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Carbonyl Diazide, $OC(N_3)_2$: Synthesis, Purification, and IR Spectrum

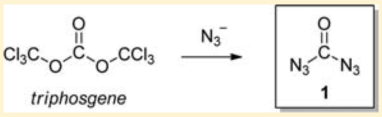
Alex M. Nolan,[†] Brent K. Amberger,[†] Brian J. Esselman,[†] Venkatesan S. Thimmakondu,[‡] John F. Stanton,*[,‡] R. Claude Woods,*[,†] and Robert J. McMahon*[,†]

[†]Department of Chemistry, University of Wisconsin−Madison, 1101 University Avenue, Madison, Wisconsin 53706-1322, United States

[‡]Institute for Theoretical Chemistry, Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas 78712, United States

Supporting Information

ABSTRACT: Carbonyl diazide (**1**), $OC(N_3)_2$, is prepared by reaction of triphosgene and tetra-*n*-butylammonium azide in a solution of diethyl ether or dimethyl ether. The advantage of this synthetic method, relative to other procedures, is that the use of triphosgene, $OC(OCCl_3)_2$, mitigates the need to use highly poisonous reagents such as phosgene, $OCCl_2$, or chlorofluorocarbonyl, OC(Cl)F. The identity and purity of $OC(N_3)_2$ are established by gas-phase IR spectroscopy, which reveals the presence of both *syn*−*syn* and *anti*−*syn* conformers. Computed anharmonic vibrational frequencies and infrared intensities of carbonyl diazide (**1**) display excellent agreement with experiment, and reveal the presence of strong Fermi resonances.



INTRODUCTION

Carbonyl diazide (**1**), $OC(N_3)_2$, is a highly explosive compound that has been the subject of recent studies concerning its synthesis, structure, and reactivity.[1] Among various interesting attributes, the compound is notable because it is a high energy structure composed of very stable diatomic species ($CO + 3N_2$), with a computed specific enthalpy of decomposition similar to industrial explosives TNT, RDX, and HMX.[2] Although known since the 1920s,[3,4] the explosive nature of carbonyl diazide (**1**) discouraged isolation attempts, making the recent synthesis, purification, and characterization by Zeng et al. quite remarkable.[1]

Recent interest in carbonyl diazide (**1**), CON_6, stems from its ability to serve as a precursor to other high energy molecules on the CON_4 and CON_2 potential energy surfaces (Figure 1). Photolysis of $OC(N_3)_2$ (**1**) in an inert matrix results in loss of N_2 to generate CON_4 isomers: acyl nitrene $N_3{-}C(O)N$ (**3**) and its Curtius rearrangement product $N_3{-}NCO$ (**4**).[5] Remarkably, flash vacuum pyrolysis of $OC(N_3)_2$ (**1**) at 400 °C yields diazirinone (**2**),[6−8] the C_{2v} conjugate of molecular nitrogen and carbon monoxide. An intriguing species in terms of structure and bonding,[9−11] diazirinone (**2**) has been the subject of a number of theoretical studies and has received recent attention because of its relevance to the chemistry of CO and N_2 under harsh reaction conditions. Kaiser and co-workers recently suggested that irradiation of N_2/CO ices generates diazirinone (**2**) under astronomically relevant conditions.[12] N_2CO isomers are also known to form under ionizing conditions in the gas phase,[13] which presents the possibility that diazirinone (**2**) or other N_2CO isomers may be formed in interstellar or circumstellar space. Mechanistic details concerning the conversion of carbonyl diazide (**1**) to diazirinone (**2**) remain unclear at this time.

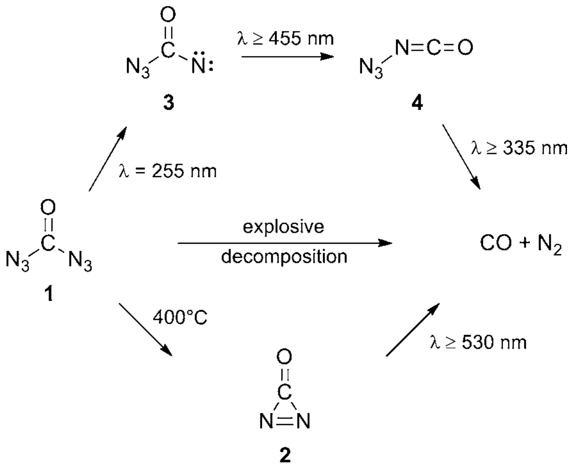


Figure 1. Experimentally observed decomposition pathways for carbonyl diazide, $OC(N_3)_2$.[5−8]

After our earlier studies established that a previous report of the experimental observation of diazirinone (**2**) was incorrect,[14] we turned our attention to the development of alternative methods for generating and detecting this species. We considered carbonyl diazide as a viable, if not especially attractive, precursor to diazirinone (**2**). Carbonyl diazide (**1**) was first synthesized in the 1920s via the diazotization of carbohydrazide (**5**)[3,4] (Figure 2, eq 1) but was not studied in pure form due to its aforementioned explosive nature. In 2007, carbonyl diazide (**1**) was produced through the incidental hydrolysis of tetraazidomethane (**6**)[15] in undried solvent (Figure 2, eq 2) and was identified by ^{13}C and ^{15}N NMR

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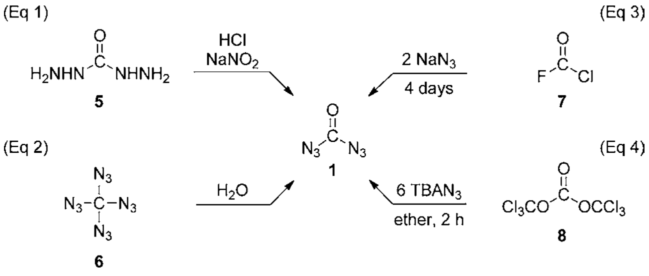


Figure 2. Synthetic routes to carbonyl diazide, $OC(N_3)_2$.

spectroscopy. In 2010, Zeng et al. reported a synthesis of carbonyl diazide from treatment of chlorofluorocarbonyl ClC(O)F (7) with sodium azide by nucleophilic substitution (Figure 2, eq 3).[1,8] The product was isolated using trap-to-trap distillation and thoroughly characterized by IR spectroscopy (gas phase and argon matrix), Raman spectroscopy, and X-ray crystallography. Here we describe an alternative procedure for the synthesis of $OC(N_3)_2$ (**1**) using triphosgene (**8**) and tetra-*n*-butylammonium azide (Figure 2, eq 4), which avoids the use of chlorofluorocarbonyl ClC(O)F (**7**), a substance that is both highly poisonous and not readily available.

■ EXPERIMENTAL SECTION

Caution! *Carbonyl diazide (1) is shock-sensitive and explosive. Proper safety precautions, which include the use of leather gloves, face shields, and blast shields, must be taken when handling this compound.*[1,16,17] Sodium azide (NaN_3) and its hydrolysis product, hydrazoic acid (HN_3) are toxic.[17] Sodium azide, as well as metal azides that may be formed by reaction of sodium azide, represent explosion hazards.[17]

Many of the manipulations involved in the preparation and purification of carbonyl diazide (**1**) were performed using a stainless-steel vacuum manifold, which is described in greater detail in Supporting Information. The purity of carbonyl diazide (**1**) samples was examined by gas-phase IR spectroscopy, and percent yield was estimated from the pressure in a stainless-steel manifold of known volume. Unless noted otherwise, chemicals were acquired from commercial sources and were used without further purification.

Tetra-*n*-butylammonium Azide. ($TBAN_3$) was prepared using a literature procedure and recrystallized from toluene.[18] On occasion, a residual toluene contaminant in $TBAN_3$ was carried through the subsequent synthetic procedures and could not be removed from the desired carbonyl diazide. In order remove the toluene contaminant, a slurry of $TBAN_3$ (ca. 5 g) in 75 mL of diethyl ether was brought to reflux with stirring. The slurry was then cooled to room temperature; crystals were collected by filtration and washed with cold diethyl ether. Residual diethyl ether solvent was removed from $TBAN_3$ under high vacuum.

Carbonyl Diazide (1): Method A. Tetra-*n*-butylammonium azide ($TBAN_3$) (1.64 g, 5.77 mmol) was added to an oven-dried round-bottom flask, followed by anhydrous diethyl ether (10 mL) under positive nitrogen pressure. The volume of solvent was not sufficient to completely dissolve the ammonium salt. Triphosgene (194 mg, 0.655 mmol) was added, and the suspension was stirred for 2 h. The solution was then passed through a silica plug to remove the suspended ammonium salts, and diethyl ether (5 mL) was used to wash the silica. The organic layer was washed with saturated aqueous sodium chloride (10 mL) and dried over magnesium sulfate, and the drying agent removed by gravity filtration.

Although a dilute solution of $OC(N_3)_2$ in diethyl ether seems comparatively safe to handle in glass, a concentrated solution or the isolated material is not. In one instance, a neat sample of $OC(N_3)_2$ detonated upon insertion of a glass pipet; the round-bottom flask containing the sample was pulverized by the blast. Therefore, all manipulations following the removal of the magnesium sulfate drying agent were conducted in a 200-mL stainless-steel flask. The solution of $OC(N_3)_2$ in diethyl ether in a stainless-steel flask was frozen at −196 °C, and the vessel was evacuated. The sample was allowed to warm to room temperature, and all volatile materials were cryopumped to a second stainless-steel flask at −196 °C to ensure that absolutely no nonvolatile or particulate matter contaminated the sample. The second flask was then held at −78 °C, a temperature at which Et_2O is volatile but $OC(N_3)_2$ is not, and the ether was removed with a diffusion pump in conjunction with a liquid nitrogen trap. To remove all traces of ether from the flask, it was necessary to perform three or four freeze−pump−thaw cycles, wherein the sample flask was isolated from the vacuum, warmed to room temperature, and cooled back to −78 °C before pumping was resumed. Carbonyl diazide synthesized and purified in this way typically afforded a yield of ca. 7.1 Torr-liter, (0.38 mmol, 19%).

Carbonyl Diazide (1): Method B. A modified version of the preparation allows the entire procedure to be carried out on the stainless-steel manifold. Use of dimethyl ether (bp −24 °C), which is more volatile than diethyl ether (bp 35 °C), improves the ease and efficiency of solvent removal from carbonyl diazide (**1**), although it also requires that the reaction be performed at low temperature or under pressure. Triphosgene (0.153 g, 0.516 mmol) and sodium azide (0.207 g, 3.184 mmol) were added to a 35-mL stainless-steel flask. The flask was attached to the stainless-steel manifold and evacuated, and gaseous dimethyl ether was condensed into the vessel at −196 °C. In the 35-mL flask, 1400 Torr-liter of dimethyl ether was calculated to afford ~4 mL as liquid solvent. After stirring for 16 h, the solvent was distilled from the flask at −78 °C. The flask was then allowed to warm to room temperature, and carbonyl diazide (**1**) was cryopumped to a clean stainless-steel flask at −196 °C. Yields as high as 32% were observed; however, this procedure proved more fickle than the synthesis in diethyl ether.

Characterization. Following either synthetic procedure, a small portion of the sample was transferred to a stainless steel, gas-phase IR cell (ca. 1 Torr) using vacuum line techniques. The purity of the sample was assessed by comparison to spectral data described previously by Zeng et al.[1] A representative IR spectrum (Figure 3) displays excellent agreement with literature data and is devoid of IR absorptions attributable to impurities (see discussion below). Carbonyl diazide can be stored at room temperature in a stainless steel flask for a few weeks with minor decomposition. Samples of $OC(N_3)_2$ must be handled gently, as physical shocks occasionally resulted in audible explosive decompositions within the steel flasks.

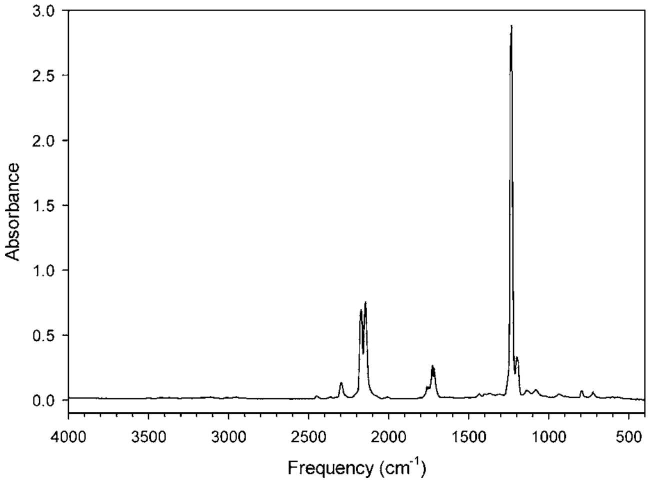
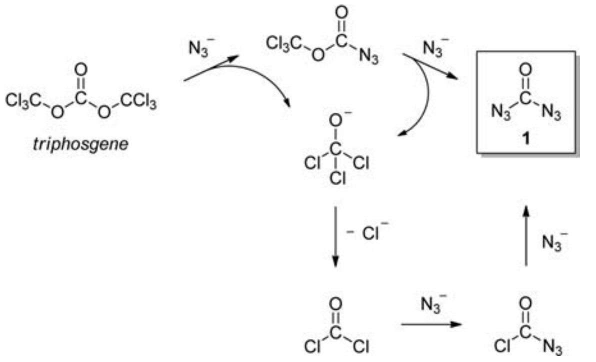


Figure 3. Infrared spectrum of gaseous carbonyl diazide, $OC(N_3)_2$ (**1**) (1 Torr, 298 K, spectral resolution of 2 cm^{-1}).

■ RESULTS AND DISCUSSION

Synthesis. A logical strategy for the preparation of carbonyl diazide (**1**) involves the use of phosgene or a "phosgene equivalent". Given the serious hazards associated with the use of phosgene, triphosgene has supplanted phosgene as the electrophile of choice in reactions of this type.[19,20] Triphosgene, $OC(OCCl_3)_2$, is a stable crystalline solid, which, in solution, serves as a surrogate for 3 equiv of phosgene. Although we have not engaged in a detailed mechanistic study of this reaction, the transformations depicted in Scheme 1 have good precedent in the literature.[21] Sequential nucleophilic attack of azide on the carbonyl carbon of triphosgene results in the formation of 1 equiv of $OC(N_3)_2$ (**1**) and the liberation of 2 equiv of trichloromethoxide ion. Trichloromethoxide ion rapidly eliminates chloride ion to generate phosgene. Phosgene generated *in situ* is more reactive than triphosgene, and subsequent reaction with azide yields additional $OC(N_3)_2$. In our initial studies, we used sodium azide as the source of azide ion and diethyl ether as solvent. Although these conditions were successful in generating carbonyl diazide (**1**), we reasoned that the very low solubility of sodium azide in diethyl ether was a factor in the slow conversion of starting material and low yield of product. We turned to tetra-*n*-butylammonium azide ($TBAN_3$) as a source of azide ion with greater solubility in organic solvents. Use of $TBAN_3$ enhanced the conversion of triphosgene to carbonyl diazide (**1**) while minimizing the risk of an explosive decomposition of solid sodium azide. Employing standard solution-phase reaction conditions also allowed the use of standard procedures to work up the reaction, including an aqueous wash of the reaction mixture to ensure that any remaining starting materials are safely neutralized and removed. The final low-temperature, low-pressure distillation of solvent from the carbonyl diazide (**1**) product is performed in a stainless-steel vessel, which increases the quantity of pure $OC(N_3)_2$ that may be handled safely. A disadvantage of this procedure stems from the relative volatilities of carbonyl diazide (**1**) and diethyl ether. Removing all of the solvent, without losing an excessive amount of product, necessitates a series of freeze−pump−thaw cycles. This procedure can be safely performed with the stainless-steel apparatus, but it is tedious.

Scheme 1. Preparation of Carbonyl Diazide (1) Using Triphosgene



The alternate procedure involving triphosgene, sodium azide, and dimethyl ether offers a different set of advantages and disadvantages. The procedure is carried out entirely within a stainless-steel apparatus, which enhances the margin of safety although diminishes the ability to monitor the reaction in real time. The higher volatility of dimethyl ether facilitates solvent removal, but upon solvent removal, the neat product remains mixed with solid sodium azide. This procedure afforded both the greatest quantity and highest chemical yield of carbonyl diazide (**1**). That the procedure is fickle may reflect an instability of the mixture of neat carbonyl diazide and sodium azide, an observation noted independently by Zeng et al.[22] Although we attempted the synthesis using tetra-*n*-butylammonium azide in dimethyl ether, we found the procedure to be complicated by experimental difficulties associated with transferring 2 g of the highly hygroscopic $TBAN_3$ to the 35-mL stainless-steel reaction vessel and ensuring that the viscous mass dissolved in dimethyl ether.

Without mitigating the dangers inherent in the preparation and handling of carbonyl diazide (**1**), our procedure addresses the complications associated with the literature procedure for the synthesis of this compound:[1] (i) the use of chlorofluorocarbonyl (**7**), which is highly poisonous and is not commercially available, (ii) the use of sodium azide under heterogeneous (gas/solid) reaction conditions, (iii) a reaction time of two hours vs four days, and (iv) the ability to quantitatively assess product yield.

Potential Energy Surface. Optimized geometries, energies, and infrared intensities were obtained using the CCSD method[23] with the cc-pVDZ[24] basis set as implemented in Gaussian 09.[25] The nature of stationary points was confirmed by calculation of the harmonic vibrational frequencies, which

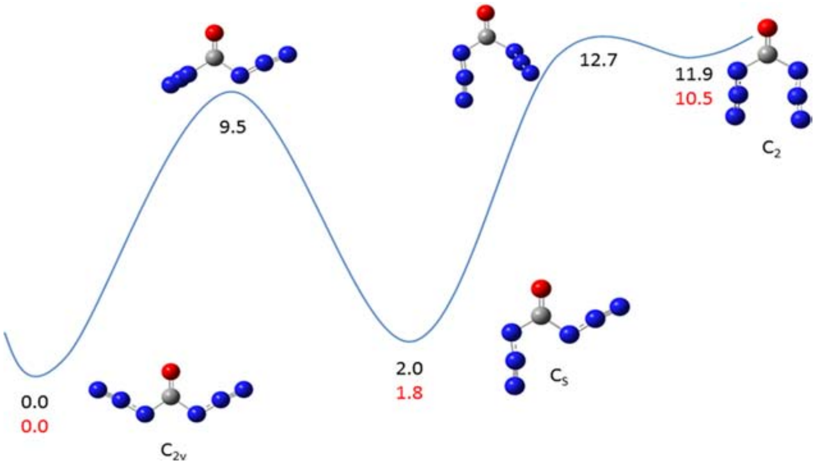


Figure 4. Potential energy surface of $OC(N_3)_2$. Relative energies (kcal/mol, including ZPVE) at CCSD/cc-pVDZ (upper, black) and CCSD(T)/cc-pVTZ (lower, red).

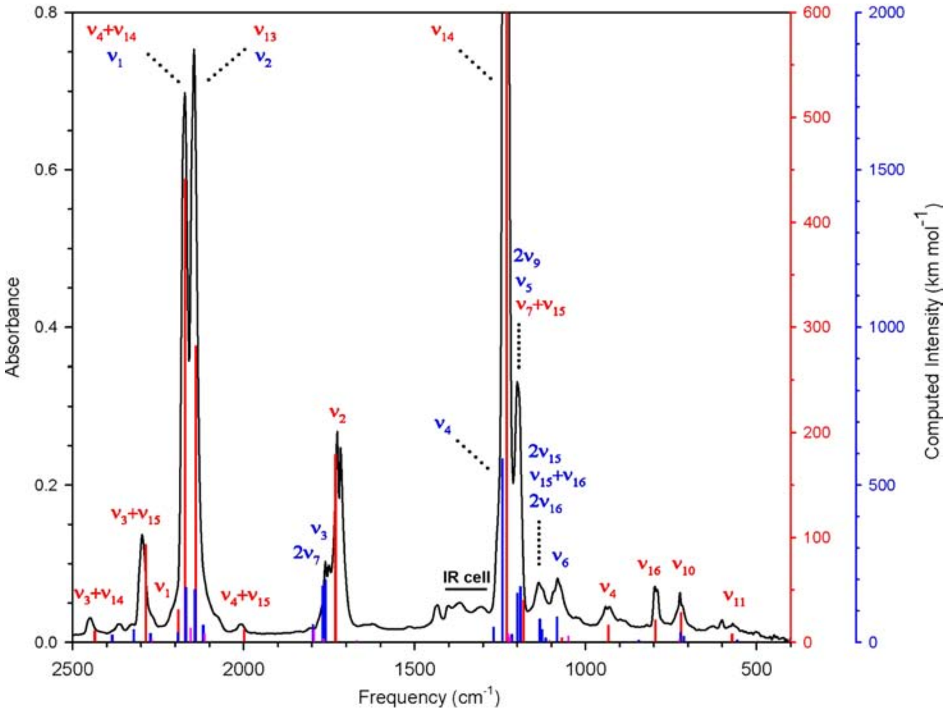


Figure 5. Infrared spectrum of gaseous carbonyl diazide, $OC(N_3)_2$ (1 Torr, 298 K) with computed vibrational frequencies and intensities of *syn*—*syn* (red) and *anti*—*syn* (blue) conformers superimposed as stick spectra. The *y*-axis scales for the computed infrared intensities have been adjusted to reflect a qualitative agreement with the experimental spectrum. Several weak absorptions arise from the IR cell.

also provided zero-point vibrational energy (ZPVE) corrections. The transition states were connected to their minima via IRC calculations. CCSD(T)/cc-pVTZ[26] optimized geometry and harmonic frequency calculations were performed using CFOUR[27] for each of the minima. Further details of the calculations can be found in Supporting Information.

The conformational isomers of carbonyl diazide (**1**) [*syn*—*syn* (C_{2v}), *anti*—*syn* (C_s), and *anti*—*anti* (C_2)] are depicted in Figure 4. In good agreement with recent literature data,[1,2] the lowest energy conformer is *syn*—*syn*, with the *anti*—*syn* conformer lying 1.8 kcal/mol higher in energy at the CCSD(T)/cc-pVTZ level of theory. The *anti*—*anti* conformer does not adopt an idealized C_{2v} structure; it exhibits a slight distortion from planarity (C_2) and lies ca. 11 kcal/mol higher in energy than the *syn*—*syn* rotamer. The barriers to rotation of the N_3 groups are modest (Figure 4).

IR Spectrum. The gas-phase infrared spectrum of carbonyl diazide (**1**) has been described previously,[1] and we rely on the IR spectrum as the criterion of purity for our synthetic method. As such, it was of some concern to us that the computed harmonic vibrational frequencies and infrared intensities for *syn*—*syn* and *anti*—*syn* conformers of carbonyl diazide (**1**) do not account for all of the prominent features in the experimental spectrum, notably 2297, 2171, and 1200 cm^{-1}. The origin of these features is unclear. While it is possible that these absorptions may arise from carbonyl diazide (**1**) through the effects of anharmonicity (combinations, overtones, Fermi resonance), it is also possible that they may be attributable to unidentified impurities. We sought to explore this matter, in greater detail, through a more sophisticated theoretical treatment of the vibrational spectrum.

To help analyze the puzzling aspects of the infrared spectrum, we undertook high-level calculations that include the effects of anharmonicity on the vibrational frequencies and infrared intensities. For each of the three conformational isomers of carbonyl diazide (**1**), geometries were optimized at CCSD(T)/ANO0 and CCSD(T)/ANO1 levels of theory using analytic gradients,[28,29] and harmonic frequencies were obtained with analytic second derivatives.[30] The cubic and quartic force constants were then calculated by numerical differentiation of analytic second derivatives calculated at displaced points, following the approach of Stanton et al.[31] Second-order vibrational perturbation theory (VPT2) was then used to compute the fundamental vibrational frequencies as well as the infrared intensities.[32,33] Fermi resonances were analyzed using the approach of Matthews and Stanton.[34]

In contrast to the harmonic analysis of the infrared spectrum, which cannot account for many of its most prominent features, the anharmonic analysis is in striking agreement with observation (Figure 5, Tables 1 and 2). The cluster of features seen from 2000 to 2300 cm^{-1} results from a strong and extensive Fermi resonance in the *syn*—*syn* conformer of $OC(N_3)_2$, whereby the combination levels $\nu_4 + \nu_{14}$, $\nu_4 + \nu_{15}$, and $\nu_3 + \nu_{15}$ borrow intensity from the very strong asymmetric —N═N═N stretching mode, ν_{13}. Similarly, the intrinsically strong ν_{14} asymmetric C—N stretching mode mixes with the combination level $\nu_7 + \nu_{15}$. When these resonances are carefully treated within the context of VPT2, a confident assignment (rightmost column in Table 1) may be made for all of the principal features seen in the spectrum (as well as most of the minor features). It is rather remarkable that almost half of the vibrational levels with predicted infrared intensities above 10 km mol^{-1} (5 of 12) correspond to two-quantum overtone and combination levels, an observation that underscores the problems that are associated with relying on the harmonic treatment for the analysis of the spectrum.

The experimental infrared spectrum also reveals the presence of the *anti*—*syn* conformer of $OC(N_3)_2$ as a minor component

Table 1. Experimental and Computed Vibrational Frequencies and Infrared Intensities for the *syn*−*syn* Conformer of $OC(N_3)_2$[a]

		fc-CCSD(T)			
mode	sym	harmonic ANO0	harmonic ANO1	VPT2+F ANO1	exptl
		Fundamentals			
1	a_1	2214 (54)	2228 (63)	2191 (31)	
2	a_1	1782 (194)	1764 (194)	1731 (179)	*1721*
3	a_1	1254 (4)	1266 (5)	1222 (4)	
4	a_1	945 (19)	953 (20)	933 (16)	*941*
5	a_1	553 (0)	553 (0)	544 (0)	
6	a_1	407 (2)	408 (2)	403 (1)	
7	a_1	122 (0)	122 (0)	114 (0)	
8	a_2	569 (0)	570 (0)	557 (0)	
9	a_2	152 (0)	155 (0)	151 (0)	
10	b_1	733 (29)	730 (25)	720 (28)	*723*
11	b_1	580 (9)	581 (7)	571 (8)	*569*
12	b_1	75 (1)	76 (1)	72 (1)	
13	b_2	2198 (858)	2212 (875)	2140 (282)	*2145*
14	b_2	1266 (1755)	1277 (1735)	1230 (1633)	*1235*
15	b_2	1095 (17)	1107 (13)	1069 (4)	
16	b_2	807 (23)	808 (26)	795 (21)	*794*
17	b_2	500 (2)	503 (3)	496 (1)	
18	b_2	206 (1)	206 (1)	204 (1)	
		Two-Quantum Levels			
3 + 14	b_2			2435 (11)	*2450*
3 + 15	b_2			2286 (93)	*2295*
4 + 14	b_2			2171 (441)	*2172*
4 + 15	b_2			1998 (12)	*2005*
7 + 15	b_2			1181 (40)	*1200*

[a] Computed harmonic and Fermi-resonance corrected (VPT2+F) frequencies (cm^{-1}), along with intensities given in parentheses (km mol^{-1}). Two-quantum (overtone and combination) levels with intensity greater than 10 km mol^{-1} also included. Computed frequencies are not scaled. Assigned experimental levels in italics.

of the gaseous mixture. The anharmonic analysis suggests that the observed C═O stretching frequency at 1756 cm^{-1} is composed of contributions from both the fundamental, ν_3, and an overtone, $2\nu_7$ vibration (Table 2). The most intense vibration of the *anti*−*syn* conformer (ν_4, 1257 cm^{-1}) appears as a shoulder on the high-energy side of the C−N stretching vibration of the *syn*−*syn* conformer (ν_{14}, 1235 cm^{-1}). Fundamental, combination, and overtone bands of the *anti*−*syn* conformer contribute to absorptions observed at 1200, 1138, and 1082 cm^{-1}. We also computed the anharmonic infrared spectrum of the *anti*−*anti* conformer (see Supporting Information section), but this conformer does not contribute to the observed spectrum.

Table 2. Experimental and Computed Vibrational Frequencies and Infrared Intensities for the *anti*−*syn* Conformer of $OC(N_3)_2$[a]

		fc-CCSD(T)			
mode	sym	harmonic ANO0	harmonic ANO1	VPT2+F ANO1	exptl
		Fundamentals			
1	a'	2212 (295)	2226 (308)	2169 (174)	*2172*
2	a'	2192 (528)	2206 (552)	2142 (167)	*2145*
3	a'	1813 (475)	1801 (482)	1760 (198)	*1756*
4	a'	1279 (766)	1290 (736)	1243 (583)	*1257*
5	a'	1226 (354)	1237 (374)	1190 (177)	*1200*
6	a'	1114 (148)	1125 (147)	1083 (80)	*1082*
7	a'	894 (7)	901 (7)	884 (6)	
8	a'	727 (34)	730 (33)	722 (30)	
9	a'	611 (2)	613 (2)	600 (2)	
10	a'	495 (1)	497 (1)	491 (1)	
11	a'	433 (1)	436 (1)	430 (1)	
12	a'	200 (2)	200 (2)	199 (2)	
13	a'	127 (0)	126 (0)	127 (0)	
14	a''	720 (27)	718 (24)	712 (18)	
15	a''	576 (2)	576 (1)	567 (2)	
16	a''	566 (11)	568 (10)	556 (7)	
17	a''	135 (0)	138 (0)	134 (0)	
18	a''	91 (0)	94 (0)	95 (0)	
		Two-Quantum Levels			
2(5)	a'			2384 (23)	
4 + 6	a'			2321 (40)	
5 + 6	a'			2272 (28)	
2(6)	a'			2192 (31)	
4 + 7	a'			2118 (54)	
6 + 8	a'			1797 (55)	
2(7)	a'			1768 (178)	*1756*
14 + 16	a'			1269 (47)	
8 + 10	a'			1215 (24)	
2(9)	a'			1199 (156)	*1200*
2(15)	a'			1133 (73)	*1138*
15 + 16	a'			1127 (40)	*1138*
2(16)	a'			1116 (13)	*1138*

[a] Computed harmonic and Fermi-resonance corrected (VPT2+F) frequencies (cm^{-1}), along with intensities given in parentheses (km mol^{-1}). Two-quantum (overtone and combination) levels with intensity greater than 10 km mol^{-1} also included. Computed frequencies are not scaled. Assigned experimental levels in italics.

■ SUMMARY

Carbonyl diazide, $OC(N_3)_2$ (**1**), serves as a precursor to several unusual, high-energy molecules; a safe and reliable preparation for this substance represents an important objective. Our synthesis provides advantages over previous methods in terms of ready availability of starting materials, scalability of the procedure, and, most importantly, safety. The infrared spectrum of $OC(N_3)_2$ serves as the criterion of purity for most synthetic procedures, which forced us to analyze this spectrum in considerable detail. The spectrum is not well-described by computed harmonic vibrational frequencies and intensities. After including the effects of anharmonicity, the computed vibrational frequencies and infrared intensities of carbonyl diazide (**1**) display excellent agreement with experiment, and reveal the presence of strong Fermi resonances.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Description of stainless-steel vacuum manifold used for synthesis and purification. Gas-phase IR spectra of $OC(N_3)_2$ obtained using various preparations. Details of computational results at CCSD/cc-pVDZ and CCSD(T)/cc-pVTZ levels of theory, including computed energies, zero-point vibrational corrections, and Cartesian coordinates. Harmonic (CCSD(T)/ANO0, CCSD(T)/ANO1) and Fermi-resonance corrected (VPT2+F) frequencies and infrared intensities for the *anti*−*anti* conformer of $OC(N_3)_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: jfstanton@mail.utexas.edu (J.F.S.), rcwoods@wisc.edu (R.C.W.), mcmahon@chem.wisc.edu (R.J.M.).

Notes

The authors declare no competing financial interest.

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