

Gas-phase Generation and Spectroscopy of the Unstable NCCNO Molecule

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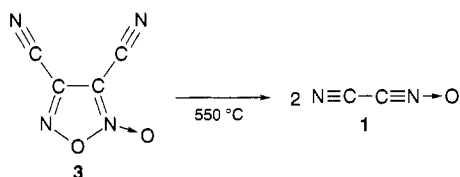
The unstable NCCNO molecule obtained from low-pressure, gas-phase pyrolysis of dicyanofuroxan is characterised spectroscopically by He I photoelectron, FT IR and photoionization mass spectroscopies; comparison with the spectroscopic results and an assessment of the structure is afforded by *ab initio* calculations.

Cyanogen *N*-oxide, NCCNO **1**, although unstable and never isolated, has been shown to undergo rapid 1,3-dipolar cycloaddition reactions in solution with dipolarophiles,^{1,2} following its *in situ* generation from the reaction of cyanohydroxamic chloride (cyanochloro-formaldehyde oxime), NC(Cl)C=NOH **2** with base. Such chemical trapping reactions of this reactive dipole provide evidence for the existence of **1** although it is unknown in the gas phase. The first direct detection was reported by Maier and Teles;³ the pyrolysis products of **2** (HCl plus **1**) were trapped into a solid argon matrix at 10 K and detected by infrared spectroscopy. This remains the only spectroscopic study of **1**. The structure is thus unknown, and methods to generate this molecule in the gas phase would provide an important step towards its full electronic and geometric characterisation. Consisting solely of C, N and O, of relatively high abundance in the interstellar medium, **1** is also of potential astrophysical interest.

Although **2** is a potential source of **1**, we have found that it can be generated efficiently, and virtually quantitatively, from vacuum flow thermolysis of the stable dimer, dicyanofuroxan (dicyano-1,2,5-oxadiazole 2-oxide) **3**, in the gas phase at 300 mTorr (Scheme 1).

Compound **3** was synthesised from cyanoacetic acid (Aldrich) using the literature method.⁴ Thermolysis was typically carried out in a quartz tube (8 mm id) heated along 15 cm; for a more efficient pyrolysis, the tube was packed with quartz chips. The pyrolysis tube was connected directly to the inlet of a combined He I photoelectron (PE) and HeI/HL_{α,β,γ} photoionization mass (PIMS) spectrometer,⁵ or to a 20 cm single-pass IR cell. The effluent from the pyrolysis was continuously pumped through either the PE-PIMS spectrometer or the IR cell. Formation of **1** commenced at 400 °C, and the conversion of **3** to **1** was complete at 550 °C. The yield of **1** was almost quantitative with only trace amounts of NCCN and CO₂ detected in the PE and He I PIMS spectra. The HL_{α,β,γ} PIMS spectrum (Fig. 1) confirms the identity of **1**. The molecular ion and only one fragment, NO⁺, are observed, entirely in keeping with PIMS spectra of the related nitrile oxides BrCNO⁵ and ONCCNO.⁶

A particular feature of simple nitrile oxides is the question of linearity or quasi-linearity, and indeed, even the parent HCNO molecule has proven to be a spectroscopic and computational challenge.^{7,8} We have calculated the equilibrium geometry of **1** at the MP3, QCISD and QCISD(T)/6-31G* levels using Gaussian-92. All calculations predict a linear molecule; from the QCISD(T)/6-31G* calculations, the rotational constant *B_e* is 2.2493 GHz with a dipole moment of 0.072 Debye. Recent *ab initio* calculations⁹ indicate that **1** exhibits a large-amplitude deformational motion, and so a detailed calculation of the energy hypersurface will be necessary in order to obtain more



Scheme 1

accurate information on vibrational frequencies, anharmonicity, and the dynamics of the large-amplitude motion. We have started such work, with preliminary calculations indicating the CCN deformation potential to be strongly anharmonic and very flat.

The He I PE spectrum (not shown) concurs (within the resolution limitations of the technique) with a linear structure. The nonbonding $\pi_{nb}(\text{CNO})$ molecular orbitals give rise to a sharp peak in the PE spectrum at 11.28 eV, with a band originating from the bonding $\pi_b(\text{CNO})$ MOs at 17.08 eV showing a much wider Franck-Condon profile, commensurate with the bonding character of this MO. The terminal nitrogen ($N_{p\sigma}$) and the cyano group $\pi(\text{CN})$ MOs lead to PE bands observed between 13.8 and 14.5 eV, with a band ascribable to the terminal oxygen lone pair orbital evident at 18.75 eV. Koopmans' calculations (MP3), and HAM/3 calculations confirm this assignment, as does a comparison with the PE spectra of BrCNO⁵ and the parent acid, HCNO.¹⁰

The IR spectrum (Fig. 2), which shows the raw spectrum obtained from the thermolysis of **3**, is also in good agreement with a linear structure, with the observed frequencies and band intensities in accord with the *ab initio* calculations. Parallel type

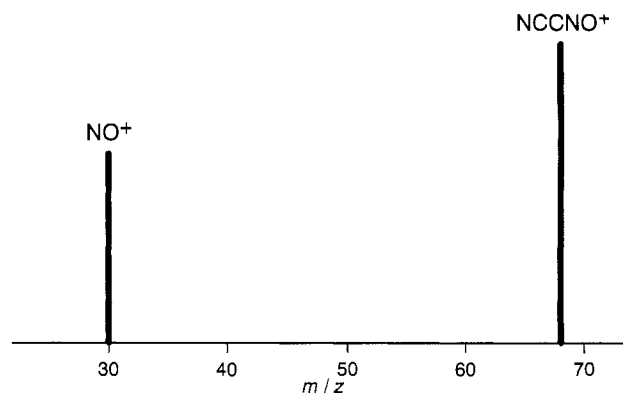


Fig. 1 HL_{α,β,γ} (10.2–12.7 eV) photoionization mass spectrum of NCCNO as produced directly from the thermolysis of **3**

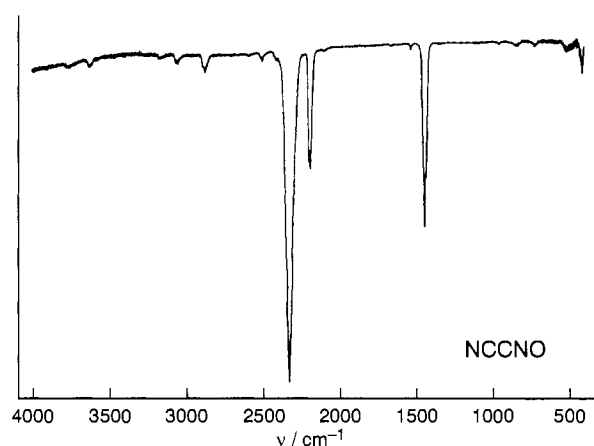


Fig. 2 Mid-IR spectrum of NCCNO as produced directly from the thermolysis of **3**

band structure, typical of linear molecules, can be observed only on the ν_2 mode, the NC stretch at 2192 cm^{-1} . The other two strong IR bands at 2328 and 1442 cm^{-1} originate from the $\nu_1(\text{CNO})$ asymmetric and $\nu_3(\text{CNO})$ symmetric stretches, respectively, and show complicated fine structure even at 0.5 cm^{-1} resolution. This detail is also observed in the corresponding IR spectra of BrCNO^5 and ONCCNO^6 and arises, in this case, from hot bands of the stretches and the low frequency CCN bend (ν_7). Such structure is clearly in need of high resolution investigation. Besides the three obvious strong bands, several weak features can be observed; the bands at 722 , 511 and 409 cm^{-1} originate from $\nu_4(\text{C-C})$ stretch, $\nu_5(\text{CNO})$ deformation and $\nu_6(\text{NCC})$ deformation respectively, and others at 3763 , 3624 , 3165 , 3058 , 2875 , 2504 and 845 cm^{-1} , which track in intensity, are either combinations or overtones of the fundamentals.

The combined spectroscopic and *ab initio* results suggest a linear structure, although a quasi-linear structure cannot be ruled out. Certainly the computational history of simple nitrile oxides⁵⁻⁸ suggests that very high levels of theory are required before definitive structural conclusions can be drawn. Experimental efforts to address this question by high resolution IR and microwave spectroscopy are required, and to this end we have initiated such high resolution IR work with colleagues at the University of Waterloo.

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References

- 1 C. Grundmann and H.-D. Frommelt, *J. Org. Chem.*, 1966, **31**, 4235.
- 2 A. P. Kozikowski and M. J. Adamczyk, *J. Org. Chem.*, 1983, **48**, 366.
- 3 G. Maier and J. H. Teles, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 155.
- 4 C. A. Parker, W. D. Emmons, H. A. Rolewicz and K. S. McCallum, *Tetrahedron*, 1962, **17**, 79.
- 5 T. Pasinszki and N. P. C. Westwood, *J. Phys. Chem.*, 1995, **99**, 6401.
- 6 T. Pasinszki and N. P. C. Westwood, *J. Am. Chem. Soc.*, in the press.
- 7 J. H. Teles, G. Maier, B. A. Hess, Jr., L. J. Schaad, M. Winnewisser and B. P. Winnewisser, *Chem. Ber.*, 1989, **122**, 753.
- 8 N. Pinnavaia, M. J. Bramley, M.-D. Su, W. H. Green and N. C. Handy, *Mol. Phys.*, 1993, **78**, 319.
- 9 M. Fehér, T. Pasinszki and T. Veszprémi, *Inorg. Chem.*, 1995, **34**, 945.
- 10 J. Bastide and J. P. Maier, *Chem. Phys.*, 1976, **12**, 177.