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Crystal Structure of 3,6-Bis(3′-aminofurazan-4-yl)-1,4-dioxa-2,5-diazacyclohexa-2,5-diyne

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Abstract: The compound of 3,6-bis(3′-aminofurazan-4-yl)-1,4-dioxa-2,5-diazacyclohexa-2,5-diyne (BADDD) was obtained and characterized. It is triclinic, *P*-1, and with parameters of a = 0.48616 (10) nm, b = 0.5237 (2) nm, c = 0.97076 (19) nm, α = 102.25 (3)°, β = 93.631 (17)°, γ = 101.88 (2)°, V = 0.23489 (12) nm^3, Z = 1, D_c = 1.783 g·cm^{-3}, λ (MoKα) = 0.071073 nm, μ(MoKα) = 0.153 mm^{-1}, F(000) = 128, T = 294 (2) k, R_1 = 0.0351 and wR_2 = 0.0875. The molecule consists of two aminofurazano rings and a 6-membered heterocycle formed by two O atoms, two N atoms and two C atoms, respectively. The molecule is centrally symmetrical.

Key words: physical chemistry; high energetic compound; 3,6-bis (3′-aminofurazan-4-yl) -1,4-dioxa-2,5-diaza-cyclohexa-2,5-diyne (BADDD); crystal structure

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1 Introduction

Furazan ring of which is comparable with two nitro groups in energetic compounds has explosive properties. The particular merits of furazano energetic compounds make them be one of the research hotspots in the energetic materials fields[1-3]. This kind of compounds has such characteristics as high formation enthalpy (ΔH_f^θ), rich nitrogen and oxygen, high-energy-density, good heat-resistance. Therefore, they become a large series of exploitable energetic materials. 3,6-bis (3′-aminofurazan-4-yl)-1,4-dioxa-2,5-diazacyclohexa-2,5-diyne (BADDD) is a novel furazano energetic compound. The detonation velocity and detonation pressure of BADDD calculated by the BKW code is 8.40 km·s^{-1} and 29.6 GPa, respectively. There are two furazan rings and a 6-membered heterocycle containing two carbon, nitrogen and oxygen atoms in the molecule. Hence, to study its chemical physical properties is significant.

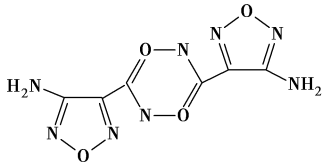
2 Experiment

2.1 Apparatus

CAD4 type 4-circle single-crystal X-ray diffractometer, Nicolet 800 type IR spectrometer (KBr), EA1108 type elemental analysis instrument, and Metller Toledo FP900 type thermal system.

2.2 Single Crystal Culture

1.0 gram BADDD was weighed, dispersed in 15.0 mL acetone, and whole dissolved at 55 ℃. The solution was filtrated. Liquid filtrated was gleaned, put into fostering utensil and left to evaporate acetone gradually for several days, and then the colorless crystals of BADDD were obtained. Its m.p. is 233.4 – 235.7 ℃. IR(KBr, cm^{-1})ν:3455, 3321(—NH_2), 1608, 1532, 1383, 1027 (C, N and O 6-membered heterocycle), 1638, 1004 (furazan ring)。Anal. calcd for $C_6N_8O_4H_4$: C 28.57, H 1.59, N 44.44; found C 27.89, H 1.37, N 44.25. The molecular structure of BADDD is as follows:



2.3 Crystal Structure Determination

The single crystal of BADDD having dimensions of 0.24 mm×0.20 mm×0.05 mm was mounted on the 4-circle single-crystal X-ray diffractometer instrument, radiated by MoKα radiation (λ = 0.071073 nm) homochromized with graphite, scanned by $\omega/2\theta$ mode at 294(2) k. In the range of 2.16°≤θ≤24.95°, −5≤h≤5, −5≤k≤6, −11≤l≤11, a total of 960 reflections were collected with 823 unique

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ones (R_{int} = 0.0229), of which 579 with $I > 2\sigma(I)$ were considered as observed. The coordinates were obtained by direct method for of non-hydrogen, and hydrogen by differential Fourier synthetic method. The results were optimized by least-squares method. Hydrogen was corrected by isotropic thermal parameters with the others by an-isotropic thermal parameters. The maximum peak and the minimum peak of the final structure μ(MoKα) = 0.153 mm^{-1}, R_1 = 0.0351, wR_2 = 0.0875 on the Fourier map were 198 e·nm^{-3} and −162 e·nm^{-3}, respectively, of which, $w = 1/[S^2(F_0)^2 + (0.0588P)^2 + 0.0141P]$, $P = (F_0^2 + 2F_c^2)/3$. S = 1.048. The crystal structure resolution and correction were processed by SHELX97 (Sheldrick, 1990)[4] and SHELX97 (Sheldrick, 1997)[5] program package, respectively.

3 Results and Discussion

The crystal structure resolution of the data tested shows that the molecular relative mass of BADDD is 252.17, the main crystallograpyical parameters of a = 0.48616(10) nm, b = 0.5237 (2) nm, c = 0.97076(19) nm, α = 102.25(3)°, β = 93.631(17)°, γ = 101.88(2)°, V = 0.23489(12) nm^3, Z = 1, D_c = 1.783 g·cm^{-3}, F(000) = 128. The non-hydrogen coordinates and thermal parameters are listed in Table 1. The bond lengths and angles are listed in Table 2, and the hydrogen bonds and angles are in Table 3. Figs 1 – 3 show the molecular structure, 2D connections and the 3D packing of BADDD molecules in the crystal, respectively.

From the testing results, one can see that the BADDD molecule is constructed by two aminofurazano rings and a 6-membered heterocycle containing two carbon, two nitrogen and two oxygen atoms, respectively, with the 6-membered heterocycle ring between the two aminofurazano rings. The plane equation of C(1), C(2), N(2), N(3) and O(1) is 3.1514 (0.0038) x − 3.0553 (0.0045) y + 6.3506 (0.0077) z = 0.0204 (0.0041) with the deviation being 0.00024 nm. BADDD molecule has a symmetrical center i. And, there are 34π electrons in the molecule according with the Hückl 4n + 2 rule. All the above-mentioned show that BADDD has excellent aromaticity and co-planarity, and its molecular structure is stable.

All the bond lengths and bond angles in BADDD molecule are in the normal range. There exists well strong conjugating effect between amino group and furazan-ring, which makes the C—N bond shorter and correspond with C═N (0.132 nm)[6]. The bonds and angles are near to the others of the other furazano derivatives (see in Table 2). In the heterocycle, the bond length of C(3)—N(4)_1 is the same as that of C(3)_1—N(4), 0.127 nm, shorter than that of C═N ; and the bond length of N(4)—O(2) is the same as that of N(4)_2—O(2)_1, 0.1432(2) nm, corresponding with that of N—O (0.1435 nm). These mentioned show that though BADDD molecule is a large planar conjugating system, for the heterocycle being, there exists some extent finite-field effect in the molecule. And, the N—O bond in the heterocycle is the weakest one in BADDD molecule, easy to rupture.

Table 1　Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (×10^5 nm^2) of BADDD

atom	x	y	z	U_{eq}
O(1)	125(3)	7701(3)	3675(2)	51(15)
O(2)	1792(4)	2501(3)	323(16)	64(5)
N(1)	−4872(4)	1774(4)	3296(2)	52(6)
N(2)	−2241(4)	6173(3)	4112(18)	46(5)
N(3)	1029(4)	6244(3)	2529(17)	47(5)
N(4)	2162(4)	471(3)	−851(17)	44(5)
C(1)	−2743(4)	3813(4)	3233(2)	36(5)
C(2)	−689(4)	3890(4)	2240(19)	35(5)
C(3)	−391(4)	1761(4)	1059(2)	38(5)

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

Table 2　Bond lengths and bond angles of BADDD

bond	length / nm	bond	length / nm
O(1)—N(3)	1.360(2)	O(1)—N(2)	1.404(2)
O(2)—C(3)	1.353(2)	O(2)—N(4)	1.432(2)
N(1)—C(1)	1.341(3)	N(1)—H(1)	0.92(3)
N(1)—H(2)	0.85(2)	N(2)—C(1)	1.310(3)
N(3)—C(2)	1.303(3)	N(4)—C(3)_1	1.270(3)
C(1)—C(2)	1.431(3)	C(2)—C(3)	1.457(3)
C(3)—N(4)_1	1.270(3)		
bond	**angle/(°)**	**bond**	**angle/(°)**
N(3)—O(1)—N(2)	111.10(15)	C(3)—O(2)—N(4)	115.31(16)
C(1)—N(1)—H(1)	118.8(17)	C(1)—N(1)—H(2)	116.9(17)
H(1)—N(1)—H(2)	123(3)	C(1)—N(2)—O(1)	105.31(16)
C(2)—N(3)—O(1)	105.69(16)	C(3)_1—N(4)—O(2)	115.56(17)
N(2)—C(1)—N(1)	123.54(19)	N(2)—C(1)—C(2)	107.97(17)
N(1)—C(1)—C(2)	128.48(18)	N(3)—C(2)—C(1)	109.92(16)
N(3)—C(2)—C(3)	121.67(18)	C(1)—C(2)—C(3)	128.41(19)
N(4)_1—C(3)—O(2)	129.14(19)	N(4)_1—C(3)—C(2)	117.51(19)
O(2)—C(3)—C(2)	113.35(19)		

Table 3　Hydrogen bond lengths and angles of BADDD

donor	H	acceptor	D-H/nm	H···A/nm	D···A/nm	D-H···A/(°)
N(1)	H(1)	N(2)	0.092(3)	0.218(3)	0.3062(3)	161(2)
N(1)	H(2)	N(4)_2	0.085(2)	0.236(2)	0.2933(3)	125(2)
N(1)	H(2)	N(3)_3	0.085(2)	0.253(3)	0.3071(3)	122.1(19)

Note: N(4)_2 and N(3)_2 are in the other BADDD molecule.

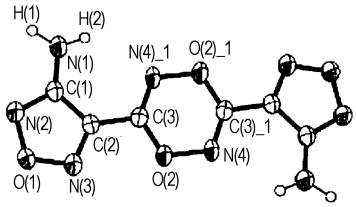

Fig. 1 Molecular structure of BADDD

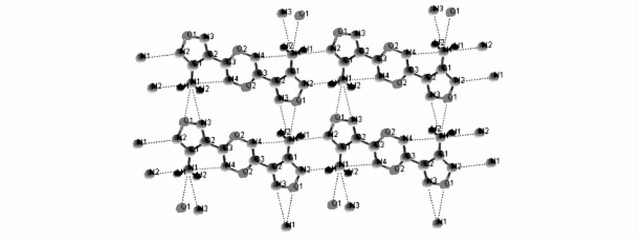

Fig. 2 2D connections of BADDD molecules in a single layer of the crystal

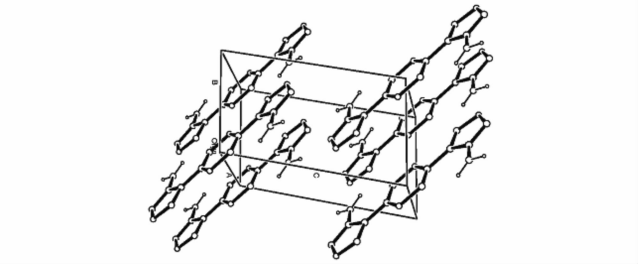

Fig. 3 3D packing of BADDD molecules in crystal

The intermolecular non-bond distance (see in Table 3) between H(1) and N(2) is 0.2178 nm, is shorter than that of the sum Vander Vales radius (0.275 nm) of H and N. It shows that there exists intermolecular hydrogen bonds in BADDD molecule. The intramolecular non-bond distance between H(2) and N(4) is 0.2359 nm; between H(2) and N(3) is 0.2532 nm, shorter than that of the sum Vander Vales radius of H and N, respectively, in the normal hydrogen bond range (0.25 – 0.30 nm)[7]. It shows there exsits intramolecular hydrogen bonds between BADDD molecules. BADDD molecules relate with each other by hydrogen bonds.

The packing of BADDD molecules in the crystal (see in Fig. 3) shows that the planar BADDD molecules are arranged by layer and layer like graphite and the distance between layers is 0.316 nm, longer than that of normal hydrogen bond length. It shows that there are no hydrogen bonds between layers, only Vander Vales effect. Although being the intramolecular hydrogen bonds, the action-force between layers is not strong, so, the packing of BADDD molecules is not well dense, and the density is 1.783 g · cm^{-3}.

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Especial note: The crystal structure of BADDD has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number CCDC 621981.

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3,6-二(3′-氨基呋咱-4-基)-1,4-二氧杂-2,5-二氮杂环己-2,5-二烯的晶体结构

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摘要: 制备并表征了化合物 3,6-二(3′-氨基呋咱-4-基)-1,4-二氧杂-2,5-二氮杂环己-2,5-二烯(BADDD)。其晶体结构参数为: M_r = 252.17, 三斜晶系, *P*-1 空间群, a = 0.48616 (10) nm, b = 0.5237 (2) nm, c = 0.97076 (19) nm, α = 102.25(3)°, β = 93.631(17)°, γ = 101.88 (2)°, V = 0.23489 (12) nm^3, Z = 1, D_c = 1.783 g · cm^{-3}, λ (MoKα) = 0.071073 nm, μ(MoKα) = 0.153 mm^{-1}, F(000) = 128, T = 294 (2) k, R_1 = 0.0351 and wR_2 = 0.0875。BADDD 分子由两个氨基呋咱环和一个由两个 O 原子,两个 N 原子和两个 C 原子组成的六元杂环构成。分子具有中心对称性。

关键词: 物理化学; 高能化合物; 3,6-二(3′-氨基呋咱-4-基)-1,4-二氧杂-2,5-二氮杂环己-2,5-二烯; 晶体结构

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