0.6773(6)	0.2988(8)	0.7126(4)	0.051(5)	0.066(5)	0.046(5)	0.013(4)	-0.003(4)	-0.007(4)
O(5)	8f	0.4134(6)	0.2298(6)	0.5768(5)	0.064(5)	0.078(4)	0.155(8)	-0.001(4)	0.016(5)	-0.017(5)
O(4)	8f	0.5520(6)	0.4322(6)	0.5773(4)	0.084(5)	0.085(5)	0.102(6)	0.015(4)	0.005(4)	0.031(4)
N(3)	8f	0.4420(8)	0.2562(9)	0.5158(4)	0.091(7)	0.104(6)	0.064(5)	0.036(5)	-0.008(5)	-0.025(5)
N(2)	8f	0.5482(7)	0.3889(8)	0.6338(5)	0.080(6)	0.074(5)	0.088(6)	0.015(5)	-0.014(5)	-0.018(5)
C(4)	8f	0.6277(6)	0.2854(7)	0.6536(4)	0.039(5)	0.069(5)	0.047(5)	0.017(4)	-0.003(4)	-0.004(4)
O(6)	8f	0.3803(6)	0.3079(7)	0.4817(3)	0.089(5)	0.113(6)	0.085(5)	0.054(5)	-0.032(4)	0.000(4)
N(4)	8f	0.6018(9)	0.0136(8)	0.3520(4)	0.095(7)	0.087(6)	0.049(5)	0.013(5)	-0.016(5)	-0.008(4)
O(8)	8f	0.6797(7)	-0.0305(7)	0.3304(3)	0.122(6)	0.099(5)	0.067(4)	0.010(5)	0.030(4)	-0.014(4)
O(1)	8f	0.9026(6)	0.1810(8)	0.8084(3)	0.091(6)	0.137(6)	0.069(4)	0.047(5)	-0.034(4)	-0.020(4)
O(7)	8f	0.512(1)	0.017(1)	0.3234(4)	0.18(1)	0.25(1)	0.075(6)	0.090(9)	-0.046(6)	-0.077(7)

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