JOC Featured Article
pubs.acs.org/joc

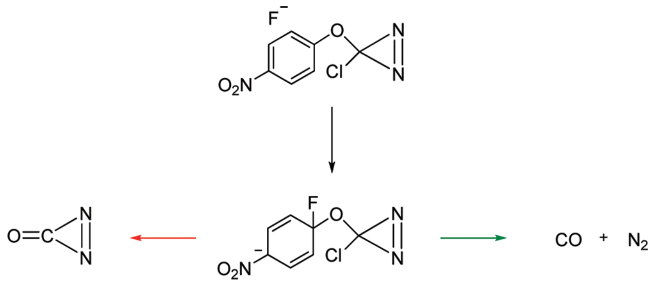
Attempted Isolation and Characterization of Diazirinone (N_2CO)

Christopher J. Shaffer,[†] Brian J. Esselman,[†] Robert J. McMahon,*[,†] John F. Stanton,*[,‡] and R. Claude Woods*[,†]

[†]*Department of Chemistry, University of Wisconsin, 1101 University Avenue, Madison, Wisconsin 53706-1322, and* [‡]*Institute for Theoretical Chemistry, Department of Chemistry and Biochemistry, University of Texas, 1 University Station A5300, Austin, Texas 78712-0165*

mcmahon@chem.wisc.edu; jfstanton@mail.utexas.edu; rcwoods@wisc.edu

Received December 14, 2009



Stimulated and intrigued by the report of the synthesis of diazirinone (**1**), a metastable adduct of N_2 and CO, we carried out further experimental and theoretical studies aimed at the detailed spectroscopic characterization of this species. Our attempts to generate and detect diazirinone (**1**) in either the condensed phase (using matrix isolation spectroscopy) or in the gas phase (using millimeter-wave rotational spectroscopy), however, have been unsuccessful. Trapping the volatile products produced from the reaction of 3-chloro-3-(*p*-nitrophenoxy)diazirine (**5**) with tetrabutylammonium fluoride (TBAF) under matrix-isolation conditions affords chlorofluorodiazirine (**8**) and carbon monoxide but fails to provide evidence for diazirinone (**1**). Moreover, sophisticated ab initio calculations of the structure and fundamental vibrational frequencies of diazirinone (**1**) produce an estimate for the fundamental band origin of the C═O stretch (2046 cm^{-1}) that is ca. 100 cm^{-1} lower in frequency than the experimental value previously attributed to this band. This discrepancy lies well outside any expected solvent shift or calculation error at this level of theory. In an effort to reconcile our findings with the earlier reports concerning diazirinone (**1**), we reconsidered the infrared spectral evidence upon which the original claim of diazirinone synthesis was based. New experiments demonstrate that these spectra may be explained and reproduced with a combination of solution-phase and gas-phase absorptions of CO, without recourse to invoke diazirinone (**1**).

Introduction

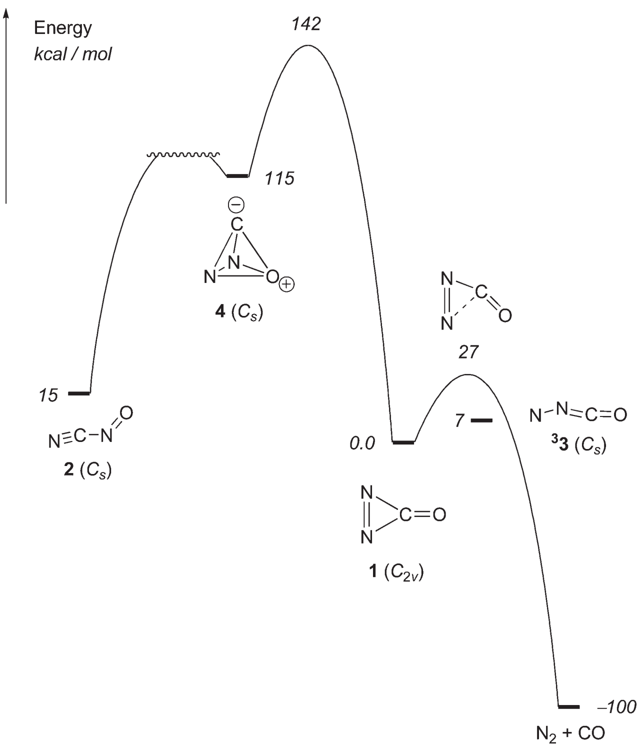
Diazirinone (**1**), the C_{2v} conjugate of molecular nitrogen and carbon monoxide, is an intriguing species, inasmuch as it is a mixed dimer of the two most strongly bonded diatomic molecules. Diazirinone (**1**), along with similar high-energy, metastable compounds[1] such as ethylenedione,[2,3] 7-norbornadienone,[4] and tetranitrogen,[5] provide opportunities to probe the limits of chemical (in)stability. Each of these molecules may undergo a highly exothermic decomposition to its respective stable constituents, presenting a potentially severe synthetic obstacle to isolation and characterization. Comparison of diazirinone (**1**) and cyclopropenone provides insight concerning the nature of weakly aromatic systems.[6,7] The anticipated polarity of diazirinone (**1**) makes it an interesting target to investigate via rotational

---

(1) Hoffmann, R.; Hopf, H. *Angew. Chem., Int. Ed.* **2008**, *47*, 4474–4481.
(2) Schröder, D.; Heinemann, C.; Schwarz, H.; Harvey, J. N.; Dua, S.; Blanksby, S. J.; Bowie, J. H. *Chem.—Eur. J.* **1998**, *4*, 2550–2557.
(3) Berson, J. A.; Birney, D. M.; Dailey, W. P.; Liebman, J. F. *Mol. Struct. Energ.* **1988**, *6*, 391–441. , 445−446.
(4) LeBlanc, B. F.; Sheridan, R. S. *J. Am. Chem. Soc.* **1985**, *107*, 4554–4556.
(5) Cacace, F.; de Petris, G.; Troiani, A. *Science* **2002**, *295*, 480–481.
(6) Korkin, A. A.; Balkova, A.; Bartlett, R. J.; Boyd, R. J.; Schleyer, P. v. R. *J. Phys. Chem.* **1996**, *100*, 5702–5714.
(7) Skancke, A.; Liebman, J. F. *J. Org. Chem.* **1999**, *64*, 6361–6365.

DOI: 10.1021/jo9026462

SCHEME 1[a]

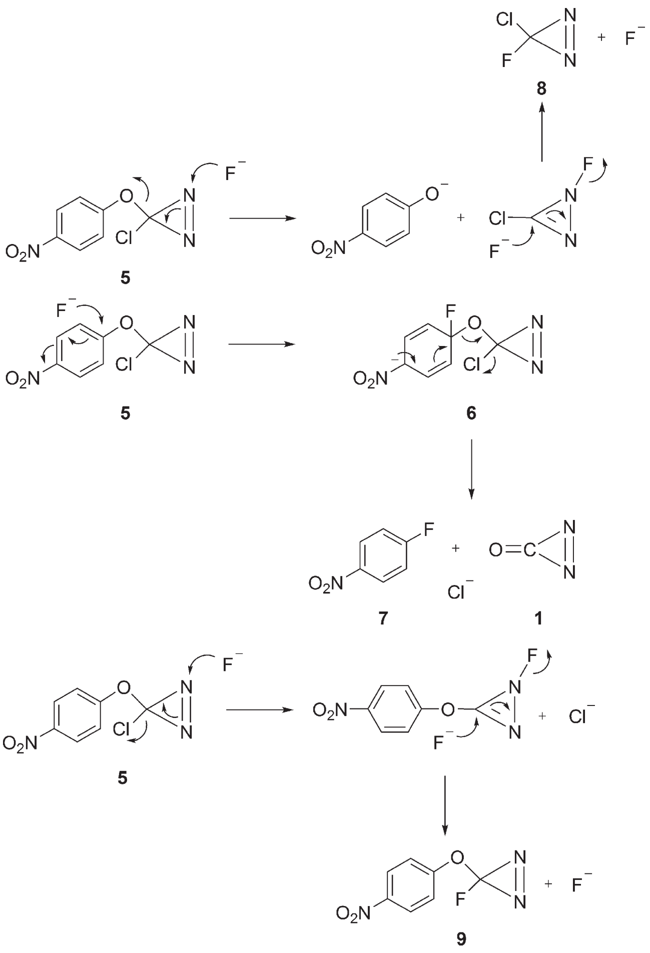


[a]Computed energies (kcal/mol) of N_2CO isomers,[6,8,9] relative to diazirinone (**1**).

spectroscopy, which could provide insights into the structure and bonding of this peculiar molecule. The laboratory rotational spectrum of **1** would also provide the basis to search for diazirinone as a possible component of the interstellar medium via radioastronomy. These considerations motivated us to initiate the studies described herein.

Diazirinone (**1**) is the lowest energy isomer on the N_2CO potential energy surface, other than CO + N_2 (Scheme 1).[3,6,8−11] Nitrosyl cyanide (**2**), which is an isolable species, lies ca. 15 kcal/mol higher in energy.[8,11] The open-chain isomer NNCO (**3**) is not bound on the singlet PES but is a low-lying minimum on the triplet PES. The enthalpy barrier for the dissociation of diazirinone (**1**) to N_2 and CO is ca. 27 kcal/mol, while the exothermicity of the reaction is ca. 100 kcal/mol.[8,11] The barrier is consistent with the rate of thermal decomposition attributed to **1**.[10] Korkin et al. noted an interesting difference between the N_2CO PES and the isoelectronic PES of N_4.[6] In the case of N_2CO, the tetrahedron-like isomer **4** is much higher in energy (115 kcal/mol) than diazirinone (**1**), which was rationalized in terms of the inherent formal charges. In the case of N_4, the tetrahedral structure is 10 kcal/mol lower in energy than the distorted structure that is analogous to diazirinone.

SCHEME 2



In terms of experimental studies, Maier and coworkers reported the photochemistry and spectroscopy of matrix-isolated N_2CO isomers (NCNO, CNNO, NCON).[12] De Petris et al. generated an N_2CO isomer in a neutralization−reionization mass spectrometry (NRMS) experiment.[9] Careful analysis suggests that the isomer generated is triplet NNCO (^{3}**3**), and persuasive arguments rule out both diazirinone (**1**) and nitrosyl cyanide (**2**). Concurrently, diazirinone (**1**) was reported as an unanticipated product obtained during the preparation of chlorofluorodiazirine.[10] When 3-chloro-3-(*p*-nitrophenoxy)diazirine (**5**) was treated with molten tetrabutylammonium fluoride (TBAF), the expected products, chlorofluorodiazirine (**8**) and *p*-nitrophenol, were obtained only as minor products, while *p*-fluoronitrobenzene (**7**) was obtained as a major product, along with a transient species exhibiting an infrared absorption at 2150 cm^{-1} (Scheme 2). As the reaction mixture warmed toward room temperature, the absorption at 2150 cm^{-1} decayed over 5−10 min, while a near-simultaneous increase of CO absorptions at 2116 and 2169 cm^{-1} was observed. The mechanism shown in Scheme 2 was used to rationalize the experimental observations, and it was concluded that the transient species produced was diazirinone (**1**). Subsequent studies to prepare other dihalodiazirines consistently produced *p*-fluoronitrobenzene (**7**), from which it was assumed that diazirinone was also produced. Diazirinone

---

(8) Korkin, A. A.; Schleyer, P. v. R.; Boyd, R. J. *Chem. Phys. Lett.* **1994**, *227*, 312–320.

(9) de Petris, G.; Cacace, F.; Cipollini, R.; Cartoni, A.; Rosi, M.; Troiani, A. *Angew. Chem., Int. Ed.* **2005**, *44*, 462–465.

(10) Moss, R. A.; Chu, G.; Sauers, R. R. *J. Am. Chem. Soc.* **2005**, *127*, 2408–2409.

(11) Zhu, R. S.; Lin, M. C. *J. Phys. Chem. A* **2007**, *111*, 6766–6771.

(12) Maier, G.; Reisenauer, H. P.; Eckwert, J.; Naumann, M.; De Marco, M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1707–1709.

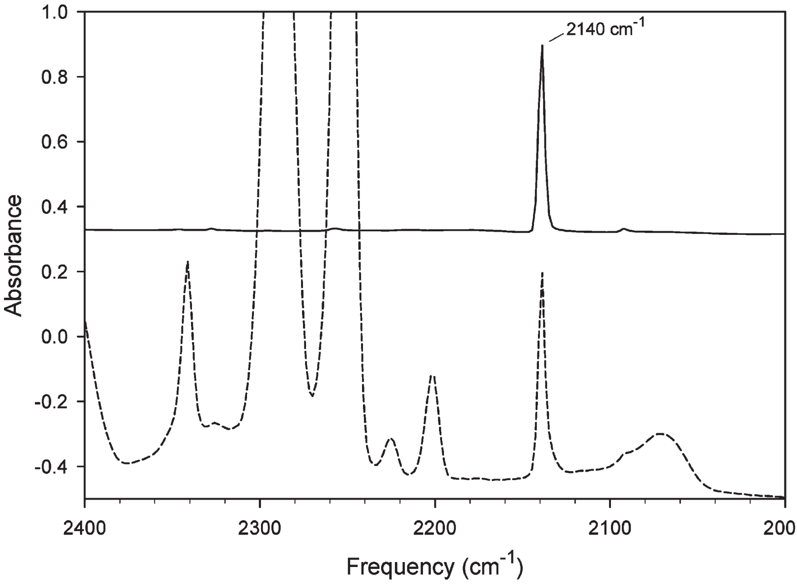


FIGURE 1. Infrared spectrum (Ar, 10 K) of the volatile components from the reaction of *p*-nitrophenoxychlorodiazirine (**5**) and $Bu_4N^+F^-$ in acetonitrile. Top: spectrum of volatile products that passed directly through a gas trap at 77 K without condensing. Bottom: spectrum obtained after warming the trap to 263 K. All peaks can be assigned to either CO (2140 cm^{-1}) or acetonitrile. Both plots are set to the same scale but are offset by 2.5 absorbance units to allow for comparison.

was not isolated as a pure compound in any of these studies.[10,13−19]

Results and Discussion

Attempted Synthesis and Isolation of Diazirinone (1). Our primary goal, to obtain the gas-phase millimeter-wave rotational spectrum of diazirinone (**1**), could be straightforwardly pursued by preparing a sample of **1**, either as a neat liquid or as a solution in a high-boiling solvent, from which **1** could be distilled. The reported rapid thermal decomposition of diazirinone (ca. 10 min at −10 °C) suggested that isolation of diazirinone (**1**) would likely require vacuum transfer of the metastable species to a cold trap. Several attempts to distill diazirinone (**1**) from the reaction mixture of 3-chloro-3-(*p*-nitrophenoxy)diazirine (**5**) and tetrabutylammonium fluoride, using a series of low volatility solvents (acetonitrile, diglyme, and butyl diglyme), into an LN2-cooled trap, failed to yield any condensed product. Our choice of solvent was influenced by a number of requirements: The solvent needed to be fluid at temperatures between −20 and +25 °C, to have a low vapor pressure at those temperatures (preventing distillation into the matrix or gas trap), and to solubilize $Bu_4N^+F^-$.

In view of the failures to capture diazirinone in an LN2 trap, we attempted the deposition of diazirinone into an argon matrix at 25 K, transferred from the same reaction mixtures. A long-path gas trap (20 cm), cooled to 77 K, was placed between the reaction solution and the matrix window. Utilizing a procedure similar to that described in the literature, 3-chloro-3-(*p*-nitrophenoxy)diazirine (**5**) was dissolved in acetonitrile and added to molten $Bu_4N^+F^-$ at −10 °C.[10] The reaction mixture bubbled steadily for 30 min before being closed off to obtain the infrared spectrum of the matrix. The spectrum exhibited a single absorption feature at 2140 cm^{-1}, which is consistent with the literature value for matrix isolated CO (Figure 1).[20,21] When the gas trap was allowed to warm from 77 to 263 K, neither increased absorption by CO nor a new absorption attributable to diazirinone was observed (Figure 1). These observations suggest that diazirinone had not condensed in the gas trap at 77 K, as it neither deposited on the matrix nor decomposed to produce more CO. Since we did not observe a peak at 2150 cm^{-1}, we were unable to confirm that diazirinone was a persistent species or an observable intermediate.

Examination of the isolable reaction products, obtained upon treatment of 3-chloro-3-(*p*-nitrophenoxy)diazirine (**5**) with $Bu_4N^+F^-$, by ^1H and ^{19}F NMR spectroscopy confirms the formation of *p*-nitrophenol, *p*-fluoronitrobenzene (**7**), and 3-fluoro-3-(*p*-nitrophenoxy)diazirine (**9**). The only points of uncertainty, therefore, appear to involve (i) the detection and characterization of diazirinone (**1**) and (ii) the suitability of utilizing *p*-fluoronitrobenzene (**7**) as a surrogate for inferring the formation of diazirinone (**1**) (Scheme 2).

Gas- and Solution-Phase Infrared Spectroscopy of Carbon Monoxide. In view of our inability to isolate diazirinone or trap it under matrix isolation conditions, as well as the significant discrepancy between our predicted band origin of the C=O fundamental stretching vibration of diazirinone (2046 cm^{-1}) (see below) and the IR peak previously attributed to this species (2150 cm^{-1}),[10] we have confronted the

---

(13) Chu, G.; Moss, R. A.; Sauers, R. R. *J. Am. Chem. Soc.* **2005**, *127*, 14206–14207.

(14) Moss, R. A. *Acc. Chem. Res.* **2006**, *39*, 267–272.

(15) Moss, R. A.; Tian, J.; Sauers, R. R.; Skalit, C.; Krogh-Jespersen, K. *Org. Lett.* **2007**, *9*, 4053–4056.

(16) Moss, R. A.; Tian, J.; Sauers, R. R.; Ess, D. H.; Houk, K. N.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* **2007**, *129*, 5167–5174.

(17) Moss, R. A.; Tian, J.; Chu, G.; Sauers, R. R.; Krogh-Jespersen, K. *Pure Appl. Chem.* **2007**, *79*, 993–1001.

(18) Moss, R. A.; Wang, L.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* **2009**, *131*, 2128–2130.

(19) Moss, R. A. *J. Phys. Org. Chem.* **2009**, early view.

(20) Ball, D. W. *A Bibliography of Matrix Isolation Spectroscopy: 1954−1985*; Rice University Press: Houston, 1988.

(21) Ochsner, D. W.; Ball, D. W.; Kafafi, Z. H. *A Bibliography of Matrix Isolation Spectroscopy: 1985−1997*; Naval Research Laboratory: Washington, DC, 1998.

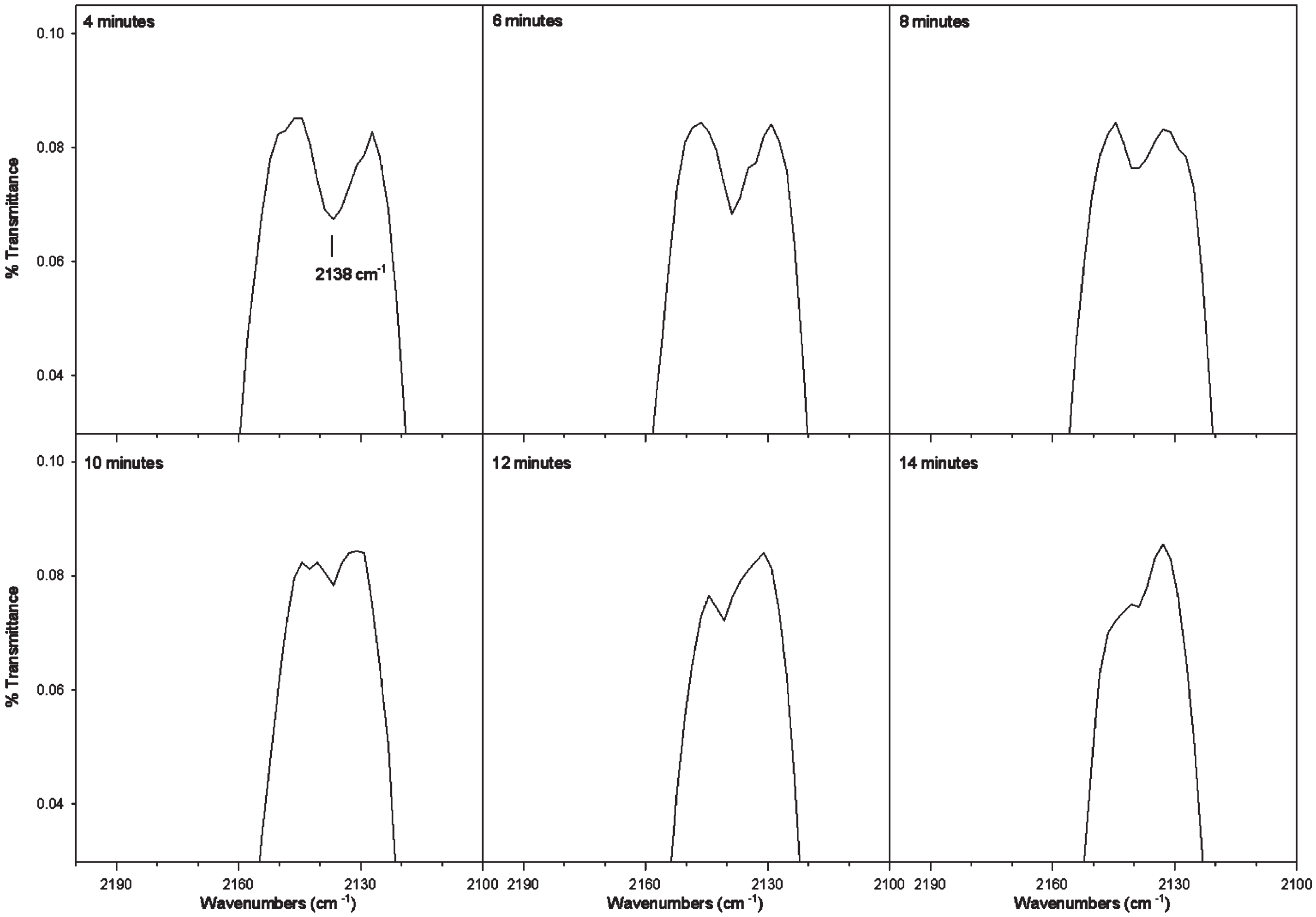


FIGURE 2. Infrared spectrum of carbon monoxide dissolved in acetonitrile (1 cm quartz cell). Top: ν_{CO} observed at 2140 cm^{-1} (4 min after saturation; warming from −35 °C). The progressive five lower plots, taken at 2 min intervals, show the decrease in intensity of solution-phase CO (2140 cm^{-1}) as CO degasses from solution upon warming.

need to reconsider the assignment of spectral features in the reported IR spectrum. We suggest that the two features (2116 and 2169 cm^{-1}) in Figure 1 of ref 10, previously attributed to solution-phase CO are, in fact, the maximum intensity positions of the P and R branches of gas-phase CO, respectively. Furthermore, we suggest that the peak at 2150 cm^{-1} that was assigned to the diazirinone (**1**) C=O stretch is actually the absorption of CO in a condensed phase. The presence of gas-phase carbon monoxide is strongly indicated by the presence of partially resolved spectroscopic features in the range 2060−2130 cm^{-1}, which correspond to individual rotational lines. Such extensive rotational structure is observed only in the gas phase, while in the condensed phase (either in solution or in a matrix), the CO absorption collapses due to the stronger intermolecular interactions.

To confirm this interpretation, we dissolved CO in acetonitrile and obtained an infrared spectrum. Literature values for carbon monoxide in acetonitrile place the fundamental frequency at 2140 cm^{-1}, but these reports are vague on solution conditions.[22−24] In view of the low solubility (0.005−0.008 M at 1 atm CO),[25−27] we attempted to saturate a solution of acetonitrile with CO at −35 °C for 30 min. To further compensate for low solubility, we employed a long path length (1.00 cm) quartz cuvette. The IR spectral window that is accessible with this cell is only 2080−2200 cm^{-1}, due to the high optical density resulting from the combined absorptions of the cuvette and acetonitrile. When the cuvette was placed in the spectrometer chamber, a structureless absorption centered at 2140 cm^{-1} was observed (Figure 2; top). Mimicking the disappearance of the 2150 cm^{-1} peak previously assigned to the decomposition of diazirinone, the intensity of this peak decreased to near zero over 10 min as the CO degassed from the gradually warming solution (Figure 2). In the spectrum previously attributed to diazirinone (**1**), the optical density of the sample was very high, corresponding to a transmittance value of 1.36−1.78% in the region of the C=O stretching absorption.[10] Although it is possible to measure intense absorption features under these conditions, the resolution at this saturation level starts to degrade and peaks begin to broaden, creating uncertainty

---

(22) Szanyi, J.; Paffett, M. T. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 5165–5175.

(23) Christensen, P. A.; Hamnett, A.; Muir, A. V. G.; Freeman, N. A. *J. Electroanal. Chem.* **1990**, *288*, 197–215.

(24) Anderson, M. R.; Blackwood, D.; Pons, S. *J. Electroanal. Chem.* **1988**, *256*, 387–395.

(25) Lopez-Castillo, Z. K.; Aki, S. N. V. K.; Stadtherr, M. A.; Brennecke, J. F. *Ind. Eng. Chem. Res.* **2006**, *45*, 5351–5360.

(26) Fujita, E.; Creutz, C.; Sutin, N.; Szalda, D. J. *J. Am. Chem. Soc.* **1991**, *113*, 343–353.

(27) Szalda, D. J.; Fujita, E.; Creutz, C. *Inorg. Chem.* **1989**, *28*, 1446–1450.

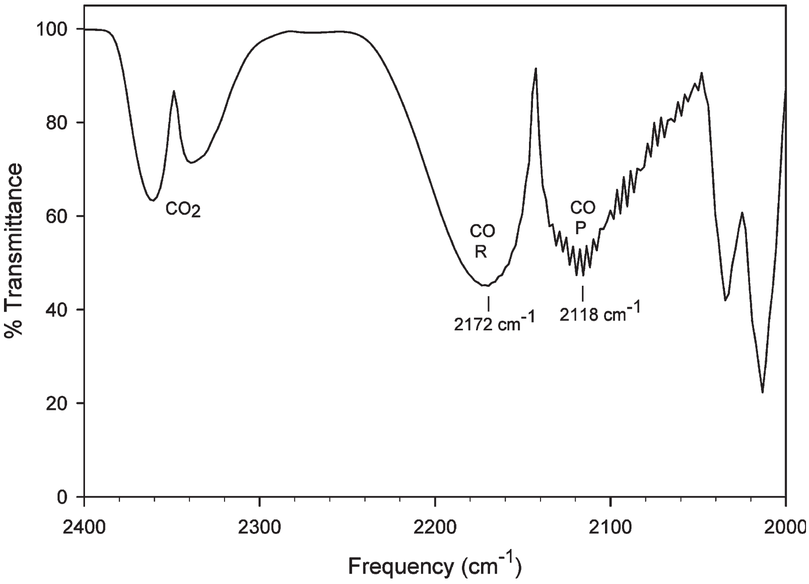


FIGURE 3. Infrared spectrum of gas phase CO exhibiting features at 2118 and 2172 cm^{-1}.

about the frequency measurement and subsequent assignment. Thus, we interpret the absorption attributed to diazirinone (**1**) at 2150 cm^{-1} as that of CO broadened by saturation; this feature is commensurate with the absorption of CO in acetonitrile at 2140 cm^{-1}.

In order to confirm our assignment of the 2116 and 2169 cm^{-1} features as gas phase CO absorptions, we collected an independent IR spectrum of gas-phase CO at 2-cm^{-1} resolution. The spectrum exhibits features at 2118 and 2172 cm^{-1} (Figure 3). At this resolution, the appearance of the spectrum is extremely similar to the published one,[10] in that partially resolved peaks were observed in the P-branch region but not in the R-branch region. This behavior is due to the closer spacing of the R-branch rotational lines relative to those in the P-branch. When the spectral resolution was increased to 0.060 cm^{-1}, all of the rotational lines in both branches were fully resolved.

Computational Studies. Our ab initio calculations estimate the fundamental C=O stretching frequency, ν_1, of diazirinone (**1**) to be 2046 cm^{-1} (Table 1). This value derives from a high-level calculation that incorporates a sophisticated treatment of electron correlation, a large basis set, and treatment of vibrational anharmonicity using second-order vibrational perturbation theory. The discrepancy between computed (2046 cm^{-1}) and experimental (2150 cm^{-1}) values is troubling in both magnitude and sign. A calculation of this type, for a molecule of this size, is expected to reproduce the experimental value to within 25 cm^{-1} (see below). Moreover, computed values are typically *higher* in frequency than experimental values. Thus, the present calculations cast considerable doubt on the assignment of the experimentally observed IR band at 2150 cm^{-1} to diazirinone (**1**).

In terms of the detailed vibrational spectroscopy of diazirinone (**1**), there is a strong Fermi resonance between the fundamental C=O stretching frequency, ν_1, and the overtone of ν_5, the latter being best described as a wagging of the CO bond perpendicular to the plane of the ring. Although the zeroth-order energy difference between ν_1 and $2\nu_5$ is not that small (186 cm^{-1}; Table 1), the magnitude of the associated cubic force constant ϕ_{155} (-307 cm^{-1}) is quite large. (The resonance has been treated here in the usual way, in which the associated fundamental and overtone levels are computed by diagonalization of a 2 × 2 effective Hamiltonian.) An accuracy of 25 cm^{-1} is typically associated with vibrational frequencies calculated at this level of theory,[28−31] but the involvement of the Fermi resonance introduces somewhat greater uncertainty. By conservative estimate, the calculated value of 2046 cm^{-1} might be in error by as much as 50 cm^{-1}.[32,33] The computed dipole moment of diazirinone (**1**) is 1.05 D, a value that is more than sufficient to permit the measurement of its rotational spectrum. The rotational constants A_0, B_0, and C_0 predicted from the VPT2 model are 41360, 8400, and 6970 MHz, where all values are rounded to the nearest 10 MHz.

TABLE 1. Computed Fundamental Vibrational Frequencies for Diazirinone (1)[a]

state	symmetry	frequency	intensity	mode description
$\nu_1{}^b$	a$_1$	2046	316.7	CO stretch
ν_2	a$_1$	1325	0.2	NN stretch
ν_3	a$_1$	903	5.2	CN symmetric stretch
ν_4	b$_1$	565	28.7	out-of-plane bend
ν_5	b$_2$	961	11.3	OCN scissor
ν_6	b$_2$	529	11.9	NCN scissor
$2\nu_5{}^b$	a$_1$	1860	120.7	

[a] CCSD(T)/ANO2; frequency (cm^{-1}). [b] Strong Fermi resonance; see text.

Analysis. In light of the evidence described above, we surmise that carbon monoxide dissolved in a condensed phase accounts for the broad peak at 2150 cm^{-1} previously

---

(28) Jochnowitz, E. B.; Zhang, X.; Nimlos, M. R.; Varner, M. E.; Stanton, J. F.; Ellison, G. B. *J. Phys. Chem. A* **2005**, *109*, 3812–3821.

(29) Zhang, X.; Nimlos, M. R.; Ellison, G. B.; Varner, M. E.; Stanton, J. F. *J. Chem. Phys.* **2006**, *124*, 084305.

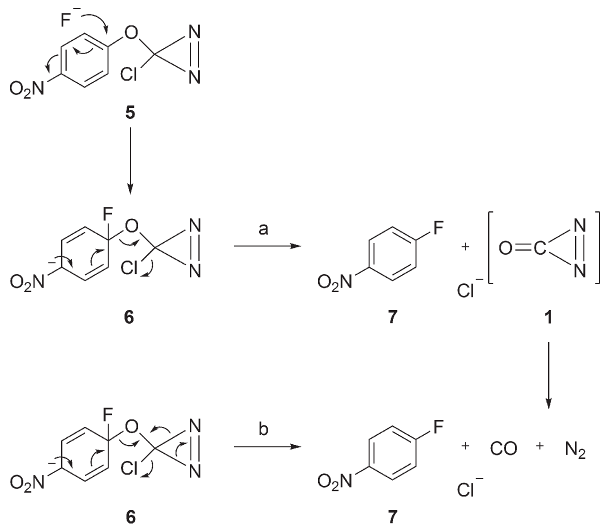
(30) Zhang, X.; Nimlos, M. R.; Ellison, G. B.; Varner, M. E.; Stanton, J. F. *J. Chem. Phys.* **2007**, *126*, 174308.

(31) Stanton, J. F.; Flowers, B. A.; Matthews, D. A.; Ware, A. F.; Ellison, G. B. *J. Mol. Spectrosc.* **2008**, *251*, 384–393.

(32) Konen, I. M.; Li, E. X. J.; Lester, M. I.; Vazquez, J.; Stanton, J. F. *J. Chem. Phys.* **2006**, *125*, 074310.

(33) Vazquez, J.; Stanton, J. F. *Mol. Phys.* **2007**, *105*, 101–109.

SCHEME 3



assigned to diazirinone (**1**). Although we cannot exclude the mechanism proposed for the formation of diazirinone (Scheme 3, path a), our observations require a much shorter lifetime for diazirinone than originally suggested. Two plausible explanations are that diazirinone is formed, but is unstable to the reaction conditions, or that N_2 and CO are produced without the intervention of diazirinone (Scheme 3, path b). The reaction of 3-chloro-3-(*p*-nitrophenoxy)diazirine (**5**) with $Bu_4N^+F^-$ undoubtedly affords *p*-fluoronitrobenzene (**7**), nitrogen, and carbon monoxide.[34] At the concentrations typically employed in these experiments, the decomposition of diazirine **5** would create a supersaturated solution of carbon monoxide. As the reaction mixture warms from −15 °C, CO will degas from solution, flooding the IR sample compartment with gas-phase CO. This rationalization is consistent with the previously reported IR experiments, in which the initially observed band at 2150 cm^{-1} gives way to the spectrum of gas-phase CO (P and R branches at 2116 and 2169 cm^{-1}, respectively). When we prepared a solution of carbon monoxide in acetonitrile at −35 °C, an absorption at 2140 cm^{-1} was observed. Convincingly, the sample degasses carbon monoxide over the same time period (10 min) as the previously reported decomposition of "diazirinone" at 2150 cm^{-1} and the unresolved P and R branches simultaneously appear at nearly identical positions to those reported in Ref. 10.

Summary. Diazirinone (**1**) was previously reported as a metastable product of the reaction of 3-chloro-3-(*p*-nitrophenoxy)diazirine (**5**) with $Bu_4N^+F^-$. The assignment was based on the decay of an infrared absorption at 2150 cm^{-1} and the increase of two peaks for carbon monoxide at 2116 and 2169 cm^{-1}. Our attempts to isolate diazirinone, however, led us to question this assignment: (i) Trapping of the volatile reaction products under matrix-isolation conditions (codeposition with argon at 10 K) led only to the observation of CO. (ii) No evidence was obtained to suggest that diazirinone was condensed in a vacuum trap cooled to 77 K. (iii) The frequency of the experimental C=O stretch attributed to diazirinone (2150 cm^{-1}) is not consistent with the value predicted (2046 cm^{-1}) by a sophisticated level of quantum theory. (iv) The high optical density (small %T) of the previously reported experimental spectrum does not allow a precise determination of the peak position. This spectrum may be interpreted in terms of the broad, featureless absorption of CO in a condensed phase. (v) The evolution of the broad IR absorption at 2150 cm^{-1} to give absorptions at 2116 and 2169 cm^{-1} may be rationalized in terms of the degassing of CO from the condensed phase into the gas phase. We therefore conclude that diazirinone (**1**), if formed at all, has a much shorter lifetime than originally suggested.[10,13−18]

Experimental Section

General Methods. The matrix isolation apparatus and general techniques for its use have been described previously.[35,36]

Computational Methods. Geometries, anharmonic force field corrections, vibrational frequencies, and rotational constants were computed for diazirinone (**1**; C_{2v}) using the coupled-cluster singles and doubles model, together with a perturbative treatment of triple excitations [CCSD(T)],[37] as implemented in the CFOUR software package.[38] The basis set used was the atomic natural orbital basis ANO2, which is based on Taylor and Almlöf's natural atomic orbitals,[39] truncated to 5s4p3d2f1g on each atom. Geometries were further optimized using analytic gradients,[40,41] and harmonic frequencies obtained with analytic second derivatives.[42] Following this, the cubic and quartic force constants were calculated by numerical differentiation of analytic second derivatives calculated at displaced points, following the approach of Stanton et al.[43] Second-order vibrational perturbation theory (VPT2) was then used to compute the fundamental vibrational frequencies and ground state rotational constants.[44] All calculations were done in the frozen-core approximation with the CFOUR program system.

Attempted Matrix Isolation Trapping of Diazirinone (1). The literature procedure for the reaction of tetrabutylammonium fluoride and 3-chloro-3-(*p*-nitrophenoxy)diazirine (**5**) was modified slightly to allow for matrix isolation. Molten tetrabutylammonium fluoride was prepared in a 25 mL round-bottom flask, equipped with a side arm, by warming tetrabutylammonium fluoride trihydrate (1.0 g, 3.2 mmol) to 50 °C under vacuum overnight (0.2 mmHg). The flask was then connected to a long path gas trap (20 cm) that could be shut off on both ends, which then fed into the deposition chamber of the matrix

---

(34) Based on the typical amount of 3-chloro-3-(*p*-nitrophenoxy)diazirine (**5**) used (35 mg) and the relative product yields, the theoretical concentration of carbon monoxide would be 0.586 M, far exceeding the room-temperature solubility in acetonitrile at 1 atm (0.005 M).

(35) McMahon, R. J.; Chapman, O. L.; Hayes, R. A.; Hess, T. C.; Krimmer, H. P. *J. Am. Chem. Soc.* **1985**, *107*, 7597–7606.

(36) Seburg, R. A.; McMahon, R. J. *J. Am. Chem. Soc.* **1992**, *114*, 7183–7189.

(37) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479–483.

(38) Stanton, J. F.; Gauss, J.; Harding, M. E.; Szalay, P. G. with contributions from Auer, A. A.; Bartlett, R. J.; Benedikt, U.; Berger, C.; Bernholdt, D. E.; Bomble, Y. J.; Christiansen, O.; Heckert, M.; Heun, O.; Huber, C.; Jagau, T.-C.; Jonsson, D.; J. Jusélius, Klein, K.; Lauderdale, W. J.; Matthews, D. A.; Metzroth, T.; D. P. O'Neill, Price, D. R.; Prochnow, E.; , Ruud, K.; Schiffmann, F.; Stopkowicz, S.; J. Vázquez, Wang, F.; Watts, J. D. and the integral packages: MOLECULE (J. Almlöf and P. R. Taylor), PROPS (P. R. Taylor), ABACUS (T. Helgaker, H. J. Aa. Jensen, P. Jørgensen, and J. Olsen), and ECP routines by A. V. Mitin, C. van Wüllen. www.cfour.de.

(39) Almlof, J.; Taylor, P. R. *J. Chem. Phys.* **1987**, *86*, 4070–4077.

(40) Scuseria, G. E. *J. Chem. Phys.* **1991**, *94*, 442–447.

(41) Lee, T. J.; Rendell, A. P. *J. Chem. Phys.* **1991**, *94*, 6229–6236.

(42) Gauss, J.; Stanton, J. F. *Chem. Phys. Lett.* **1997**, *276*, 70–77.

(43) Stanton, J. F.; Lopreore, C. L.; Gauss, J. *J. Chem. Phys.* **1998**, *108*, 7190–7196.

(44) Mills, I. M. In *Molecular Spectroscopy: Modern Research*; Rao, K. N., Mathews, C. W., Eds.; Academic Press: New York, 1972; p 115.

isolation apparatus. The system was evacuated and the matrix window cooled to 25 K. The gas trap was cooled in an LN2 bath (77 K). 3-Chloro-3-(*p*-nitrophenoxy)diazirine (**5**) (50 mg, 0.23 mmol) was dissolved in 1 mL of solvent (typically CH_3CN or $CHCl_3$). This solution was added through the rubber-septum sealed side arm of the 25 mL round-bottom flask with stirring at −10 °C. The side arm was closed, and the reaction bubbled steadily for 30 min while the temperature was maintained at −10 °C, before being closed off to allow infrared characterization of the matrix.

Product Analysis. The reaction residual reaction mixture from the matrix isolation experiment was dissolved in 5 mL of CH_2Cl_2 and washed twice with 5 mL of water before drying with Na_2SO_4 and concentrated by rotary evaporation. This crude mixture contained the expected 3-fluoro-3-(*p*-nitrophenoxy)diazirine (**9**), *p*-fluoronitrobenzene (**7**), and *p*-nitrophenol as primary products.[10] Flash column chromatography (10% EtOAc in hexanes) of the concentrate resulted in an inseparable mixture of 3-fluoro-3-(*p*-nitrophenoxy)diazirine (**9**) and *p*-fluoronitrobenzene (**7**); these species were identified by NMR spectroscopy.

3-Fluoro-3-(*p*-nitrophenoxy)diazirine (**9**) exhibited spectroscopic data in excellent agreement with that reported previously:[10] ^{1}H NMR (δ, $CDCl_3$) 7.38 (m, 2H), 8.27 (m, 2H); ^{13}C NMR (δ, $CDCl_3$) 86.8 (diazirine C, d, $J_{C-F} = 275$ Hz giving rise to resonances at 85.4 and 88.2), 117.4, 126.1, 144.7, 156.2; ^{19}F NMR (δ, $CDCl_3$, referenced to *o*-difluorobenzene) −119.0;[10] (δ, $CDCl_3$, referenced using unified scale based on proton TMS reference): −123.5.[45] Attempts to identify 3-fluoro-3-(*p*-nitrophenoxy)diazirine (**9**) using EI^+ and ESI^+ mass spectrometry were unsuccessful. There is little literature precedent for exact mass identification of halodiazirines, as these molecules commonly undergo complex fragmentation pathways once ionized.[46] Attempts to interpret fragmentation data were further complicated by contamination with *p*-fluoronitrobenzene (**7**).

p-Fluoronitrobenzene (**7**) was identified by comparison to commercially available material: ^{1}H NMR (δ, $CDCl_3$) 7.18 (m, 2H), 8.21 (m, 2H); ^{19}F NMR (δ, $CDCl_3$ referenced using unified scale based on proton TMS reference) −106.5.

An EtOAc flush of the column afforded spectroscopically pure *p*-nitrophenol: ^{1}H NMR (δ, $CDCl_3$) 6.90 (m, 2H), 8.13 (m, 2H); HRMS (EI^+) calcd for $[C_6H_5NO_3]^+$ requires m/z 139.0264, found 139.0261.

IR Spectrum of CO: Gas Phase. A balloon of carbon monoxide (Matheson) was emptied into the cavity of the infrared spectrometer and sealed from atmosphere. Thirty-two scans were taken at a lower resolution setting (1.928 cm^{-1}) before background subtraction and identification of the P and R branches at 2116 and 2169 cm^{-1}.

IR Spectrum of CO: Acetonitrile Solution. A Hellma 260 QS 282 1.000 cm path length quartz cell was filled with acetonitrile. A balloon of CO (Matheson) was filled at atmospheric pressure and bubbled through the acetonitrile in the cuvette for 30 min at −35 °C. The cell was immediately placed on a stand in the IR chamber and measured approximately every two min over the course of 16 min. The observed transition at 2140 cm^{-1} neared complete decay over 16 min and was absent from the spectrum of pure acetonitrile.

Acknowledgment. We gratefully acknowledge financial support from the National Science Foundation (NSF-0715305 (R.J.M.) and NSF-0710146 (J.F.S.)). We thank Mitch Daane for meaningful discussions and valuable insight.

Note Added after ASAP Publication. This paper was published on the Friday, February 12, 2010, with errors in Table 1 and some of the text. The corrected version was reposted on February 18, 2010.

Supporting Information Available: NMR spectra of diazirine **5** and its reaction products. This material is available free of charge via the Internet at http://pubs.acs.org.

---

(45) Harris, R. K.; Becker, E. D.; Cabral De Menezes, S. M.; Goodfellow, R.; Granger, P. *Pure Appl. Chem.* **2001**, *73*, 1795–1818.

(46) Burkholder, C. D.; Jones, W. E.; Wasson, J. S.; Liu, M. T. H. *J. Am. Chem. Soc.* **1980**, *102*, 2847–2848.