PERKIN 2

Monomer, dimers and trimers of cyanogen *N*-oxide, N≡C–C≡N→O. An X-ray, FVT-MS/IR and theoretical investigation

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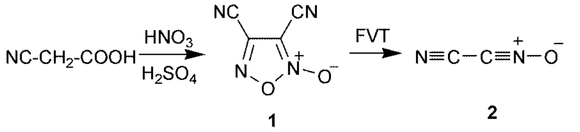
The structures of the trimers **4** and **5** of cyanogen *N*-oxide, NC–CNO **2** are established by X-ray crystallography and ^{13}C NMR spectroscopy. Triethyl phosphite reduction of **4** and **5** affords the 1,2,4-oxadiazolyl-1,2,5-oxadiazole **6**. Deoxygenation of the *N*-oxide moieties in furoxans **1**, **4**, and **5** also takes place easily on the walls of the mass spectrometer. FVT-MS and FVT-IR investigations of furoxans **1**, **4**, and **5** reveal that small amounts of cyano isocyanate, NC–NCO **3** accompany the formation of the main thermolysis product, NC–CNO **2**. The isomerisation of **2** to **3** has a high calculated activation barrier but is catalysed efficiently by Ag_2S. The IR and mass spectra of **3** are analysed.

Introduction

3,4-Dicyano-1,2,5-oxadiazole-2-oxide (3,4-dicyanofuroxan) **1** is obtained by treatment of cyanoacetic acid with a mixture of nitric and sulfuric acids [eqn. (1)].[1]



(1)

1 2

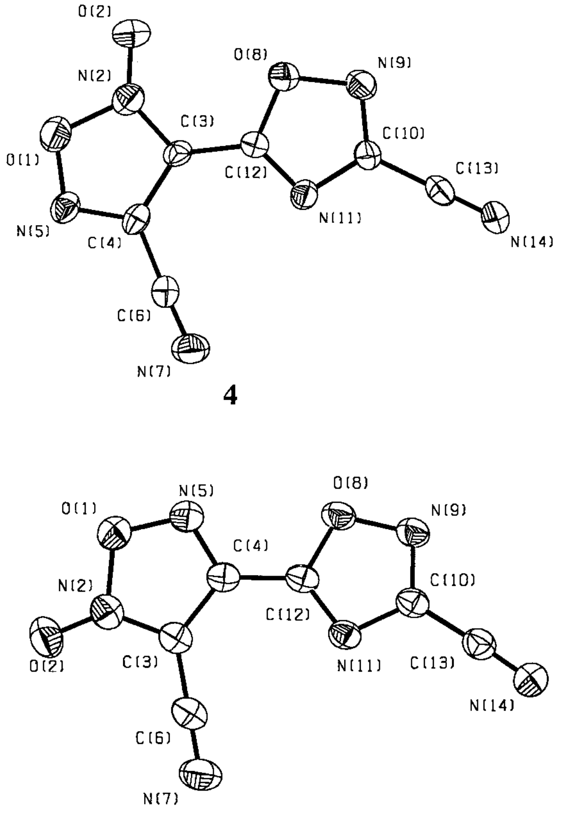
Upon short contact time flash vacuum thermolysis (FVT), **1** is cleaved almost quantitatively into the metastable cyanogen *N*-oxide, NC–CNO **2**.[2–5]

As part of our research on the R–C≡N→X family of reactive molecules (R = O, S, Se),[6–9] we have investigated furoxan **1** and cyanogen *N*-oxide **2** under the conditions of collisional activation (CA) and neutralisation–reionisation (NR) mass spectrometry.[9] Here, we report the isolation and characterization of the trimers **4** and **5** of **2**. While byproducts have been reported before,[10] their actual structures remained uncertain. We also report a thorough analysis by on-line MS of the FVT of **1**, **4**, and **5** as well as the isomerisation of **2** to the isocyanate, NC–NCO **3**.

Results and discussion

NC–CNO dimer and trimers

Two formal trimers of cyanogen *N*-oxide of the composition $C_6N_6O_3$ were isolated from a preparation of furoxan **1** and separated into the pure compounds **4** and **5** by HPLC. The structures of these compounds were established by X-ray crystal structure analysis (Fig. 1). In the crystals, the two rings are almost but not quite coplanar, with dihedral angles of 4.56(0.59)° in the case of **4** and 9.43(0.17)° in the case of **5**. The characteristic bond lengths and angles are reported in Table 1.



4

5

Fig. 1 ORTEP drawings of compounds **4** and **5** (30% probability level).

The structures **4** and **5** are also in complete accord with the ^{13}C NMR spectra, which are listed together with the theoretical values obtained at the GIAO-B3LYP/6-311G** level in Scheme 1.

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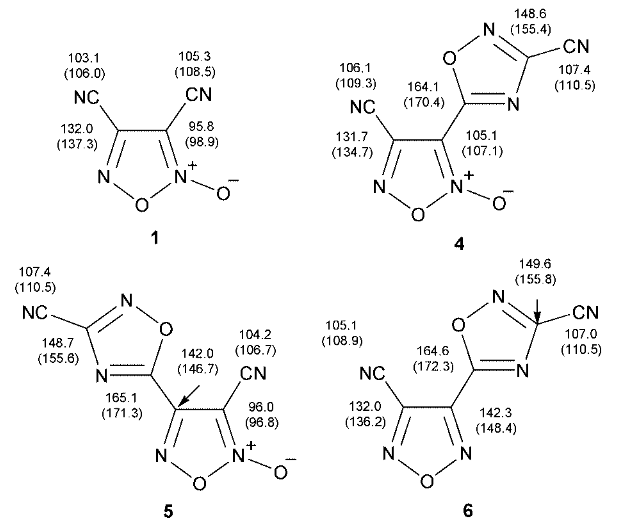
Table 1 Bond lengths (Å) and angles (degrees) for **4** and **5**

	4		**5**
O(1)–N(5)	1.353(9)		1.348(3)
O(1)–N(2)	1.468(10)		1.459(3)
N(2)–O(2)	1.215(10)		1.200(3)
N(2)–C(3)	1.330(11)	C(4)–C(12)	1.329(4)
C(3)–C(12)	1.407(13)		1.441(3)
C(3)–C(4)	1.424(13)		1.412(3)
C(4)–N(5)	1.302(10)	C(3)–C(6)	1.305(3)
C(4)–C(6)	1.425(4)		1.412(4)
C(6)–N(7)	1.141(11)		1.140(4)
O(8)–C(12)	1.362(10)		1.342(3)
O(8)–N(9)	1.414(10)		1.391(3)
N(9)–C(10)	1.294(10)		1.300(3)
C(10)–N(11)	1.370(11)		1.373(3)
C(10)–C(13)	1.463(14)		1.425(4)
N(11)–C(12)	1.283(11)		1.287(3)
C(13)–N(14)	1.110(11)		1.140(4)
N(5)–O(1)–N(2)	108.7(7)		108.5(2)
O(2)–N(2)–C(3)	135.5(9)		135.8(3)
O(2)–N(2)–O(1)	118.6(8)		118.4(3)
C(3)–N(2)–O(1)	105.9(8)	N(5)–C(4)–C(12)	105.8(2)
N(2)–C(3)–C(12)	125.2(9)		121.57(19)
N(2)–C(3)–C(4)	106.3(9)	C(12)–C(4)–C(3)	106.9(2)
C(12)–C(3)–C(4)	128.5(9)	N(2)–C(3)–C(6)	126.9(2)
N(5)–C(4)–C(6)	120.8(9)	N(2)–C(3)–C(4)	121.0(2)
N(5)–C(4)–C(3)	112.3(8)	C(6)–C(3)–C(4)	106.9(2)
C(6)–C(4)–C(3)	126.8(9)	C(3)–N(2)–O(1)	132.1(2)
C(4)–N(5)–O(1)	106.8(7)	N(7)–C(6)–C(3)	105.8(2)
N(7)–C(6)–C(4)	177.8(11)		178.5(3)
C(12)–O(8)–N(9)	106.7(7)		106.58(17)
C(10)–N(9)–O(8)	101.5(7)		102.46(18)
N(9)–C(10)–N(11)	116.9(9)		115.9(2)
N(9)–C(10)–C(13)	121.5(9)		122.0(2)
N(11)–C(10)–C(13)	121.4(9)		122.1(2)
C(12)–N(11)–C(10)	102.1(9)		101.08(19)
N(11)–C(12)–O(8)	112.8(8)		113.9(2)
N(11)–C(12)–C(3)	127.6(9)		127.53(18)
O(8)–C(12)–C(3)	119.4(9)		118.5(2)
N(14)–C(13)–C(10)	117.6(12)		176.7(3)



Scheme 1 Experimental and calculated (in parentheses, GIAO-B3LYP/6-311G**) chemical shifts of **1**, **4**, **5** and **6**. Experimental data (δ in ppm) in CD_3CN (**1**, **4** and **5**) or $CDCl_3$ (**6**).

Triethyl phosphite reduction of the mixture of **4** and **5** afforded the furazan **6**, identified by its ^{13}C NMR spectrum (Scheme 1) as well as the electron ionisation mass spectrum (Table 2).

FVT-MS and FVT-IR

The main product of FVT of furoxan **1** appears at *m*/*z* 68, corresponding to NC–CNO **2**. The CA mass spectrum of the *m*/*z* 68 ions confirms the structure NC–CNO, of which the peaks at *m*/*z* 26, 30, 38, 42, and 52 are characteristic. However, there are additional low intensity signals at *m*/*z* 40, 28, and 54 which, as we will show, are indicative of the presence of the isomeric isocyanate, NC–NCO, **3** (Fig. 2a). The relative intensities of these signals do not increase significantly at higher pyrolysis temperatures (750–850 °C), thus indicating that the NC–CNO→NC–NCO isomerization[11] is difficult and very inefficient thermally.

Table 2 Relative intensities (%) of some significant peaks in the EIMS of **6** at different oven temperatures[a]

m/*z*	188 ($M^{\cdot+}$)	158	136	120	76	68	52	44
200 °C	56	16	30	4	24	100	20	8
400 °C	—	—	22	30	2	100	48	8
600 °C	—	—	4	12	—	58	100	26
750 °C	—	—	—	—	—	52	100	32

[a] The intensity of *m*/*z* 40 was 5–6% at all temperatures listed.

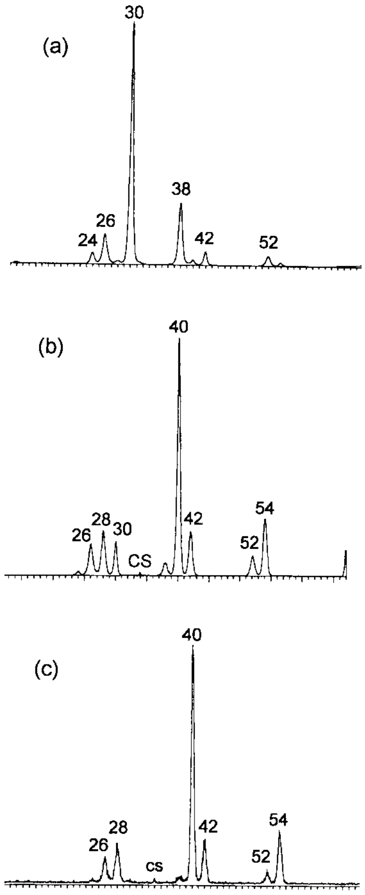


Fig. 2 (a) $CA(O_2)$ mass spectrum of the *m*/*z* 68 ions (largely NC–CNO **2**) resulting from the product of FVT of **1** at 750 °C through a clean quartz tube. (b) Spectrum from the same experiment using an Ag_2S coated FVT tube. (c) CAMS of NC–NCO **3** produced from AgOCN.[13] CS = charge stripping = M^{2+}.

The thermal formation of small amounts of isocyanate **3** was confirmed by FVT with Ar matrix isolation of the products at *ca.* 10 K for IR spectroscopy. Thus, thermolysis of **1** through a clean and empty quartz tube at 430 °C produced essentially only peaks due to the nitrile oxide NC–CNO **2** (and unreacted starting material **1**). At 610 °C, small peaks due to the isocyanate NC–NCO **3** appeared, and these became stronger at 750 °C, although **2** was still by far the dominant absorber in the spectrum. The strongest IR absorptions of **3** are at 2338 and 2283/2277 cm^{-1}. The experimental and calculated IR spectra of **2** and **3** are reported in Table 4.

Additional experiments revealed that the isomerisation of **2**

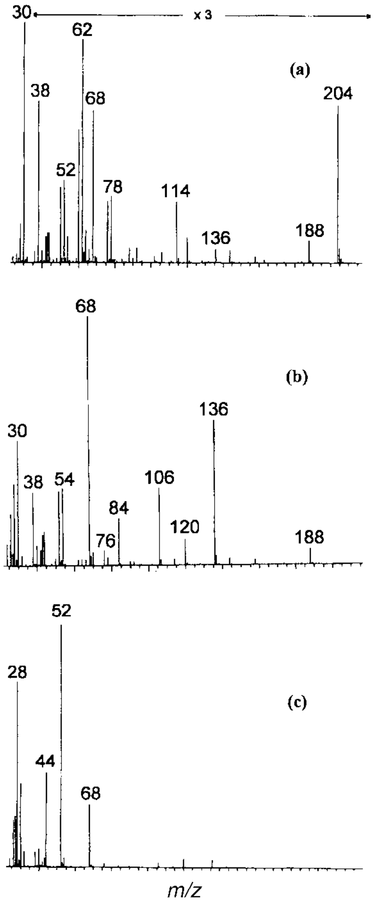


Fig. 3 EIMS of the products of FVT of **4** at (a) 200 °C, (b) 400 °C, and (c) 750 °C.

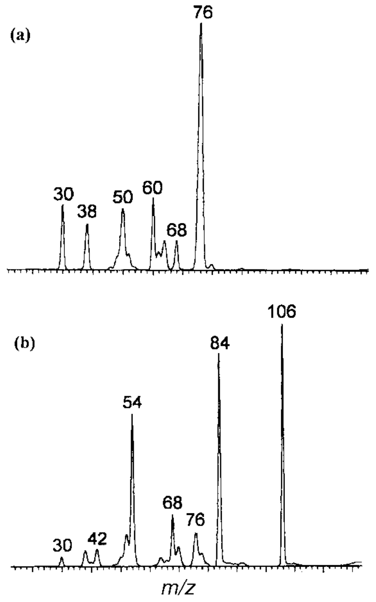


Fig. 4 CA(He) mass spectra of the *m*/*z* 136 ions produced by (a) ionisation of dicyanofuroxan **1**; (b) FVT-MS of **4** at 500 °C.

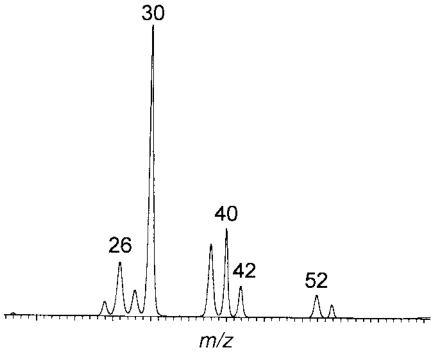


Fig. 5 CA(He) mass spectrum of the *m*/*z* 68 ions produced by FVT-MS of **6** at 750 °C. An identical spectrum was obtained by FVT-MS of **4** at 750 °C (mixture of **2** and **3**).

to **3** can be catalysed very efficiently by silver sulfide. Ag_2S was deposited as a thin film inside the quartz FVT tube by pyrolysis of silver *N*-methoxydithiocarbamate ($CH_3ONCSSAg_2$) at 140 °C, a reaction that generates methoxy isothiocyanate (CH_3O-NCS).[12] Subsequent FVT of furoxan **1** through this quartz tube resulted in a dramatic increase in the intensity of *m*/*z* 40, as well as *m*/*z* 28 and 54 (Fig. 2b). The catalytic effect increased with the extent of coating with Ag_2S and disappeared when the FVT tube was cleaned.

Authentic cyano isocyanate **3** was prepared by vacuum pyrolysis of solid silver cyanate using Gottardi's method.[13] In the CA mass spectrum the peaks at *m*/*z* 40 (NCN), 54 (CNCO), and 28 (CO) are characteristic of the NC–N=C=O connectivity and distinguish it from that of NC–CNO (**2**) (Fig. 2c). Comparison of the spectra in Fig. 2 reveals that FVT of **1** produces largely nitrile oxide **2**; the Ag_2S catalysed reaction produces a mixture of **2** and **3**, with a large proportion of the latter.

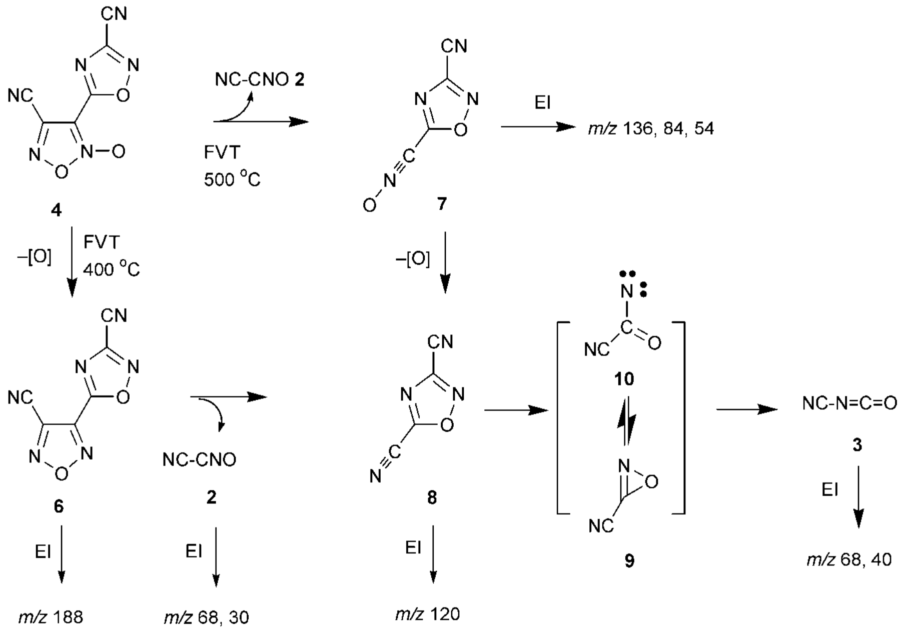
Next, the thermal fragmentation of trimers **4** and **5** was investigated by on-line FVT-MS. Most experiments described are for isomer **4**, but **5** behaves in the same manner. In the low temperature regime (200 °C), **4** and **5** have nearly identical mass spectra dominated by very intense peaks for NO^+ (*m*/*z* 30) (Fig. 3a).

At mild pyrolysis temperatures (*ca.* 300–400 °C, Fig. 3b), a facile deoxygenation reaction takes place: the molecular ion at *m*/*z* 204 has disappeared, and a *m*/*z* 188 species is formed instead. The CA mass spectrum of these *m*/*z* 188 ions is identical with that of the reduced compound **6**. This initially surprising reaction also occurs, albeit to a lesser extent, in the case of dicyanofuroxan **1** and may proceed *via* collision with the walls of the pyrolyser or of the ion source.[14]

FVT at 400–500 °C also produces an isomer of dicyanofuroxan **1** (*m*/*z* 136; HRMS 136.0021; Fig. 3b). The main fragmentation process is now the extrusion of cyanogen *N*-oxide **2**. The new compound so produced is entirely different from **1** as evidenced by the CA mass spectra (Fig. 4). The molecular ions of **1** eliminate two molecules of NO to produce dicyanoacetylene ions, $NCC{\equiv}CCN^{+\bullet}$ (*m*/*z* 76, Fig. 4a). The new *m*/*z* 136 ions eliminate only one NO to produce *m*/z 106 (Fig. 4b). The peaks at *m*/*z* 84 and 54 suggest the ONC–CNO and ONCC connectivities.[15] The most likely structure of the new *m*/*z* 136 compound is therefore the nitrile oxide of 3,5-dicyano-1,2,4-oxadiazole **7** (see Scheme 2).

FVT/Ar matrix IR spectroscopy of a mixture of the trimers **4** and **5** confirmed the production of mainly NC–CNO **2**, with small amounts of NC–NCO **3**. At the lowest temperature, 400 °C, additional weak bands at 2347, 2349 cm^{-1} may be due to the intermediate formation of nitrile oxide **7**. These bands disappeared completely at temperatures above 450 °C.

On FVT of **4** at still higher temperatures (750 °C, Fig. 3c), cleavage to cyanogen (*m*/*z* 52) and to three molecules of cyanogen *N*-oxide **2** (*m*/*z* 68) becomes prominent. The CA spectrum of these *m*/*z* 68 ions again exhibits an increased intensity of the peak at *m*/*z* 40 indicative of cyano isocyanate ions, $NC{-}NCO^{\bullet +}$ ($\mathbf{3}^{\bullet +}$) (and this is without any Ag_2S catalyst). The CAMS of these ions is identical with the one shown in Fig. 5, which is actually of the *m*/*z* 68 ions generated by FVT of **6** at 750 °C. Comparison with Fig. 2 reveals the formation of a mixture of **2** and **3**, with the former dominating. FVT of **4** in the presence of the Ag_2S catalyst again led to a dramatic increase in the peaks at *m*/*z* 28, 40, and 54 due to the enhanced formation of isocyanate **3**. The resulting CAMS was similar to that shown in Fig. 2b.



Scheme 2

Table 3 Calculated relative energies (kJ mol^{-1}) of NC–CNO isomers and $NC–NCO^{•+}$ fragmentation products[a]

Species	Relative energies	Species	Relative energies
NC–CNO **2**	0.0	$NC–NCO^{•+}$ ($\mathbf{3}^{•+}$)	0.0
TS2–9	273.0	CO + $NCN^{•+}$ (*m*/*z* 40)	339.2
Cyanooxazirine **9**	80.1	NCN + $CO^{•+}$ (*m*/*z* 28)	596.6
TS9–3	211.8	$N^{•}$ + $CNCO^{+}$ (*m*/*z* 54)	622.5
NC–NCO **3**	−246.9	$CN^{•}$ + NCO^{+} (*m*/*z* 42)	634.0
		$NCO^{•}$ + CN^{+} (*m*/*z* 26)	692.8
		O + $NCNC^{•+}$ (*m*/*z* 52)	929.0
		NCNC + $O^{•+}$ (*m*/*z* 16)	1095.9
		$CNCO^{•}$ + N^{+} (*m*/*z* 14)	1209.2

[a] G2(MP2,SVP) level. Calculated G2(MP2,SVP) energies include: −260.44734 (NCCNO) and −260.12012 ($NCNCO^{•+}$) hartrees.

Two plausible pathways for the production of **2** and **3** in the uncatalysed reactions are summarised in Scheme 2 (**4**→**2** + **7**→**8**→**3** and **4**→**6**→**2** + **8**→**3**). Other 1,2,4-oxadiazoles have been reported to be cleaved into nitriles and isocyanates.[16] Oxazirine **9** and/or nitrene **10** may be involved as intermediates in the cleavage of oxadiazole **8** and in the isomerisation of nitrile oxide **2** to isocyanate **3**. This question is examined theoretically below.

Molecular orbital calculations

The isomerisation of cyanogen *N*-oxide **2** to cyano isocyanate **3** was investigated at the G2(MP2,SVP)[17,18] level (Table 3) unless otherwise noted. **2** is predicted to be 247 kJ mol^{-1} higher in energy than **3**. The calculated N–O bond in oxazirine **9** is rather long (1.729 Å), and it is therefore somewhat debatable whether this species is an oxazirine or a singlet nitrene (**10**).[19] At the MP2/6-31G* level, a discrete singlet nitrene **10** is not a stable species, collapsing without a barrier to the oxazirine **9** upon geometry optimization. The triplet nitrene is less stable than **9** by 89 kJ mol^{-1}. Oxazirine **9** lies 80 kJ mol^{-1} above **2**. Rearrangement of **2** to **9** *via* a 1,2-O shift transition structure has a large activation barrier (273 kJ mol^{-1}, **TS2-9** in Table 3). Rearrangement of oxazirine **9** to isocyanate **3** *via* a 1,2-CN shift has a smaller barrier (132 kJ mol^{-1}; **TS9-3** in Table 3). Thus, the uncatalysed rearrangement of NCCNO to NCNCO is calculated to be a difficult, high energy process, in accord with the experimental observations.

Calculated fragmentation energies (G2(MP2,SVP)) of the $NCNCO^{•+}$ radical cation $\mathbf{3}^{•+}$ are also given in Table 3. The calculated fragmentation pattern is in excellent agreement with the observed CA spectrum (Fig. 2c) with loss of CO as the lowest-energy fragmentation pathway. In sharp contrast, the isomeric nitrile oxide, $NCCNO^{•+}$ $\mathbf{2}^{•+}$, predominantly loses $NO^{•}$ and NO^{+}.[9] The nitrile oxide radical cation $NCCNO^{•+}$ is much less stable than the isocyanate ion $NCNCO^{•+}$, by 266 kJ mol^{-1}, but the MP2/6-31G* activation barrier for the $NCCNO^{•+}$→$NCNCO^{•+}$ rearrangement is 212 kJ mol^{-1}. Accordingly, $NCCNO^{•+}$ is stable in the gas phase, although a partial isomerization to $NCNCO^{•+}$ under MS conditions cannot be ruled out.

Computations of the vibrational spectra of NCCNO and NCNCO at the MP2/6-31G* level were reported by Feher *et al.*[20] We have calculated the IR spectra of NCCNO **2** and NCNCO **3** using the DFT method B3LYP/6-31G*,[21] which has been shown often to provide more reliable vibrational frequencies than MP2.[22,23] As evidenced in Table 4, the B3LYP values tend to agree much better with the experimental data.

Our results reveal that the IR spectrum of **3** in the gas-phase reported by Devore[24] is undoubtedly erroneous: it bears no resemblance to our spectra and to that of Mayer.[25] The sample of **3** generated by Maier and Teles[11] was also in agreement with that of Mayer[25] and ours.[26] In Devore's IR spectrum, the band at 2330 cm^{-1}, in particular, is missing. Feher's assignment[20] of a theoretically calculated IR spectrum of **3** using a mixture of bands from Mayer[25] and Devore[24] as the experimental values is therefore inappropriate.

^{13}C NMR chemical shifts of **1**, **4**, **5** and **6** (Scheme 1) were calculated using the gauge-including atomic orbital (GIAO)[27] method at the B3LYP/6-311G** level, based on the B3LYP/6-31G* optimized geometry. The average deviation between calculated and experimental values is just 4 ppm, which is half that obtained using the smaller 6-31G* basis set.

Conclusions

The structures of the cyanogen *N*-oxide trimers **4** and **5** have been established. These compounds are formed by cycloaddition of NC–CNO **2** onto either of the CN groups in furoxan **1**. FVT of **1**, **4** and **5** causes formation of monomeric NC–CNO **2**, together with varying amounts of cyano isocyanate, NC–NCO **3**. Formation of isocyanate **3** is strongly catalysed by Ag_2S. Theory confirms a high activation barrier for

Table 4 Calculated[a] and experimental IR spectra[b] of NCCNO **2** and NCNCO **3**

NC–N=C=O **3**				NC–C≡N→O **2**[c]			
Calculated				Calculated			
MP2[d]	B3LYP[e]		Experiment	MP2[d]	B3LYP[e]		Experiment
2288	2345	(1254)	2338,[f] 2330[g]	2260	2403	(649)	2355,[f] 2356[i]
2115	2274	(81)	2283/2277,[f] 2284/2272[g]	2124	2216	(22)	2192,[f] 2192[i]
1405	1489	(4)	1430[g]	1451	1458	(185)	1445[f,i]
816	827	(9)	869[h]	708	730	(12)	717[i]
568	560	(27)	610[g]	458	479	(4)	
525	527	(18)	567[h]	446	479[j]	(4)	
436	456	(17)	455[g]	387	450	(9)	407[i]
420	440	(22)	365[g]	330	450[j]	(9)	
120	111	(3)		64	117	(6)	
				64	117[j]	(6)	

[a] 6-31G* basis set. [b] Frequencies in cm^{-1} (B3LYP intensities in parentheses in km mol^{-1}). [c] MP2 predicts a bent structure while B3LYP predicts a linear structure. [d] MP2/6-31G* frequencies are scaled by 0.9427 (Ref. 23). [e] B3LYP/6-31G* frequencies are scaled by 0.9613 (Ref. 22). [f] This work, Ar matrix values. [g] Ref. 25; gas phase values. [h] Ref. 25; bands observed only in the solid **3** at −196 °C. [i] Ref. 2*b*; matrix values. The gas phase values are also reported in this reference. [j] Degenerate modes.

the thermal rearrangement of nitrile oxide **2** to isocyanate **3**. Thorough MS investigations indicate that the FVT of **4** and **5** proceeds *via* oxadiazole intermediates **7** and **8**. *N*-oxides **1**, **4**, and **5** also undergo a deoxygenation reaction on the walls of the mass spectrometer.

Experimental

Apparatus

The mass spectrometric data were obtained on a large scale tandem mass spectrometer of EBEEBE geometry (where E stands for electric sector and B for magnetic sector; Micromass AutoSpec 6F, Manchester).[28] General conditions were 8 keV accelerating voltage, 200 μA trap current and 70 eV ionizing electron energy. Collisional activation was performed in the collision cell preceding the third electric sector by using oxygen or helium as the collision gas, and the CA spectra were recorded by scanning the field of this sector and collecting the ions in the fifth field-free region with an off-axis photomultiplier detector.

The FVT-MS unit consists of a quartz tube of 50 mm length and 3 mm internal diameter heated electrically (tantalum wire).[29] This unit is installed directly in the ion source (outer block). Ag_2S coating of the quartz tube was achieved by pyrolysis of silver *N*-methoxydithiocarbamate, $CH_3ONCSSAg_2$ at 140 °C in vacuum.[12] The FVT-IR unit and Ar matrix isolation conditions were as previously described.[30]

3,4-Dicyano-1,2,5-oxadiazole-2-oxide (1)

This compound was prepared according to the literature.[1] Mp 42 °C. ^{13}C NMR: see Scheme 1. EIMS: *m*/*z* 136 (20), 76 (13), 38 (14), 30 (100%). IR (KBr): $\nu = 2270$, 2255 (CN) cm^{-1}. UV (acetonitrile): $\lambda_{max} = 275$ nm ($\varepsilon = 3990$).

4-Cyano-3-(3-cyano-1,2,4-oxadiazolyl-5-yl)-1,2,5-oxadiazole-2-oxide (4) and 3-cyano-4-(3-cyano-1,2,4-oxadiazolyl-5-yl)-1,2,5-oxadiazole-2-oxide (5)

In order to improve the yields of trimers **4** and **5** in the synthesis of **1**, the procedure of Parker *et al.*[1] was modified in the following way. Concentrated nitric acid (28.5 ml) was added slowly to a refluxing mixture of 51 g of cyanoacetic acid in 150 ml of trifluoroacetic acid. After the addition was completed, reflux was continued for 2 h. After cooling, the reaction mixture was poured onto ice (*ca.* 600 g) and extracted with dichloromethane. The combined organic layers were washed with water until neutrality. After drying, the solvent was evaporated under reduced pressure, yielding a crude reaction mixture containing 62% of furoxan **1**, 21% of the trimer **4** and 17% of the trimer **5** according to HPLC analysis. Compounds **4** and **5** were separated from **1** by column chromatography on silica gel, eluting with a 1:1 mixture of dichloromethane and hexane. **4** was separated from **5** by preparative HPLC (Novapak C_{18}, 25 mm × 100 mm, methanol–water (25:75), 10 ml min^{-1}). Both compounds were recrystallised from CCl_4. Data for **4**: mp 114–117 °C; ^{13}C NMR: see Scheme 1; EIMS: see Fig. 3a; IR (KBr): $\nu = 2271$ and 2253 (CN) cm^{-1}; UV (acetonitrile): $\lambda_{max} = 230$ ($\varepsilon = 9250$) and 282 nm ($\varepsilon = 5790$). Data for **5**: mp 95–96 °C; ^{13}C NMR: see Scheme 1; EIMS: *m*/*z* 204 (7), 30 (100%); IR (KBr): $\nu = 2268$ and 2251 (CN) cm^{-1}; UV (acetonitrile): $\lambda_{max} = 225$ ($\varepsilon = 13166$) and 271 nm ($\varepsilon = 4994$).

Table 5 Crystal data and refinement parameters for 4(3)-cyano-3(4)-(3-cyano-1,2,4-oxadiazol-5-yl)-1,2,5-oxadiazole-2-oxides, **4** and **5**

	4	**5**
Formula	$C_6N_6O_3$	$C_6N_6O_3$
Mass	204.12	204.12
Temperature/K	293(2)	293(2)
Crystal system, space group	Orthorhombic, *Pcab*	Monoclinic, $P2_1$
Unit cell dimensions/Å	$a = 9.393(2)$ $b = 11.199(4)$ $c = 15.277(4)$	$a = 6.093(3)$ $b = 7.5041(8)$ $c = 9.297(4)$
Volume/$Å^3$	1606.9(8)	403.5(3)
Z, Calculated density/Mg m^{-3}	8, 1.687	2, 1.680
μ (Mo-Kα)/mm^{-1}	0.141	0.141
Reflections collected/unique	1404/1404 [$R_{int} = 0.0000$]	2017/2017 [$R_{int} = 0.0000$]
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0907$, $wR_2 = 0.1960$	$R_1 = 0.0570$, $wR_2 = 0.1485$
R indices (all data)	$R_1 = 0.2274$, $wR_2 = 0.2576$	$R_1 = 0.0616$, $wR_2 = 0.1551$

Crystal data.† The crystal data and details of the data acquisition and refinement for compounds **4** and **5** are summarised in Table 5. Compound **5** crystallised in the acentric space group $P2_1$. The absolute configuration could not be determined. There was no decay during data collection. A CAD4 diffractometer, ω/θ mode with ω scan width = 1.0 + 0.34tan θ, and graphite monochromated Mo-Kα radiation were used. Structure analysis and refinement: direct methods found all the atoms. Full matrix least-squares refinement gave $R_1 = 0.09$ and $wR_2 = 0.20$, where $w = 1/[\sigma^2(F_o) + (0.10 \cdot P)^2]$ and $P = (\text{Max}\,(F_o^2, 0) + 2 \cdot F_c^2)/3$, with $\sigma(F_o)$ from counting statistics. Programs and sources of scattering factor data are given in reference 31.

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† CCDC reference number 188/216. See http://www.rsc.org/suppdata/p2/a9/a908653f for crystallographic files in .cif format.

4-Cyano-3-(3-cyano-1,2,4-oxadiazol-5-yl)-1,2,5-oxadiazole (6)

A solution of 3.93 g (19.3 mmol) of a mixture of **4** and **5** (*ca.* 1 : 1) in 10 ml of anhydrous benzene was added slowly to 5 g of cold triethyl phosphite. The mixture was heated for 1 h at 30–40 °C, washed with 15 ml H_2SO_4 (1 M) and then with water (4 × 30 ml). After drying over magnesium sulfate, the solvent was evaporated and the residue recrystallised from carbon tetrachloride to give 1.2 g (33%; yield not optimised). Mp 65 °C; ^{13}C NMR: see Scheme 1; EIMS: see Table 2; IR (KBr): $\nu = 2271$ and 2255 (CN) cm^{-1}; UV (acetonitrile): $\lambda_{max} = 225$ ($\varepsilon = 7500$) and 285 nm ($\varepsilon = 1180$).

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