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Cyanogen Di-*N*-oxide (ONCCNO): Gas Phase Generation and a HeI Photoelectron, Photoionization Mass Spectroscopy, Midinfrared, and *Ab Initio* Study

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Abstract: The cyanogen di-*N*-oxide molecule (ONCCNO) has been generated in high yield from *in situ* flow pyrolysis reactions of gaseous dichloroglyoxime or dibromofuroxan precursors and studied for the first time in the gas phase. This structurally novel transient species is characterized by HeI photoelectron, HeI/HL$_\alpha$ photoionization mass, and mid-infrared spectroscopies. To complement the experimental aspects, an assessment of the structure and bonding of ONCCNO is obtained from *ab initio* calculations at the HF, MP2, MP,3 and MP4SDQ/6-31G* levels of theory. Both the calculations and the spectroscopic results suggest that the molecule has a linear or quasi-linear structure

Introduction

Cyanogen di-*N*-oxide, (ONCCNO, **1**), although unstable, is of considerable interest for both synthetic chemistry and spectroscopic/theoretical studies. Although first prepared in 1911,[1] its chemical formula and isolation in dilute solution were only achieved some half a century later by HCl elimination from the stable dichloroglyoxime (HON=CCl−ClC=NOH, **2**) precursor.[2,3] Since dilute solutions of **1**, a difunctional nitrile oxide, are stable at 0 °C for some hours (followed by polymerization to polyfuroxan[3]), it has found considerable use in organic chemistry for 1,3-dipolar cycloaddition reactions[4−6] and as a building block for new polymers.[2,3,5,6]

As a six-atom palindromic molecule, ONCCNO, also has the potential to become a classic system for both spectroscopic and structural studies due to its high symmetry and possible quasi-linear behavior. Spectroscopic studies to date have, however, been limited entirely to investigation in solution, *viz.* infrared (IR) and ultraviolet−visible (UV−vis),[3,5] since although crystalline, monomeric **1** is stable at −78 °C (at least for a couple of hours), it begins to decomposes at −45 °C in vacuum, and then detonates.[7] Maier and Teles[8] have reported the formation of **1** following condensation of the flash vacuum pyrolysis products of **2** with argon onto a cold (10 K) window, although no spectroscopic data were reported.

The structure is thus unknown, and methods to generate this molecule into the dilute gas phase would provide an important *entrée* toward its full electronic and geometric characterization. Certainly the very large number of resonance structures that **1** can exhibit, of which some of the symmetrical variants are shown in Scheme 1, implies that the bonding and structure are of particular spectroscopic and, indeed, theoretical interest.

1a,b represent the all-octet structures, **1c,d** the 1,3-dipolar structures, **1e** a N^V formulation, **1f,g** biradical structures with a CC multiple bond, and **1h** a dinitroso acetylenic formulation, probably not linear. Other resonance structures exist, including asymmetric ones not shown here, but clearly, the bonding in this molecule, with back-to-back CNO groups is unusual, with the potential for considerable *π* delocalization.

Of particular relevance is the parent species, fulminic acid HCNO, one of the few nitrile oxides to have been subjected to intense experimental (high-resolution IR and microwave spectroscopy[9,10]) and theoretical (*ab initio* calculations[10−16]) scrutiny due to its structure, especially quasi-linear behavior, and alternative isomeric forms. We anticipate **1** to exhibit some of these features. In addition, consisting solely of C, N, and O, of relatively high abundance in the interstellar medium, **1** is of potential astrophysical interest.

In this work we report the first gas phase generation and characterization of the unstable ONCCNO molecule and an investigation of its electronic and geometric structure by *ab initio* methods and gas phase spectroscopy. The latter includes

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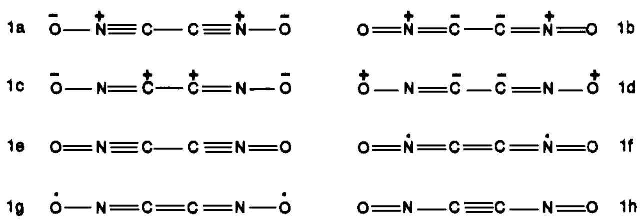
Scheme 1



ultraviolet photoelectron (PE) spectroscopy, HeI and $HL_{\alpha,\beta,\gamma}$ photoionization mass spectroscopy (PIMS), and mid-infrared (IR) spectroscopy. Relevant to this work is our recent study of the BrCNO monomer and its dimer, dibromofuroxan ($Br_2C_2N_2O_2$, **3**),[17] the latter molecule being one precursor to **1**.

Experimental Section

The specifics of the generation of **1** from thermolysis of **2** or **3** are given below in the Results and Discussion. **2** was synthesized from glyoxime (Fluka) and chlorine using the literature method.[18] **3** was synthesized as described recently.[17] **3** has sufficient vapor pressure to be used at ambient temperature; **2** is heated to 60 °C.

The HeI PE spectrum was recorded on a fast pumping PE spectrometer specifically designed to study reactive/unstable species. The spectrometer was connected directly to the pyrolysis tube used for generation of **1** (see below). The spectrum was calibrated with the known ionization potentials (IPs) of the side products CO, CO_2, NO, and HCl; resolution was 45 meV during the experiment. This PE spectrometer, adapted from an earlier version,[19] can also mass analyze ions produced in the photoionization process using a quadrupole mass analyzer (Hiden Analytical, 320 amu, with the electron impact (EI) source removed) mounted directly above the photoionization point. Single-wavelength PIMS spectra were obtained with either HeI (21.2 eV) 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.

IR spectra were collected on a Nicolet 20SXC interferometer equipped with a 20 cm single-pass gas cell. The cell, with KBr windows, gave a spectral range from 4000 to 400 cm^{-1}. The effluent from the pyrolysis tube was pumped continuously through the cell using a rotary pump while maintaining the pressure constant between 500 and 600 mTorr. The spectrum was recorded at 0.5 cm^{-1} resolution.

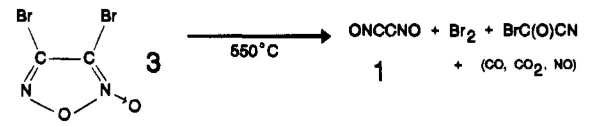
Computational Methods

Ab initio calculations for **1** were carried out at the HF, MP2, MP3 and MP4SDQ levels using a standard 6-31G* basis set.[20] All electrons were included in the correlation energy calculations (*i.e.*, "full"). Equilibrium molecular geometries were fully optimized, and harmonic vibrational frequencies were then calculated at the minimum energy geometries using numeric second derivatives. All calculations were performed with the Gaussian-92 quantum chemistry package[21] implemented on a Silicon Graphics Inc. Challenge/XL workstation.

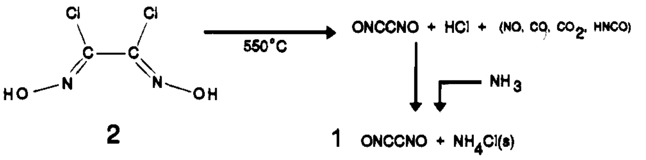
Results and Discussion

Generation of ONCCNO. We have found that **1** can be conveniently generated in the gas phase by two methods: (A) the thermolysis of dibromofuroxan and (B) the thermolysis of dichloroglyoxime. Reactions are typically carried out at 550 °C in a quartz tube (8 mm i.d.) heated along 15 cm; for a more efficient pyrolysis, the tube is packed with quartz chips. All of the following observations were confirmed by concurrent PE, PIMS, and IR measurements.

Scheme 2



Scheme 3



Method A. We initially observed ONCCNO in the gas phase while investigating the thermolysis of dibromofuroxan (**3**).[17] Pyrolysis of **3** does not lead to the expected BrCNO product but to the formation of Br_2, ONCCNO, BrC(O)CN (cyanoformyl bromide), and smaller amounts of NO, CO, and CO_2 (Scheme 2). In the IR spectrum, **1** and BrC(O)CN appear as the main products with approximately equal band intensities. Cyanoformyl bromide is a new molecule, and its identification is based on the IR spectrum and that of the chloro- analog produced by thermolysis of dichlorofuroxan.[22] In the PE spectrum, Br_2 shows as a major component.

Method B. Thermal elimination of HCl from **2** gives a much superior route to **1** with only trace amounts of the side products, NO, CO, CO_2, and HNCO. The yield of **1** plus HCl is essentially quantitative, and the latter could be carefully titrated in the gas phase with $NH_3(g)$ to form involatile $NH_4Cl(s)$ (Scheme 3). This method, involving removal of HCl, was used to record the PIMS and PE spectra shown in Figures 1 and 3, respectively. The IR spectrum (Figure 2) shows the raw pyrolysis products, including HCl. If the flow of **1** through the IR cell is interrupted by isolating **1** in the cell, its spectrum completely disappears in 2–3 min; no side products are observed, and we conclude that **1** polymerizes on the walls of the cell.

Calculated Structure. A critical question is whether or not the molecule is linear or bent. The parent nitrile oxide HCNO is routinely described as a quasi-linear molecule, since analysis of rotational–vibrational spectra leads to an effective deformation potential function with a bent structure and low barrier (below 20 cm^{-1}) to linearity. It has been shown that the equilibrium structure of HCNO is linear with excitation of stretching vibrations giving rise to the HCN bending potential having its minimum at a nonlinear configuration.[23,24] *Ab initio* calculations, however, have exhibited difficulty in determining if HCNO has a bent or linear structure. Calculations performed at the HF, MP3, CISD, and CCSD levels of theory favor a linear structure, whereas MP2, MP4SDTQ, MCSCF, and CCSD(T) calculations give a bent structure;[10–16] in general, the effects of triple substitutions favor the bent structure. In the case of the bromo derivative, BrCNO, we have found a similar dependence of the calculated equilibrium geometry on the level of theory.[17]

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Table 1. Calculated Equilibrium Structure, Energies, Barrier to Linearity, Dipole Moment, and Rotational Constants of ONCCNO[a]

	HF	MP2	MP3	MP4SDQ
C−C	1.371	1.351	1.361	1.365
C−N	1.134	1.208	1.163	1.172
N−O	1.189	1.205	1.203	1.215
CCN	180.0	155.4	180.0	180.0
CNO	180.0	171.2	180.0	180.0
total energy	−334.10364	−335.11089	−335.05222	−335.08655
barrier to linearity	0	227	0	0
A[b]		635.4911		
B	1.2839	1.2548	1.2535	1.2355
C		1.2523		

[a] Bond angles in deg, bond lengths in Å, total energies in au, and barrier to linearity in cm^{-1}; a 6-31G* basis set was used, and all electrons were included in the correlation energy calculations ("full"). [b] Rotational constants in GHz; isotopes: ^{12}C, ^{14}N, ^{16}O.

Due to computational limitations we were not able to explore **1** at higher levels of theory. The MP2 calculation gives a slightly bent equilibrium structure with a *trans*-bend at the C atoms (C_{2h} symmetry) and a barrier of 227 cm^{-1} (0.65 kcal mol^{-1}), while the HF, MP3, and MP4SDQ calculations prefer a linear structure ($D_{\infty h}$) (Table 1). For both HCNO (experiment known) and BrCNO (experiment unknown), the MP2 method overestimates any barrier at the linear configuration. Although the MP3 and MP4SDQ calculations for **1** predict a linear geometry, the computational history of the parent HCNO molecule suggests that this is not the final word on the linear *versus* bent question for **1**. We have also found, from similar studies on the equilibrium structure of ClCNO that increasing the basis set size from 6-31G* to 6-311G(2d) results in a lower barrier to linearity at all levels of theory.[25] On the basis of the above comments, and the flatness of the potential, we conclude that **1** is most likely linear or quasi-linear.

Rather than speculate at length on the validity, or otherwise, of the calculated bond lengths, given the limitations of the computational methods, and the fact that no structural data are available for **1**, we would point first to the heavy-atom bond lengths of the structurally characterized HCNO[26] and H_3CCNO[27] molecules which have CN bond lengths of 1.168 and 1.169 Å and NO bond lengths of 1.199 and 1.217 Å, respectively. A comparison with Table 1 suggests that the HF bond lengths are too short, whereas MP2 errs (as is often the case) in making the nominal CN triple bond too long. For the simple cyanogen molecule NCCN, the CC bond length is 1.389 Å and that for CN is 1.154 Å.[28] A comparison of MP3(full)/6-31G* calculations on NCCN and ONCCNO shows that, in the former, the calculated CC bond length is 1.393 Å, and in the latter, 1.361 Å. The implication is that the CC bond in **1** is very short, as might be expected from a delocalized model of the structure, the CN bond is somewhat less than triple, and the NO bond is closer to double, suggesting that, although **1a,b** may be the dominant resonance structures, there are significant contributions from structures involving an extended π system.

Photoionization Mass Spectra. The HeI and HL$_{\alpha,\beta,\gamma}$ PIMS spectra (Figure 1a,b) are relatively simple and confirm the identification of **1**; the molecular peak and only two fragments, NO^+ and $ONCC^+$, are observed with HeI radiation. The relative intensity of the NO^+ peak is very strong in the HeI spectrum, as also observed with BrCNO.[17] Fragmentation is usually reduced in the HL$_{\alpha,\beta,\gamma}$ PIMS, and this is reflected in the strong increase in parent ion signal and the disappearance of the $ONCC^+$ fragment.

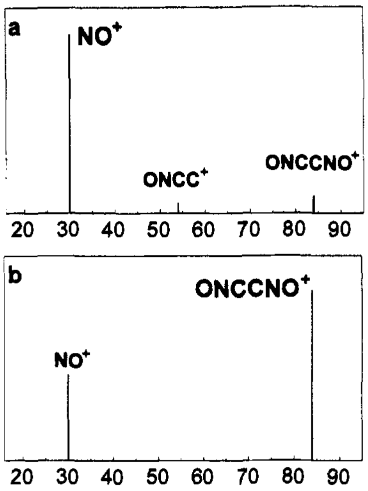

Figure 1. (a) HeI and (b) HL$_{\alpha,\beta,\gamma}$ photoionization mass spectra (amu) of ONCCNO produced by method B. The main additional product of the formation reaction is HCl, titrated to $NH_4Cl(s)$ with gaseous NH_3.

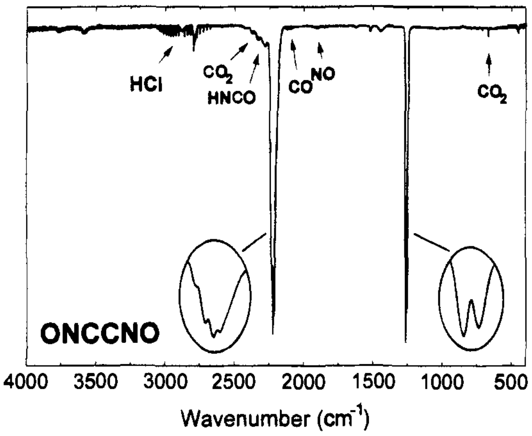

Figure 2. Infrared spectrum of ONCCNO plus HCl, as produced by method B. The IR bands of side products, NO, CO, CO_2, and HNCO, are indicated. Insets show details (0.5 cm^{-1} resolution) of the two strong IR-active bands of ONCCNO.

Infrared Spectrum. The IR spectrum of **1** plus HCl produced by method B is shown in Figure 2, and the observed and calculated vibrational frequencies are given in Table 2 for both MP2 and MP3 geometries. Weak bands attributable to the side products, NO, CO, CO_2, and HNCO, are indicated, and as illustrated, HCl appears weakly in the IR spectrum. The bent (C_{2h}) and linear ($D_{\infty h}$) structures allow only six and four IR active modes, respectively, the deformation modes for the linear case being degenerate. We will discuss assignments based on the linear case; for such a centrosymmetric molecule, the IR and Raman active bands are mutually exclusive. Since the CCN deformations are expected well below 400 cm^{-1}, only species of *ungerade* symmetry, the two CNO stretches (σ_u) and the two CNO deformations (π_u), are IR active in the investigated region from 4000 to 400 cm^{-1}. The calculated IR intensities of the deformation modes are some 1−2 orders of magnitude weaker than those of the stretching modes, with the result that only two strong bands are observed above 400 cm^{-1}: one with a maximum at 2226 cm^{-1}, the antisymmetric combination of the two antisymmetric CNO stretches, ν_4, and the other with a band center close to 1260 cm^{-1}, the antisymmetric combination of

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Table 2. Experimental and Calculated[a] Vibrational Frequencies (cm^{-1}) of ONCCNO

	MP2 (C_{2h})		MP3 ($D_{\infty h}$)		
exptl freq[b]	freq	intensity[c]	freq	assignment and description	PED[d]
3760 (vw)				—	
3587 (vw)				—	
2882 (vw)				—	
2793 (w)				—	
IR inactive	2359 (A_g)	0	2620 (Σ_g^+)	ν_1 CNO as. str.	CN(70), NO(12), CC(18)
2226[e] (s)	**2303** (B_u)	**1200**	**2471** (Σ_u^+)	ν_4 **CNO as. str.**	**CN(80), NO(20), CC(0)**
IR inactive	1658 (A_g)	0	1658 (Σ_g^+)	ν_2 CNO sym. str.	CN(1), NO(69), CC(30)
1521 (vw)				—	
1446 (vw)				—	
1264 R (s) **1255 P**	**1338** (B_u)	**212**	**1344** (Σ_u^+)	ν_5 **CNO sym. str.**	**CN(15), NO(85), CC(0)**
IR inactive	681 (A_g)	0	646 (Σ_g^+)	ν_3 C−C str.	CN(26), NO(18), CC(56)
454 (vw)	435 (B_u)[f]	7	526 (Π_u)	ν_8 CNO linear bend	CNO(94), CCN(6)
	434 (A_u)[g]	11			
	427 (A_g)[f]	0	488 (Π_g)	ν_6 CNO linear bend	CNO(91), CCN(9)
	418 (B_g)[g]	0			
	254 (A_g)[f]	0	198 (Π_g)	ν_7 CCN linear bend	CNO(18), CCN(82)
	151 (B_u)[f]	7	91 (Π_u)	ν_9 CCN linear bend	CNO(8), CCN(92)
	132 (A_u)[h]	5			

[a] Unscaled harmonic frequencies. [b] Additional very weak bands at 1627 and 2423 cm^{-1}, origin unknown. [c] In km/mol. Not available for MP3 due to numeric derivatives. [d] Potential energy distribution from force field analysis based on MP3(full)/6-31G* force constants. [e] Band position taken from the most intense hot band; does not represent the band center. [f] In-plane bend. [g] Out-of-plane bend. [h] C-C torsion.

the two symmetric CNO stretches, ν_5. These two bands were observed earlier in CCl_4 solution at 2190 and 1235 cm^{-1}.[3] The gas phase band at 1260 cm^{-1} shows a typical parallel band structure indicative of a linear or quasi-linear structure (inset to Figure 2), with P and R branch maxima at *ca.* 1255 and 1264 cm^{-1}. The other band with a maximum at 2226 cm^{-1}, however, shows rather complicated fine structure which can be observed even at 0.5 cm^{-1} resolution (inset to Figure 2). Such detail, also observed on ν_{as}(CNO) of BrCNO,[17] arises from hot bands. Much detailed information on these bands is evident from recent high-resolution IR studies initiated with colleagues at the University of Waterloo;[29] these seem to confirm the linear or quasi-linear formulation.

Additionally, some weak structure is observed. The band at 454 cm^{-1} probably originates from the CNO deformation, ν_8, observed in the IR spectrum of HCNO(g) at 537 cm^{-1},[10] and in H_3CCNO (solution) at 478 cm^{-1}.[30] Weak bands, listed in Table 2, are noted to track in intensity with the strong bands, especially those under the HCl rotational profile. These are, most likely, overtone/combination bands but cannot be unambiguously assigned since we do not know the values for either the IR inactive or low-wavenumber bands.

Overall, the calculated vibrational positions, where observed, are in good agreement with experiment, being calculated somewhat too high, partially as a result of the harmonic approximation and the deficiencies of the applied electronic structure calculations. Better agreement could be achieved by a scaling of 0.91 (MP3). The calculated intensities predict correctly that the CNO antisymmetric and symmetric stretches are intense, but the intensity of the symmetric, compared to the antisymmetric stretch, is too small. For a potentially quasi-linear molecule the positions of the lower energy vibrations, especially the bending potential, will have significant errors due to our inability to accommodate anharmonicity.

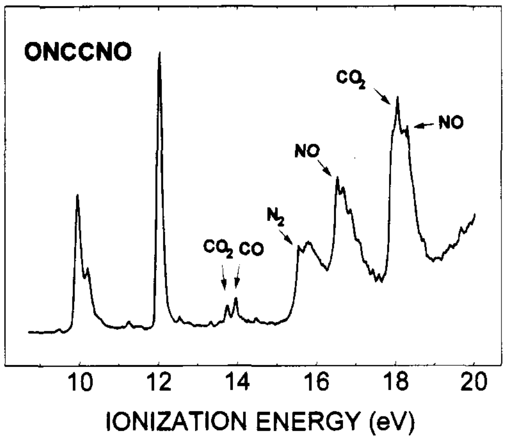

Figure 3. HeI photoelectron spectrum of ONCCNO produced by method B. The main additional product of the reaction is HCl, titrated to NH_4Cl(s) with gaseous NH_3. Weak, individual sharp bands of NO, CO, N_2, and CO_2 are indicated.

A preliminary force field analysis for **1** using unscaled MP3/6-31G* force constants as input to the BMAT program[31] indicates that, although the IR active CNO antisymmetric and symmetric stretches, ν_4 and ν_5, may best be described as νCN and νNO, respectively, there is considerable coupling between the modes involving the CNO group. This is shown in the last column of Table 2, which gives the calculated potential energy distribution (PED). For the stretches of *gerade* symmetry, substantial CC coupling is also incurred, and for the key structural feature of this molecule, the CC bond, the corresponding stretch, ν_3, has only 56% CC character. We note that the CC stretches in NCCN[32] and H_3CCNO[30] are located at 846 and 778 cm^{-1}; the calculated CC stretch for **1**, 646 cm^{-1} (MP3), must thus be regarded as exceptionally low.

Photoelectron Spectrum. The PE spectrum of **1** is shown in Figure 3; the weak bands due to side products are marked. The other product of the thermolysis of **2**, HCl, shows strongly in PE spectra and has been removed by titration with NH_3. A small band of N_2 is observed at 15.58 eV, either from the thermolysis or from trace air in the spectrometer. The experimental and calculated IPs are presented in Table 3, the calculated (Koopmans') results for both linear and bent optimized struc-

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Table 3. Experimental and Calculated Ionization Potentials (eV) of ONCCNO

	calcd			
exptl IP[a]	MP2[b]	MP3[b]	HAM/3[c]	orb sym and char
9.95	10.51 ($9a_g$) 10.55 ($2b_g$)	10.66 ($2\pi_g$)	10.03 ($2\pi_g$)	π_{nb}(CNO)
12.02	13.56 ($2a_u$) 13.59 ($8b_u$)	13.51 ($2\pi_u$)	12.01 ($2\pi_u$)	π_{nb}(CNO)
15.8	18.93 ($8a_g$) 19.09 ($1b_g$)	19.27 ($1\pi_g$)	16.67 ($1\pi_g$)	π_b(CNO)
16.67	19.65 ($7b_u$) 19.75 ($1a_u$)	19.99 ($1\pi_u$)	17.22 ($1\pi_u$)	π_b(CNO)
17.8	20.97 ($7a_g$)	20.89 ($7\sigma_g$)	18.58 ($4\sigma_g$)	$\sigma(n_O)$
|	21.22 ($6b_u$)	21.07 ($6\sigma_u$)	18.72 ($3\sigma_u$)	$\sigma(n_O)$
18.4				
	26.48 ($6a_g$)	26.64 ($6\sigma_g$)	22.19 ($3\sigma_g$)	σ(C−C)

[a] Vertical ionization potentials. [b] Calculated via Koopman's theorem (unscaled). [c] The MP3 geometry was used.

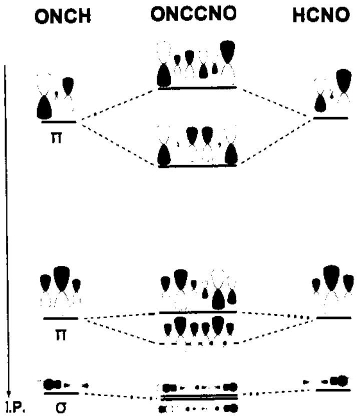

Figure 4. Correlation diagram showing the formation of the MOs of ONCCNO from two separated CNO fragments. Experimental IPs for HCNO and ONCCNO were used for this purpose, together with eigenvectors from the HAM/3 calculation.

tures. From comparison with the known PE spectrum of HCNO,[33] as well as from the calculated IPs, the assignment is relatively straightforward, especially since, for a linear $D_{\infty h}$ molecule, there is complete π/σ separation. Three bands are observed in the HeI PE spectrum of HCNO, the degenerate nonbonding π_{nb}(CNO) and bonding π_b(CNO) molecular orbitals (MOs) as well as the oxygen lone pair orbital n_O.[33] By combining two CNO groups and assuming a linear structure, six bands are expected in the HeI region of **1**, four of which are doubly degenerate (Figure 4). The first two bands at 9.95 and 12.02 eV (Figure 3) with narrow Franck−Condon profiles can be assigned to the π_{nb}(CNO) MOs, the $2\pi_g$ and $2\pi_u$ orbitals, destabilized and stabilized, respectively, from the mean location in HCNO, 10.83 eV. The next pair occur at 15.8 eV ($1\pi_g$) and 16.67 eV ($1\pi_u$), with substantially broader Franck−Condon profiles, which reflect their assignment to the bonding CNO π orbitals; again these are disposed about the corresponding broad band in HCNO at 15.92 eV. Vibrational fine structure is partially resolved on the first and fourth bands. Since only symmetric (σ_g) modes (which we have not observed) are allowed in units of 1 quantum, we can estimate only that the structure on the first band (2097 cm^{-1}) represents a small decrease from the molecular ground state vibrational value (which must be close to ν_4, Table 2), whereas the structure on the fourth band (1613 cm^{-1}) represents a very large decrease from the neutral value. We assume that ν_2 is not involved here, since this would be incommensurate with the assignment of these orbitals to nonbonding and bonding MOs, respectively. The two π_{nb}(CNO) and two π_b(CNO) orbitals, degenerate if the ONCCNO chain is linear, split into $a_{g,u}$ and $b_{g,u}$ orbitals as the molecule bends at carbon (see MP2 result, Table 3). In the experimental PE spectrum, no splitting can be observed. Since the first two bands at 9.95 and 12.02 eV are sharp and narrow, we conclude that the molecule must be linear or close to linear.

The broad and relatively intense last band between 17.8 and 18.4 eV (maximum around 18.1 eV) is assigned to the two nondegenerate oxygen terminal lone pair orbitals, $7\sigma_g$ and $6\sigma_u$. Such a terminal lone pair orbital (n_O) leads to a strong sharp band in the individual PE spectra of HCNO[33](17.79 eV) and BrCNO[17](17.14 eV). The calculated split for the symmetric and antisymmetric combinations of these orbitals in **1** is less than 0.25 eV; experimentally no separation is observable, although the band profile is somewhat corrupted by sharp single peaks due to CO_2 (18.08 eV) and NO (18.32 eV). No other bands are observed, in agreement with the calculations (Table 3) predicting the next IP beyond the HeI range, 21.2 eV.

The separation between the π_{nb} orbitals (2.07 eV) is, as expected, larger than that between the π_b orbitals (0.87 eV) and reflects the substantial resonance interaction between the two halves of the molecule. The interaction between the cyano group π orbitals in NCCN is quite comparable, amounting to some 2.09 eV.[34] Figure 4 illustrates, through a correlation diagram, the formation of the ONCCNO valence MOs from two CNO fragments (IP values for HCNO are used). The MOs for ONCCNO serve to illustrate the delocalized nature of the π structure, and the not inconsiderable CC π interaction. The terminal $p\sigma$ orbitals, not surprisingly, show essentially no splitting, a reflection of their physical remoteness (Figure 4). We note, however, that for each *g*/*u* pair of orbitals the barycenter has moved some 0.2−0.3 eV to higher IE, due to the inductive effect.

Although the calculated Koopmans' IPs are not scaled, they are in reasonable agreement with the experiment. HAM/3 (hydrogenic atoms in molecules) has been shown to give an accurate representation of IPs for molecules containing first-row atoms.[35] Such calculations for **1**, performed at the MP3 geometry, give the best agreement with experiment (average deviation <0.5 eV), although it should be pointed out that similar results are obtained for the MP2 and MP3 values with a simple scaling (IP = 1.68 + 0.77IP(MP)).

Conclusion

Simple nitrile oxides are short-lived reactive species, and ONCCNO is no exception. This novel molecular species, containing only C, N, and O, can be generated in good yield in the gas phase by thermolysis of the dichloroglyoxime precursor. An alternate route, thermolysis of dibromofuroxan, gives reasonable yields but leads also to the parallel formation of the new molecule BrC(O)CN in addition to Br_2. *Ab initio* calculations establish that ONCCNO is most probably linear, or quasi-linear, but as in the case of HCNO, where higher level computational approaches and high-resolution spectroscopy are *de rigeur*, this conclusion will require extensive verification. Ultimately, a careful structural study is required; with no dipole moment, the linear molecule is best characterized with electron diffraction and infrared/Raman spectroscopy. Although low resolution, the present infrared and photoelectron data also indicate that the frame of the molecule must be linear or very close to linear. The vibrational results, although limited by

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wavenumber range and mutual exclusion, indicate, through the potential energy distribution, that the modes are somewhat coupled. The photoelectron analysis provides a picture of substantial interaction between the two halves of the molecule. The calculated vibrational frequencies and IPs are in reasonable agreement with experiment and support the assignment of the IR and PE spectra. Preliminary work to address some of the issues raised herein is being undertaken by high-resolution IR spectroscopy; the initial investigation indicates intensity alternation in the rotational structure, suggesting a linear or quasi-linear structure.

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