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The Crystal and Molecular Structure of 4,6-Dinitrobenzfuroxan

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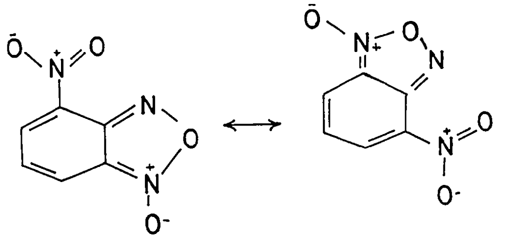
The crystal and molecular structure of 4,6-dinitrobenzfuroxan (monoclinic; $a=7\cdot40$, $b=9\cdot78$, $c=6\cdot19$ Å, $\gamma=108\cdot0°$; space group $P2_1$) has been determined by three-dimensional X-ray techniques. The structure was determined by direct methods from X-ray reflexions observed for Cu $K\alpha$ radiation with a four-circle diffractometer. The structure was refined by the least-squares method assuming anisotropic thermal motion for only the nitrogen and oxygen atoms. The final R was 0·063. In the molecule the 6-nitro group is very nearly coplanar with the benzfuroxan entity to give a short 'non-bonded' N···O contact of 2·63Å. The relevance of the structure to the rearrangement of 6-nitrofuroxans to 2-nitrofuroxans is discussed.

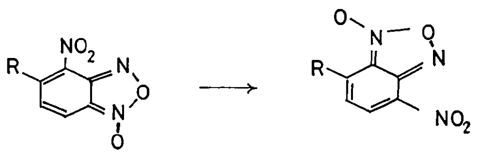
Introduction

Bailey & Case (1957, 1958) suggested that a 6-nitrobenzfuroxan might be capable of a fast tautomeric interconversion of the type I ↔ II.



(I) (II)

N.m.r. studies (Harris, Katritzky, Øksne, Bailey & Paterson, 1963) showed that the fast interconversion does not occur below 160° but a slow interconversion is not ruled out. The isolation of (III) ($R=CH_3$ or Cl) and the conversion into the isomeric products (IV) (Boulton & Katritzky, 1962) showed that rearrangement could occur.



(III) (IV)

In (III) the nitro group is unlikely to be in the plane of the benzfuroxan because of steric interference. The loss of planarity may result in a loss of resonance stabilization compared with (IV) in which the molecule may be planar. The ultraviolet spectra of the molecules (III) and (IV) show that they are not identical. If a 6-nitrobenzfuroxan is planar then the N···O contact between the oxygen of the nitro-group and the furoxan nitrogen atom may be remarkably short. If this contact is short it will enhance the possibility of a slow I ↔ II conversion. We report the crystal and molecular structure 4,6-dinitrobenzfuroxan, prepared by the method of Bailey & Case (1957) and supplied by Dr A. S. Bailey as a yellow-brown beautifully crystalline solid.

Experimental

The crystal data are: $C_6H_2N_4O_6$, $M=226\cdot11$; monoclinic; $a=7\cdot40\pm0\cdot01$, $b=9\cdot78\pm0\cdot01$, $c=6\cdot19\pm0\cdot01$ Å; $\gamma=108\cdot0\pm0\cdot1°$; $U=426\cdot1$ Å^3; $D_m=1\cdot752$; $Z=2$; $D_c=1\cdot761$ g.cm^{-3}; Cu $K\alpha$ 1·5418 Å; $\mu=14\cdot47$ cm^{-1}; Space group $P2_1$ (C_2^2, No. 4, first setting). Optically biaxial, piezoelectric.

The crystal class and space group $P2_1$, were uniquely determined by the observed piezoelectric properties and reflexions systematically absent from Weissenberg photographs. The unit-cell dimensions and relative intensities of X-ray reflexions were measured, at room temperature, with a Hilger and Watts four-circle diffractometer. Copper $K\alpha$ radiation was used with a β filter and pulse-height analyser. A θ, 2θ step scan was used to observe significant counts ($I\geq3\sigma$) for 656 of the accessible reflexions (those with $2\theta\geq150°$). The observations were corrected for Lorentz and polarization effects but not for absorption.

Structure determination

The structure was solved by direct methods with programs developed by Kennard (1971) and co-workers. Starting sets were derived from three reflexions ($1\bar{2}1$, $E=3\cdot53$; 540, $E=2177$; 030, $E=2\cdot22$) chosen, by the rules of Hauptman & Karle (1956), to have phase angles of zero to define the origin, and three general reflexions ($1\bar{3}1$, $E=3\cdot66$; 154, $E=2\cdot17$; $1\bar{8}3$, $E=2\cdot21$) for which 32 phase combinations were generated. The possible values of $1\bar{3}1$ were restricted to define the enantiomorph. From six 'known' phases those of 180 reflexions, $E\geq1\cdot1$, were determined, and refined by iterative use of the tangent formula. Of the 32 starting sets used three gave very good values for the several consistency parameters supplied by the program. The first E map to be calculated was on the set with starting parameters $\alpha_{1\bar{3}1}$, $\pi/4$; α_{154}, $7\pi/4$ and $\alpha_{1\bar{4}3}$, $\pi/4$ with the minimum value of R_{Karle} (24%) (Karle & Karle 1966). This map showed 13 peaks in positions compatible with a 4,6-dinitrobenzfuroxan molecule with an orientation very similar to that suggested by the sharpened Patterson function. A structure-factor calculation gave $R=(\sum|F|-|F_o|/\sum|F_o|)$ of 0·405 and the subsequent electron-density map showed clearly the whole molecule. The structure was refined by the full-matrix least-squares method. Four cycles were calculated with isotropic temperature factors and the five more with anisotropic temperature factors for the nitrogen and oxygen atoms. At no time during the refinement was it possible to see the two hydrogen atoms in the difference syntheses. The final R value was 0·063. The weighting scheme used was $w=18\cdot8/(0\cdot021|F_o|^2+$

Table 1. *Observed and calculated structure amplitudes and calculated phases*

H	K	L	FO	FC	ALPHA
0	0	2	13.5	14.1	76.1
0	0	4	17.5	17.1	167.4
0	0	6	2.7	1.3	90.0
0	1	0	10.7	10.0	0.0
0	1	1	25.7	25.7	155.5
0	1	2	30.4	29.5	-151.1
0	1	3	11.4	10.0	-95.9
0	1	4	13.0	12.6	-105.6
0	1	5	3.7	4.0	14.4
0	2	0	26.1	26.2	180.0
0	2	1	32.5	31.0	165.4
0	2	2	2.8	2.5	82.1
0	2	3	12.4	12.2	97.4
0	2	4	14.8	14.4	-52.3
0	2	5	5.1	4.7	-14.5
0	3	0	41.5	41.7	0.0
0	3	1	14.0	14.0	-100.7
0	3	2	16.8	17.2	95.8
0	3	3	7.4	7.8	-77.3
0	3	4	5.0	4.7	131.9
0	3	5	4.5	4.6	-149.1
0	4	1	10.9	11.0	29.0
0	4	2	13.7	13.8	-123.3
0	4	3	5.0	5.6	-52.9
0	4	4	6.9	7.4	-43.5
0	4	5	7.1	7.1	133.0
0	5	0	13.8	13.6	0.0
0	5	1	7.8	7.9	-141.8
0	5	2	3.7	4.3	-66.5
0	5	3	1.3	1.6	-174.3
0	5	4	9.4	9.2	-103.4
0	5	5	2.9	3.8	-147.6
0	6	0	17.7	16.8	0.0
0	6	1	2.8	2.7	-142.4
0	6	2	5.1	5.7	132.9
0	6	3	9.1	9.1	13.5
0	6	4	7.9	8.2	-170.4
0	6	5	1.5	1.7	130.2
0	7	0	5.0	5.3	0.0
0	7	1	2.7	2.4	123.3
0	7	2	2.4	2.1	11.1
0	7	3	7.1	7.1	-57.3
0	7	4	2.1	1.7	7.0
0	7	5	1.6	1.1	79.7
0	8	0	4.6	4.0	180.0
0	8	1	6.0	6.2	155.8
0	8	2	1.6	0.9	60.4
0	8	3	5.8	5.8	-163.8
0	8	4	3.6	3.2	158.7
0	9	1	2.4	2.6	-100.9
0	9	2	2.3	2.2	-54.3
0	9	3	2.0	2.4	61.2
0	9	4	1.5	1.3	-140.4
0	10	1	1.5	1.5	-100.9
0	10	2	1.3	1.2	-97.0
1	-11	1	2.3	1.8	-177.6
1	-10	1	3.1	3.0	153.8
1	-10	2	4.2	3.9	-113.2
1	-9	0	3.1	3.0	180.0
1	-9	1	1.3	1.4	83.0
1	-9	2	5.8	5.7	-68.2
1	-9	3	3.8	3.7	-80.2
1	-8	0	4.8	4.7	180.0
1	-8	1	4.7	4.4	3.5
1	-8	2	4.6	4.5	44.6
1	-8	4	2.9	3.2	146.7
1	-7	1	2.9	1.6	-67.7
1	-7	2	3.7	3.6	-72.6
1	-7	3	5.0	4.9	54.8
1	-7	4	3.1	2.6	85.6
1	-6	0	4.5	5.6	180.0
1	-6	1	7.6	7.7	91.6
1	-6	2	7.1	6.8	-131.2
1	-6	3	5.7	5.5	-159.3
1	-6	4	7.0	7.4	145.5
1	-6	5	1.6	2.3	-113.0
1	-5	1	11.5	11.1	-73.6
1	-5	2	17.3	16.4	33.9
1	-5	3	6.9	7.4	34.3
1	-5	4	2.9	3.0	-126.9
1	-5	5	3.5	3.6	43.5
1	-4	0	21.5	22.4	180.0
1	-4	1	13.5	12.2	174.3
1	-4	2	8.4	7.1	-11.5
1	-4	3	2.7	2.8	-78.1
1	-4	5	5.7	5.7	-49.6
1	-4	6	1.7	1.4	172.2
1	-3	0	35.5	38.3	180.0
1	-3	1	64.8	67.0	71.8
1	-3	2	28.8	27.9	-69.8
1	-3	3	7.6	7.2	-132.8
1	-3	4	8.9	8.2	59.5
1	-3	5	5.0	5.7	-126.7
1	-3	6	1.7	1.6	-123.9
1	-2	0	24.9	22.9	180.0
1	-2	1	73.7	77.8	-22.5
1	-2	2	13.4	13.1	-31.5
1	-2	3	21.5	21.0	-13.5
1	-2	4	6.6	6.5	93.2
1	-2	5	3.3	3.5	-147.1
1	-2	6	1.2	1.0	14.0
1	-1	0	2.2	2.3	0.0
1	-1	1	6.8	7.1	-74.9
1	-1	2	17.4	17.2	-125.1
1	-1	3	21.3	19.9	91.6
1	-1	4	10.1	10.0	161.8
1	-1	5	5.5	5.2	-28.1
1	-1	6	5.2	4.8	60.6
1	0	0	30.2	31.1	0.0
1	0	1	14.0	14.0	123.6
1	0	2	23.7	22.7	-50.6
1	0	3	15.1	14.8	155.7
1	0	4	3.7	4.0	55.6
1	0	5	2.7	3.2	-87.5
1	0	6	1.4	1.3	-118.2
1	1	0	18.7	20.5	180.0
1	1	1	39.3	39.8	-18.2
1	1	2	17.1	16.8	59.7
1	1	3	7.1	7.2	13.9
1	1	4	2.9	2.2	-143.8
1	1	5	4.5	4.2	70.3
1	1	6	7.3	7.2	-151.5
1	2	0	9.9	11.2	180.0
1	2	1	24.7	24.5	68.6
1	2	2	15.6	14.5	-48.9
1	2	3	1.3	1.8	-73.5
1	2	4	5.9	6.1	-38.7
1	2	5	8.1	8.4	-45.6
1	2	6	1.3	1.0	-91.2
1	3	1	15.0	14.6	50.0
1	3	2	7.8	8.2	-103.2
1	3	3	3.9	4.0	-102.5
1	3	4	10.0	10.3	83.4
1	3	5	8.4	8.9	-98.7
1	3	6	2.8	2.7	-167.0
1	4	0	7.6	6.4	180.0
1	4	1	16.6	16.7	10.2
1	4	2	1.7	1.9	-86.7
1	4	3	9.8	9.7	96.4
1	4	4	7.8	8.2	12.1
1	4	5	2.4	2.3	152.7
1	5	0	5.1	3.9	180.0
1	5	1	10.1	9.3	-59.8
1	5	2	8.5	8.0	-108.6
1	5	3	3.9	3.1	-118.9
1	5	4	9.6	8.9	-76.3
1	5	5	2.3	2.3	-97.6
1	5	6	1.8	1.4	78.6
1	6	0	12.3	12.0	0.0
1	6	1	3.6	3.8	53.3
1	6	2	1.0	0.9	68.1
1	6	3	6.5	5.9	-4.4
1	6	4	1.6	2.8	149.3
1	7	0	4.7	4.1	0.0
1	7	1	1.9	1.8	54.7
1	7	2	3.4	4.1	-65.8
1	7	3	3.3	2.1	28.7
1	7	4	3.9	3.6	24.4
1	8	0	3.6	3.4	180.0
1	8	2	2.0	2.1	-173.5
1	8	3	1.6	1.6	145.1
1	8	4	1.6	1.1	-173.6
1	9	0	1.2	1.1	0.0
1	9	2	3.7	3.4	70.2
1	9	3	1.2	1.6	-7.3
1	10	1	1.7	1.4	-164.8
1	10	2	1.0	1.3	-123.1
2	-10	1	1.5	1.0	-151.0
2	-10	2	3.5	3.5	-144.9
2	-9	1	1.7	1.2	-1.1
2	-9	2	2.5	2.0	-119.6
2	-9	3	5.4	5.4	-97.6
2	-9	4	1.4	1.7	-6.6
2	-8	0	2.4	2.4	0.0
2	-8	1	4.4	5.0	126.5
2	-8	2	2.2	2.9	60.8
2	-8	3	2.5	2.1	61.7
2	-7	0	3.0	2.3	0.0
2	-7	1	7.5	6.8	-104.0
2	-7	2	8.0	7.4	-128.0
2	-7	3	6.6	6.5	43.4
2	-7	4	1.9	2.1	3.1
2	-7	5	1.1	1.1	-136.1
2	-6	0	8.2	8.0	180.0
2	-6	1	1.7	1.3	-38.1
2	-6	2	17.4	16.6	136.0
2	-6	3	5.0	4.4	-21.8
2	-6	4	1.3	1.9	-104.3
2	-6	5	2.0	1.6	107.7
2	-5	0	4.2	5.7	0.0
2	-5	1	18.3	17.6	153.5
2	-5	2	33.6	32.3	69.4
2	-5	3	9.7	9.0	-103.5
2	-5	4	3.7	3.8	9.7
2	-5	5	3.1	3.2	93.6
2	-5	6	1.6	1.5	-123.8
2	-4	0	20.8	20.5	180.0
2	-4	1	9.4	8.8	169.2
2	-4	2	11.3	11.0	-132.7
2	-4	3	13.4	13.5	-63.1
2	-4	4	3.3	3.4	105.8
2	-4	5	4.1	3.8	-164.5
2	-3	0	8.5	9.1	0.0
2	-3	1	27.5	27.3	77.0
2	-3	2	13.9	13.6	-119.4
2	-3	3	7.3	7.9	-25.9
2	-3	4	4.0	3.3	159.5
2	-3	5	3.3	3.7	-151.5
2	-3	6	3.9	4.0	-42.1
2	-2	1	16.9	17.2	176.3
2	-2	2	14.2	14.0	64.6
2	-2	3	6.1	6.7	-87.7
2	-2	4	2.7	2.4	158.9
2	-2	5	4.8	5.7	-30.3
2	-2	6	3.4	2.9	57.4
2	-1	0	37.3	38.1	180.0
2	-1	1	9.8	11.1	-155.0
2	-1	2	6.6	6.6	110.5
2	-1	3	15.3	15.6	35.8
2	-1	4	2.7	2.1	4.6
2	-1	5	4.3	5.0	45.4
2	-1	6	6.7	6.0	63.5
2	0	0	7.5	7.3	180.0
2	0	1	8.0	7.9	121.2
2	0	2	19.5	19.5	104.2
2	0	3	8.0	7.8	-94.2
2	0	4	2.2	2.6	-30.7
2	0	5	3.8	4.7	162.6
2	0	6	5.6	5.5	-52.3
2	1	0	10.0	10.4	180.0
2	1	1	9.2	8.8	151.0
2	1	2	13.7	13.5	113.2
2	1	3	9.1	8.5	-84.2
2	1	4	5.6	6.0	179.0
2	1	5	7.8	8.3	68.7
2	1	6	3.2	3.1	-86.0
2	2	0	8.6	8.4	0.0
2	2	1	4.5	4.5	163.5
2	2	2	21.8	20.5	5.5
2	2	3	8.4	8.5	-24.0
2	2	4	3.1	2.8	109.0
2	2	5	4.6	5.0	-6.6
2	3	0	15.3	16.7	180.0
2	3	1	17.2	16.7	95.7
2	3	2	9.1	8.8	105.0
2	3	3	2.9	3.5	-171.1
2	3	4	3.5	2.1	146.9
2	3	5	7.3	7.1	-99.7
2	3	6	3.7	2.8	-112.2
2	4	0	4.8	5.0	180.0
2	4	1	10.3	10.5	42.3
2	4	2	7.5	7.5	135.9
2	4	3	1.5	0.8	13.6
2	4	4	2.4	2.8	-36.3
2	4	5	3.6	3.4	40.9
2	4	6	3.8	4.0	-16.4
2	5	0	2.5	2.9	0.0
2	5	1	1.6	1.2	-95.7
2	5	3	7.4	7.8	-97.8
2	5	5	1.9	1.9	4.9
2	6	0	2.4	1.3	180.0
2	6	1	4.1	4.3	152.5
2	6	3	2.4	2.4	97.6
2	6	5	1.1	1.0	54.4
2	7	0	2.0	2.0	0.0
2	7	1	3.6	3.3	-75.7
2	7	2	1.1	0.9	-106.6
2	7	3	2.9	2.7	71.7
2	7	4	1.2	1.2	-51.7
2	8	1	3.7	3.5	46.6
2	8	3	1.6	1.6	-96.8
2	9	1	1.9	1.4	24.1
3	-11	0	1.3	1.2	180.0
3	-10	0	4.2	3.9	0.0
3	-9	0	3.2	3.1	180.0
3	-9	2	1.6	1.6	-75.0
3	-9	3	5.7	5.4	-146.0
3	-9	4	2.3	2.5	40.5
3	-8	0	4.0	3.2	180.0
3	-8	1	3.2	2.4	-142.8
3	-8	2	3.0	2.7	-58.3
3	-8	3	9.6	9.5	126.7
3	-8	4	2.9	2.3	-70.8
3	-7	0	6.8	6.0	0.0
3	-7	1	11.4	11.6	-68.9
3	-7	2	2.4	2.0	133.5
3	-7	3	3.0	2.6	60.9
3	-7	4	4.1	3.8	-49.6
3	-6	0	8.5	7.8	180.0
3	-6	1	7.9	7.5	32.7
3	-6	2	10.6	10.1	133.6
3	-6	3	4.9	4.6	-84.5
3	-6	4	4.5	4.9	-3.9
3	-6	5	2.4	1.9	76.8
3	-5	0	2.2	3.4	0.0
3	-5	1	3.4	4.0	-19.5
3	-5	2	5.8	5.6	66.3
3	-5	3	1.0	2.4	140.3
3	-5	4	4.0	4.8	36.4
3	-5	5	4.4	4.2	150.3
3	-4	0	8.5	9.0	0.0
3	-4	1	10.8	11.0	-113.9
3	-4	2	8.7	8.6	172.8
3	-4	3	1.5	2.9	116.4
3	-4	4	6.7	6.7	141.3
3	-4	5	4.7	4.5	-145.8
3	-3	1	10.7	10.1	-142.0
3	-3	2	3.9	4.5	-121.8
3	-3	3	6.1	6.1	163.0
3	-3	4	4.5	4.5	-21.6
3	-3	5	2.9	2.8	-17.6
3	-3	6	2.7	2.1	-108.9
3	-2	1	14.8	15.0	-71.5
3	-2	2	3.8	3.7	52.0
3	-2	3	7.8	7.6	144.4
3	-2	4	2.9	2.7	-18.9
3	-2	5	2.0	1.3	-179.1
3	-2	6	3.6	3.5	139.2
3	-1	1	13.6	13.8	88.3
3	-1	2	7.8	7.4	153.3
3	-1	3	9.5	9.3	89.2
3	-1	4	3.7	4.1	-26.0
3	-1	5	5.1	5.2	-159.5
3	-1	6	4.3	3.9	57.0
3	0	0	12.4	12.9	180.0
3	0	1	22.0	22.2	-113.2
3	0	2	13.8	13.0	173.8
3	0	3	7.7	7.1	-16.4
3	0	4	5.6	5.5	-1.9
3	0	5	1.6	1.1	-13.5
3	0	6	3.1	3.3	-36.8
3	1	0	10.8	11.9	180.0
3	1	1	14.0	14.0	-109.0
3	1	2	4.8	6.2	84.5
3	1	3	6.3	6.4	95.3
3	1	4	5.8	6.2	99.1
3	1	5	7.5	6.9	92.3
3	1	6	1.7	1.8	166.2
3	2	0	6.0	7.5	180.0
3	2	1	4.4	4.6	1.1
3	2	2	11.8	11.5	9.7
3	2	3	4.1	4.7	131.9
3	2	4	1.7	2.7	-21.9
3	2	5	6.7	6.4	-173.3
3	2	6	1.2	1.0	121.0
3	3	1	5.5	5.4	-44.7
3	3	2	6.7	6.0	135.1
3	3	3	2.9	2.8	40.6
3	3	4	3.7	3.8	-174.0
3	3	5	3.9	3.4	-122.6
3	4	0	6.1	6.7	0.0
3	4	1	2.6	2.6	102.1
3	4	2	3.7	4.1	-124.3
3	4	3	2.3	1.5	80.7
3	4	4	2.6	3.1	125.8
3	4	5	2.8	2.6	2.0
3	5	0	8.5	8.4	180.0
3	5	2	2.7	1.4	-45.1
3	5	3	1.4	1.6	177.4
3	5	4	1.7	1.4	20.8
3	6	0	6.5	6.2	180.0
3	6	1	3.8	3.7	-154.7
3	6	2	4.5	4.6	68.7
3	6	3	3.5	3.5	108.0
3	7	0	3.3	2.7	180.0
3	7	1	3.1	2.9	-75.8
3	7	2	4.4	4.0	-93.3
3	8	1	5.7	4.7	-2.3
3	8	2	2.4	1.9	-38.1
4	-10	0	3.7	3.3	0.0
4	-10	1	1.7	1.3	125.1
4	-10	2	2.5	2.5	-15.5
4	-9	0	6.2	5.9	180.0
4	-9	1	1.0	1.5	-103.5
4	-9	2	1.5	1.3	0.5
4	-9	3	3.0	3.5	167.6
4	-8	0	3.3	2.7	180.0
4	-8	1	2.1	2.5	169.9
4	-8	2	2.4	2.1	26.3
4	-8	3	5.0	5.1	157.5
4	-8	4	3.5	3.4	-115.0
4	-7	1	3.6	3.6	-68.1
4	-7	2	3.1	3.7	-62.1
4	-7	3	2.5	3.5	-85.6
4	-7	4	3.7	2.5	-28.5
4	-6	0	2.4	2.3	0.0
4	-6	1	3.5	4.1	31.1
4	-6	2	3.7	4.2	-81.1
4	-6	4	1.4	1.9	49.7
4	-6	5	1.3	1.7	71.0
4	-5	0	6.3	6.4	0.0
4	-5	1	2.1	1.7	138.9
4	-5	2	2.8	3.7	-24.1
4	-5	3	1.0	1.6	167.0
4	-5	4	4.9	4.8	-159.2
4	-5	5	1.7	1.1	38.9
4	-4	0	13.5	13.4	180.0
4	-4	1	5.4	5.0	-95.3
4	-4	2	2.7	2.5	-122.0
4	-4	5	1.6	1.5	42.1
4	-3	0	15.8	15.6	0.0
4	-3	1	4.9	5.6	-95.0
4	-3	2	7.6	7.0	16.5
4	-3	3	8.5	8.7	178.3
4	-3	4	6.7	7.0	64.0
4	-3	5	1.3	1.5	1.4
4	-3	6	1.8	1.8	-142.3
4	-2	0	16.7	16.3	0.0
4	-2	2	7.0	7.7	-139.2
4	-2	3	9.8	9.9	-170.6
4	-2	4	7.0	6.9	-156.3
4	-1	0	2.4	1.1	180.0
4	-1	1	10.4	10.0	151.9
4	-1	2	5.6	5.5	-106.2
4	-1	3	1.5	1.9	65.0
4	-1	4	8.0	8.6	-75.1
4	-1	5	2.5	2.3	15.0
4	-1	6	1.4	0.9	68.2
4	0	0	1.1	2.0	180.0
4	0	1	13.1	13.4	-168.3
4	0	2	2.5	2.8	27.4
4	0	3	5.7	5.5	-112.6
4	0	4	7.1	6.7	22.3
4	0	5	4.1	4.3	-21.4
4	0	6	1.5	1.7	177.2
4	1	0	3.4	4.3	180.0
4	1	1	7.5	7.6	-6.7
4	1	2	5.4	5.0	-152.5
4	1	3	2.5	3.2	-59.8
4	1	4	3.6	4.2	83.7
4	1	5	5.7	5.2	110.9
4	2	0	5.2	3.7	0.0
4	2	3	2.6	2.3	-102.2
4	2	4	1.9	1.4	-107.3
4	2	5	4.3	4.0	162.5
4	3	0	6.6	6.4	0.0
4	3	1	11.6	11.5	-165.2
4	3	2	3.7	3.7	-128.0
4	3	3	2.4	3.1	149.6
4	3	4	1.5	2.4	173.9
4	3	5	2.6	2.2	-44.5
4	4	0	10.5	10.4	0.0
4	4	1	4.1	3.4	-105.9
4	4	3	2.8	2.5	-6.7
4	4	4	1.6	1.4	173.1
4	5	0	2.5	2.4	180.0
4	5	1	7.1	7.0	119.8
4	5	2	4.2	4.3	89.9
4	5	3	3.4	4.0	-110.5
4	5	4	1.8	1.8	-81.6
4	6	0	6.0	5.7	180.0
4	6	1	6.0	6.1	160.1
4	-5	5	1.7	1.7	38.9
4	-4	0	13.5	13.4	180.0
4	-4	1	5.4	5.0	-95.3
4	-4	2	2.7	2.5	-122.0
4	-4	5	1.6	1.5	42.1
4	-3	0	15.8	15.6	0.0
4	-3	1	4.9	5.6	-95.0
4	-3	2	7.6	7.0	16.5
4	-3	3	8.5	8.7	178.3
4	-3	4	6.7	7.0	64.0
4	-3	5	1.3	1.5	1.4
4	-3	6	1.8	1.8	-142.3
4	-2	0	16.7	16.3	0.0
4	-2	2	7.0	7.7	-139.2
4	-2	3	9.8	9.9	-170.6
4	-2	4	7.0	6.9	-156.3
4	-1	0	2.4	1.1	180.0
4	-1	1	10.4	10.0	151.9
4	-1	2	5.6	5.5	-106.2
4	-1	3	1.5	1.9	65.0
4	-1	4	8.0	8.6	-75.1
4	-1	5	2.5	2.3	15.0
4	-1	6	1.4	0.9	68.2
4	0	0	1.1	2.0	180.0
4	0	1	13.1	13.4	-168.3
4	0	2	2.5	2.8	27.4
4	0	3	5.7	5.5	-112.6
4	0	4	7.1	6.7	22.3
4	0	5	4.1	4.3	-21.4
4	0	6	1.5	1.7	177.2
4	1	0	3.4	4.3	180.0
4	1	1	7.5	7.6	-6.7
4	1	2	5.4	5.0	-152.5
4	1	3	2.5	3.2	-59.8
4	1	4	3.6	4.2	83.7
4	1	5	5.7	5.2	110.9
4	2	0	5.2	3.7	0.0
4	2	3	2.6	2.3	-102.2
4	2	4	1.9	1.4	-107.3
4	2	5	4.3	4.0	162.5
4	3	0	6.6	6.4	0.0
4	3	1	11.6	11.5	-165.2
4	3	2	3.7	3.7	-128.0
4	3	3	2.4	3.1	149.6
4	3	4	1.5	2.4	173.9
4	3	5	2.6	2.2	-44.5
4	4	0	10.5	10.4	0.0
4	4	1	4.1	3.4	-105.9
4	4	3	2.8	2.5	-6.7
4	4	4	1.6	1.4	173.1
4	5	0	2.5	2.4	180.0
4	5	1	7.1	7.0	119.8
4	5	2	4.2	4.3	89.9
4	5	3	3.4	4.0	-110.5
4	5	4	1.8	1.8	-81.6
4	6	0	6.0	5.7	180.0
4	6	1	6.0	6.1	160.1
4	6	3	1.6	1.2	-102.8
4	7	1	3.3	3.2	-86.0
4	7	2	2.4	2.8	-97.6
5	-10	0	2.3	3.2	0.0
5	-9	0	2.9	2.2	180.0
5	-9	2	1.4	1.5	151.9
5	-8	1	1.7	2.3	100.1
5	-8	3	1.6	1.5	-74.2
5	-7	0	3.5	3.1	0.0
5	-7	1	2.7	2.9	-122.5
5	-7	2	1.9	1.5	66.0
5	-7	3	1.6	1.9	5.1
5	-6	1	6.2	5.8	128.6
5	-6	2	5.6	5.7	-92.3
5	-6	3	2.2	2.6	140.3
5	-6	4	2.4	2.2	-94.6
5	-5	0	1.9	1.3	180.0
5	-5	1	3.4	3.7	18.5
5	-5	2	6.4	6.7	-44.5
5	-5	3	6.4	6.5	-56.1
5	-5	4	2.4	2.7	-151.3
5	-5	5	1.0	1.1	20.4
5	-4	0	4.4	4.2	180.0
5	-4	1	7.2	6.9	-16.0
5	-4	2	1.4	1.7	15.3
5	-4	3	7.9	8.3	30.1
5	-4	4	2.9	2.8	144.7
5	-3	0	9.5	9.9	0.0
5	-3	1	1.1	1.2	-107.6
5	-3	2	2.6	2.5	-70.6
5	-3	3	7.9	8.3	116.8
5	-3	4	1.7	2.2	107.3
5	-3	5	1.6	1.5	-117.6
5	-2	0	6.8	6.8	0.0
5	-2	1	2.2	1.6	-69.7
5	-2	2	5.9	5.6	81.5
5	-2	3	5.5	6.3	-147.2
5	-2	4	5.7	6.2	-160.7
5	-2	5	1.2	0.7	9.2
5	-1	0	8.5	8.6	180.0
5	-1	1	4.0	2.4	25.6
5	-1	2	3.6	3.4	17.3
5	-1	4	6.1	7.1	-74.3
5	-1	3	1.3	0.8	-93.9
5	-1	5	1.4	1.4	44.8
5	0	0	5.5	5.9	0.0
5	0	1	5.6	3.8	16.4
5	0	2	5.2	6.2	-84.3
5	0	4	2.0	2.1	40.7
5	0	5	2.6	2.1	-104.2
5	1	0	10.3	8.9	0.0
5	1	1	8.9	9.3	48.0
5	1	2	1.8	2.7	-106.7
5	1	3	1.3	1.5	-98.0
5	1	4	4.2	4.6	124.8
5	2	0	9.1	10.1	180.0
5	2	1	7.5	7.6	-52.7
5	2	2	4.6	3.3	-109.2
5	2	3	2.5	3.8	84.5
5	2	4	3.4	3.8	-65.2
5	3	0	5.7	5.5	0.0
5	3	1	6.9	7.7	-75.6
5	3	2	2.2	2.9	102.7
5	3	3	5.2	5.5	98.1
5	4	0	10.5	11.2	0.0
5	4	1	2.7	3.1	48.6
5	4	2	2.9	3.0	102.2
5	4	3	2.5	2.5	-131.4
5	5	0	3.2	1.9	180.0
5	5	1	2.1	1.9	48.9
5	5	2	1.5	1.5	-141.1
5	5	3	1.1	1.1	-98.9
5	7	0	1.3	1.3	0.0
6	-8	0	1.9	1.6	0.0
6	-8	1	2.8	2.8	55.9
6	-8	2	3.3	3.3	79.2
6	-7	1	3.8	4.1	167.6
6	-7	2	4.6	4.8	115.5
6	-6	1	2.9	3.1	125.8
6	-6	2	6.4	6.5	-121.4
6	-6	3	1.5	1.4	-87.0
6	-5	1	1.3	1.8	38.4
6	-5	2	5.0	5.3	-59.1
6	-5	3	2.8	3.5	-60.1
6	-5	4	1.5	0.9	14.1
6	-4	1	2.8	3.0	-115.3
6	-4	2	2.3	3.3	48.3
6	-4	3	6.6	6.9	43.4
6	-4	4	1.4	1.3	-173.9
6	-3	1	3.5	2.5	113.8
6	-3	2	1.2	1.2	-177.7
6	-3	3	2.5	2.9	74.2
6	-2	0	7.5	6.6	180.0
6	-2	1	3.5	4.9	45.3
6	-2	2	2.7	3.7	108.2
6	-2	3	5.4	5.5	-90.7
6	-2	4	1.3	1.1	7.[illegible]
6	-1	0	3.5	3.3	0.0
6	-1	1	1.8	2.5	-135.3
6	-1	2	5.3	6.0	57.8
6	-1	3	4.2	4.1	-37.1
6	-1	4	2.0	2.0	157.5
6	0	1	8.9	9.3	144.7
6	0	2	6.7	7.4	-79.9
6	0	3	1.5	1.5	-160.1
6	0	4	1.7	2.4	146.3
6	1	0	6.6	7.8	180.0
6	1	1	3.2	3.9	64.3
6	1	2	5.4	5.9	-66.3
6	2	0	4.1	4.7	180.0
6	2	1	3.8	4.5	-41.1
6	2	2	4.0	4.0	49.9
6	2	3	1.6	1.9	10.8
6	3	1	2.8	1.5	126.2
6	5	0	1.0	0.8	180.0
7	-11	0	3.0	2.9	180.0
7	-9	0	1.4	2.0	0.0
7	-7	1	2.1	2.7	156.0
7	-6	2	3.2	3.5	-140.6
7	-5	1	1.0	1.2	-84.7
7	-5	2	2.2	2.2	38.0
7	-4	0	2.0	1.7	180.0
7	-4	1	1.4	1.7	175.1
7	-4	2	1.5	1.2	37.4
7	-4	3	2.2	3.1	128.8
7	-3	1	4.9	5.0	-12.6
7	-3	2	4.1	4.8	-158.2
7	-3	3	3.5	3.8	7.0
7	-2	0	4.1	3.4	0.0
7	-2	1	2.2	2.3	17.8
7	-2	2	4.9	5.1	118.6
7	-2	3	1.5	2.5	-25.0
7	-1	0	1.5	1.4	0.0
7	-1	1	4.6	5.5	175.8
7	-1	2	1.7	3.3	69.2
7	0	1	2.3	2.0	-139.8
7	0	2	1.7	1.3	-146.4
7	1	1	1.3	1.6	49.0
8	-9	0	1.0	1.4	0.0
8	-5	0	4.3	4.3	180.0
8	-3	0	2.4	2.8	0.0

$1{\cdot}0|F_o|+9{\cdot}5)$ when $|F_o|\geq 9{\cdot}5$ and $w=0{\cdot}001|F_o|^2$ when $|F_o|<9{\cdot}5$.

In Table 1 the observed structure amplitudes are listed and those calculated from the final atomic parameters are given in Table 2. The atomic scattering factors used were those from *International Tables for X-ray Crystallography* (1962).

Fig. 1 shows the crystal structure projected down the *c* axis and Fig. 2 gives the interatomic distances and interbond angles with their standard deviations. The crystal contains isolated, essentially planar 4,6-dinitrobenzfuroxan molecules.

The carbon atoms of the benzene ring have maximum and mean deviations from their least-squares best plane of 0·016 and 0·013 Å respectively. The mean C–C bond length in the benzene ring is 1·39 Å [*cf.* benztrifuroxan (Cady, Larson & Cromer, 1966) 1·434 Å mean] but the difference in length between the longest and the shortest bonds, C(4)–C(5), 1·44, and C(2)–C(3), 1·36 Å, may be significant although the differences in bond length are not readily interpreted in terms of the possible electronic structures of the molecule. Within the benzene the bond angles of C(3) and C(5) which have nitro-group substituents are greater than 120°, C(2)–C(3)–C(4), 124°, C(4)–C(5)–C(6), 128°. The angle at C(1), 128°, is also in excess of 120° unlike the angle at carbon (5) in 1,3-dinitrobenzene (Trotter & Williston, 1966) which is not significantly different from that at carbon (4) or carbon (6). A similar but less pronounced enlargement of the internal ring angles is found in benztrifuroxan. The large angle at C(1) may suggest that the nitrogen atom at C(1) is more electrophilic than the corresponding atoms in benztrifuroxan.

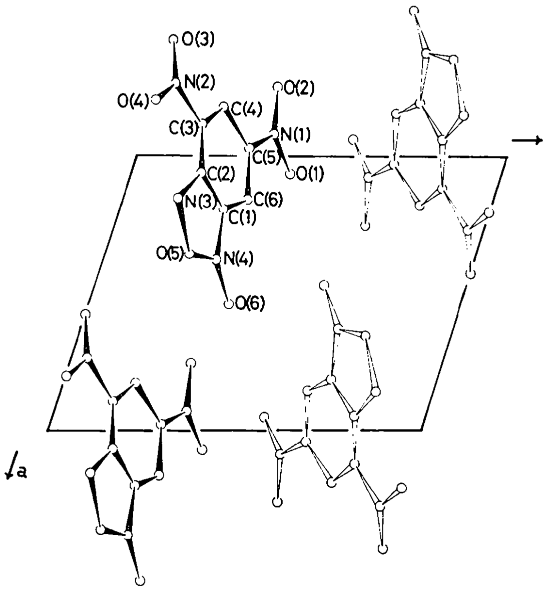


Fig. 1. The crystal structure of 4,6-dinitrobenzfuroxan seen projected down **c**

The pair of *ortho* nitroso groups link in the expected manner to form a furoxan (furazan-*N*-oxide) system. The five atoms of the furazan group are very nearly coplanar (maximum and mean deviations from the least-squares best plane are 0·012 and 0·008 Å) but the *N*-oxide oxygen atom is 0·07 Å from this plane. The plane of the furazan group makes and angle of only 1·1° with the plane of the benzene ring so that the whole benzfurazan entity can be regarded as planar. Comparison of the dimensions given in Fig. 2 with those found by Cady *et al.* (1966) in benztrifuroxan shows that in 4,6-dinitrobenzfuroxan the carbon–nitrogen bonds are longer and more nearly equal in length than those in the benztrifuroxan.

The dimensions of the two nitro groups are not significantly different from those observed in other nitrobenzenes (see bibliography in *Molecular Structures and Dimensions*, 1970). Both nitro groups are planar. The plane of that containing N(1) and attached to C(5), *i.e.* the group furthest from the furoxan ring, is

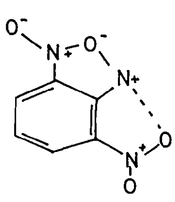
Table 2. *Fractional atomic coordinates and thermal factors with standard deviations in parentheses*

Fractional coordinates and anisotropic thermal parameters are multiplied by 10^3.
The anisotropic temperature factor $T=\exp[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+U_{23}klb^*c^*+U_{13}hla^*c^*+U_{12}hka^*b^*)]$.

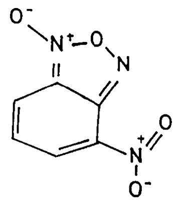
	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	B(Å^2)
C(1)	196 (1)	286 (1)	55 (1)	–	–	–	–	–	–	4·0 (2)
C(2)	63 (1)	186 (1)	185 (2)	–	–	–	–	–	–	4·6 (2)
C(3)	−119 (1)	149 (1)	116 (2)	–	–	–	–	–	–	4·0 (2)
C(4)	−174 (1)	197 (1)	−79 (2)	–	–	–	–	–	–	4·5 (2)
C(5)	−23 (1)	297 (1)	−195 (2)	–	–	–	–	–	–	3·5 (2)
C(6)	166 (1)	343 (1)	−140*	–	–	–	–	–	–	4·2 (2)
N(1)	−80 (1)	356 (1)	−401 (1)	53 (3)	9 (1)	28 (3)	−1 (2)	−6 (3)	9 (2)	
N(2)	−265 (1)	45 (1)	237 (2)	39 (3)	13 (1)	46 (4)	0 (2)	14 (3)	7 (2)	
N(3)	154 (1)	151 (1)	360 (2)	61 (4)	22 (2)	30 (3)	3 (2)	−9 (3)	18 (2)	
O(1)	55 (1)	429 (1)	−512 (2)	64 (3)	15 (1)	29 (2)	6 (1)	6 (2)	14 (1)	
O(2)	−248 (1)	328 (1)	−432 (2)	43 (2)	34 (2)	55 (4)	13 (2)	−23 (3)	7 (2)	
O(3)	−426 (1)	3 (1)	174 (2)	38 (2)	24 (1)	40 (3)	4 (2)	7 (2)	15 (2)	
O(4)	−208 (1)	6 (1)	409 (2)	48 (3)	26 (1)	44 (3)	17 (2)	7 (2)	15 (2)	
O(5)	350 (1)	230 (1)	345 (2)	30 (2)	28 (1)	41 (3)	2 (2)	−17 (2)	6 (1)	
O(6)	533 (1)	383 (1)	95 (2)	33 (2)	27 (1)	57 (4)	−3 (2)	−2 (3)	3 (1)	

* Parameter fixed to define origin with respect to *z*.

inclined at an angle of 8·9° to the benzene ring and that of the nitro group containing N(2) attached to C(3), adjacent to the furoxan ring, is inclined at an angle of only 2·7° to the benzene ring. The oxygen atom O(4) of this latter nitro group is only 2·63 Å from the nitrogen atom N(3) of the furoxan. Several short non-bonded N···O contacts have been reported and it is difficult to establish the van der Waals contact distance between a nitrogen and an oxygen atom both with chemical environments similar to those found in aromatic nitro compounds, furoxans *etc.* For example, the shortest intermolecular N···O contact in the 4,6-dinitrobenzfuroxan crystal is 3·13 Å, in benztrifuroxan it is 2·997 Å and in 2,3,4,6-tetranitroaniline (Dickinson, Stewart & Hodder, 1966) is 3·09 Å, all suggesting rather small van der Waals radii. Even shorter intramolecular contacts were found in picryl azide in the bis-8-hydroxyquinolinatocopper(II)–picryl azide molecular complex (Bailey & Prout, 1965). These intramolecular N···O contacts of 2·52 and 2·82 Å, observed between a nitro-group oxygen atom and the nitrogen atoms of the azide, are due to the steric requirements of the crystal packing and not to the overcrowding of the substituent groups and there is no reason to suppose that they represent any form of bonding interaction. By analogy, the short contact in 4,6-dinitrobenzfuroxan does not, in itself, provide any urgent reason for supposing that there is a bonding interaction between these atoms. However, when the molecule is compared with benztrifuroxan there is a marked absence of lengthening of the C–C bonds in the benzene ring, an elongation of the bonds in the furoxan ring and a greater equivalence of the bonds at the furazan oxygen atom. These, together with the coplanarity of the *ortho* nitro group and the short N···O contact, indicate that there is an increase in the importance of the resonance form (V) with respect to that of (VI).



(V)



(VI)

If 6-nitrobenzfuroxans are stabilized by a contribution from the resonance form (V) then the molecule (III), which is sterically prevented from adopting a planar form, might be expected to be less stable than the isomer (IV) which is potentially a planar molecule. The shape of the 4,6-dinitrobenzfuroxan indicates that the rearrangement of I–II is possible but the distances that the nitrogen and oxygen atoms are required to move in the rearrangement are sufficiently great to make it most unlikely that the rearrangement would be fast.

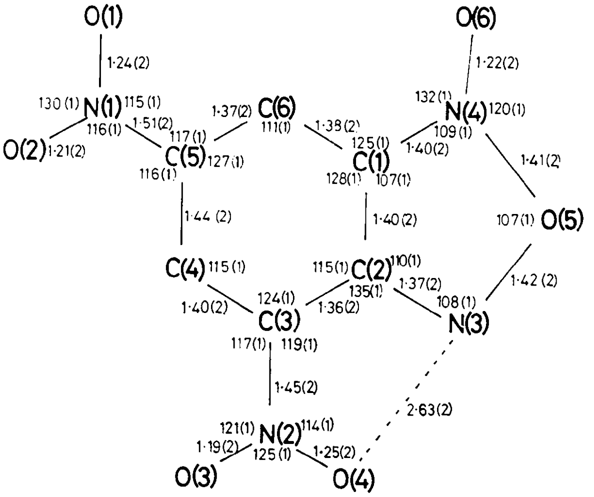


Fig. 2. 4,6-Dinitrobenzfuroxan; interatomic distances and interbond angles with standard deviations in parentheses.

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