Geometric and electronic structure of dicyanofuroxan by experiment and theory

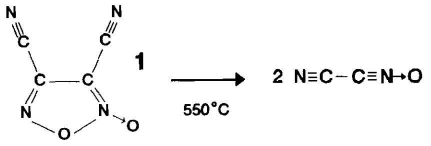
Tibor Pasinszki,† George Ferguson and Nicholas P. C. Westwood*

Guelph-Waterloo Centre for Graduate Work in Chemistry, Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1

Dicyanofuroxan (3,4-dicyano-1,2,5-oxadiazole 2-oxide), the precursor to the novel NCCNO species, has been studied in the solid and gas phases to obtain both structural and electronic information. The solid-state structure determined by X-ray diffraction gives an orthorhombic space group *Pna*2$_1$, with a = 10.2578(14), b = 10.8818(12) and c = 10.2259(15) Å. There are two independent molecules with similar geometries in the asymmetric unit. The gas-phase molecule is characterized by HeI photoelectron, HeI and HL$_{\alpha,\beta,\gamma}$ photoionization and IR spectroscopies. The vibrational data is also supported by a Raman study of the solid. The equilibrium geometry of dicyanofuroxan obtained from *ab initio* calculations at the HF and MP2/6-31G* levels lends support to the crystallographic result of an asymmetric planar five-membered ring with three quite different N–O bonds, including a very short (and strongly polarized) exocyclic *N*-oxide group. Nevertheless, both HF and MP2 calculations are in poor quantitative agreement with the solid-state structure. Density functional theory (B3-LYP) is, however, much more in accord with the crystallographic result, as indeed, it is with the vibrational data.

Furoxans (1,2,5-oxadiazole 2-oxides), also known as furazan *N*-oxides, have a long and fascinating history with much debate and controversy.[1–3] In the 1850s,[4] the first preparation of a furoxan, dibromofuroxan (from mercury fulminate and bromine), went unrecognised since for a couple of decades the reaction product was believed to be dibromonitroacetonitrile. After a century of debate, NMR spectroscopy and X-ray crystallography clarified the general form of furoxans as planar five-membered rings with an exocyclic *N*-oxide group.[2] The electronic structure of furoxans is less understood; the furoxan ring, especially in the parent furoxan $H_2C_2N_2O_2$, which is unknown, is best described as electron-overcrowded.[5,6] Substitution permits delocalization of this excess charge onto the substituents, offering stability to the furoxans, and may explain the non-existence of the unsubstituted parent furoxan and the lability of monosubstituted furoxans.[5] Indeed, the sum of the calculated [HF/6-31G(d)] total atomic charges for the six atoms of the furoxan moiety is $-0.44\,e$‡ in the parent furoxan and is only $-0.07\,e$ in the stable dibromo derivative.[7] Dipole moment measurements confirm that the electron distribution in furoxans is unusual and cannot be described by just two or three simple mesomeric structures.[8] Such electron-rich and unsaturated systems are especially interesting from a theoretical point of view since any description of their electronic and geometric structure requires the best possible description of electron correlation. Unfortunately this effect was neglected in earlier semiempirical and *ab initio* HF calculations;[5,6,9,10] thus these methods were not entirely successful in describing accurately the structure, especially the three interconnected N–O bonds. The only study performed at the correlated level is the MP2/6-31G* calculation on the parent furoxan,[11] which confirms the importance of electron correlation, although, as suggested recently,[7] even this fails to give a true representation of the structure. Since the actual structure of the parent molecule is unknown, a comparison between theory and experiment is not possible.

The electronic and geometric structure of dicyanofuroxan, **1**, (3,4-dicyano-1,2,5-oxadiazole 2-oxide) is especially interesting since two highly unsaturated CN groups are attached to the unsaturated furoxan moiety, providing an opportunity for investigating the effect of inductive electron-withdrawing substitution on the ring. This is also relevant to the observation that **1** can undergo thermolytic cycloreversion to produce cleanly two moles of the novel penta-atomic molecule, NCCNO,[12] a linear or quasi-linear molecule of potential astrophysical interest (Scheme 1).



Scheme 1

1 was first prepared in 1925 from the tetramer of fulminic acid, isocyanilic acid, HON=CH[$C_2N_2O_2$]CH=NOH, or from fulminic acid, HCNO.[13] The strongly unsaturated character of the molecule has attracted special interest in using it as an explosive.[14] Like many of the furoxans, **1** reacts with dipolarophiles in toluene or xylene at refluxing temperatures. It has been shown that such reactions do not go *via* an *N*-oxide 1,3-dipolar cycloaddition, but give nitrone-type 1,3-dipolar cycloadducts.[15] Spectroscopic studies have been limited to the negative ion mass spectrum[16] and the infrared band positions of a capillary melt[17] have been obtained.

In this work we report the first solid-phase crystallographic study of **1** and the first detailed gas-phase characterization, which collectively provide information on the geometric and electronic structure. The gas-phase studies include ultraviolet photoelectron (PE) spectroscopy, HeI and HL$_{\alpha,\beta,\gamma}$ photoionization mass spectroscopy (PIMS) and mid-infrared (IR) spectroscopy. The vibrational component of this work is complemented by Raman spectra of the solid. Our intent is to evaluate the crystal structure of this dicyano-derivative in the context of other furoxan structures and to gain an insight into the electronic structure of such an electron-rich species. To these ends the experimental aspects of this work are complemented by conventional Hartree-Fock (HF) and Møller–Plesset (MP2) quantum mechanical methods, and, in addition, by density functional theory (DFT).

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† Permanent address: Department of Inorganic Chemistry, Technical University, H-1521 Budapest, Hungary.

‡ $e \approx 1.602 \times 10^{-19}$ C.

Table 1 Summary of crystal data, data collection, structure solution and refinement details

(*a*) Crystal data	
Empirical formula	$C_4N_4O_2$
Molar mass	136.08
Colour, habit	Colourless, needle
Crystal size/mm	0.40 × 0.21 × 0.21
Crystal system	Orthorhombic
a/Å	10.2578(14)
b/Å	10.8818(12)
c/Å	10.2259(15)
α/degrees	90
β/degrees	90
γ/degrees	90
V/Å^3	1141.4(3)
Space group	$Pna2_1$
Z	8
Molecular symmetry	None
F(000)	544
d_{calc}/g cm^{-3}	1.584
μ/mm^{-1}	0.133
(*b*) Data acquisition[a]	
Temp/K	294(1)
Unit-cell reflcns (θ-range°)	25 (11.1 18.0)
Max. θ (°) for reflcns	26.9
hkl range of reflcns	0 13; 0 13; 0 12
Variation in 3 standard reflcns	1.5%
Reflcns measured	1302
Unique reflcns	1302
Reflcns with $I > 2\sigma(I)$	849
(*c*) Structure solution and refinement[b]	
Refinement on	F^2
Solution method	Direct methods
No. of variables in L.S.	182
k in $w = 1/(\sigma^2F_o^2 + k)$ $[P = (F_o^2 + 2Fc^2)/3]$	$(0.0671P)^2$
R, R_w, *gof*	0.034, 0.102, 0.99
Density range in final Δ-map, e Å^{-3}	−0.143, 0.215
Final shift/error ratio	0.000
Sec. extnct. type	SHELXL
Sec. extnct. correction	0.0323(43)

[a] Data collection on an Enraf-Nonius CAD4 diffractometer with graphite monochromatized Mo-Kα radiation (λ 0.7107 Å). [b] All calculations were done on a Silicon Graphics 4D-35TG computer system with the NRCVAX system of programs[18] and with SHELXL-93[19] for refinement with all data on F^2.

Experimental

Dicyanofuroxan **1** was synthesized from cyanoacetic acid (Aldrich) using the literature method.[17] It was purified by vacuum sublimation to afford white crystals, melting point 42 °C. **1** reacted with the epoxy adhesive normally used to mount crystals and because it sublimed readily at room temperature, a suitable crystal was mounted in a glass capillary for the X-ray structure determination. Concise details of crystal data, data collection, structure solution and refinement are provided in Table 1, and full details are provided in the Supplementary material.§ The systematic absences allow the space group to be either $Pna2_1$ or *Pnam*. Analysis of the E-statistics indicated that the orthorhombic $Pna2_1$ was the correct choice (with two independent molecules in the asymmetric unit) and this was confirmed by the successful refinement. Space group $Pna2_1$ is polar, but we were not able to establish the direction of the polar axis. The full CIF (Crystallographic Information File) for **1** has been deposited with the Cambridge Crystallographic Data Centre and is also available from the authors.

The HeI (21.2 eV) PE spectrum was recorded on a fast pumping PE spectrometer at an operational resolution of 45 meV. The spectrum was calibrated with the known ionization potentials (IPs) of O_2 and N_2. The spectrometer, a modification of an earlier version,[20] can also mass analyse ions produced in the photoionization process using a quadrupole mass analyser (Hiden Analytical, 320 amu) mounted directly above the photoionization point. The conventional EI source of the mass analyser is removed, ionization being provided by HeI or unfiltered $HL_{\alpha,\beta,\gamma}$ (10.2–12.7 eV) radiation. Although not done in coincidence, PE and PIMS spectra can be recorded within seconds of each other; thus it is assumed that for a given PE spectrum the subsequent PIMS is of the same compound. For both PE and IR measurements **1** has sufficient vapour pressure at ambient temperatures.

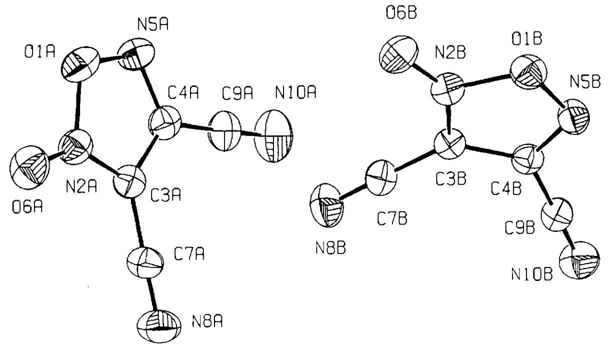

Fig. 1 View of the two independent molecules of dicyanofuroxan, A and B, in the asymmetric unit showing the numbering scheme. Thermal ellipses are drawn at the 30% level.

The IR spectrum, recorded at 0.5 cm^{-1} resolution, was collected on a Nicolet 20SXC interferometer using a 20 cm single pass gas cell. The cell, with KBr windows, gave a spectral range from 4000–400 cm^{-1}. The sample pressure was maintained constant between 140–150 mTorr by pumping **1** continuously through the cell using a rotary pump.

The Raman spectrum of the solid crystalline material was recorded, using Nd:YAG excitation (1.064 μm), on a Bruker RFS 100 FT–Raman spectrometer at 2 cm^{-1} resolution and a laser power of 100 mW.

Computational methods

Ab initio calculations for **1** were carried out at the HF and MP2 levels using a standard 6-31G* basis set. All electrons were included in the correlation energy calculations at the MP2 level (*i.e.* 'full'). Density functional theory was also used to calculate the equilibrium structure in the form of Becke's three-parameter exchange functional in combination with the Lee, Yang and Parr (LYP) correlation functional (B3-LYP) as implemented in the GAUSSIAN-92/DFT quantum chemistry package[21] using a 6-31G* basis set. Equilibrium molecular geometries were fully optimized and harmonic vibrational frequencies were then calculated at the HF, MP2 and B3-LYP levels using numeric second derivatives. All calculations were performed on a Silicon Graphics Inc. Challenge/XL workstation.

Results and discussion

Crystal and molecular structure from X-ray diffraction measurements

A view of the two independent molecules (A and B) of **1** is shown in Fig. 1, together with the labelling of the atoms. Examination of the structure with PLATON[22] showed that the two molecules were not related by any symmetry elements and that there were no voids in the crystal lattice. Table 2 lists the final fractional coordinates for **1** and Table 3 contains the

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§ Crystallographic data has been deposited. For details of the CCDC deposition scheme, see 'Instructions for Authors (1996)', *J. Chem. Soc. Perkin Trans. 2*, 1996, issue 1.

molecular dimensions. In both independent molecules the five-membered rings are individually planar, but the cyano groups are asymmetrically displaced slightly to the same side of the ring plane. Deviations are, for molecule A (all values in Å): C7, +0.085(6); N8, +0.172(8); C9, +0.013(5); N10, + 0.040(7). The corresponding values for molecule B are: C7, + 0.058(5); N8, +0.105(7); C9, +0.012(5); N10, +0.068(7). This results in the C7–C3–C4–C9 torsion angles being 3.5(6) and 3.9(5)° for molecules A and B, respectively.

There are no untoward contacts between molecules in the crystal lattice; the shortest intermolecular contacts [3.132(4) to 3.319(4) Å] all involve the exocyclic O atoms and correspond with normal van der Waals contacts.

The two sets of bond lengths and angles in Table 3 generally agree, although there are some differences, *e.g.* O1–N2, C4–C9 and C9–N10. This may be a reflection of the different molecular environments in the solid phase. The third column of experimental data in Table 3 shows the mean values and their esds. The bond lengths and angles in the furoxan substructure generally track those in other substituted derivatives determined by crystallographic methods,[2,23] but nevertheless all bonds, except C4–N5, are outside either the upper or lower quartiles determined from a critical analysis of the mean bond lengths of 14 substituted furoxans of known structure.[23] Even the C4–N5 bond length is right at the lower limit. For ease of comparison the mean values of these literature data[23] are included in Table 3, column 8. A comparison with these values shows that the endocyclic O1–N2 and N2–C3 bonds are especially long (by 0.016 and 0.028 Å, respectively), whereas the exocyclic N2–O6 bond is much shorter (by 0.028 Å), as are the endocyclic O1–N5 (by 0.0261 Å) and C3–C4 (by 0.016 Å) bonds. What this suggests is that the structure of **1** is not typical of those for other known furoxans, although it should be remarked that the three interconnected N–O bonds still follow the trend, N2–O6 < O1–N5 < O1–N2. The shortened N2–O6 bond is seen to accompany lengthened N2–C3 and O1–N2 bonds, the latter parameter of relevance as a point of thermal cleavage.[12]

Table 2 Final fractional coordinates and U_{eq}

	x	y	z	U_{eq}
O1A	0.2312(2)	0.4844(3)	0.0000(3)	0.0740(7)
N2A	0.2853(3)	0.3657(3)	−0.0000(3)	0.0612(7)
C3A	0.3624(3)	0.3598(3)	−0.1065(3)	0.0523(7)
C4A	0.3536(3)	0.4741(3)	−0.1691(3)	0.0547(8)
N5A	0.2767(3)	0.5487(3)	0.1066(3)	0.0645(8)
O6A	0.2570(3)	0.2982(3)	−0.0892(3)	0.0846(9)
C7A	0.4398(3)	0.2544(3)	−0.1351(3)	0.0614(9)
N8A	0.5029(4)	0.1721(3)	−0.1571(4)	0.0839(10)
C9A	0.4179(3)	0.5116(3)	−0.2843(4)	0.0627(9)
N10A	0.4696(4)	0.5438(4)	0.3754(4)	0.0949(11)
O1B	0.0426(2)	0.2389(2)	0.5169(4)	0.0654(6)
N2B	0.1595(2)	0.3155(2)	0.5159(3)	0.0533(6)
C3B	0.1509(3)	0.3824(2)	0.4063(3)	0.0466(7)
C4B	0.0339(3)	0.3491(3)	0.3453(3)	0.0493(7)
N5B	−0.0288(3)	0.2646(2)	0.4091(3)	0.0587(7)
O6B	0.2357(2)	0.3054(3)	0.6049(3)	0.0724(7)
C7B	0.2456(3)	0.4730(3)	0.3748(3)	0.0574(8)
N8B	0.3201(3)	0.5450(3)	0.3484(3)	0.0806(10)
C9B	−0.0156(3)	0.3987(3)	0.2250(4)	0.0528(8)
N10B	−0.0557(3)	0.4424(3)	0.1320(3)	0.0747(9)

It has been noted previously[2] that the exocyclic N2–O6 bond length does not show much shortening upon conjugation with electron-withdrawing substituents at C3, and this is reflected in the small range for this parameter.[2,23] This is probably because the structures investigated to date involve mainly CH_3, $CONR_2$ and substituted aryl substituents. Nevertheless, in the present case, C3 and C4 substitution by cyano groups has a pronounced effect with a reduction, in what is already a short bond, of some 0.028 Å.

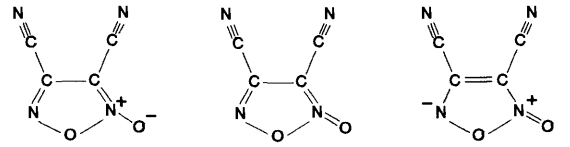
The bond orders of the C–C, C–N and N–O bonds in **1** can be estimated by comparing the experimental bond lengths with those of typical single, double and triple bonds, which can be estimated from the covalent radii[24] using the Schomaker–Stevenson rule.[25] The bond lengths are as follows (all values in Å); C–C bond (single, 1.544), (double 1.334), (triple 1.206); C–N bond (single, 1.473), (double 1.248), (triple 1.114); N–O bond (single, 1.448), (double 1.208), (triple 1.068). The calculated bond orders using the mean of the two sets of experimental bond lengths are included in the final column of Table 3.

Table 3 Calculated (equilibrium)[a] and experimental (crystal)[b] structure of dicyanofuroxan

				Experimental (X-ray diffraction)				
	HF	MP2	B3-LYP	Mol. A	Mol. B	Mean	Ave. lit.[c]	Calc. bond order[d]
N2–O6	1.192	1.200	1.205	1.207(4)	1.205(3)	1.206(4)	1.234	2.0
O1–N5	1.350	1.310	1.351	1.356(4)	1.352(4)	1.354(4)	1.380	1.4
O1–N2	1.336	1.649	1.476	1.446(4)	1.461(3)	1.454(8)	1.438	1.0
N2–C3	1.315	1.355	1.345	1.348(5)	1.339(4)	1.344(5)	1.316	1.6
C3–C4	1.424	1.407	1.430	1.402(5)	1.400(4)	1.401(5)	1.417	1.7
C4–N5	1.275	1.343	1.314	1.300(4)	1.299(4)	1.300(4)	1.304	1.8
C3–C7	1.419	1.412	1.410	1.425(5)	1.421(5)	1.423(5)	(1.427)	1.6
C7–N8	1.134	1.184	1.163	1.129(4)	1.127(4)	1.128(4)	(1.136)	2.9
C4–C9	1.436	1.420	1.425	1.410(5)	1.435(5)	1.423(12)	(1.427)	1.6
C9–N10	1.133	1.183	1.161	1.128(5)	1.140(4)	1.134(6)	(1.136)	2.9
O1–N2–O6	118.5	120.8	119.1	118.0(3)	118.4(3)	118.2(3)		
O1–N2–C3	108.5	100.2	105.2	105.6(3)	105.2(2)	105.4(2)		
N2–C3–C4	104.5	110.5	106.9	106.8(3)	106.8(3)	106.8(3)		
C3–C4–N5	110.6	112.5	111.5	111.6(3)	112.5(3)	112.1(5)		
O1–N5–C4	106.1	109.2	107.4	107.6(3)	106.8(2)	107.2(4)		
C3–C4–C9	127.3	126.1	126.5	127.5(3)	126.0(3)	126.8(8)		
C4–C3–C7	132.3	129.7	131.0	131.0(3)	131.6(3)	131.3(3)		
C3–C7–N8	178.6	179.8	179.1	178.8(4)	179.1(4)	179.0(4)		
C4–C9–N10	178.5	178.6	178.5	178.7(4)	177.2(3)	178.0(8)		
Total energy:	−518.751 220	−520.328 448	−521.664 256					

[a] Bond angles in degrees, bond lengths in Å, total energies in au (1 au = 4.360 × 10^{-18} J); 6-31G* basis set was used; all electrons were included in the correlation energy calculation at the MP2 level ('full'). [b] Geometries of the two independent molecules in the asymmetric unit, and their mean values. For numbering of atoms see Fig. 1. [c] Literature values of average bond lengths from 14 furoxan crystal structures (ref. 23); values in parentheses are for the (C–CN) grouping in similar chemical environments (ref. 23). [d] Calculated using the mean value of the two experimental bond lengths; see text for details.

Thus, the short exocyclic N–O bond may be regarded as a double bond (calculated bond order of 2), whereas N5–O1 lies between a single and double bond with a bond order of 1.4. O1–N2 is a single bond, the longest of the three N–O bonds, this being the point of cleavage upon thermal reversion to two NCCNO molecules.[12] The two C–N bonds of the furazan ring have substantial double bond character, particularly C4–N5 (bond order, 1.8), which is on the opposite side to the exocyclic oxygen. The C–C bond in the ring, although normally represented as a single bond, also has a strong double bond character (bond order, 1.7). The three most important mesomeric structures of the furoxan moiety which partially explains these findings are shown in Scheme 2. Additional mesomeric structures are required for a full description, especially to describe the effect of the two cyano groups. Their C–N bonds are essentially triple bonds and the strong interaction between the furoxan ring and cyano groups is reflected by some double bond character in the exocyclic C3–C7 and C4–C9 bonds (bond orders = 1.6).



Scheme 2

Calculated structure. The various calculated structures are included in Table 3. Although the calculated equilibrium structure cannot be compared directly with the experimental data determined by crystallographic methods owing to solid-phase effects, we expect the difference between equilibrium and experimental bond lengths and angles in the case of rigid molecules like **1** to be less than 0.01 Å and 2.0°. All three quantum chemical methods give a planar ring structure for **1**, which extends to the exocyclic atoms. The largest drawback of the HF method, noted previously,[7] is that it cannot describe the relative lengths of the three interconnected N–O bonds. In fact, it makes O1–N2 shorter than O1–N5 which is clearly incorrect. In addition, all ring bonds (except C3–C4) are calculated too short, with the critical endocyclic O1–N2 bond calculated far too short. The introduction of electron correlation at the MP2 level overcompensates, increasing O1–N2 by 0.313 Å. Other bond lengths especially the C–N multiple bonds are also exaggerated by this method. The MP2 method actually performs worse than HF (average deviation for MP2, 0.043 Å; for HF, 0.024 Å), illustrating that MP2 does not provide a sufficient description of electron correlation in the case of this molecule. A larger basis set and a higher level of theory is required which is, given our computational limitations, not feasible for this size of molecule. A possible alternative to traditional electron correlation methods (at least in comparison with MP2) is density functional theory.[26] It has the advantage of performing well with modest basis sets, which describe only the strongly occupied orbitals, not the difficult correlation orbitals. The three-parameter exchange-correlation function of Becke[27] is particularly noteworthy for its good reproduction of geometries and force constants of organic molecules.[28,29] The calculated geometry of **1** using the B3-LYP/6–31G* method is shown in Table 3 and indeed it gives the best agreement with the solid-state structure among the three methods applied herein. Some of the bond lengths are slightly too long, especially the CN triple bonds (*ca.* 0.03 Å too long), a well known deficiency of DFT methods, but the overall average deviation is a reasonable 0.015 Å. The angles are especially well reproduced by the DFT method, the average deviation being only 0.4°, with the maximum, 0.9°.

A recent critical analysis[30] of HF, MP2, MP4, QCISD and DFT (B3-LYP) calculations on the structure of pyrazole compared with the known microwave spectrum, concluded that the QCISD and DFT methods were comparable and closest to experiment. The performance of DFT concurs with that found here for **1** and is also supported by crystallographic and DFT data on dibromofuroxan.[31]

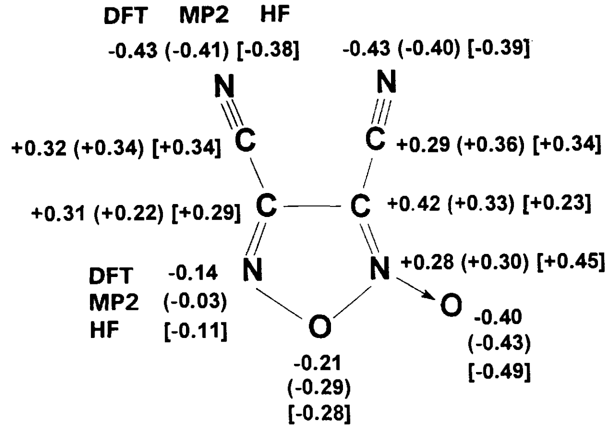


Fig. 2 Calculated charge distribution (in *e*) in dicyanofuroxan using the B3-LYP/6-31G*, MP2/6-31G* (in brackets) and HF/6-31G* (in square brackets) methods

The calculated total atomic charges are shown in Fig. 2. The electron richness of the parent furoxan ring (−0.44 *e*, HF/6-31(d);[7] −0.31 *e*, B3-LYP[31]) is considerably reduced owing to the electron-withdrawing CN substituents, possibly explaining the stability of the molecule. Thus the charge on the furoxan moiety in **1** is positive, +0.09, +0.10 and +0.26 *e* from HF, MP2 and B3-LYP calculations, respectively. The large negative charge on the exocyclic oxygen and large positive charge on N2 is maintained, keeping the exocyclic N2–O6 bond very polarized. The endocyclic oxygen is also negative, but less so than the exocyclic oxygen and the negative charge on N5 is even smaller. Most of the change in electron density in **1** compared with the parent furoxan[32] is a result of removal of electron density from C3 and C4, which ends up on the cyano N atoms. The large positive charge on C3, together with the large negative charge on O6 explains the typical nitrone-type 1,3-dipolar cycloaddition reactions of this molecule.[15,33] Thus the molecule, through the CN groups, can behave as a 1,2-dipolarophile, although this has not been widely investigated so far. The formation of $(NCCNO)_5$ in the thermolysis of **1** has, however, been explained by a [3 + 2] dipolar cycloaddition reaction between intermediate NCCNO and **1**, where **1** is the 1,2-dipole (CN group) and also the source of the 1,3-dipole NCCNO.[34]

HeI and $HL_{\alpha,\beta,\gamma}$ photoionization mass spectra. The HeI PIMS of **1** can be best characterized as a single peak at mass 30 (NO^+) [Fig. 3(*a*)]. The PIMS of dibromofuroxan[7] and conventional mass spectroscopic studies of substituted furoxans[35] have also noted the dominant NO^+ fragment. This can be attributed to easy cleavage of C–N and N–O bonds in furoxans and preservation of the C–C bond. With higher detector sensitivity, the molecular ion at $m/z = 136$ and fragments at $m/z = 76, 60, 46$ and 38 corresponding to $C_4N_2^+$, $N_2O_2^+$, NO_2^+ and C_2N^+, respectively, can be observed with intensities some two to three orders smaller than those of NO^+ [inset to Fig. 3(*a*)]. We note that the $(M-NO)^+$ ion, although evident only very weakly in the PIMS of dibromofuroxan[7] and the mass spectroscopy of substituted furoxans,[35] is not observed here. Other extremely weak fragments in the HeI PIMS at $m/z = 68$, 54 and 48 correspond to $C_2N_2O^+$, C_2NO^+ and C_4^+(?), respectively. The NO^+ signal is very strong in the $HL_{\alpha,\beta,\gamma}$ PIMS spectrum also [Fig. 3(*b*)], although the parent ion signal has increased to *ca.* 10% of the NO^+ intensity due to the reduced fragmentation. Only one weak additional fragment $(N_2O_2)^+$ is observed.

Table 4 Experimental and calculated vibrational frequencies (cm^{-1}) of dicyanofuroxan

Experimental		Calculated		Assignment and description
IR[a]	Raman[b]	Freq.[c]	Intensity[d]	
2264vw	2269vs	2383 (a′)	0.7	ν_1 CN str.
	2254vs	2365 (a′)	4.7	ν_2 CN str.
1662vs	1638w	1742 (a′)	453.0	ν_3 ring str. (C=N–O)
—[e]	—	1530 (a′)	5.1	ν_4 ring str. (C=N)
1461m	1471ms	1485 (a′)	37.6	ν_5 ring str.
1303w	1307ms	1338 (a′)	18.0	ν_6 ring vibr.
1099w	1103m	1129 (a′)	21.9	ν_7 ring vibr.
1043mw	1046w	1085 (a′)	55.5	ν_8 ring vibr.
831w	843w	849 (a′)	19.3	ν_9 ring vibr.
736vw	745vw	752 (a′)	3.8	ν_{10} in-plane vibr.
—	688vw	702 (a″)	4.5	ν_{18} ring out-of-plane def.
—	635m	643 (a′)	1.0	ν_{11} in-plane vibr.
—	588w	602 (a″)	2.2	ν_{19} ring out-of-plane def.
—	525m	526 (a″)	1.6	ν_{20} CCN out-of-plane def.
		525 (a′)	0.6	ν_{12} in-plane vibr.
485w	497m	497 (a′)	19.6	ν_{13} in-plane vibr.
—	454mw	479 (a″)	0.4	ν_{21} CCN out-of-plane def.
438vw	446mw	462 (a′)	6.1	ν_{14} CCN in-plane-def.
	406mw	406 (a′)	3.1	ν_{15} in-plane def.
	304w	303 (a″)	0.01	ν_{22} out-of-plane def.
	184w	182 (a″)	16.6	ν_{23} out-of-plane def.
	(148)w	178 (a′)	8.3	ν_{16} in-plane def.
	112s	109 (a″)	0.5	ν_{24} out-of-plane def.
		104 (a′)	1.7	ν_{17} C–CN in-plane def.
				Lattice mode

[a] Gas phase. [b] Solid phase. [c] Unscaled harmonic frequencies; calculated at the B3-LYP/6-31G* level of theory. [d] IR intensities in km mol^{-1}. [e] Not observed.

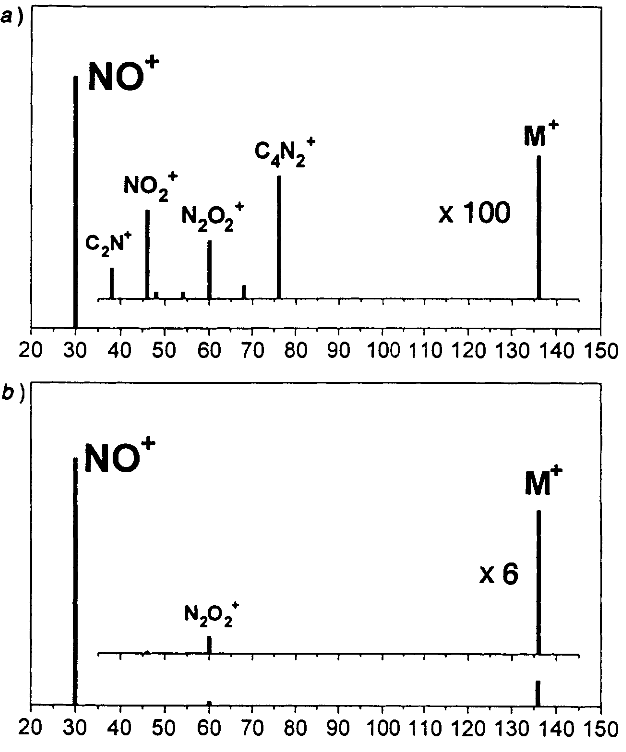


Fig. 3 (*a*) HeI and (*b*) $HL_{\alpha,\beta,\gamma}$ photoionization mass spectra (amu) of gaseous dicyanofuroxan. Insets show expanded ordinates.

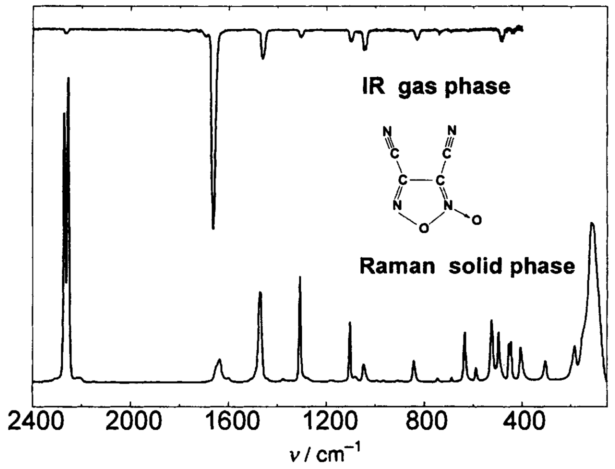


Fig. 4 Gas-phase IR and solid-phase Raman spectra of dicyanofuroxan placed on a common abscissa

IR and Raman spectra. The IR (gas) and Raman (solid) spectra are shown in Fig. 4 with experimental and calculated (B3-LYP/6-31G*) frequencies listed in Table 4. The IR of melt[17] and solid (KBr pellet)[36] have been noted before and are in general accord with the gas-phase data given here. The complementary character of IR and Raman spectroscopy (albeit gas *versus* solid) is illustrated in Fig. 4 since weak bands in the IR spectrum correspond to strong ones in the Raman and *vice versa*. The DFT calculated frequencies are in good agreement with experiment; indeed, they are much better than HF or MP2 values (not shown), but an unambiguous assignment for all bands is not entirely possible owing to the strong mixing of normal modes, arising from similar atomic masses. The very weak band at 2264 cm^{-1} in the IR spectrum corresponding to very strong bands at 2269 and 2254 cm^{-1} in the Raman can be unambiguously assigned to the CN stretches of the two cyano groups. The IR spectra of several aryl-, acyl- and alkyl-furoxans in various solvents have been investigated earlier[37] with the conclusion that no absorption bands characteristic of the furoxan group appear between 4000–1800 cm^{-1}, although there is strong IR absorption in the 1635–1600 cm^{-1} region characteristic of the furoxan group which is assigned to the C=N double bond. The same holds true for dibromofuroxan[7] and is confirmed by the present work on dicyanofuroxan. According to the calculations this normal mode also possesses some N→O character. Most spectra of aryl-, acyl- and alkyl-substituted derivatives[37] also show an additional band, anywhere between weak and strong, in the

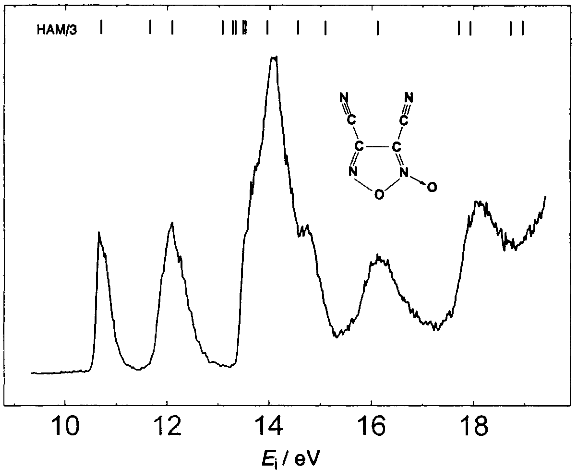


Fig. 5 HeI photoelectron spectrum of gaseous dicyanofuroxan, showing the positions of the calculated HAM/3 ionization potentials

Table 5 Experimental and calculated ionization potentials (eV) of dicyanofuroxan

Experimental E_i[a]	Calculated HAM/3[b]	Orbital character
10.65	10.68 (a″)	π(n_o)
12.09	11.70 (a″)	π
	12.07 (a′)	σ(n_o)
13.4	13.03 (a′)	π(CN)
|	13.27 (a″)	π(CN)
|	13.29 (a′)	π(CN)
|[c]	13.46 (a′)	n_N
|	13.50 (a′)	n_N
|	13.93 (a″)	π(CN)
|	14.56 (a′)	σ
15.3	15.12 (a″)	π
16.1	16.15 (a′)	σ(ring oxygen)
18.1	17.73 (a′)	σ
	17.95 (a″)	π
	18.76 (a′)	σ
	19.00 (a′)	σ($n_{O,terminal}$)

[a] Vertical ionization potentials. [b] The B3-LYP/6-31G* geometry was used. [c] Broad feature between 13.4 and 15.3 eV containing at least seven and possibly eight separate bands. A distinct shoulder occurs at 14.8 eV.

1600–1500 cm^{-1} region, identified as the second C=N ring stretch. This band was not observed in the IR spectrum of dibromofuroxan[7] and also is not seen in the case of **1**, in good agreement with the calculation which predicts a very low IR intensity (Table 4). It is surprising, however, that this mode is not observed in the Raman spectrum of **1** either, because it shows up in the Raman spectrum of dibromofuroxan at 1452 cm^{-1}.[31] The assignment of the next five bands between 1500 and 800 cm^{-1} is straightforward; they have been observed in the IR spectra of all furoxan derivatives investigated so far[37] and can be assigned to the furoxan group. The two C–C stretches and deformations of the two cyano groups are expected in the 800–400 cm^{-1} region with weak IR intensity (Table 4) and are mixed with the normal modes of the furoxan group. The IR spectrum is therefore relatively simple, but all normal modes, including those of the furoxan group, belonging to in- and out-of-plane deformations are observed at a weak to medium intensity in the Raman. Four other bands have been observed below 400 cm^{-1}, the lowest frequency modes possibly being the C–C(N) deformations.

HeI photoelectron spectrum. The HeI photoelectron spectrum of **1** is shown in Fig. 5 and experimental and calculated ionization potentials E_i, are listed in Table 5. Since the breakdown of Koopmans' theorem in the case of molecules containing the cyano group is now well known,[38] the HAM/3 (Hydrogenic Atoms in Molecules) method,[39] which has been shown to give an accurate representation of IPs for molecules containing first-row atoms,[40] has been used herein. Such a calculation for **1**, performed at the B3-LYP geometry, gives very good agreement with experiment (Table 5 and Fig. 5).

A possible starting point to describe the electronic structure of **1** is to consider the molecular orbitals (MOs) of a furazan ring, modified with an exocyclic oxygen atom and mixed to some extent with MOs arising from two CN groups. Furazan has three π orbitals, two high lying at 11.8 eV and one deeper at 16.3 eV.[41] The two high energy π orbitals will mix strongly with the exocyclic oxygen lone pair orbital, O6 pπ and the O6 pσ orbital will mix with the ring σ framework. Three π orbitals and two σ orbitals together with another three σ orbitals from the furazan ring are thus expected below 18 eV. This total of eight MOs will be supplemented by six more arising from the two cyano groups, two terminal nitrogen lone pair n_N and four CN π MOs, all usually observed as a cluster in the 12–15 eV range.[42]

The oxygen pπ and pσ orbitals in relatively simple *N*-oxides, *e.g.* pyridine *N*-oxides,[43] are high lying (8–10 eV) and are separated by *ca.* 1 eV. Furthermore the corresponding oxygen pσ orbital in nitrosyl and carbonyl groups appears in the 10–12 eV region.[44,45] The first band in the spectrum of **1** at 10.65 eV can thus be assigned to the O6 oxygen π lone pair (n_o) with some contribution from the ring. The second band at 12.09 eV is assigned to two MOs; one is the in-plane O6 pσ orbital mixed with the ring σ orbitals and the other is a furazan-like π orbital mixed to some extent with the CN groups. The next intense, broad feature in the spectrum between 13.4–15.3 eV is a result of the overlapping of six strongly localized cyano-based MOs assigned to the four π(CN) and two terminal nitrogen lone pair (n_N) orbitals, together with at least one σ and possibly one π orbital of the furoxan group. A clear identification to individual orbitals is not possible, but the HAM/3 calculations clearly show the clustering of the six CN based MOs (all calculated positions are within 1 eV). The calculations also suggest that the furoxan ring σ orbital is to be located near the shoulder at 14.8 eV, on the high energy side of the cluster; the same MO in dibromofuroxan[7] is observed at *ca.* 13.3 eV. A mute point is whether the π orbital, calculated at 15.12 eV, is located on the high energy side of the cluster, together with the σ orbital, or is associated with the band at 16.1 eV; in Table 5 we have indicated the former. On the basis of the calculations and comparison with the PE spectrum of dibromofuroxan,[7] the next two bands at 16.1 and 18.1 eV can be assigned to a σ orbital with dominant contribution from the ring oxygen and to a σ orbital together with the lowest lying (all bonding) π furazan-type orbital, respectively.

Comparing the E_i values of **1** with those of dibromofuroxan,[7] the latter being the only other furoxan derivative studied by PE spectroscopy so far, it can be seen that all furoxan-type orbitals are stabilized by *ca.* 1.3 eV owing to the electron-withdrawing cyano groups. The HOMO, although mainly localized on O6, is stabilized by 1.18 eV, a remarkably high value. This indicates that the HOMO(furoxan)–LUMO(dipole) controlled 1,3-dipolar cycloadditions may be less important in the case of **1**, depending also on the reagent type, and that HOMO(dipole)–LUMO(furoxan) controlled reactions may become more favourable. Further justification for this is provided by the HF/6-31G* calculations predicting a 1.3 eV stabilization of the LUMO of **1** compared with that of dibromofuroxan.

Conclusion

The crystal structure of dicyanofuroxan, **1**, has been determined; it has an orthorhombic space group, *Pna*2_1, with two independent molecules with similar geometries in the asymmetric unit. The molecular geometry determined by X-ray methods characterizes **1** as a planar five-membered ring with a very short exocyclic N–O bond and a long endocyclic N–O bond. Comparison with other known furoxan structures shows that the crystal structure of **1** is somewhat unique in that the bond lengths lie outside the standard range. The perturbations brought about by the 3,4-cyano substituents could most meaningfully be compared with the parent furoxan (molecule unknown) or the corresponding C_{2v} species, dicyano-1,2,5-oxadiazole (structure unknown), which does not have the exocyclic *N*-oxide group. A comparison with data from HF, MP2 and DFT electronic structure calculations shows that both HF and MP2 perform poorly, whereas DFT (B3-LYP) shows surprisingly good agreement for both the structure and the vibrational frequencies. The gas-phase spectroscopy applied to this molecule has provided information on the valence occupied levels and on the fundamental vibrations. In both cases considerable mixing occurs, commensurate with the delocalized electronic structure and the heavy atom framework based on only C, N and O atoms. Cyano substitution is seen to stabilize the molecule by providing a sink for the electron density on the ring.

Of relevance to the cycloreversion reaction to form NCCNO is the question of the potential energy surface for this cleavage process. Now that we have shown that the DFT method is computationally viable, both in terms of calculated structures and economy, we are actively pursuing this problem.

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