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Crystal Structure of 3,4-Bis (nitrofurazano) furoxan

WANG Jun, DONG Hai-shan, HUANG Yi-gang, LI Jin-shan, ZHOU Xiao-qing

(*Institute of Chemical Materials, CAEP, Mianyang* 621900, *China*)

Abstract: The single crystal of 3,4-bis (nitrofurazano) furoxan (BNFF) was obtained using acetone as solvent. Its molecular structure was characterized by elemental analysis, IR, MS, ^{13}C NMR and single-crystal X-ray diffraction. The results indicate that BNFF crystal belongs to orthorhombic, space group P212121 with $a = 0.6794$ (3) nm, $b = 1.0755$ (5) nm, $c = 1.5137$ (4) nm, $V = 1.1060$ (7) nm^3, $M_r = 312.14$, $Z = 4$, $D_x = 1.874$ g·cm^{-3}, $D_c = 1.875$ g·cm^{-3}, $F(000) = 624$, μ(MoKα) = 0.176 mm^{-1}, $R_1 = 0.0757$, $wR_2 = 0.1206$. Three 5-membered furazan rings of BNFF molecule are planar and the dihedral angles between them are 62.16 (0.29)° and 25.67 (0.36)°

Key words: organic chemistry; high energetic compound; 3,4-bis (nitrofurazano) furoxan(BNFF); crystal structure

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1 Introduction

Furazano or furoxano derivatives have merits of high-energy, high standard formation enthalpy (ΔH_f^θ), rich nitrogen and excellent stability[1,2]. Explosive density can be increased by 0.06 – 0.08 g·cm^{-3} and detonation velocity by 300 m·s^{-1} as nitro groups substituted by furoxano groups. Hence, furazan-ring is an effective structure unit for designing new high-energy density explosive. 3,4-Bis (nitrofurazano) furoxan (BNFF)[3,4] is a novel high-energy density material with zero-hydrogen and excellent general performances. Especially, mixed with pertinent explosive, it will exalt energy of mixed explosive in a new rank. So, it is significant to study the physicochemical properties of BNFF.

2 Experimental

2.1 Instruments

The crystal structure of BNFF was determined by a CAD4 type 4-circle single-crystal X-ray diffraction instrument. IR and elemental analysis were carried out on a Nicolet 800 type IR spectrometer (KBr) and an EA1108 type elemental analysis instrument, respectively. MS was conducted by a Large B-E MS spectrometer. ^{13}C NMR was dealed with a Bruker AVANCE-300 MHz NMR spectrometer. The determination of Melting point was conducted by a Metller Toledo FP900 type thermal system.

2.2 Single crystal culture and molecular structure characterization

1.0 g BNFF purified by ethanol was weighed, dispersed and wholly dissolved in 10.0 mL acetone at room temperature. The solution was filtrated. The filtration was gleaned, put into fostering utensil and left to evaporate gradually for 7 days, and then the colorless crystals of BNFF were obtained. m.p. 108.6 – 110.0 ℃. Anal. calcd for $C_6N_8O_8$: C 23.08, N 35.90, O 41.02; found C 23.15, N 35.25. IR ν: 1640, 1565, 1411, 1355 (furazan ring), 1515, 1448 (furoxan ring), 1586, 1355 (C—NO_2), 1001, 961 (N—O), 906 (C—N) cm^{-1}. MS m/z (%): 312 (M^+), 282 (M—NO), 46 (NO_2). ^{13}C NMR δ ($CDCl_3$): 161.535, 161.408, 144.402, 140.938, 138.463, 104.953 ppm.

2.3 Crystal structure determination

The single crystal of BNFF having dimensions of 0.30 mm × 0.18 mm × 0.15 mm was mounted on the single-crystal X-ray diffractometer instrument, radiated by MoKα radiation ($\lambda = 0.071073$ nm) monochromized with graphite, scanned by $\omega/2\theta$ mode ($2.32° \leqslant \theta \leqslant 25.00°$) at 293 (2). Within the range of $-2 \leqslant h \leqslant 8$, $-4 \leqslant k \leqslant 12$, $-17 \leqslant l \leqslant 18$ a total of 1443 reflections were collected with 1174 unique ones (Rint = 0.0068), of which 533 with $I > 2\sigma(I)$ were considered as observed. The coordinates of non-hydrogen were obtained by direct method. The results

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Biography: WANG Jun (1970 –), male, MS degree. research field synthesis and performance of energetic materials. e-mail: icm@caep.ac.cn

were optimized by least-squares method with an-isotropic thermal parameters. The molecular weight of BNFF is 312.14. The crystal of BNFF belongs to orthorhombic, space group P212121 with a = 0.6794 (3) nm, b = 1.0755 (5) nm, c = 1.5137 (4) nm, V = 1.1060 (7) nm^3, Z = 4, D_x = 1.874 g·cm^{-3}, D_c = 1.875 g·cm^{-3}, $F(000)$ = 624. The maximum peak and the minimum peak on the Fourier map were 249 e·nm^{-3} and −255 e·nm^{-3}, respectively. The refinement was converged with R_1 = 0.0757, wR_2 = 0.1206, of which, $w = 1/[S^2(F_0)^2 + (0.0377P)^2 + 0.0000P]$, $P = (F_0^2 + 2F_c^2)/3$, S = 0.979. The crystal structure resolve and correction were processed using SHELXS-97 (Sheldrick, 1990) [5] and SHELXL-97 (Sheldrick, 1997) [6] program package, respectively.

3 Results and discussions

The non-hydrogen coordinates and thermal parameters are listed in Table 1. The bond lengths and bond angles are listed in Table 2. Figs 1, 2 show the molecular structure and the 3D packing of BNFF molecules.

Table 1 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\times 10^5$ nm^2) of BNFF

atom	x	y	z	U_{eq}
O(1)	1419(16)	1707(7)	6408(4)	79(3)
O(2)	4479(11)	5166(7)	5894(5)	64(2)
O(3)	6227(12)	3511(9)	5537(6)	90(3)
O(4)	−1601(10)	6425(7)	6505(5)	69(2)
O(5)	−1800(12)	7513(8)	5243(5)	78(3)
O(6)	2363(12)	4769(6)	3391(4)	67(2)
O(7)	−3320(14)	6318(9)	3754(6)	88(3)
O(8)	−1670(2)	7462(9)	2910(7)	151(6)
N(1)	3254(17)	2103(8)	6191(5)	69(3)
N(2)	73(15)	2648(8)	6385(4)	63(3)
N(3)	4763(16)	4016(9)	5794(6)	63(3)
N(4)	−794(10)	5319(7)	6778(5)	55(2)
N(5)	−1195(11)	6564(7)	5601(5)	48(2)
N(6)	2088(12)	4739(6)	4293(5)	50(2)
N(7)	950(15)	5494(7)	2988(5)	60(3)
N(8)	−1871(19)	6683(10)	3442(7)	76(4)
C(1)	3031(17)	3286(9)	6044(3)	43(3)
C(2)	1074(13)	3621(9)	6161(3)	47(3)
C(3)	39(9)	4853(7)	6074(5)	38(2)
C(4)	−166(8)	5587(7)	5338(5)	36(3)
C(5)	506(11)	5434(5)	4439(6)	30(2)
C(6)	−144(15)	5872(7)	3626(7)	49(3)

Note: U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2 Bond lengths (nm) and angles (°) of BNFF

bond	length/nm	bond	length/nm
O(1)-N(1)	1.357(13)	O(1)-N(2)	1.364(11)
O(2)-N(3)	1.261(10)	O(3)-N(3)	1.199(12)
O(4)-N(4)	1.374(10)	O(4)-N(5)	1.404(9)
O(5)-N(5)	1.227(10)	O(6)-N(6)	1.379(9)
O(6)-N(7)	1.378(11)	O(7)-N(8)	1.160(12)
O(8)-N(8)	1.170(11)	N(1)-C(1)	1.301(11)
N(2)-C(2)	1.293(11)	N(3)-C(1)	1.463(13)
N(4)-C(3)	1.307(10)	N(5)-C(4)	1.323(10)
N(6)-C(5)	1.328(11)	N(7)-C(6)	1.284(12)
N(8)-C(6)	1.488(16)	C(1)-C(2)	1.389(13)
C(2)-C(3)	1.506(12)	C(3)-C(4)	1.372(11)
C(4)-C(5)	1.445(11)	C(5)-C(6)	1.390(12)
bond	**angle/(°)**	**bond**	**angle/(°)**
N(1)-O(1)-N(2)	112.1(7)	N(4)-O(4)-N(5)	107.9(7)
N(6)-O(6)-N(7)	110.9(8)	C(1)-N(1)-O(1)	104.0(10)
C(2)-N(2)-O(1)	104.7(8)	O(3)-N(3)-O(2)	127.6(12)
O(3)-N(3)-C(1)	120.5(10)	O(2)-N(3)-C(1)	111.8(10)
C(3)-N(4)-O(4)	105.0(7)	O(5)-N(5)-C(4)	134.8(8)
O(5)-N(5)-O(4)	117.0(9)	C(4)-N(5)-O(4)	108.2(8)
C(5)-N(6)-O(6)	105.1(8)	C(6)-N(7)-O(6)	104.5(8)
O(8)-N(8)-O(7)	128.5(16)	O(8)-N(8)-C(6)	117.0(13)
O(7)-N(8)-C(6)	113.3(10)	N(1)-C(1)-C(2)	110.0(11)
N(1)-C(1)-N(3)	118.4(12)	C(2)-C(1)-N(3)	131.6(10)
N(2)-C(2)-C(1)	109.1(10)	N(2)-C(2)-C(3)	119.3(7)
C(1)-C(2)-C(3)	131.6(8)	N(4)-C(3)-C(4)	113.5(8)
N(4)-C(3)-C(2)	117.9(7)	C(4)-C(3)-C(2)	128.7(6)
N(5)-C(4)-C(3)	105.4(7)	N(5)-C(4)-C(5)	122.7(8)
C(3)-C(4)-C(5)	131.9(8)	N(6)-C(5)-C(6)	107.5(9)
N(6)-C(5)-C(4)	118.4(8)	C(6)-C(5)-C(4)	134.0(8)
N(7)-C(6)-C(5)	112.0(10)	N(7)-C(6)-N(8)	120.1(10)
C(5)-C(6)-N(8)	127.9(10)		

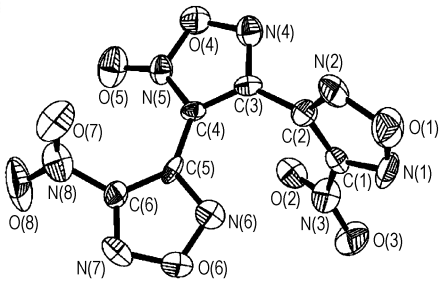

Fig. 1 Molecular structure of BNFF

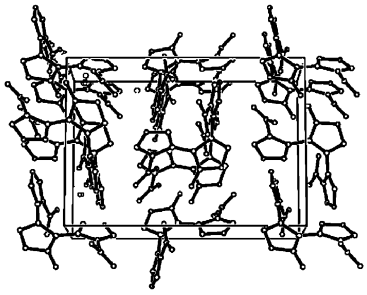

Fig. 2 Packing of BNFF molecules in the crystal

From Fig. 1, two nitrofurazano rings and one furoxano ring with the furoxano ring between the two nitrofurazano rings consist of BNFF molecule with zero-hydrogen. It can be seen from Tables 1,2 and Figs 1,2 that the structure of furazan-ring in BNFF molecule is planar. Six electrons of which two come from carbon atoms [C(1) and C(2) or C(5) and C(6)], two from nitrogen atoms [N(1) and N(2) or N(6) and N(7)] and two from oxygen atom[O(1) or O(6)] in furazan-ring form a conjugation system. From the bond data tested, the average bond length of C—C is 0.1420 nm, of N—O is 0.1298 nm, and of C—N is 0.1348 nm, between the single and double bond length of C—C, N—O[7] and C—N each. The angles tested are similar to those of the furazan-ring of the other furazano derivatives (Table 2). Consequently, the three furazan-rings form a stable conjugation system, respectively. But the two nitro groups connected with the two furazano rings and the oxygen atom bonded with furoxano ring do not take part in the furazano conjugating system.

C(1), C(2), N(2), O(1) and N(1); C(3), C(4), N(5), O(4) and N(4); C(5), C(6), N(7), O(6) and N(6) partly constitute the three furazan-rings of BNFF molecule. The least-squares plane equations of the three 5-membered furazan-rings are $1.2431(0.0252)x + 2.0897(0.0351)y + 14.5878(0.0159)z = 9.8782(0.0071)$ with the average deviation 0.00021 nm, $5.7764(0.0112)x + 5.1048(0.0301)y + 3.4439(0.0442)z = 4.5923(0.0291)$ with 0.00021 nm and $3.9574(0.0179)x + 8.6725(0.0216)y + 1.5495(0.0497)z = 5.5999(0.0189)$ with 0.00028 nm. It demonstrates that the three furazan-rings have very good aromaticity and are planar, respectively. Otherwise, the two dihedral angles between the three furazan-ring planes are 62.16 (0.29)° and 25.67(0.36)° show that BNFF molecule is twist, and not aromatic. This is consistent with the reported $C_6N_8H_4O_4$[8] [3,4-bis (aminofurazano) furoxan]. The space configuration of BNFF molecule is chair-like makes the molecules of BNFF in crystal accumulate denser with the density 1.875 g·cm^{-3}.

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3,4-二(硝基呋咱基)氧化呋咱的晶体结构研究

王 军, 董海山, 黄奕刚, 李金山, 周小青

(中国工程物理研究院化工材料研究所, 四川 绵阳 621900)

摘要: 在丙酮中培养出了3,4-二(硝基呋咱基)氧化呋咱(BNFF)的单晶。用单晶X射线衍射、元素分析、红外、质谱和^{13}C核磁共振谱对其结构进行了表征。测试结果表明: BNFF晶体属正交晶系,空间群P212121。主要晶体学参数为: a = 0.6794 (3) nm, b = 1.0755 (5) nm, c = 1.5137 (4) nm, V = 1.1060 (7) nm^3, M_r = 312.14, Z = 4, D_x = 1.874 g·cm^{-3}, D_c = 1.875 g·cm^{-3}, $F(000)$ = 624, μ(MoKα) = 0.176 mm^{-1}, R_1 = 0.0757, wR_2 = 0.1206。BNFF分子中三个五员呋咱环分别处于3个不同的面中,在空间呈椅型结构,三环面扭曲,面间夹角为62.16 (0.29)° 和25.67 (0.36)°

关键词: 有机化学; 高能化合物; 3,4-二(硝基呋咱基)氧化呋咱(BNFF); 晶体结构

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