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Crystal Structure of 3-Amino-4-acylaminoximinofurazan

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Abstract: The single crystal of 3-amino-4-acylaminoximinofurazan (AAOF) was cultured using the mixed solvent of water and ethanol. The structure was characterized by 4-circle single-crystal X-ray diffraction analysis, IR and elemental analysis. The results indicate that the crystal belongs to monoclinic, space group $P21/C$ with the crystallographcial parameters of a = 0.7651(3) nm, b = 1.1702(3) nm, c = 1.9216(10) nm, M_r = 143.12, β = 96.47(4)°, V = 1.7095(12) nm^3, Z = 4, D_c = 1.668 g·cm^{-3}, $F(000)$ = 888. The AAOF molecule is good planar. There are inter- and intramolecular hydrogen bonds in the crystal.

Key words: physical chemistry; energetic compound; 3-amino-4-acylaminoximinofurazan (AAOF); crystal structure

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1 Introduction

Many studies show that furazan ring is a perfect structure unit for constructing new high-energy-density material compound[1-3]. 3-Amino-4-acylaminoximinofurazan (AAOF) is an important precursor of synthesizing new furazano (furoxano) energetic compound. Energetic compounds such as 3,4-bis (aminofurazano) furoxan (BAFF) and its isomer can be synthesized through diazotization, 1,3-diploar ring-closure reaction and bimolecular bond-linked reaction[4] from AAOF. The detonation velocity and detonation pressure of AAOF calculated by the BKW code is 7.98 km·s^{-1} and 23.3 GPa, respectively. So, it is significant to study the chemicophysical properties of AAOF.

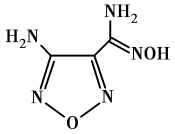
2 Experiment and results

2.1 Apparatus

The crystal structure of AAOF was determined by a ACD4 type 4-circle single-crystal X-ray diffraction instrument. The determination of Melting point was conducted by a Metller Toledo FP900 type thermal system. IR and elemental analysis were carried out on a Nicolet 800 type IR spectrometer (KBr) and an EA1108 type elemental analysis instrument, respectively.

2.2 Single crystal culture

1.0 gram AAOF was dispersed and whole dissolved in 10.0 ml mixed solvent of water and ethanol (V/V = 1.0/1.0) at room temperature. The solution was filtrated. Liquid filtrated was gleaned, put into fostering utensil and left to evaporate the solvent gradually, and the colorless single crystals of AAOF were obtained. m.p. = 189.3 – 192.2 ℃. Anal. calcd for $C_3N_5O_2H_5$: C 25.17, H 3.50, N 48.95; found C 24.93, H 3.35, N 48.74. IR(KBr, cm^{-1}) ν: 3441, 3386, 3333(—NH_2); 3200(N—OH); 1669, 1006 (furazano ring). Its structure is shown in Scheme 1.



Scheme 1 Structure of AAOF

2.3 Crystal structure resolution

The single crystal with dimensions of 0.15 mm × 0.20 mm × 0.23 mm was mounted on the X-ray single-crystal diffraction instrument, radiated by Mo Kα radiation (λ = 0.071073nm) homochromized with graphite, scanned by $\omega/2\theta$ mode (2.04° ≤ θ ≤ 23.97°) at 293 K. Within the range of $-8 \leqslant h \leqslant 8, 0 \leqslant k \leqslant 13, 0 \leqslant l \leqslant 21$, a total of 2837 reflections were collected with 2644 unique ones (R_{int} = 0.0000), of which 944 with $I > 2\sigma(I)$ were considered as observed. The coordinates of non-hydrogen were obtained by direct method, and of 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 molecular relative weight of

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AAOF is 143.12. The crystal belongs to monoclinic, space group $P21/C$ with crystallographic parameters of a = 0.7651(3) nm, b = 1.1702(3) nm, c = 1.9216(10) nm, M_r = 143.12, β = 96.47(4)°, V = 1.7095(12) nm^3, Z = 4, D_c = 1.668 g · cm^{-3}, $F(000)$ = 888. The maximum peak and the minimum peak of the final structure R_1 = 0.0672, wR_2 = 0.1571 on the Fourier map were 290 e · nm^{-3} and −389 e · nm^{-3}, respectively, of which, $w = 1/[S^2(F_0)^2 + (0.1048P)^2 + 0.0000P]$, $P = (F_0^2 + 2F_c^2)/3$. The crystal structure resolution and correction were processed with the SHELX97 (Sheldrick, 1990) and SHELX97 (Sheldrick, 1997) program packages, repectively. The non-hydrogen coordinates and thermal parameters are listed in Table 1. The bond lengths and bond angles are listed in Table 2. The hydrogen bond lengths and bond angles can be seen in Table 3. Figs. 1,2 and 3 show the molecular structure and three different space configuration, hydrogen bonds of AAOF molecules and the 3D packing of AAOF molecules, respectively.

3 Discussion

The plane equation of the 5-membered furazan ring [C(5), C(6), N(7), O(8) and N(9)] in AAOF molecule calculated by least-squares method is 0.3423(0.0249)x + 9.7721(0.0215)y + 10.3717(0.0530)z = 15.783(0.0410) with the deviation being 0.00056 nm. There are 18π electrons in AAOF molecule in according with HÜckl 4n + 2 rule. From Fig. 1, AAOF molecule is well co-planar.

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

atom	x	y	z	U_{eq}	atom	x	y	z	U_{eq}
N(1)	16362(8)	5967(6)	9121(3)	33(2)	C(17)	18407(8)	9699(6)	8776(3)	21(2)
N(2)	14910(7)	7018(6)	8172(3)	28(2)	N(18)	18300(7)	10284(5)	8202(2)	26(1)
O(4)	16664(7)	7168(5)	8015(3)	33(1)	O(19)	20070(6)	10504(4)	8026(2)	27(1)
C(5)	13195(9)	6166(6)	8965(3)	23(2)	N(20)	19823(9)	9318(7)	9165(3)	38(2)
C(6)	11495(9)	6534(6)	8689(3)	22(2)	C(21)	9830(9)	2882(6)	8929(3)	23(2)
N(7)	10303(8)	6163(6)	9067(3)	34(2)	C(22)	8158(8)	3258(6)	8617(3)	22(2)
O(8)	11284(6)	5552(4)	9614(2)	39(1)	N(23)	6927(7)	2845(6)	8968(3)	34(2)
N(9)	13072(7)	5590(6)	9525(3)	29(2)	O(24)	7868(6)	2205(4)	9516(2)	37(1)
N(10)	11057(12)	7176(8)	8069(4)	37(2)	N(25)	9650(7)	2247(5)	9486(3)	29(2)
C(11)	16668(9)	9469(6)	9004(3)	21(2)	N(26)	7772(10)	3874(6)	8021(3)	32(2)
C(12)	14962(8)	9845(6)	8716(3)	20(2)	C(27)	11588(9)	3116(6)	8709(3)	24(2)
N(13)	13779(7)	9425(6)	9082(3)	31(2)	N(28)	11536(7)	3747(5)	8157(3)	25(1)
O(14)	14729(6)	8794(4)	9618(2)	39(1)	O(29)	13280(6)	3937(5)	7977(2)	30(1)
N(15)	16483(7)	8826(5)	9559(3)	33(2)	N(30)	13018(8)	2672(7)	9075(3)	36(2)
N(16)	14517(9)	10440(6)	8111(3)	30(2)	C(2)	14944(9)	6403(6)	8746(3)	25(2)

Table 2 Bond lengths and bond angles for AAOF

bond	length / nm	bond	length / nm	bond	length / nm
N(1)—C(2)	0.1334(9)	N(1)—H(11)	0.090(6)	N(1)—H(303)	0.083(7)
N(2)—C(2)	0.1314(8)	N(2)—O(4)	0.1419(8)	O(4)—H(28)	0.068(5)
C(5)—N(9)	0.1282(8)	C(5)—C(6)	0.1415(9)	C(5)—C(2)	0.1474(10)
C(6)—N(7)	0.1302(9)	C(6)—N(10)	0.1416(10)	C(6)—H(23)	0.146(7)
N(7)—O(8)	0.1416(7)	O(8)—N(9)	0.1399(8)	N(10)—H(23)	0.053(6)
N(10)—H(12)	0.097(6)	C(11)—N(15)	0.1326(8)	C(11)—C(12)	0.1429(9)
C(11)—C(17)	0.1471(9)	C(12)—N(13)	0.1304(9)	C(12)—N(16)	0.1364(9)
N(13)—O(14)	0.1402(7)	O(14)—N(15)	0.1360(8)	N(16)—H(161)	0.087(6)
N(16)—H(162)	0.084(6)	C(17)—N(18)	0.1293(8)	C(17)—N(20)	0.1322(9)
N(18)—O(19)	0.1455(7)	O(19)—H(10)	0.092(12)	N(20)—H(14)	0.082(6)
N(20)—H(9)	0.090(6)	C(21)—N(25)	0.1322(8)	C(21)—C(22)	0.1420(9)
C(21)—C(27)	0.1480(10)	C(22)—N(23)	0.1311(9)	C(22)—N(26)	0.1358(9)
N(23)—O(24)	0.1420(7)	O(24)—N(25)	0.1372(7)	N(26)—H(261)	0.064(6)
N(26)—H(262)	0.100(7)	C(27)—N(28)	0.1291(8)	C(27)—N(30)	0.1336(9)
N(28)—O(29)	0.1433(8)	O(29)—H(22)	0.084(8)	N(30)—H(301)	0.075(6)
N(30)—H(302)	0.101(10)				

Table 2 (continued)

bond	angle/(°)	bond	angle/(°)	bond	angle/(°)
C(2)—N(1)—H(11)	110(3)	C(2)—N(1)—H(303)	123(5)	H(11)—N(1)—H(303)	127(6)
C(2)—N(2)—O(4)	108.4(5)	N(2)—O(4)—H(28)	115(5)	N(9)—C(5)—C(6)	108.8(6)
N(9)—C(5)—C(2)	119.6(6)	C(6)—C(5)—C(2)	131.5(6)	N(7)—C(6)—C(5)	111.3(6)
N(7)—C(6)—N(10)	122.0(7)	C(5)—C(6)—N(10)	126.6(7)	N(7)—C(6)—H(23)	117(3)
C(5)—C(6)—H(23)	126(3)	N(10)—C(6)—H(23)	21(2)	C(6)—N(7)—O(8)	103.6(5)
N(9)—O(8)—N(7)	109.7(5)	C(5)—N(9)—O(8)	106.6(5)	C(6)—N(10)—H(23)	84(8)
C(6)—N(10)—H(12)	107(3)	H(23)—N(10)—H(12)	116(10)	N(15)—C(11)—C(12)	108.1(6)
N(15)—C(11)—C(17)	121.7(6)	C(12)—C(11)—C(17)	130.2(6)	N(13)—C(12)—N(16)	122.0(6)
N(13)—C(12)—C(11)	109.5(6)	N(16)—C(12)—C(11)	128.1(7)	C(12)—N(13)—O(14)	105.1(5)
N(15)—O(14)—N(13)	111.0(5)	C(11)—N(15)—O(14)	106.2(5)	C(12)—N(16)—H(161)	115(4)
C(12)—N(16)—H(162)	101(4)	H(161)—N(16)—H(162)	141(6)	N(18)—C(17)—N(20)	129.0(7)
N(18)—C(17)—C(11)	112.2(6)	N(20)—C(17)—C(11)	118.8(6)	C(17)—N(18)—O(19)	108.7(5)
N(18)—O(19)—H(10)	93(9)	C(17)—N(20)—H(14)	115(4)	C(17)—N(20)—H(9)	111(4)
H(14)—N(20)—H(9)	134(5)	N(25)—C(21)—C(22)	110.1(6)	N(25)—C(21)—C(27)	121.0(6)
C(22)—C(21)—C(27)	128.8(6)	N(23)—C(22)—N(26)	121.9(6)	N(23)—C(22)—C(21)	109.6(6)
N(26)—C(22)—C(21)	128.4(7)	C(22)—N(23)—O(24)	104.0(5)	N(25)—O(24)—N(23)	111.9(5)
C(21)—N(25)—O(24)	104.4(5)	C(22)—N(26)—H(261)	103(6)	C(22)—N(26)—H(262)	107(4)
H(261)—N(26)—H(262)	115(8)	N(28)—C(27)—N(30)	127.0(7)	N(28)—C(27)—C(21)	113.3(6)
N(30)—C(27)—C(21)	119.7(6)	C(27)—N(28)—O(29)	110.1(5)	N(28)—O(29)—H(22)	99(7)
C(27)—N(30)—H(301)	119(5)	C(27)—N(30)—H(302)	135(6)	H(301)—N(30)—H(302)	102(7)
N(2)—C(2)—N(1)	126.9(7)	N(2)—C(2)—C(5)	114.2(6)	N(1)—C(2)—C(5)	118.9(6)

Table 3 Hydrogen bond lengths and bond angles for AAOF

donor	H	acceptor	D-H/nm	H···A/nm	D···A/nm	D-H···A/(°)
N(26)	H(261)	N(28)	0.0643	0.2437	0.2886	126.51
N(26)	H(262)	O(29)	0.100	0.2552	0.3429	146.38
N(26)	H(262)	N16	0.100	0.2696	0.3209	112.15
N(20)	H(14)	N(13)	0.0822	0.2301	0.3051	152.11
N(10)	H(23)	O(19)	0.0525	0.2453	0.2932	153.32
N(10)	H(12)	O(4)	0.0973	0.2619	0.3351	132.13
N(20)	H(9)	N(15)	0.0902	0.2342	0.2806	111.90
N(20)	H(9)	N(25)	0.0902	0.2353	0.3163	149.53
N(30)	H(301)	N(15)	0.0750	0.2428	0.3144	160.25
N(30)	H(302)	N(23)	0.1006	0.2035	0.3027	168.61
N(1)	H(11)	N(7)	0.0896	0.2265	0.3037	144.12
N(1)	H(303)	N(9)	0.0831	0.2387	0.3167	156.52
N(16)	H(161)	N(18)	0.0871	0.2297	0.2886	125.06
N(16)	H(161)	N(2)	0.0871	0.2574	0.3151	124.62
N(16)	H(162)	O(19)	0.0845	0.2546	0.3389	175.34
O(4)	H(28)	O(29)	0.0681	0.2143	0.2819	171.65
O(4)	H(28)	N(28)	0.0681	0.2694	0.3329	156.19
O(29)	H(22)	N(18)	0.0841	0.2308	0.2909	128.73

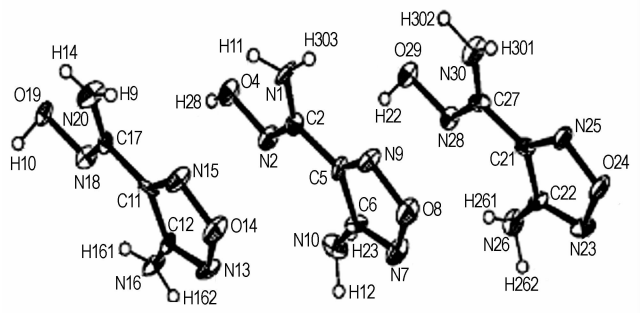

Fig. 1 Molecular structure of AAOF

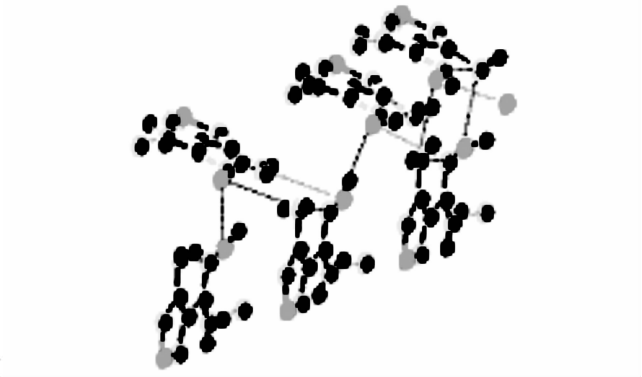

Fig. 2 Hydrogen bonds of AAOF molecule

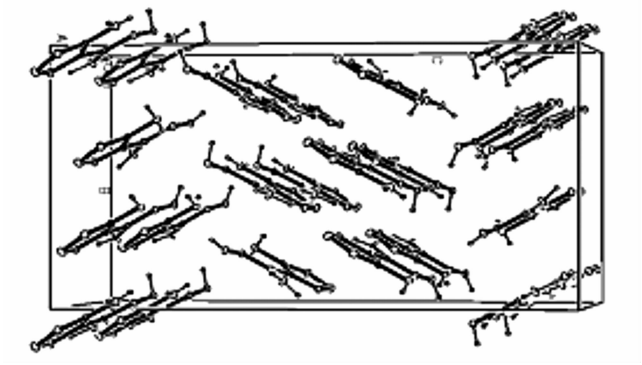

Fig. 3 Packing arrangement of AAOF molecule in a unit cell

From Fig. 1 and Table 2, all bonds and angles in AAOF molecule are in the natural range. In AAOF molecule structure, the bonds and angles of furazan ring are

similar to those of the other furazan derivatives. The length of C—N bond of N(10) in amino group bonded with C(6) in furazan ring is 0.142 nm approaching that of the normal C—N single bond (0.147 nm). It shows that the finite-field characteristic of this part in AAOF molecule is well obvious. The length of C—N bond of N(1) in amino group bonded with C(2) in oximino group is 0.133 nm approaching that of the normal C═N (0.132 nm)[5], showing that there is the well strong conjugating characteristic. The length of N═O double bond in oximino group is 0.142 nm (8) approaching that of the normal N—O single bond (0.144nm)[6]. The length of double bond in AAOF molecule increases, of single bond decreases. These demonstrate that the conjugating characteristic of AAOF molecule is stronger than that of finite-field.

The plane equation of the 5-membered furazan ring [C(5), C(6), N(7), O(8) and N(9)] in AAOF molecule calculated by least-squares method is $0.3423(0.0249)x + 9.7721(0.0215)y + 10.3717(0.0530)z = 15.783(0.0410)$ with the deviation being 0.00056 nm. There are 18π electrons in AAOF molecule in according with HÜckl 4n + 2 rule. From Fig.1, AAOF molecule is well co-planar.

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From Table 3 and Fig. 2, the hydrogen bond effective in AAOF molecule is faintish. The non-bond distance of H…O and H…N between molecules is less than that of the sum of Vander vales radius (0.272 nm) and (0.275 nm)[7], respectively, and is partly in the range of that of the normal hydrogen bond (0.25 – 0.30 nm)[8]. These show that there are two kinds of N—H…O and N—H…N hydrogen bonds between molecules. AAOF molecules relate with each other by hydrogen bonds. From Fig. 3, the arrangement of AAOF molecules in the crystal is layered. But there are space-baffling effectives of oximino and amino groups, so, the packing of AAOF molecules in the crystal is not dense, and the density of AAOF crystal is 1.668 g · cm^{-3}.

4 Conclusion

The single crystal of 3-amino-4-acylaminoximinofurazan (AAOF) was cultured using the mixed solvent of water and ethanol ($V/V = 1.0/1.0$). The structure was characterized by 4-circle single-crystal X-ray diffraction, IR and elemental analysis. Its molecular relative mass is 143.12. The crystal is yellow-golden, monoclinic with space group $P21/c$ and the density is 1.668 g · cm^{-3}.

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3-氨基-4-酰胺肟基呋咱的晶体结构

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摘要: 从水和乙醇的混合溶剂中培养出了 3-氨基-4-酰胺肟基呋咱(AAOF)的单晶,用四圆单晶 X-射线衍射仪、IR 和元素分析对其结构进行了表征。结果表明,AAOF 晶体属单斜晶系,空间群 $P21/C$。晶体学参数为: M_r = 143.12, a = 0.7651(3) nm, b = 1.1702(3) nm, c = 1.9216(10) nm, β = 96.47(4)°, V = 1.7095(12) nm^3, Z = 4, D_c = 1.668 g·cm^{-3}, $F(000)$ = 888。AAOF 分子平面性好,晶体中存在分子内和分子间氢键。

关键词: 物理化学; 含能化合物; 3-氨基-4-酰胺肟基呋咱(AAOF); 晶体结构

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Synthesis Improvement of 5-Amino-3-nitro-1,2,4-triazole (ANTA)

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Abstract: 5-Amino 3-nitro-1,2,4-triazole (ANTA) as well as its intermediate was synthesized from 3,5- diamino-1,2,4-triazole after diazotization, neutralization and reduction. Its structure was characterized by IR, MS, ^{1}H NMR and elemental analysis. In addition, the effects of reaction temperature on yield and purity were investigated. The synthetic procedures of ANTA were optimized with the overall yield to be 64%, and purity to be 98%.

Key words: organic chemistry; synthesis; purity; triazole

读者·作者·编者

2006 年火炸药新技术研讨会召开

由西安近代化学研究所火炸药燃烧国防重点实验室、中国兵工学会火炸药专业委员会、总装部火炸药技术专业组联合主办的 2006 年火炸药新技术研讨会于 2006 年 10 月 26 日至 28 日在深圳召开。本次会议共收录了 158 篇论文,来自全国从事含能材料研究、生产和使用及其相关领域的大学、研究所、工厂和公司的科技人员 100 余人参加了会议交流,主题覆盖了含能材料的各个领域。其中,HEDM、IHE、含能粘结剂、高氮化合物、高品质 RDX、温压炸药以及新材料新技术等的研究和应用引起了参会者的广泛关注。

从会议论文集和交流报告来看,CL-20、DNTF、FOX-7、ADN 等在推进剂中的应用研究已成为当今的研究热点之一,DNTF、FOX-7 在炸药中的应用研究也已有有益的探索; PBAMO、BAMO-AMMO、BAMO-THF、GAP 等含能粘结剂的合成及应用在火炸药中具有乐观的前景; 高品质 RDX 的制备和降感取得显著效果;纳米含能复合材料、毁伤增强型材料及破片、含能离子液体等新材料的探索研究悄然进行并取得一定进展; PBAMO 的一步合成、微反应器中芳烃硝化反应、分子烙印技术处理火炸药废水、原位聚合包覆 HMX、甲苯氟两相硝化一步合成 TNT、TNT 选择性氧化等新方法、新技术,以及一些分析检测新技术如光谱法测定燃烧火焰温度等正在拓展含能材料研究新领域并推动学科发展。此外,炸药安全和爆轰性能研究的独特方法,也为含能材料的表征和评估注入了新的活力。

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