

## ARE THERE TWO DIFFERENT GEOMETRIC ISOMERS OF THE O=C=N=C=O CATION?

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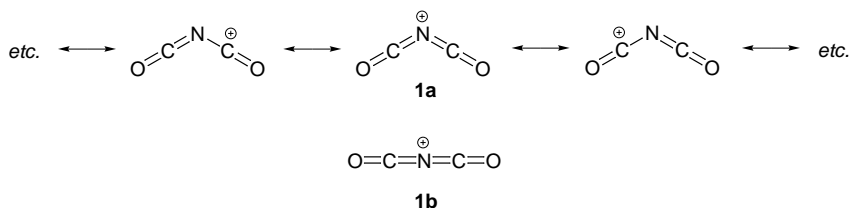
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Re-examination of the O=C=N=C=O<sup>+</sup> cation reported previously by Eberlin *et al.* (*J. Chem. Soc., Perkin Trans. 2* **1997**, 2347) yielded a single local minimum for the C<sub>2v</sub> bent structure (**1a**). The D<sub>∞h</sub> linear structure (**1b**) reported previously as a local minimum was found to be a second-order stationary point that, upon slight geometry perturbation, collapsed to a C<sub>2v</sub> transition state (**1c**) for degenerate inversion of the N–C–N angle in **1a**. The ion enthalpy of formation was obtained from the enthalpies of three reactions as  $\Delta H_{f,298}(\mathbf{1a}) = 718 \pm 6 \text{ kJ mol}^{-1}$ . **Keywords:** Heterocumulenes; C<sub>2</sub>NO<sub>2</sub> cation; Ion structure; Ion enthalpy of formation; *Ab initio* calculations; DFT; Mass spectrometry.

In recent papers, Eberlin and coworkers<sup>1–3</sup> and Cooks and coworkers<sup>4,5</sup> reported on several ion-molecule reactions involving the C<sub>2</sub>NO<sub>2</sub><sup>+</sup> cation generated by dissociative ionization of O=C=N–COOC<sub>2</sub>H<sub>5</sub>. To support the postulated mechanisms for the gas-phase reactions of this ion, the authors reported *ab initio* calculations that revealed two different geometrical isomers.

Cooks *et al.* used Møller–Plesset (MP2) calculations to report a linear structure as a local energy minimum<sup>4</sup>. Eberlin *et al.*<sup>2,3</sup> used Gaussian 2 (MP2) calculations and obtained a bent isomer (**1a**) as an energy minimum, which was slightly more stable than a linear isomer (**1b**), which was also reported as an energy minimum. The authors also suggested that structures **1a** and **1b** were separated by an unspecified energy barrier<sup>2</sup>. Although unnoticed by Eberlin *et al.*, the existence of local potential energy minima for both **1a** and **1b** is somewhat puzzling. The linear structure **1b** has precedents in several closed shell cations, *e.g.*, O=N=O<sup>+</sup>, CH<sub>2</sub>=N=CH<sub>2</sub><sup>+</sup> (ref.<sup>6</sup>), and CH<sub>2</sub>=N=O<sup>+</sup> (ref.<sup>7</sup>) which also have linear geometries about the nitrogen atoms. The bent structure **1a** can be written as a combination of canonical structures that differ in their formal (valence bond) electron distributions. Of necessity, this set of canonical structures also includes a bent form of **1b**.

The existence of a linear and bent **1b** is therefore equivalent to the existence of linear and bent isomers of ozone,  $N_3^-$ , and  $I_3^-$ , which are all known to exist as single isomers. The question of heterocumulene structures was addressed previously by Pykkö and Runeberg who reported Hartree-Fock and MP2-level calculations for a variety of molecular and ionic systems<sup>8</sup>. These authors reported a bent structure for the O=C=N=C=O<sup>+</sup> ion. In a related work, Bernhardt *et al.* recently reported the crystal structure of an Sb-complex of O=C=N=C=O<sup>+</sup> in which the ion moiety showed a bent geometry with large N-C-O angles (173.1 and 173.6°) and a 130.7° angle for the N-C-N bonds<sup>9</sup>. In view of the contradicting results from calculations carried out at different levels of theory, it became of interest to re-examine the structures of **1a**, **1b** and bring new thermochemical data pertinent to the stability of this interesting cation.



## CALCULATIONS

Standard *ab initio* and density functional theory calculations were performed using the Gaussian 98 suite of programs<sup>10</sup>. Geometries were optimized at two levels of theory. Density functional theory calculations used Becke's hybrid functional<sup>11</sup> (B3LYP) and the 6-311+G(d) or 6-311+G(d,p) basis sets. Another set of optimized geometries were obtained by perturbational Møller-Plesset calculations<sup>12</sup> with full excitations that were truncated at second order MP2(FULL). These calculations also used the 6-311+G(d) or 6-311+G(d,p) basis sets. In addition, structures **1a** and **1b** were reoptimized with coupled-clusters calculations using single and double excitations<sup>13,14</sup>, CCSD/6-311+G(d). The optimizations were carried out with tight convergence criteria that were  $3 \cdot 10^{-5}$  ångströms for maximum displacement and  $1.5 \cdot 10^{-5}$  atomic unit/ångström for maximum gradient. The predicted energy changes in optimized structures were  $<10^{-12}$  hartree. Optimized structures were characterized by harmonic frequency calculations as local minima (all frequencies real) or higher-order stationary points (one or more imaginary frequencies). The B3LYP frequencies were scaled<sup>15</sup>

by 0.963 and used to calculate zero-point energy and thermal corrections. Single-point energies were calculated at the G2(MP2) level of theory<sup>16</sup> using the B3LYP/6-311+G(d,p) geometries and zero-point corrections. In addition, B3LYP single-point energies were calculated with the larger 6-311+G(3df,2p) basis set. Comparison of B3LYP and MP2/6-311+G(3df,2p) relative energies can provide an indication of pathological behavior of the species in question.

## RESULTS AND DISCUSSION

**Structures of 1a–1c.** Geometry optimizations with B3LYP, MP2(FULL), and CCSD/6-311+G(d) yielded stationary states for **1a** and **1b** (Fig. 1). The bent structure was a local minimum at all levels of theory, as documented by frequency analysis. In contrast, the linear structure that was obtained with  $D_{\infty h}$  symmetry constraint showed two imaginary frequencies for the degenerate  $\Pi_u$  bending mode ( $i82\text{ cm}^{-1}$  by B3LYP). Upon releasing the  $D_{\infty h}$  symmetry constraint, the linear structure **1b** collapsed to a slightly bent  $C_{2v}$  structure **1c** of a total energy that was only  $1\text{--}3 \cdot 10^{-6}$  hartree lower than for **1b** (Table I). Structure **1c** showed one imaginary frequency due to the symmetrical ( $4a_1$ ) bending mode of the C–N–C atoms. Since the previous calculations of Eberlin *et al.*<sup>2</sup> may have used the packaged version of the G2(MP2) which employs the smaller 6-31G(d) basis set for geometry optimizations<sup>10</sup>, the geometry of **1c** was re-optimized with MP2(FULL)/6-31G(d). However, frequency analysis at this level of theory again gave one imaginary frequency for the  $4a_1$  bending mode (Fig. 1). Hence, the discrepancy between the present and previous data was not due to a basis set effect. We also compared our G2(MP2) total energies for **1a** and **1c** (Table I) with those of Eberlin *et al.*<sup>2</sup> and found those to agree within 1.6 millihartree, which may be due to slight differences in the optimized geometries. It is therefore concluded that the previous conclusions by Eberlin *et al.* and also Cooks *et al.* regarding the linear isomer **1b** were in error. Ion **1** exists as a single bent structure **1a** in the ground singlet state in line with the calculations of Pykkö and Runeberg<sup>8</sup>, and the X-ray data of Bernhardt *et al.*<sup>9</sup>. The linear structure **1b** is not a local minimum but a *second-order stationary point* that results from a symmetry constraint in the geometry optimization. Upon releasing the symmetry constraint, a slight bending distortion converts **1b** to **1c**, which is a *first-order stationary point* for vibrational inversion in **1a**.

**Energetics of 1a.** Having established the bent isomer **1a** as the only stable structure, we were interested in this ion's thermochemistry. This was inves-

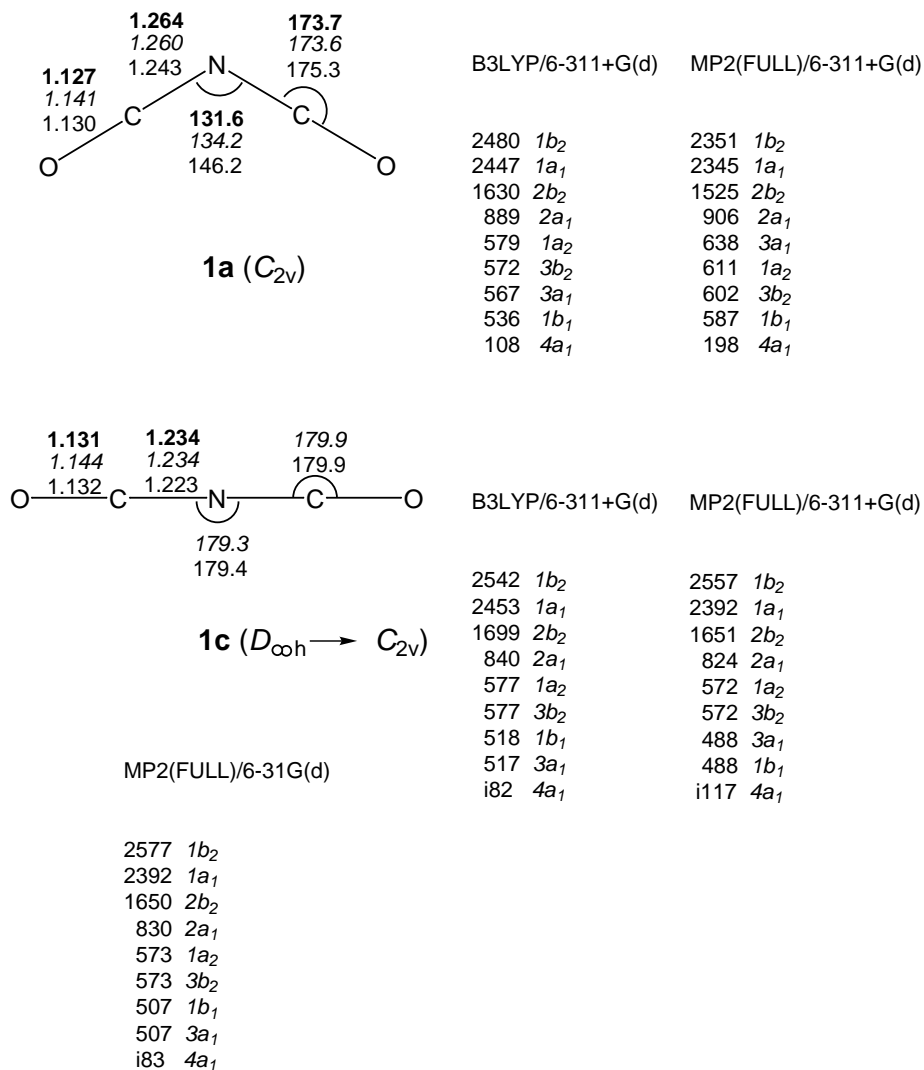


FIG. 1

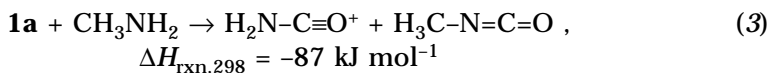
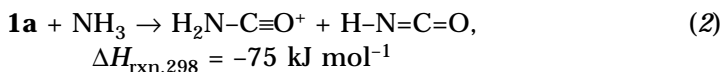
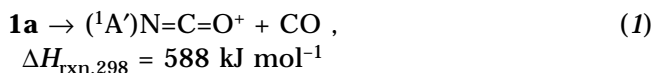
Calculated optimized geometries of **1a** and **1b**; bond lengths in Å, bond angles in °, frequencies in  $\text{cm}^{-1}$ . Roman numerals: B3LYP/6-311+G(d) parameters, italic numerals: MP2(FULL)/6-311+G(d) parameters, bold numerals: CCSD/6-311+G(d) parameters. The harmonic frequencies are uncorrected

TABLE I  
 Total energies

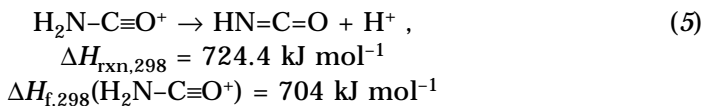
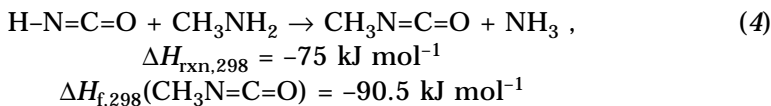
Species	Energy, hartree <sup>a</sup>							
	B3LYP/MP2(FULL) <sup>b</sup> 6-311+G(d,p)	ZPVE <sup>c</sup>	H <sub>298</sub> <sup>c</sup>	B3LYP/ 6-311+G(3df,2p)	MP2/ 6-311+G(3df,2p)	MP2/ 6-311G(d,p)	QCISD(T)/ 6-311G(d,p)	G2(MP2) <sup>d</sup>
<b>1a</b>	-281.150807	58.7	14.1	-281.174036	-280.625506	-280.466654	-280.496712	-280.694047
	-280.568170	58.4	14.0					
<b>1b</b>	-281.149964	58.2						
	-280.564904	57.1						
<b>1c</b>	-281.149967	58.2		-281.172442	-280.622613	-280.464005	-280.493589	-280.690865
	-280.564905	57.1						
H <sub>2</sub> N=C=O <sup>+</sup>	-169.021989	88.9	11.8	-169.034921	-168.691927	-168.596717	-168.624049	-168.726636
	-168.599988							
CH <sub>3</sub> -N=C=O	-208.055099	132.6	15.0	-208.070404	-207.617126	-207.487332	-207.529403	-207.665561
	-207.495866							
HN=C=O	-168.738735	55.8	11.1	-168.409098	-168.751516	-168.303939	-168.328112	-168.452807
	-168.311785							
HN=C=O <sup>+</sup>	-168.310085	50.3	11.5	-168.323793	-167.966155	-167.874543	-167.918800	-168.027142
( <sup>-</sup> A)N=C=O <sup>+</sup>	-167.554592	21.2	11.1	-167.567383	-167.224681	-167.137199	-167.181720	-167.296413
	-167.140713							
CH <sub>3</sub> NH <sub>2</sub>	-95.893840	167.5	11.6	-95.900313	-95.652241	-95.587209	-95.625991	-95.664592
NH <sub>3</sub>	-56.582636	89.8	10.0	-56.586839	-56.450534	-56.408536	-56.428137	-56.457191
	-56.434445							
CO	-113.349050	13.2	8.7	-113.356769	-113.136603	-113.074491	-113.093687	-113.175947
H <sup>+</sup>	-0.502156	0	6.2	-0.5021559	-0.4998098			-0.500000

<sup>a</sup> In units of hartree, <sup>b</sup> 1 hartree = 2 625.5 kJ mol<sup>-1</sup>, <sup>c</sup> B3LYP energies in upper lines, MP2(FULL) energies in lower lines, <sup>d</sup> In kJ mol<sup>-1</sup> from uncorrected B3LYP/6-311+G(d,p) harmonic frequencies, <sup>d</sup> Including corrections for scaled ZPVE and number of valence electrons.

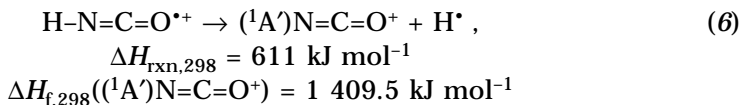
tigated using the enthalpies of dissociation by loss of CO (Eq. (1)) and two isodesmic reactions (Eqs (2), (3)). Combining the calculated  $\Delta H_{\text{rxn},298}$  for reactions (1)–(3) with the standard enthalpies of formation ( $\Delta H_{\text{f},298}$ ) of the other reactants and products yields  $\Delta H_{\text{f},298}(\mathbf{1a})$ . Evaluated  $\Delta H_{\text{f},298}$  for  $\text{NH}_3$ ,



$\text{CH}_3\text{NH}_2$ , CO, and HNCO were obtained from the NIST database<sup>17</sup> (Table II), which unfortunately does not include thermochemical data for methyl isocyanate and the cations in Eqs (1)–(3). The  $\Delta H_{\text{f},298}(\text{H}_3\text{C}-\text{N}=\text{C}=\text{O}) = -75 \text{ kJ mol}^{-1}$  was obtained from the G2(MP2) enthalpy of an isodesmic reaction with methylamine (Eq. (4)). Similarly, the  $\Delta H_{\text{f},298}$  of the remaining species needed to evaluate Eqs (1)–(3) were obtained according to Eqs (5) and (6). The G2(MP2) energies reproduced very well the tabulated proton affinity of isocyanic acid<sup>17</sup> (724 kJ mol<sup>-1</sup>),



lending credence to the calculated  $\Delta H_{f,298}(\text{H}_2\text{N}-\text{C}\equiv\text{O}^+)$  (Eq. (5)). The  $\Delta H_{f,298}$  of the  $\text{N}=\text{C}=\text{O}^+$  ion was difficult to verify, because the only available experiment-based result<sup>18,19</sup> did not report the ion spin multiplicity and may have



corresponded to the more stable triplet state. It is worth noting, however, that G2(MP2) reproduced very well the adiabatic ionization energy of  $\text{H}-\text{N}=\text{C}=\text{O}$  (calculated 11.59 eV, measured<sup>20</sup> 11.595 eV) and hence also the  $\Delta H_{f,298}(\text{HN}=\text{C}=\text{O}^{\bullet+}) = 1\,016.6 \text{ kJ mol}^{-1}$  when compared with the tabulated value<sup>17</sup> (1 017.1 kJ mol<sup>-1</sup>). Combining the  $\Delta H_{\text{rxn},298}$  from reactions (1)–(3)

TABLE II  
Relative energies

Species/Reaction	Relative enthalpy, kJ mol <sup>-1</sup>		
	B3LYP/ 6-311+G(3df,2p)	MP2/ 6-311+G(3df,2p)	G2(MP2)
$\mathbf{1a} + \text{NH}_3 \rightarrow \text{H}_2\text{N}-\text{C}=\text{O}^+ + \text{HN}=\text{C}=\text{O}$	-70.7	-69.2	-74.1 <sup>a</sup> -75.2 <sup>b</sup>
$\mathbf{1a} + \text{CH}_3\text{NH}_2 \rightarrow \text{H}_2\text{N}-\text{C}=\text{O}^+ + \text{CH}_3\text{N}=\text{C}=\text{O}$	-85.8	-86.6	-88.1 -86.9
$\mathbf{1a} \rightarrow ({}^1\text{A}')\text{N}-\text{C}=\text{O}^+ + \text{CO}$	632.8	670.4	582.0 587.8
$\text{H}_2\text{N}-\text{C}=\text{O}^+ \rightarrow \text{HN}=\text{C}=\text{O} + \text{H}^{\bullet}$	712.2	710.6	718.9 724.4
$\text{HN}=\text{C}=\text{O} \rightarrow \text{HN}=\text{C}=\text{O}^{\bullet+}$	1117.7 11.58 <sup>c</sup>	1124.1 11.65 <sup>c</sup>	1118.0 11.59 <sup>c</sup>
$\text{HN}=\text{C}=\text{O}^{\bullet+} \rightarrow ({}^1\text{A}')\text{N}=\text{C}=\text{O}^+ + \text{H}^{\bullet}$	639.5	640.1	605.4 611.2
$\text{H}-\text{N}=\text{C}=\text{O} + \text{CH}_3\text{NH}_2 \rightarrow \text{CH}_3\text{N}=\text{C}=\text{O} + \text{NH}_3$	-15.0	-17.4	-14.1 -11.7

<sup>a</sup> At 0 K. <sup>b</sup> At 298 K. <sup>c</sup> Adiabatic ionization energies in eV.

with the enthalpies of formation of the reactants and products provided the  $\Delta H_{f,298}(\mathbf{1a})$  as 711, 719, and 723 kJ mol<sup>-1</sup>, for reactions (1), (2), and (3), respectively. On the basis of these calculations, one can best estimate the enthalpy of formation of ion  $\mathbf{1a}$  as  $\Delta H_{f,298}(\mathbf{1a}) = 718 \pm 6$  kJ mol<sup>-1</sup>.

## CONCLUSIONS

Re-examination of the structure of the O=C=N=C=O<sup>+</sup> cation ( $\mathbf{1a}$ ) revealed a single potential energy minimum with a bent C<sub>2v</sub> geometry. The enthalpy of formation of  $\mathbf{1a}$  was calculated to be  $718 \pm 6$  kJ mol<sup>-1</sup> from two isodesmic and one dissociation reactions.

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He is Editor of *Journal of Mass Spectrometry*, an international journal published by John Wiley & Sons, and member of Editorial or Advisory Boards of *International Journal of Mass Spectrometry*, *Spectroscopy Letters*, and *Collection of Czechoslovak Chemical Communications*. In 1996–1999 he was appointed Affiliate Staff Scientist of the Pacific Northwest National Laboratory and in 1999 he co-founded Intelligent Ion, Inc. where he is Chief Scientist.

His research interest range from chemical physics to biology. Focus is on instrument development and applications of mass spectrometric techniques to the generation and study of transient intermediates of chemical reactions, bioinorganic chemistry in the gas phase, clinical enzymology, and proteomics. In addition to some 250 research articles, he co-authored the books *Synthesis of Natural Products* (with Pavel Kočovský and Josef Hájíček, CRC Publishers, 1986), *Interpretation of Mass Spectra* (with Fred W. McLafferty, University Science Books, 1993) and *edited Applications of Mass Spectrometry to Organic Stereochemistry* (with Janet. S. Splitter, VCH Publishers, 1994).

More details can be found on the Turecek Group web page at <http://dogbert.chem.washington.edu> or <http://depts.washington.edu/chemfac/turecek.html>. If you cannot reach him in the lab, he is probably climbing glaciers in the Cascade Mountains, so leave a message and hope he is going to make it back.