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Article

α- and *β*-FOX-7, Polymorphs of a High Energy Density Material, Studied by X-ray Single Crystal and Powder Investigations in the Temperature Range from 200 to 423 K

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The α–*β* phase transition in the novel energetic material 1,1-diamino-2,2-dinitroethylene, $C_2H_4N_4O_4$ (FOX-7), has been studied by single-crystal X-ray investigations at five different temperatures over the 200–393 K range. In these investigations, the positions of the hydrogen atoms were experimentally determined without any geometric constraints. In addition, X-ray powder investigations using the Guinier technique have been performed to characterize the *β*-phase up to 423 K. The α–*β* phase transition at 389 K is first order, shows a discontinuous increase of the molar volume and entropy ($\Delta V = 1.75$ cm^3/mol, X-ray investigation; $\Delta S = 1.5$ cal/K mol, DSC analysis), and can be classified as displacive. The hitherto unknown structure of *β*-FOX-7 was solved at 393 K and showed simple structural relations to the α-polymorph. The characteristic bonding in wave-shaped layers is now found for *β*-FOX-7 ($P2_12_12_1$, $z = 4$, $a = 6.9738(7)$ Å, $b = 6.635(1)$ Å, $c = 11.648(2)$ Å, 393 K), as well as for α-FOX-7 ($P2_1/n$, $z = 4$, $a = 6.9467(7)$ Å, $b = 6.6887(9)$ Å, $c = 11.350(1)$ Å, $\beta = 90.143(13)°$, 373 K). Interestingly, whereas the intramolecular C–C, C–N, N–O, and N–H bond distances remain nearly unchanged for both polymorphs over the whole temperature range from 200 to 393 K, the two nitro groups deviate strongly from the molecular plane formed by the two carbon and two amino nitrogen atoms. In α-FOX-7 at 373 K, the nitro groups are twisted –47 and +6° with respect to the carbon–carbon bond, but in *β*-FOX-7 at 393 K, these twist angles are changed to –36 and +20°. Within the layers, the FOX-7 molecules show strong *π*-conjugation and extensive intra- and intermolecular hydrogen bonding. In this investigation, we have been able to show that α- and *β*-FOX-7 build up different nets of intermolecular hydrogen bonds. In α-FOX-7, each oxygen atom of the nitro groups is involved in two hydrogen bonds resulting in two intramolecular and six intermolecular hydrogen bonds. But in *β*-FOX-7 this coordination changes, and half of the oxygen atoms build up two and the other half build up three hydrogen bonds leading to two intramolecular and eight intermolecular hydrogen bonds. The average intermolecular hydrogen bond distance increases slightly from 2.31 Å in α-FOX-7 to 2.52 Å in *β*-FOX-7. The C–NO_2 bonds are of particular interest because they are referred to as the detonation trigger. It has been suggested that these bonds could be strengthened by the extensive intermolecular hydrogen bonding within the layers in both polymorphs. Such bond strengthening via cooperative effects was proposed in earlier DFT calculations on FOX-7 and may be one key to understanding its low sensitivity and high activation energy to impact.

Introduction

FOX-7, 1,1-diamino-2,2-dinitroethylene, $C_2H_4N_4O_4$, is a novel high explosive which combines two important properties: high performance and low sensitivity. This compound may be described as a push−pull ethylene with two donor amino groups ("head") and two withdrawing nitro groups ("tail") within its molecular framework.[1] Its crystal structure was solved independently by single-crystal investigations[2,3] and showed a structure consisting of molecules with strong *π*-conjugation. The dipolar FOX-7 molecules are packed "head-to-tail" forming wave-shaped layers with extensive

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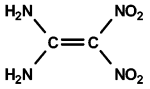
intra- and intermolecular hydrogen bonding within the layers and weak van der Waals interactions between the layers.

Until now, considerable experimental work has been performed on FOX-7 (I)[4,5] to establish the properties of this novel explosive in comparison to such materials as RDX (II) or HMX (III), which are among the currently most widely used explosives and propellants. Interestingly, although compounds (I$-$III) possess the same molecular ratio of 2:4:4:4 C/H/N/O,[6] they show quite different properties.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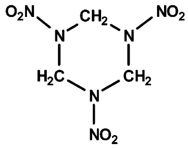
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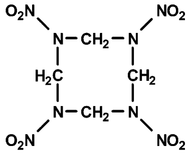
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Particularly important is the much higher activation energy for decomposition ($E_a \approx 58$ kcal/mol in the range of 210$-$250 °C)[7] of I in comparison with that of II ($E_a \approx 40$ kcal/mol)[8$-$10] and III ($E_a \approx 35$ kcal/mol).[11] In addition, the solution behavior of compounds I$-$III in polar solvents is also very different. An inspection of the formulas of I$-$III shows their quite different molecular frameworks. Although compounds I$-$III consist of very polar nitro groups with a carbon to nitro group ratio of 1:1, the general bonding situation in I is considerably different from that in II and III. In I, hydrogen is bonded to nitrogen, and the nitro groups are bonded to carbon. In II and III, these bonding functions are interchanged. Therefore strong intra- and intermolecular hydrogen bonds can be built up in FOX-7 (I) between the hydrogen atoms of the polar amino groups and the oxygen atoms of the polar nitro groups. But in RDX (II) and HMX (III), where hydrogen is present in methylene groups which show very low polarity, formation of strong intra- and intermolecular hydrogen bonds is difficult.

It has been pointed out by Bemm and co-workers,[1] that the molecular packing built up by the extensive intermolecular hydrogen bonding within the layers and the van der Waals interactions between them, is one reason for the unique properties of FOX-7. It has also been stated, that explosives with strong intermolecular hydrogen bonding usually have lower sensitivities to friction and impact. In addition, the $C-NO_2$ bonds are referred to as the detonation trigger in FOX-7.[12] Interestingly, from density functional theory (DFT) calculations, it was found that such hydrogen bonds make the reactive $C-NO_2$ bonds stronger via cooperative effects of the intermolecular interactions, and therefore, they lower the sensitivity this explosive.[12]

The key to understanding the unique properties of FOX-7 (e.g., its high activation energy for detonation) lies in obtaining precise knowledge of both the atomic and molecular arrangements. Therefore a series single-crystal structural investigations were undertaken with various temperatures from 200 to 393 K. In these investigations, the positions of the hydrogen atoms were also determined without any geometric constraints to characterize the intermolecular hydrogen bonding.

Two phase transitions in FOX-7 have been identified, using X-ray powder diffraction measurements and thermal analyses, in earlier experiments.[4,5] The first phase transition ($\alpha-\beta$) takes place at 389 K and is fully reversible.[4] Lattice parameters and thermal expansion data have been published for α-FOX-7 between 193 and 373 K.[4] For β-FOX-7, only the lattice parameters at 403 K, the thermal expansion coefficients and the space group $P2_12_12_1$ were presented, as well as a structural plot of the $b-c$ plane.[4] The positional parameters of the constituent atoms were not given. A second phase transition ($\beta-\gamma$) occurs at 446 K;[4] however, in contrast to the $\alpha-\beta$ phase transition, this phase transition is not reversible.

In this study, single-crystal X-ray investigations are reported on α-FOX-7 at 200, 298, 333, and 373 K. In addition, the crystal structure of β-FOX-7 at 393 K was also solved using single-crystal X-ray diffraction. Unfortunately, measurements at temperatures higher than 400 K could not be performed on our four-circle diffractometer. Therefore, X-ray powder investigations using the Guinier technique were undertaken at temperatures up to 433 K to obtain additional structural information on β-FOX-7 until it becomes γ-FOX-7 at 446 K.[5] The Gunier diffractograms were analyzed by the Rietveld technique with the program FullProf.[13]

Experimental Section

Single-Crystal Preparation. From powdered crude material dissolved in warm DMF or DMSO, single crystals of α-FOX-7 were prepared by slow cooling. The crystals obtained were then vacuum-dried; small crystals with well-developed faces were selected, and their quality was checked with X-ray rotation and Weissenberg photographs.

Powder Preparation. For X-ray powder experiments, finely ground material was carefully sieved through a very fine sieve (140 mesh) to decrease the effects of preferred orientation.

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Table 1. Single-Crystal Crystallographic Data[a] for I−V

	I	II	III	IV	V
T (K)	200	298	333	373	393
phase	α	α	α	α	β
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_12_12_1$
a (Å)	6.9209(7)	6.9340(7)	6.9414(7)	6.9467(7)	6.9738(7)
b (Å)	6.5515(9)	6.6228(8)	6.6534(9)	6.6887(9)	6.6350(10)
c (Å)	11.2741 (14)	11.3119(13)	11.3316(13)	11.3500(13)	11.6475(16)
β (deg)	90.060(14)	90.065(13)	90.08 (1)	90.143 (13)	90
V (Å^3)	511.19(11)	519.47(10)	523.34(11)	527.37(11)	538.94(12)
Z	4	4	4	4	4
D_{calcd} (g cm^{-3})	1.924(1)	1.894(1)	1.880(1)	1.865(1)	1.825(1)
reflns measured	4257	4348	4397	4496	4516
reflns unique	1111	1135	1147	1172	1182
$R(\sigma)$	0.0478	0.0583	0.0588	0.0605	0.0341
$R(F_o)$	0.0361	0.0402	0.0 410	0.0542	0.0359
$R_w(F_o^2)$	0.0926	0.0995	0.0977	0.1435	0.0878
GOF	1.080	1.041	1.065	1.069	1.019

[a]Standard deviations in parentheses.

Single-Crystal X-ray Diffraction Experiments. A FOX-7 single crystal was measured on a Stoe-IPDS diffractometer with Mo Kα radiation (graphite monochromator, $\lambda = 0.71073$ Å) applying the image plate technique. A yellow single-crystal block of α-FOX-7 with dimensions of $0.44 \times 0.36 \times 0.25$ mm^3 was investigated in the θ range from 3.5 to 27.8° ($d(hkl)$ range from 10.679 to 0.753 Å), and 5000 reflections were used for the cell measurement. The temperature of the single crystal was controlled by a Oxford cryosystem apparatus with an upper temperature limit of 400 K. About 4300 data (Table 1) were collected at 200, 298, 333, 373 K for the α-phase and at 393 K for the β-phase. The reflection range was $-8 < h < 8$, $-8 < k < 8$, and $-14 < l < 14$, and after they were merged, about 1100 unique reflections (Table 1) remained. The heated crystal of the β-phase was retransformed into the α-phase, and after the crystal had cooled, the clear and transparent crystal was measured again at 293 K to check the crystal quality. The single-crystal structural data were obtained using Stoe-IPDS software and the *SHELXL*-97 program package.[14] The thermal parameters of the non-hydrogen atoms were refined anisotropically, and those of the hydrogen atoms were refined isotropically. The positions of the hydrogen atoms were experimentally derived from difference Fourier analyses and were refined without any geometric constraints.

The crystallographic data of the single-crystal refinement for α-FOX-7 at 200, 298, 333, and 373 K and for β-FOX-7 at 393 K are summarized in Table 1. Atomic coordinates and thermal displacement parameters are presented in Tables 3 and 4 for α-FOX-7 at 373 K and β-FOX-7 at 393 K, respectively. The atomic coordinates and thermal displacement parameters for α-FOX-7 at 200, 298, and 333 K are summarized as Supporting Information. Selected interatomic distances are shown in Table 6. It is well-known that intramolecular bond distances in structures with high anisotropic displacement parameters are underestimated.[15−17] Therefore these distances were corrected by calculation of the thermal motion tensors T, L, and S[15−17] using the program THMA11[18,19] and are summarized in Table 7. Interatomic angles are shown in Table 8. Numbering of the atoms and the atomic coordinates of α-FOX-7 are presented here in accordance with those of Bemm and Östmark[2]

Table 2. Crystallographic Data[a] for VI−VII Obtained from Powder Investigations

	VI	VII
T (K)	403	423
phase	β	β
cryst syst	orthorhombic	orthorhombic
space group	$P2_12_12_1$	$P2_12_12_1$
a (Å)	6.972(2)	6.974(2)
b (Å)	6.663(2)	6.675(2)
c (Å)	11.666(4)	11.673(4)
V (Å)^3	541.9(4)	543.4(4)
Z	4	4
D_{calcd} (g cm^{-3})	1.83(1)	1.84(1)
R_w	0.1000	0.0999
R_{wp}	0.1230	0.1240

[a] Standard deviations in parentheses.

X-ray Powder Experiments. Investigations were performed on a Huber G644 Guinier diffractometer with Mo Kα1 radiation ($\lambda = 0.7093$ Å) (quartz monochromator) in Lindemann capillaries (0.5 mm diameter) sealed under vacuum. The angle calibration of the diffractometer was performed with electronic grade germanium ($a = 5.6575$ Å). In the 2θ range between 6 and 36° with an increment of 0.04°, 750 data points were collected with a counting time of 10 s for each increment. In this manner, the diffractograms showed a very low signal-to-noise ratio. The heating and cooling cycles were performed with a Huber heating attachment. The temperature was calibrated by measuring Guinier diffractograms with NaCl under the same heating conditions as in the FOX-7 samples. For NaCl, the variation of the lattice parameter with temperature is tabulated.[20]

The Rietveld refinement parameters for β-FOX-7 at 403 and 423 K were analyzed with the program FULLPROF[13] and with soft constraints applied for the bond distances. The crystallographic data of the powder investigations are given in Table 2; atomic coordinates are given in Table 5, and interatomic distances are listed in Table 9. The Rietveld plot for the refinement at 423 K ($R_w = 0.0999$, $R_{wp} = 0.1240$) is shown in Figure 2.

DSC Analyses. A heating measurement of 10.27 mg of FOX-7 in a differential scanning calorimeter (DSC) from 55 to 140 °C

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Table 3. Atomic Coordinates and Thermal Displacement Parameters[a] (Å)^2 for α-FOX-7 at 373 K Obtained from a Single-Crystal Investigation[b]

atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
O11	0.0244(3)	0.0658(3)	0.74947(18)	0.0479(14)	0.0697(11)	0.0389(9)	0.0080(8)	−0.0091(8)	0.0067(9)	0.0521(6)
O12	0.0814(4)	0.2042(4)	0.5815(2)	0.0341(14)	0.0963(15)	0.0471(11)	0.0155(10)	0.0075(9)	−0.0015(10)	0.0592(6)
O21	−0.5159(4)	0.0658(3)	0.71276(15)	0.0448(13)	0.0762(13)	0.0364(8)	0.0022(7)	0.0015(8)	−0.0149(10)	0.0525(6)
O22	−0.3002(4)	0.1696(4)	0.8344(2)	0.0517(15)	0.0938(15)	0.0249(8)	−0.0035(8)	−0.0040(8)	−0.0054(10)	0.0568(6)
N11	−0.0348(4)	0.1491(3)	0.65798(17)	0.0367(13)	0.0509(11)	0.0298(10)	0.0019(7)	−0.0016(7)	0.0017(8)	0.0391(5)
N12	−0.3532(4)	0.1331(3)	0.73293(16)	0.0406(13)	0.0458(9)	0.0257(8)	0.0023(6)	−0.0003(8)	−0.0001(7)	0.0374(5)
C1	−0.2313(4)	0.1730(3)	0.6373(2)	0.0350(14)	0.0452(10)	0.0261(9)	0.0006(7)	0.0007(8)	0.0005(8)	0.0354(53)
C2	−0.31177(41)	0.2414(3)	0.52572(18)	0.0409(14)	0.0402(9)	0.0251(8)	−0.0011(7)	−0.0006(9)	0.0028(8)	0.0354(5)
N21	−0.2004(5)	0.2983(4)	0.4398(2)	0.0503(18)	0.0745(14)	0.0292(9)	0.0113(9)	0.0030(10)	0.0050(11)	0.0513(6)
H11	−0.244(8)	0.338(6)	0.369(4)							0.066(12)
H12	−0.065(9)	0.297(5)	0.455(4)							0.055(10)
N22	−0.4992(4)	0.2537(3)	0.51034(19)	0.0435(15)	0.0590(11)	0.0336(10)	0.0054(8)	−0.0061(11)	0.0011(10)	0.0454(6)
H21	−0.551(10)	0.296(6)	0.446(5)							0.075(13)
H22	−0.595(7)	0.208(5)	0.561(3)							0.050(9)

[a] ADPs are defined as $-2\pi^2\sum U_{ij}h_ih_ja_i{}^*a_j{}^*$. [b] Standard deviations in parentheses.

Table 4. Atomic Coordinates and Thermal Displacement Parameters (Å)^2 for β-FOX-7 at 393 K[a] Obtained from a Single-Crystal Investigation

atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
O11	0.8084(2)	0.3179(3)	0.71229(13)	0.0451(10)	0.0997(12)	0.0526(8)	−0.0015(7)	−0.0138(7)	0.0231(8)	0.0658(5)
O12	0.8285(2)	0.5064(3)	0.56336(14)	0.0316(11)	0.1295(15)	0.0618(9)	0.0118(9)	0.0096(6)	−0.0132(9)	0.0743(5)
O21	0.2609(2)	0.3628(3)	0.73342(12)	0.0347(9)	0.0960(11)	0.0484(8)	0.0053(7)	0.0104(6)	−0.0096(6)	0.0597(4)
O 22	0.5176(2)	0.4235(3)	0.82820(10)	0.0578(11)	0.0989(11)	0.0274(6)	−0.0025(6)	0.0001(6)	−0.0007(8)	0.0614(4)
N11	0.7333(3)	0.4206(3)	0.63770(11)	0.0305(10)	0.0643(9)	0.0340(6)	−0.0073(6)	−0.0031(6)	0.0030(7)	0.0429(4)
N12	0.4342(2)	0.4049(2)	0.73534(12)	0.0394(10)	0.0510(8)	0.0297(6)	−0.0003(6)	0.0044(5)	0.0024(6)	0.0401(4)
C1	0.5326(3)	0.4369(3)	0.63255(12)	0.0263(10)	0.0517(10)	0.0292(7)	−0.0012(6)	0.0010(6)	0.0020(7)	0.0357(4)
C2	0.4329(3)	0.4881(3)	0.52753(14)	0.0336(11)	0.0456(9)	0.0292(7)	−0.0029(7)	−0.0024(6)	−0.0000(7)	0.0361(4)
N21	0.5277(3)	0.5332(3)	0.43372(14)	0.0444(13)	0.0824(13)	0.0304(7)	0.0061(7)	−0.0008(7)	−0.0043(9)	0.0524(5)
H11	0.479(4)	0.559(4)	0.374(3)							0.080(9)
H12	0.642(9)	0.548(5)	0.438(4)							0.048(7)
N22	0.2454(3)	0.4892(3)	0.52365(18)	0.0323(10)	0.0851(12)	0.0424(8)	0.0028(8)	−0.0081(8)	0.0064(8)	0.0533(4)
H21	0.193(4)	0.527(4)	0.467(2)							0.060(7)
H22	0.180(4)	0.459(4)	0.584(3)							0.069(8)

[a] Standard deviations in parentheses.

Table 5. Atomic Coordinates for β-FOX-7 at 403 and 423 K[a] Obtained from Powder Investigations

	403 K			423 K		
atom	x/a	y/b	z/c	x/a	y/b	z/c
O11	0.806(3)	0.318(3)	0.712(3)	0.806(3)	0.318(3)	0.712(3)
O12	0.829(3)	0.507(3)	0.564(3)	0.829(3)	0.507(3)	0.564(3)
O21	0.260(3)	0.364(3)	0.733(3)	0.261(3)	0.364(3)	0.733(3)
O 22	0.518(3)	0.426(3)	0.829(3)	0.517(3)	0.424(3)	0.828(3)
N11	0.734(3)	0.421(3)	0.638(3)	0.733(3)	0.421(3)	0.638(3)
N12	0.434(3)	0.405(3)	0.735(3)	0.434(3)	0.406(3)	0.735(3)
C1	0.533(3)	0.437(3)	0.633(3)	0.533(3)	0.438(3)	0.632(3)
C2	0.432(3)	0.488(3)	0.527(3)	0.433(3)	0.489(3)	0.527(3)
N21	0.528(3)	0.533(3)	0.433(3)	0.527(3)	0.534(3)	0.434(3)
N22	0.245(3)	0.489(3)	0.524(3)	0.245(3)	0.490(3)	0.524(3)

[a] Standard deviations in parentheses.

Table 6. Selected Interatomic Distances (Å) for α- and β-FOX-7 at 200, 298, 333, 373, and 393 K[a] Obtained from Single-Crystal Investigations

	α				β
	200 K	298 K	333 K	373 K	393 K
C1−N11	1.389(3)	1.388(2)	1.393(3)	1.394(4)	1.405(3)
C1−N12	1.417(2)	1.417 (2)	1.412(2)	1.404(3)	1.397(2)
C1−C2	1.460(2)	1.458(2)	1.456 (2)	1.456(3)	1.447(2)
C2−N21	1.309(2)	1.308(2)	1.307(2)	1.304(4)	1.312(2)
C2−N22	1.320(3)	1.316(3)	1.317(3)	1.315(4)	1.308(3)
N11−O11	1.254(2)	1.250(2)	1.249(2)	1.248(3)	1.222(2)
N11−O12	1.243(2)	1.242(2)	1.241(3)	1.243(3)	1.231(2)
N12−O21	1.237(2)	1.235(2)	1.237(2)	1.238(3)	1.241(2)
N12−O22	1.238(2)	1.235(2)	1.234(2)	1.233(3)	1.234(2)
N21−H11	0.94(4)	0.95(4)	0.90(4)	0.90(6)	0.79(4)
N21−H12	1.02(3)	0.94(3)	0.93(3)	0.95(5)	0.80(3)
N22−H21	0.89(3)	0.91(4)	0.83(4)	0.86(6)	0.80(3)
N22−H22	0.88(3)	0.85(3)	0.86(3)	0.93(5)	0.86(3)

[a] Standard deviations in parentheses.

(heating rate of 2.0 K/min) is shown in Figure 3. From sixteen different DSC measurements, an averaged value of $\Delta H = 18.0 \pm 1.5$ J/g was obtained, which corresponds to $\Delta H = 2664$ J/mol = 636 cal/mole. The α−β phase transition occurs at 116 °C (389 K). From these data an entropy increase, $\Delta S = \Delta H/T = 1.6$ cal/K mol, is obtained.

Results and Discussion

For monoclinic α-FOX-7, single-crystal data were obtained at 200, 298, 333, and 373 K. At 389 K, α-FOX-7 is transformed into orthorhombic β-FOX-7. Therefore, the crystal with the β-phase was measured at 393 K, slightly higher than the transition temperature. An inspection of the *R* values in Table 1 shows that the structural refinement of the data for β-FOX-7 at 393 K leads to a very good $R(F_o)$ value (0.0359) and a good $R(F_o{}^2)$ value (0.0878). These values are substantially lower than those obtained with α-FOX-7 at 373 K ($R(F_o) = 0.0542$, $R(F_o{}^2) = 0.1435$, Table 1). At approximately 16 K below the equilibrium transition temperature, the structure of α-FOX-7 seems to be thermally stresssed. It is probable that the high mobility of the atoms very near to the phase transition leads to the higher *R* value. The measured crystal block of FOX-7 remained clear and yellow after the heating and cooling cycle through the phase transition. Cooling the crystal to room temperature leads again to good *R* values for the α-phase.

Table 7. *TLS* Correction[19] for Intramolecular Distances (Å) and Averaged Experimental Uncertainties σ (Å) for α- and β-FOX-7 at 200, 298, 333, 373, and 393 K Obtained from Single-Crystal Investigations

	α				β
	200 K	298 K	333 K	373 K	393 K
C1−N11	0.0034	0.0050	0.0059	0.0066	0.0128
C1−N12	0.0045	0.0069	0.0079	0.0086	0.0124
C1−C2	0.0031	0.0048	0.0056	0.0063	0.0100
C2−N21	0.0042	0.0064	0.0074	0.0080	0.0118
C2−N22	0.0033	0.0049	0.0057	0.0064	0.0120
N11−O11	0.0028	0.0044	0.0051	0.0057	0.0096
N11−O12	0.0040	0.0061	0.0071	0.0077	0.0118
N12−O21	0.0034	0.0052	0.0061	0.0068	0.0117
N12−O22	0.0030	0.0047	0.0055	0.0061	0.0086
σ_{av}	0.0022	0.0022	0.0024	0.0033	0.0023

Table 8. Selected Interatomic Angles (deg) for α- and β-FOX-7 at 200, 298, 333, 373, and 393 K[a] Obtained from Single-Crystal Investigations

	α				β
	200 K	298 K	333 K	373 K	393 K
N11−C1−N12	116.5	116.2	116.1	116.1	116.2
N11−C1−C2	124.1	124.4	124.2	123.8	122.2
N12−C1−C2	119.4	119.4	119.7	120.1	121.6
N21−C2−N22	118.2	118.3	118.2	118.1	118.3
N21−C2−C1	120.7	120.5	120.6	121.1	121.0
N22−C2−C1	121.1	121.2	121.2	120.8	120.7
O12−N11−O11	120.3	120.3	120.3	120.0	121.8
O12−N11−C1	119.1	119.0	119.0	119.1	118.1
O11−N11−C1	120.5	120.7	120.7	120.8	120.0
O21−N12−O22	121.7	121.7	121.4	121.0	119.8
O21−N12−C1	118.4	118.3	118.4	118.6	119.8
O22−N12−C1	119.9	120.0	120.2	120.4	120.3
C2 −N21−H11	121	123	122	124	124
C2 −N21−H12	115	117	117	117	119
C2 −N22−H21	120	118	117	123	119
C2 −N22−H22	123	124	122	128	120
H11−N21−H12	124	121	120	119	117
H21−N22−H22	116	118	120	109	121

[a] Experimental uncertainties: ∠ C, N, O = ± 0.2°, ∠ C, N, H = ± 2°, ∠ H, N, H = ± 3°.

Table 9. Selected Interatomic Distances (Å) for β-FOX-7 at 403 and 423 K[a] obtained from Powder Investigations

	403 K	423 K
C1−N11	1.41	1.40
C1−N12	1.39	1.40
C1−C2	1.46	1.45
C2−N21	1.32	1.30
C2−N22	1.30	1.31
N11−O12	1.23	1.23
N11−O11	1.21	1.22
N12−O21	1.24	1.24
N12−O22	1.25	1.24

[a] Experimental uncertainties: C−N, C−C, N−O = ±0.02 Å.

The phase transition between α- and β-FOX-7 can be classified as displacive. For such a change, a "mere distortion from one network into another" is expected;[21] therefore, a search for structural relations between α- and β-FOX was promising. An inspection of Table 1 shows that the lattice parameters are only slightly changed for both phases during the transition. In Figure 4, the lattice parameters and the unit-cell volumes of both FOX-7 polymorphs are shown in the range of 200−423 K.

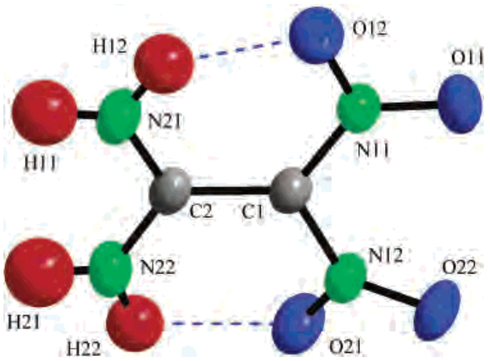

Figure 1. View of a molecule of α-FOX-7 at 373 K. Thermal parameters are drawn at 50% probability. The C, N, and O atoms were refined anisotropically, and the H atoms were refined isotropically. The same numbering scheme is used for β-FOX-7.

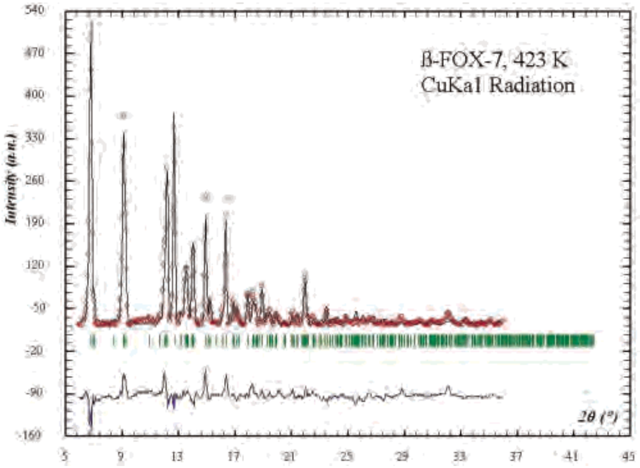

Figure 2. Rietveld Plot of β-FOX-7 at 423 K.

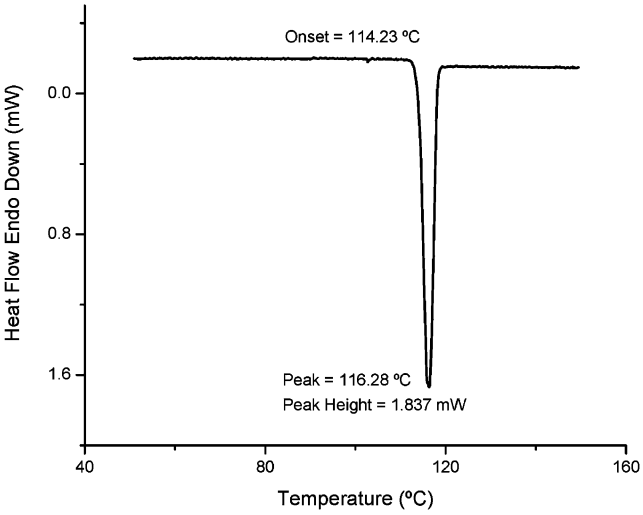

Figure 3. DSC heating measurement of 10.27 mg of FOX-7 with the endothermic α−β peak at 116 °C.

In the graphs from 200 to 393 K (Figure 4), X-ray single-crystal data (Table 1) have been used. The additional data from 403 to 423 K for the β-phase were obtained from X-ray powder data (Table 2). These plots show that the phase transition has only a small influence on the *a* and *b* axes and a greater one on the *c* axis. It can also be observed in Figure 4 that the *b* axis of α-FOX-7 has the strongest

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(21) Dunitz, J. D. *Acta Crystallogr*. **1995**, *B51*, 619−631.

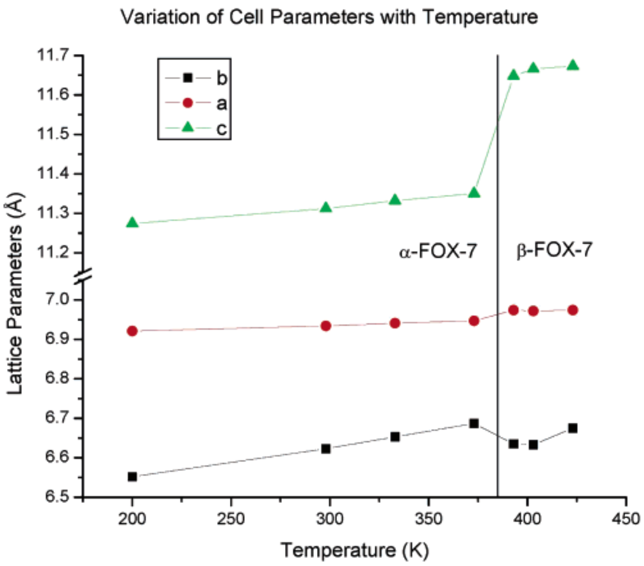

Figure 4. Lattice parameters of α- and β-FOX-7 between 200 and 423 K. Solid lines serve as guides to the eyes.

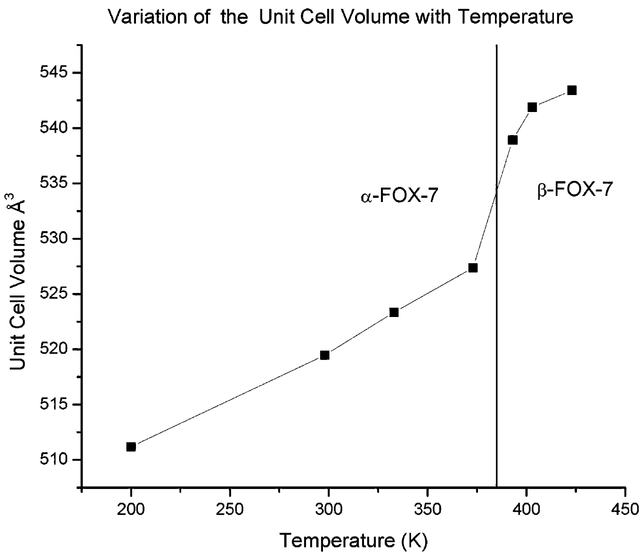

Figure 5. Unit cell volumes for α- and β-FOX-7 between 200 and 423 K. Solid lines serve as guides to the eyes.

temperature dependence. The slope of the graph for the *b* axis is about three times steeper than those for the *a* and *c* axes. It is therefore evident that bonding in the direction of the *b* axis is weaker than in the direction of the *a* and *c* axes.

In Figure 5, the volumes of the unit cells between 200 and 423 K are plotted as function of temperature. The unit-cell volume of α-FOX-7 (527.37(3) Å^3, 373 K, Table 1) increases by $\Delta V = 11.57$ Å^3 to a value of 538.94(3) Å^3 for β-FOX-7 at 393 K. This converts to $\Delta V = 1.8$ cm^3/mol, an increase of approximately 2%.

α- and β-FOX-7 are structurally related, whereby simple relations for transformation of coordinates have been derived

$$x_\alpha - 1/4 \approx x_\beta \quad y_\alpha + 1/4 \approx y_\beta \quad z_\alpha \approx z_\beta.$$

A substantiating example of this simple relationship between atomic coordinates in α-FOX-7 and β-FOX-7 can be drawn from the coordinates of O11. The oxygen atom O11 of α-FOX-7 at 373 K (0.0244, 0.0658, and 0.74947) (Table 3) is changed by the above instruction to −0.2256, 0.3158, and 0.74947 and then to 0.7744, 0.3158, and 0.74947. An inspection of Table 4 shows for O11 in β-FOX-7 at 393 K the coordinates 0.8084, 0.3179, and 0.71229 with a difference of 0.49 Å between the calculated and observed coordinates.

Therefore, one could expect a group theoretical relation for the transformation of the coordinates of α- and β-FOX-7. The α-phase crystallizes in the centrosymmetric monoclinic space group $P2_1/n$ (No. 14), while the β-phase crystallizes in the orthorhombic space group $P2_12_12_1$ (No. 19). Since the $P2_12_12_1$ space group does not possess a center of symmetry, a group theoretical relation to $P2_1/n$ is only possible via a centrosymmetic supergroup. In the *International Tables for Crystallography*, Vol. A1,[22] two orthorhombic space groups *Pbca* (No. 61) and *Pnma* (No. 62) are tabulated for this case. Between *Pbca* and the subgroups $P2_1/n$ and $P2_12_12_1$ there is only an interchange of axes required for $P2_1/n$ (*c*, *a*, *b*), but no origin shift for both.[22] This is not in agreement with the above-mentioned empirical relations, and therefore, *Pbca* could not be a supergroup for α- and β-FOX-7. Between *Pnma* and the subgroups $P2_1/n$ and $P2_12_12_1$, there is again an interchange of axes required for $P2_1/n$, but only one shift (x, y, z + 1/4) is required. Therefore the empirical relation $y_\alpha + 1/4 \approx y_\beta$ with a shift of $b/4 \approx 1.7$ Å is not in agreement with a group theoretical relation between α- and β-FOX-7.

As it can be observed in Figure 6, the shift of $b/4$ is responsible for a different arrangement of the wave-shaped layers of FOX-7 molecules along [010]. In α-FOX-7 at 373 K (Figure 6a) the wave-shaped layers are centered at $y = \sim 1/4$ and $\sim 3/4$, in contrast to β-FOX-7 (Figure 6b) where they are centered at $y = \sim 0$ and $\sim 1/2$.

In both polymorphs (Figure 6a and b), characteristic wave-shaped layers are shown. The dipolar FOX-7 molecules are arranged by “head-to-tail” intermolecular hydrogen bonding, where the “heads” of the FOX-7 molecules are the donating amino groups and the “tails” are the withdrawing nitro groups. To build up intermolecular hydrogen bonds, the head of one molecule is bonded to the tail of the next molecule, which is then rotated 180° around the C−C-bond axis. Upon inspection of these figures, it can be deduced that the two carbon and two amino nitrogen atoms form the molecular plane. However, the four oxygen atoms deviate from the molecular plane. Additionally, the two nitro nitrogen atoms also deviate slightly from the plane defined by the carbon atoms and amine nitrogens.

The head-to-tail-bonded FOX-7 molecules within the wave-shaped layers lie in the *a*−*c* plane. They are packed above each other in the direction of the *b* axis. In this direction, a stronger dependence of the lattice parameter on temperature is derived (Figure 5) because the van der Waals bonds between the layers are weaker than in the *a*−*c* plane.

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(22) *International Tables for Crystallography, Volume A1 Symmetry Relations between Space Groups*; Wondratschek, H., Müller, U., Eds.; Kluwer Academic Publshers: Dordrecht, The Netherlands, 2004.

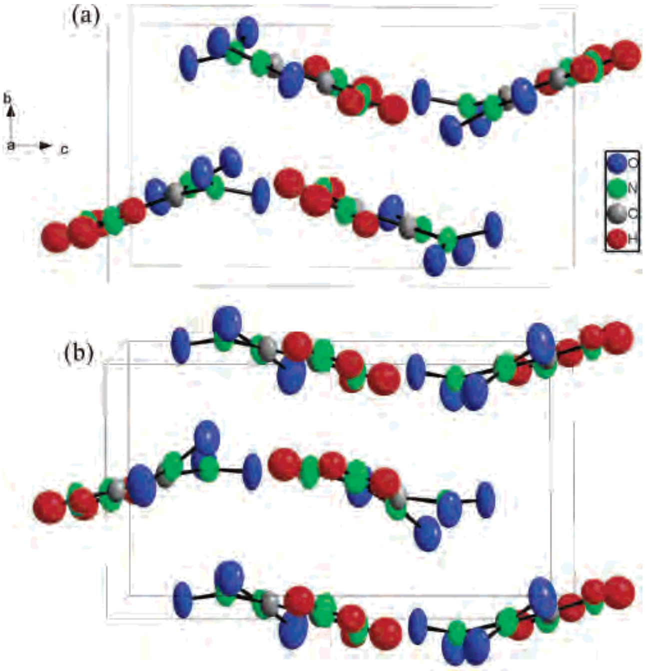

Figure 6. View along [100] of the wave-shaped layers of head-to-tail-bonded FOX-7 molecules. Thermal displacement parameters are drawn at the 50% probability level (O, C, and N anisotropically; H isotropically): (a) α-FOX-7 at 373 K with layers centered at $y = \sim 1/4$ and $\sim 3/4$ and (b) β-FOX-7 at 393 K with layers centered at $y = \sim 0$ and $\sim 1/2$.

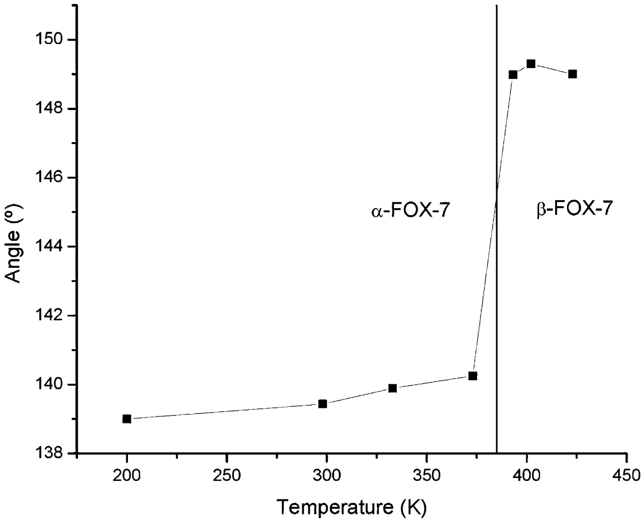

Figure 7. Dependence of the angle between the wave-shaped layers on temperature. Single-crystal data from measurements at 200, 298, 333, 373, and 393 K and powder data at 403 and 423 K. The solid line serves as a guide to the eyes.

If it is assumed that the main orientation of the FOX-7 molecules is determined primarily by the carbon−carbon bond of the ethylene molecule (Figure 6), then, from the positional parameters y and z of the two carbon atoms (α-FOX-7, 200K), an incident angle of the wave-shaped layers of 139.0° can be calculated. However, this angle increases in the α-phase at 373 K by only ~1° to a value of 140.3°, whereas in the β-phase at 393 K a steep increase of ~9° to a value of 149.0 ° is found. Heating of FOX-7 molecules to 393 K flattens the wave-shaped layers. In Figure 7, the angle of the wave-shaped layers at 200, 298, 333, 373, 393 (single-crystal data), 403, and 423 K (powder data) are plotted as function of temperature.

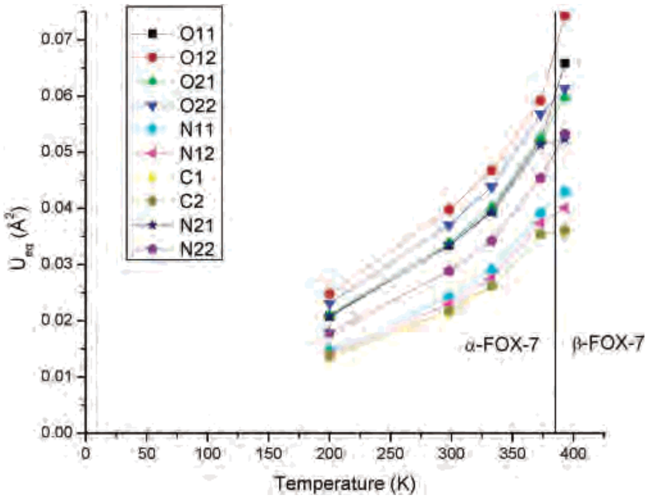

Figure 8. Isotropic displacement parameters for the O, N, and C atoms of α- and β-FOX-7 between 200 and 393 K. Solid lines serve as guides to the eyes.

The weaker bonding perpendicular to the wave-shaped layers is also manifested by the anisotropical thermal displacement parameters (ADPs) for α-FOX-7 at 373 K (Table 3) and β-FOX-7 at 393 K (Table 4). For orthogonal crystal systems, the ADPs U_{11}, U_{22}, and U_{33} represent the principal axes of the thermal ellipsoids in the a, b, and c directions, respectively. Orthorhombic β-FOX-7 is orthogonal per se, but monoclinic α-FOX-7 with $\beta = 90.06°$ (e.g., at 200 K, Table 1) deviates only slightly from such a system. In Tables 3 and 4, it is summarized that with the exception of carbon atom C2 (α-FOX-7, 373 K) the U_{22} values are always the largest ones, and they fall in sequence for the values of O, N, and C. However, the greatest U_{22} value is obtained for the oxygen atom O12 for both α- and β-FOX-7. At 393 K, $U_{22} = 0.1295(15)$ Å^2 (Table 4) is the largest value for β-FOX-7, and at 373 K, $U_{22} = 0.0963(15)$ Å^2 (Table 3) is the largest value for α-FOX-7. The oxygen atoms O12 have the largest U_{22} values for both phases, and interestingly, these atoms form intramolecular hydrogen bonds in both phases.

In Figure 8, the isotropic thermal displacement parameters, U_{eq} (Å^2), for the O, N, and C atoms at 200, 298, 333, 373, and 393 K are plotted as function of temperature. Extrapolation[23] of the U_{eq} graphs for α-FOX-7 from values with $200 \leq T \leq 298$ K shows that at 0 K the intercepts on the ordinate have very low values. From this extrapolation, one can derive that the static disorder in the investigated crystal is low. However, the plot shows also that the slopes increase in the intervals 200−298, 298−333, and 333−373 K, especially for oxygen atoms O11 and O12. It seems that dynamic disorder, with a strong part of the oxygen atoms, in FOX-7, increases with increasing temperature. Probably, the thermal behavior of the oxygen atoms contributes largely to the entropy increase, $\Delta S = 1.6$ cal/K mol, during the α−β phase

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(23) Willis, B. T. M.; Pryor, A. W. *Thermal Vibrations in Crystallography*; Cambridge University Press: New York, 1975; p 126.

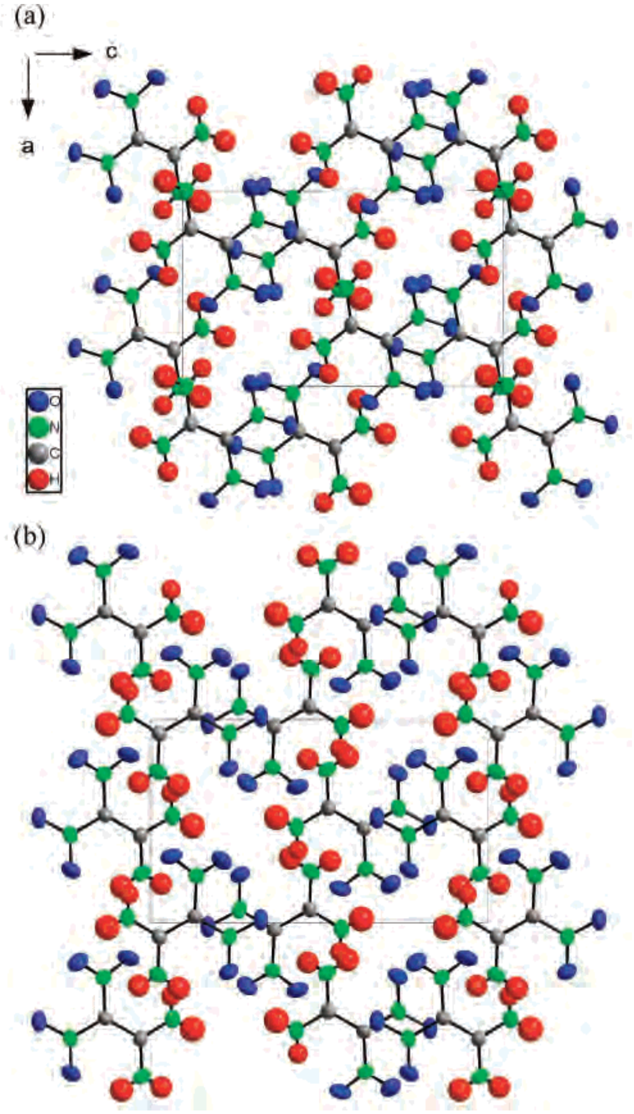


Figure 9. View along [010] of two layers of FOX-7 at 373 K. Thermal displacement parameters are drawn at the 50% probability level: (a) α-FOX-7 at 373 K and (b) *β*-FOX-7 at 393 K.

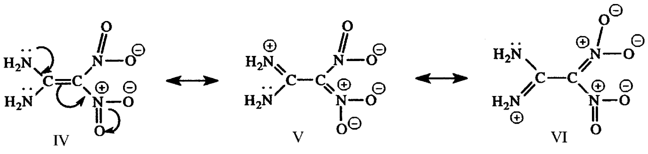
transition (Figure 3). Is there a structural background for the large thermal motion?

Views along [010] on the wave-shaped layers of α- and of *β*-FOX-7 are shown in Figure 9a and b. If the carbon−carbon bonds of the ethylene molecules are considered, one realizes that, in α-FOX-7, although the molecules are head-to-tail bonded, the carbon−carbon bonds are at first sight uniformly orientated, whereby rows of carbon−carbon bonds exist, in which the center of the C−C bond lies at $x \approx 1/4$ and 3/4. These bonds are rotated 24° against the *c* axis (Figure 9a). Astonishingly, in *β*-FOX-7, a different arrangement of the carbon−carbon bonds of the ethylene molecules is observed. There are also rows of carbon−carbon bonds but with the center at $x \approx 0$ and 1/2. However, at $x \approx 0$, the C−C bonds have an angle of +29°, and at $x \approx 1/2$, they are rotated in the opposite direction (−29° against the *c* axis; Figure 9b).

If the intramolecular distances and angles in both FOX-7 phases (Table 6) are compared, the C1−C2 distance in α-FOX-7 shows at first sight a tendency to decrease upon heating: 1.460(2) (200 K), 1.458(2) (298 K), 1.457(2) (333 K), and 1.456(2) Å (373 K). The same tendency is also found for the C1−N12, C2−N21, C2−N22, N11−O11, and N12−O22 distances (Table 6). However, this tendency results from the increasing atomic motion with increasing temperature.[15] Nevertheless, intramolecular distances can be corrected for thermal motion by calculating tensors *T*, *L*, and *S* using the program THMA11.[18,19] The corrections for intramolecular distances are summarized in Table 7. They are compared with the averaged standard deviation, σ_{av}, which is obtained by the structure analyses with the SHELX-97 program.[14] At low temperature ($T = 200$ K), the calculated *TLS* correction is approximately only $2\sigma_{av} \approx 0.004$ Å, whereas at 393 K, it is $5\sigma_{av} \approx 0.012$ Å (Table 7). By applying the additive correction for the C1−C2 distance, one obtains 1.463(2) (200 K), 1.463(3) (298 K), 1.462(2) (333 K), and 1.463(2) Å-(373 K), and no significant indication of decreasing bond distances on heating can be observed.

Now, the corrected interatomic distances could be examined for differences resulting from the destabilization on heating of FOX-7. Of particular interest are the precise C−N distances because the $C-NO_2$ bond is known as the detonation trigger.[12] The C1−N11 distance in α-FOX-7 increases from 1.392(3) Å at 200 K to 1.401(3) Å at 373 K (Tables 6 and 7), whereas the C1−N12 distance shows a slight decrease from 1.421(2) Å at 200 K to 1.413(3) Å at 373 K. Therefore it can be concluded that heating α-FOX-7 from 200 to 373 K does not lead to a significant change of the intramolecular C1−N11 and C1−N12 bond distances or of the N11−O11, N11−O12, N12−O21, and N12−O22 bond lengths.

The bond order (BO) of the C−C, C−N, and N−O bonds in FOX-7 is very interesting; three mesomeric structures of FOX-7 are shown below (IV−VI).



If one interpretes FOX-7 as ethylene which is substituted by two amino and two nitro groups (IV), then the BO of the C−C bond should be 2.0, that of the C−N bonds should be 1.0, and that of the N−O bonds should be 1.5. However, the two mesomeric structures (V and VI) suggest that the BO of the C−C bond in FOX-7 should be lower and that of the C−N bonds higher than indicated in IV. If all the structures in the scheme (IV−VI) are considered, the same BO (1.33) is obtained for the C−C, C−N, and N−O bonds. With tabulated single and double bond radii for carbon, nitrogen, and oxygen of 0.77/0.67, 0.70/0.60, and 0.60/0.56 Å, respectively,[24] one calculates, after graphical interpolation for BO = 1.33, the C−C bond distance to be 1.47 Å, the C−N bond distance to be 1.40 Å, and the N−O bond distance to be 1.29 Å. Comparison with the experimental

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(24) Wiberg, N. *Holleman-Wiberg, Lehrbuch der Anorganischen Chemie*; Walther de Gruyter: Berlin, 1995; p 136.

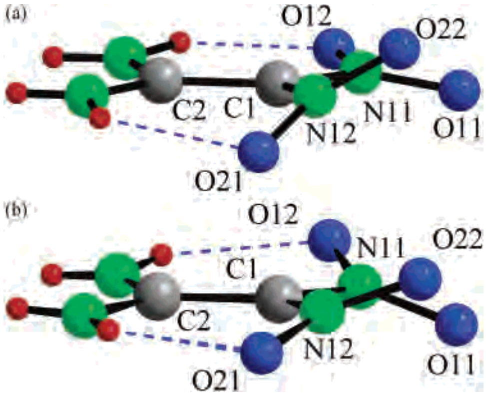

Figure 10. Four oxygen atoms in FOX-7 lie out of the molecular plane of the two carbon and two amino nitrogen atoms. For clarity, no experimental thermal displacement parameters are plotted because the large ellipsoids hide the bond sticks. (a) α-FOX-7 at 373 K: nitro group 2 with O21, N12, O22 is twisted out of the molecular plane (−46.6°) considerably more than nitro group 1 with O11, N11, O12 (+6.0°). (b) *β*-FOX-7 at 393 K: nitro group 2 with O21, N12, O22 is out of the molecular plane (−35.6°) considerably more than nitro group 1 with O11, N11, O12 (+20.3°).

Table 10. Twist Angle (deg) of O11−O12 and O21−O22 Groups against the C1−C2 Bond in the *b*−*c* plane

T (K)	phase	O11−O12	O21−O22
200	α	+5.5	−47.4
298	α	+5.8	−47.0
333	α	+6.0	−46.8
373	α	+6.0	−46.6
393	*β*	+20.3	−35.6

single-crystal data (Tables 6 and 7) shows that the (calcd/exptl) C−C (1.47/1.46 Å) and C−N_{nitro} (1.40/1.40 Å) bonds agree with BO = 1.33, but a deviation is found for the C−N_{amino} (1.40/1.31 Å) and N−O (1.29/1.24 Å) bonds. The experimental N−O distances (1.24 Å) are better fitted for BO = 1.5, and the experimental C−N_{amino} distances (1.32 Å) are better fitted for BO = 1.67.

These observations can be clearly explained by Figure 10, in which the two amino groups lie in the molecular plane in both polymorphs of FOX-7, in sharp contrast to the two nitro groups. Although the mesomeric structures (V and VI) suggest that the oxygen atoms with approximate sp^2 hybridization are located in the C2, C1, N11, N12 molecular plane, the nitro groups in both polymorphs of FOX-7 are twisted around the two C−N_{nitro} bonds (Figure 13a and b). In α-FOX-7 at 373 K, nitro group 2 with O21, N12, O22 is twisted −46.6° against the C1−C2 bond in the *b*−*c* plane, whereas nitro group 1 with O11, N11, O12 is twisted significantly less with only +6.0 ° (Figure 10a). On the other hand, in comparison to α-FOX-7, the twist angle of nitro group 1 in *β*-FOX-7 is decreased to −36.6° and that for nitro group 2 increased to +20.3°.

The twist angles O11−O12 and O21−O22 in the range of 200−393 K with respect to the carbon−carbon bond show a slight temperature dependence and are summarized in Table 10 and plotted in Figure 11. The O11−O12 twist angle for α-FOX-7 increases slightly from 5.5 to 6.0° in the range of 200−373 K, and then it increases abruptly to 20.3° in *β*-FOX-7. The reverse is true for the O21−O22 twist angle which changes from −47.4° at 200 K to −46.6° at 373 K for α-FOX-7 and then abruptly to −35.6° for *β*-FOX-7 at 393 K.

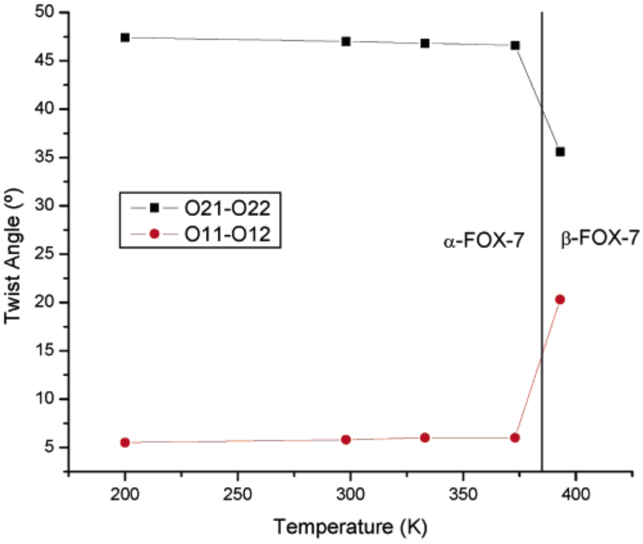

Figure 11. Twist angles of the O11−O12 and O21−O22 groups in α- and *β*-FOX-7 in the range of 200−393 K. The strongly asymmetric twisting angles of −47 and +6 ° in α-FOX-7 are changed to more averaged ones in *β*-FOX-7 with values of −36 and +20° (for further explanation, see text).

Table 11. Deviation (Å) of the O11, O12, O21, and O22 Oxygen Atoms and of the Nitro Nitrogen Atoms, N11 and N12, from Planarity

T (K)	phase	N11	N12	O11	O12	O21	O22
200	α	0.09	0.16	0.25	0.14	0.40	0.83
298	α	0.09	0.15	0.25	0.14	0.39	0.81
333	α	0.09	0.16	0.25	0.14	0.38	0.81
373	α	0.09	0.14	0.25	0.14	0.39	0.79
393	*β*	0.10	0.11	0.52	0.26	0.20	0.53

To examine the structural details for the deviation of both oxygen groups from a planar arrangement, the positional parameters for the four oxygen atoms, O11,O12, O21, and O22) and for the two nitro nitrogen atoms, N11 and N12, have been analyzed. The deviation of these atoms from the molecular plane of the two carbon atoms and the amino nitrogen atoms has been calculated in the range of 200−393 K, bearing in mind that this arrangement is also slightly distorted. The C2 carbon atom deviates 0.04 Å from the center of the triangle formed by the N21, N22, and C1 atoms. The results of the calculations are shown in Table 11 and Figure 12.

The two nitro nitrogen atoms, N11 and N12, deviate only slightly from the molecular plane, and the four oxygen atoms, O11, O12, O21, and O22, deviate strongly. In α- FOX-7, between 200 and 373 K, the N11 atom lies 0.09 Å and the N12 atom 0.15 Å out of the plane, and in *β*-FOX-7 at 393 K, an averaged value of ∼0.10 Å is found for both atoms. However, the largest deviation from the plane is found for the oxygen atoms with O22 and O21 being 0.83 and 0.40 Å, respectively, and with O11 and O12 being 0.25 and 0.14 Å, respectively, in α-FOX-7 at 200 K. Up to 373 K, these values remain nearly constant, but then in *β*-FOX-7 at 393 K, an abrupt change for the deviation from the molecular plane is observed: 0.53/0.20 Å for O22/O21 and 0.52/0.26

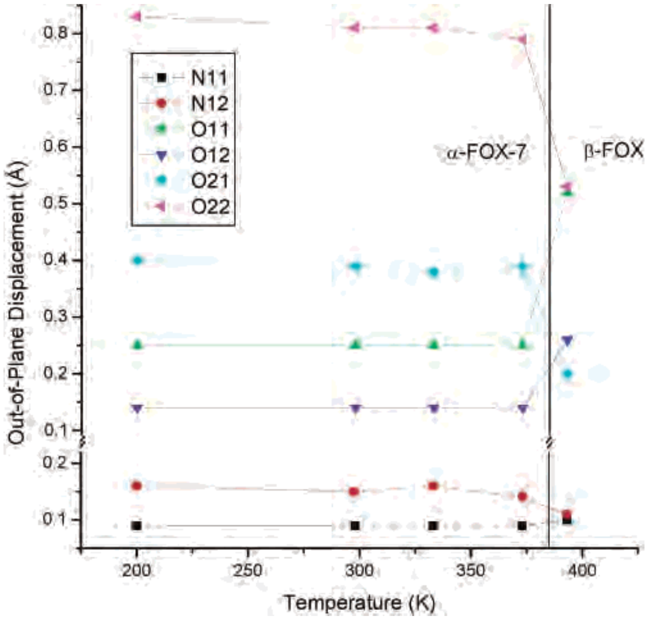

Figure 12. Deviation of the O11, O12, O21, and O22 oxygen atoms and of the nitro nitrogen atoms, N11 and N12, from the molecular plane C1, C2, N21, N22 in α- and β-FOX-7 in the range of 200−393 K.

Å. Interestingly, the O21−O22 oxygen group in α-FOX-7 (deviation 0.40 and 0.83 Å, 200 K, Table 11) is arranged less symmetrically than O11−O12 (0.25 and 0.14 Å) group, but in β-FOX-7, these relations are interchanged. In β-FOX-7, O11−O12 (0.52 and 0.26 Å) is in a a slightly less symmetrical arrangement than O21−O22 (0.20 and 0.53 Å), since the deviation from the molecular plane for O21 (0.20 Å) is slightly lower than that for O12 (0.26 Å).

If the C−N$_{nitro}$ bond distances (Tables 6 and 7) are considered, it is shown that, in α-FOX-7, the C1−N11 bond distance of 1.401(4) Å (Tables 6 and 7) is shorter than that of C1−N12 (1.413(3) Å) but, in β-FOX-7 at 393 K, the latter (1.409(2) Å) is shorter than the former (1.418(3) Å) with a greater separation for α-FOX-7 (1.401(4)/1.413(4) Å) than for β-FOX-7 (1.418(3)/1.409(2) Å).

The oxygen atoms in the wave-shaped layers in FOX-7 also influence the hydrogen-bonding network. Indeed, the O12 and O21 oxygen atoms in β-FOX-7 at 393 K, which show the smallest deviation from the molecular plane, are involved in the two intramolecular hydrogen bonds (Figure 1). For α-FOX-7, this observation also holds for O12. However, during the phase transition, half of the FOX-7 molecules rearrange their position and are rotated 29° against each other (Figure 6). Therefore, the hydrogen-bonding net in α-FOX-7 must be rebuilt at the α−β phase transition. In Figure 13a and b, the net of hydrogen bonds is shown for one wave-shaped layer of FOX-7 molecules for both phases. Intramolecular hydrogen bonds are blue, and the intermolecular ones are red. The donor−acceptor (D−A) geometries for α-FOX-7 at 373 K are summarized in Table 12, and those for β-FOX-7 at 393 K are given in Table 13.

An inspection of Figure 13a shows that each oxygen of the two nitro groups is involved in two hydrogen bonds, resulting in eight hydrogen-acceptor bonds of this type: six are intermolecular, and two are intramolecular. In β-FOX-7, the hydrogen-bonding net is less symmetrical than that in α-FOX-7 (Figure 13b). Now, only one oxygen atom per nitro group is involved in two hydrogen bond, while the other is involved in three hydrogen bonds. Therefore, 10 hydrogen-acceptor bonds are formed: eight of them are intermolecular, and two are intramolecular.

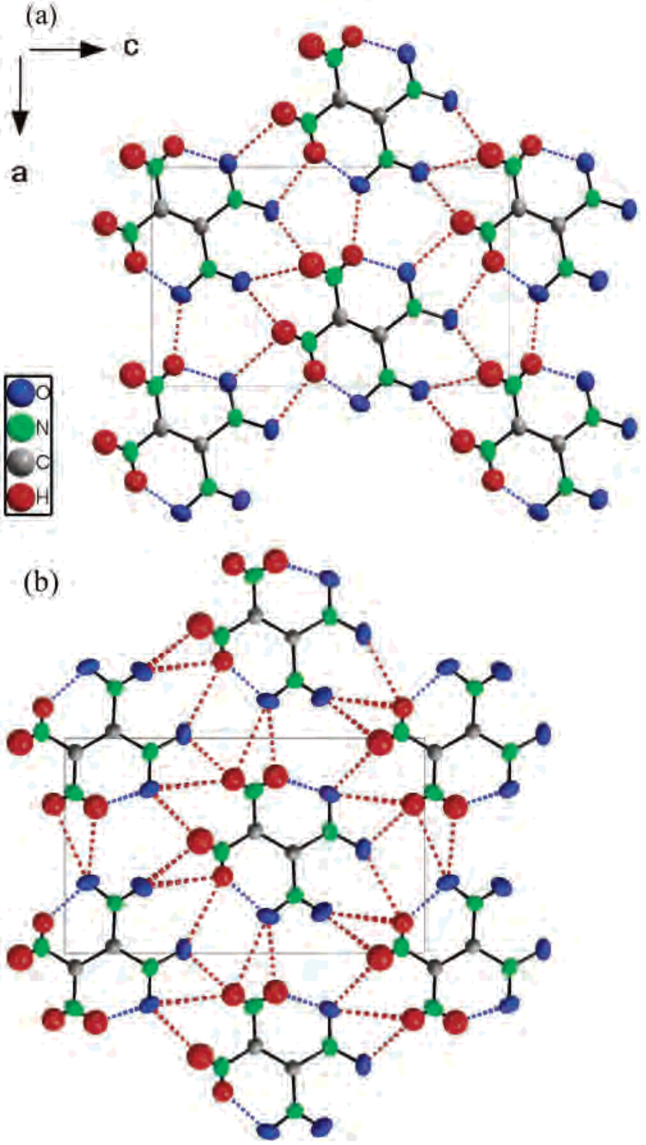

Figure 13. View along [010] on one layer of FOX-7. Thermal displacement parameters are drawn at the 50% probability level. Intramolecular hydrogen bonds are blue, and intermolecular ones are red. (a) α-FOX-7 at 373 K: each oxygen atom forms two hydrogen bonds within one wave-shaped layer, which results in two intramolecular and six intermolecular hydrogen bonds. (b) β-FOX-7 at 393 K: O11 and O22 form two and O12 and O22 atoms form three hydrogen bonds. This results in two intramolecular and eight intermolecular hydrogen bonds.

To decide which of the nets is stronger, D−H···A in α-FOX-7 at 373 K can be compared with that in β-FOX-7.(Tables 12 and 13). Inspection of these tables shows that the average D−H and D···A distances and the average D−H···A bond angles remain nearly unchanged, in contrast to the average H···A distances: they increase from 2.22 Å in α-FOX-7 to 2.47 Å in β-FOX-7. In α-FOX-7, there six intermolecular distances to be compared, and in β-FOX-7, there are eight. If only six of these distances for both phases

Table 12. Donor−Acceptor (D−A) Geometry (Å, deg) for Hydrogen Bonds in α-FOX-7 at 373 K[a] Obtained from a Single-Crystal Investigation

D−H$\cdots$A	D−H (Å)	H$\cdots$A (Å)	D$\cdots$A (Å)	D−H$\cdots$A (deg)
N21−H11$\cdots$ O11	0.90	2.20	3.021	152
N21−H11$\cdots$ O21	0.90	2.47	3.020	120
N21−H12$\cdots$O12[b]	0.95	1.87	2.608	132
N21−H12$\cdots$O22	0.95	2.31	3.036	133
N22−H21$\cdots$O22	0.86	2.15	2.933	150
N22−H21$\cdots$O11	0.86	2.47	3.202	143
N22−H22$\cdots$O21[b]	0.93	2.04	2.621	119
N22−H22$\cdots$O12	0.93	2.26	3.043	141
average	0.92	2.22	3.04	136

[a] Experimental uncertainties: D−H = ±0.04 Å, H$\cdots$A = ±0.04 Å, D$\cdots$A = ±0.004 Å, ∠D−H$\cdots$A = ±2°. [b] Intramolecular bonds.

Table 13. Donor−Acceptor (D−A) Geometry (Å, deg) for Hydrogen Bonds in β-FOX-7 at 393 K[a] Obtained from a Single-Crystal Investigation

D−H$\cdots$A	D−H (Å)	H$\cdots$A (Å)	D$\cdots$A (Å)	D−H$\cdots$A (deg)
N21−H11$\cdots$O11	0.79	2.53	2.989	118
N21−H11$\cdots$O21	0.79	2.40	3.158	161
N21−H12$\cdots$O12[b]	0.80	1.98	2.591	133
N21−H12$\cdots$O22	0.80	2.71	3.413	148
N21−H12$\cdots$O11	0.80	2.79	2.989	96
N22−H21$\cdots$O22	0.79	2.21	2.980	164
N22−H21$\cdots$O12	0.79	2.78	2.946	94
N22−H21$\cdots$O21	0.79	2.83	2.585	146
N22−H22$\cdots$O21[b]	0.86	1.94	2.585	131
N22−H22$\cdots$O12	0.86	2.48	2.946	115
average	0.81	2.47	2.92	130

[a] Experimental uncertainties: D−H = ±0.04 Å, H$\cdots$A = ±0.04 Å, D$\cdots$A = ± 0.004 Å, ∠D−H$\cdots$A = ±2°. [b] Intramolecular bonds.

are taken into account, the average H$\cdots$A value increases from 2.31 Å in α-FOX-7 to 2.52 Å in β-FOX-7. Therefore, the intermolecular hydrogen-bonding network in β-FOX-7 is slightly weakened in comparison to that in α-FOX-7, even though there two additional long intermolecular distances in β-FOX-7.

It has been suggested[1] that the molecular packing built up by extensive intermolecular hydrogen bonding within the wave-shaped layers and van der Waals interactions between them is one of the reasons for the stability of FOX-7 phases before detonation. The two stable phases are α- and β-FOX-7. Detonation occurs only after the phase transition from β- into γ-FOX-7 (446 K) occurs, and it requires further heating to ∼500 K. It has been also suggested that the $C-NO_2$ bonds are known as the detonation trigger in FOX-7.[12] They have to be sharpened before detonation. In addition, from the DFT calculations on FOX-7, it was proposed that, via cooperative effects of intermolecular interactions, a net of hydrogen bonds should make the $C-NO_2$ bonds stronger, and this should lower the sensitivity of the explosives.[12]

Our results indicate that the $C-NO_2$ bonds are not significantly destabilized during the heating of FOX-7 from 200 to 393 K, although the intermolecular network of hydrogen bonds is slightly weakened. On the molecular level of FOX-7, the oxygens are powerful actors. Therefore, one could focus on the behavior of the oxygen atoms of the nitro groups in FOX-7 and on their influence on the strengths of the $C-NO_2$ bonds. As it has been already discussed, in α-FOX-7 up to 373 K, the $C-NO_2$ bonds for C1−N11 are slightly shorter than those for C1−N12, but in β-FOX-7 at 393 K, this relationship is reversed. Probably, as a result of the temperature-dependent deviation of the oxygen atoms from the molecular plane, the C1−N12 bond becomes shorter than the C1−N11 bond. Therefore, a rearrangement of the oxygen atoms of the two nitro groups could also play a significant role in the stability of the $C-NO_2$ bonds in FOX-7 and, therefore, on the sharpening of the trigger before detonation. Preliminary results of single-crystal investigations on β-FOX-7 up to 423 K appear to confirm this suggestion.[25]

Summary

(1) At 393 K, the hitherto unknown crystal structure of β-FOX-7 has been solved.

(2) The $\alpha-\beta$ phase transformation in FOX-7 is displacive and first order. Since a FOX-7 single crystal is not destroyed by heating and cooling cycles through the $\alpha-\beta$ transition, simple relations for the transformation of coordinates have been derived

(3) Wave-shaped layers of head-to-tail-bonded dipolar FOX-7 molecules have been found for both phases. The angle between the wave-shaped layers increases only slightly upon heating for the α-phase, but after the transition to the β-phase, it increases abruptly. The layers are more flattened at higher temperatures.

(4) The four oxygen atoms of the nitro groups in FOX-7 lie out of the molecular plane of the carbon and the amino nitrogen atoms. In α-FOX-7, nitro group 2 lies much more out of the plane than nitro group 1. In β-FOX-7, this relationship is reversed.

(5) It has been suggested that the molecular packing built up by extensive intermolecular hydrogen bonding within the layer is one reason for the unique properties of FOX-7, namely, its high performance and low sensitivity. This investigation shows that the network of intermolecular hydrogen bonds is slightly weakened by heating FOX-7 to 393 K. However, this does not cause a significant change of the $C-NO_2$ bond distances.

(6) In the $C-NO_2$ groups of FOX-7, the four oxygen atoms could also play a dominant role on the detonation trigger because our temperature-dependent single-crystal investigations show that the oxygens belong to the very active part of the FOX-7 molecules. They can be rearranged during the phase transition changing the twist angle and also influencing, at first slightly, the $C-NO_2$ bond distances.

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Supporting Information Available: Tables of atomic coordinates and thermal displacement parameters and the donor−acceptor geometry of the hydrogen bonds for the FOX-7 phases at various temperatures. This material is available free of charge via the Internet at http://pubs.acs.org.

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