



Heterocycles Hot Paper

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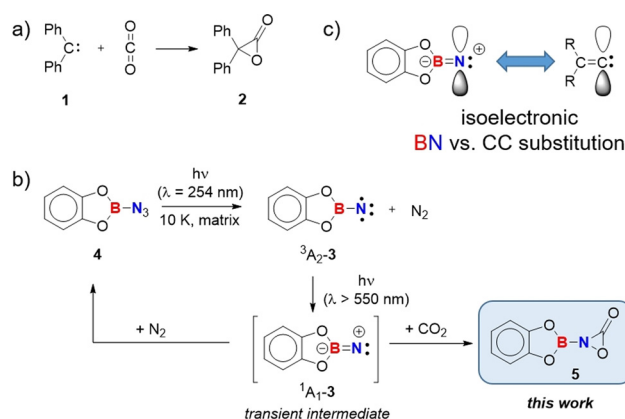
The Reaction of CO₂ with a Borylnitrene: Formation of an 3-Oxaziridinone

Virinder Bhagat, Julia Schumann, and Holger F. Bettinger*

Abstract: The reaction of a borylnitrene with carbon dioxide is studied under cryogenic matrix isolation conditions. Photo-generated CatBN (Cat = catecholato) reacts with CO₂ under formation of the cycloaddition product CatBNCO₂, a 3-oxaziridinone derivative, after photoexcitation (> 550 nm). The product shows Fermi resonances between the CO stretching and ring deformation modes that cause unusual ¹³C and ¹⁸O isotopic shifts. A computational analysis of the 3-oxaziridinone shows this cyclic carbamate to be less strained than an α -lactone or an α -lactame.

Carbon dioxide is one important contributor to the greenhouse effect, and its increasing emission from various sources triggers research of its capture and recycling into chemicals.^[1–13] The use of CO₂, which is non-toxic and abundantly present in nature, as a C1 building block in chemical reaction systems is still not very common due to its high thermodynamic and kinetic stability.^[14] However, despite this, there are systems which are known to show reactivity towards CO₂. The reduction of CO₂ using many heterogenous and homogenous transition metal catalysts is well documented.^[15–22] Furthermore, the use of metal-free CO₂ reductants has evolved over the years considering the toxicity and cost of the metal-based reducing/activation agents. These involve frustrated Lewis pairs, N-heterocyclic carbene (NHC), and nitrogen bases (e.g. 1,5,7-triazabicyclo[4.4.0]dec-5-ene and 1,8-diazabicyclo[5.4.0]undec-7-ene).^[23–33]

Electrophilic carbenes can also react with CO₂.^[34] Sander has shown that the reaction of diphenylcarbene **1** with CO₂ yields both thermally and photochemically the corresponding α -lactone, diphenyloxiranone **2**, in cryogenic matrix isolation experiments (Scheme 1a).^[34] Nitrenes are analogues of carbenes that generally undergo similar reactions, but for these the related cycloaddition reaction with CO₂ was never demonstrated. We have previously identified a class of particularly reactive nitrenes, borylnitrenes, carrying two oxygen atoms at the boron center that preclude isomerization



Scheme 1. a) Formation of diphenyloxiranone **2** as the result of the reaction of diphenylcarbene **1** with CO₂.^[34] b) Photogeneration of borylnitrene ³A₂-**3** under matrix isolation conditions and its photoreaction with closed-shell molecules N₂ and CO₂ (this work) via the transient singlet nitrene ¹A₁-**3**. c) Isoelectronic relationship between ¹A₁-**3** and vinylidenes and the in-plane p-type orbital that comprises the LUMO of both.

to iminoboranes.^[35–41] The catechol derivative **3** (CatBN, Cat = catecholato), accessible under matrix isolation conditions from azide **4** (Scheme 1b), has a triplet electronic ground state (³A₂-**3**) and shows high reactivity towards small molecules even under matrix isolation conditions (N₂, CO, D₂, CH₄, O₂).^[35–41] The reaction with closed-shell molecules requires photoactivation ($\lambda > 550$ nm) presumably involving the closed-shell singlet state (S₁) ¹A₁-**3**. The electronic structure of ¹A₁-**3** is reminiscent of vinylidenes as their reactive centers are related by an isoelectronic substitution of the C=C by the B=N unit (Scheme 1c). The ¹A₁ state of **3** and vinylidene have both a $\pi^2\sigma^0$ type configuration that causes low-lying vacant orbitals at their monocoordinate carbon or nitrogen atoms and high electrophilicity.^[35,42] A particular reactive derivative is super electrophilic difluorovinylidene that inserts into methane and dihydrogen at 20–40 K.^[43–49]

We here report for the first time the reaction of a borylnitrene with CO₂ and show that this results in an 1,2-oxaziridin-3-one derivative.^[50] These are the smallest possible cyclic carbamates, which were suggested as reactive intermediates^[51–57] and have been studied computationally before,^[58–61] but never could be isolated.

To investigate the reaction of **3** with carbon dioxide, azide **4** was isolated at 10 K in nitrogen doped with carbon dioxide (5% CO₂). Photolysis of **4** using UV irradiation ($\lambda = 254$ nm) resulted in the complete disappearance of **4** and the concomitant formation of nitrene **3**. Annealing of the matrix isolated nitrene in the presence of CO₂ to 35 K did not result in new

[*] V. Bhagat, Dr. J. Schumann, Prof. Dr. H. F. Bettinger
Institut für Organische Chemie, Universität Tübingen
Auf der Morgenstelle 18, 72076 Tübingen (Germany)
E-mail: Holger.Bettinger@uni-tuebingen.de

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:
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signals. Long-wavelength irradiation ($\lambda > 550$ nm), on the other hand, resulted primarily in the growth of the signals of the azide **4** owing to the efficient reaction of **3** with N_2 as reported previously.^[40] However, also a set of rather weak new signals at 1934, 1457, 1393, 1332, 1312, 1303, 1237, 1019, 919, 803, and 748 cm^{-1} (see Figure 1, Table S1) was observed. A similar new set of bands is also observed in solid argon, but also in this matrix the photo generation of azide **4** dominates (see Figure S3).

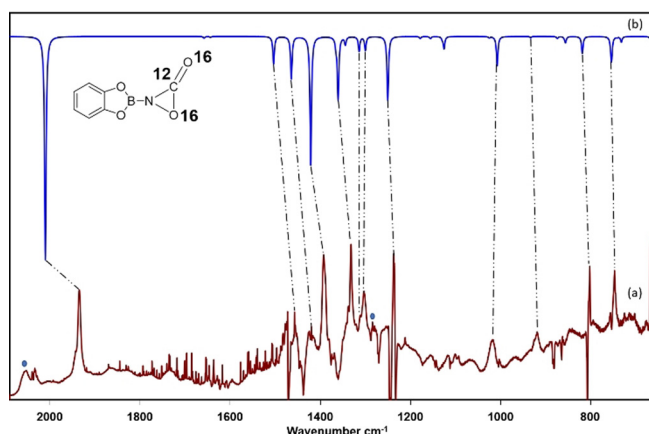


Figure 1. a) Difference spectrum obtained after irradiation of N_2 matrix with $\lambda > 550$ nm (following the irradiation with $\lambda = 254$ nm) in the presence of CO_2 . b) Calculated spectrum for ^{11}B and ^{10}B isotopologues (81:19) of 3-oxaziridinone **5** at the B3LYP/6–311++G(2d,p) level (with $^{16}O_2$). ● correspond to the signals for overtones/combination bands of the resulting product.

The strong signal at 1934 cm^{-1} excludes nitroso borane **6**, acyl nitrene **7**, and isocyanatoxy borane **8** (Figure 2) as the carrier of these bands based on their computed (B3LYP/6–311++G(2d,p) level of theory, see Figure S1 for details) harmonic vibrational spectra. Note the short N–O distance in **7** of 1.850 Å, which is similar to that computed earlier for singlet formylnitrene, indicates a structure in between acylnitrene and oxazirine.^[62]

3-Oxaziridinones are not known to date, and hence no experimental data is available for their $\nu(CO)$ stretching vibrations. For the α -lactone **2**, a very strong vibration at 1890 cm^{-1} was observed by Sander.^[34] The computational study by Liebman et al. showed the presence of harmonic C=O stretch of 1,2-oxaziridine-3-one at 1974 cm^{-1} at MP2/6–311++G(2d,2p) which is very close (1969 cm^{-1}) to the C=O stretch that we calculated for **5** at the MP2/6–311++G(2d,p) level.^[58] The computed harmonic value of the C=O stretching vibration in the 3-oxaziridinone derivative **5** is 2009 cm^{-1} at B3LYP/6–311++G(2d,p), in support of an assignment to **5**. Additional strong bands are computed for **5** in the 1500–700 cm^{-1} range, in agreement with the experiment (see Figure 1).

To further support the assignment to **5**, we investigated the reactions with $^{13}C(^{16}O)_2$ and $^{12}C(^{18}O)_2$ that produce two additional isotopologues of **5**. The ^{18}O isotopic shift of 35 cm^{-1} for the strong band at 1934 is similar to that observed for **2** (30.4 cm^{-1}) previously,^[34] and in line with a carbonyl group.

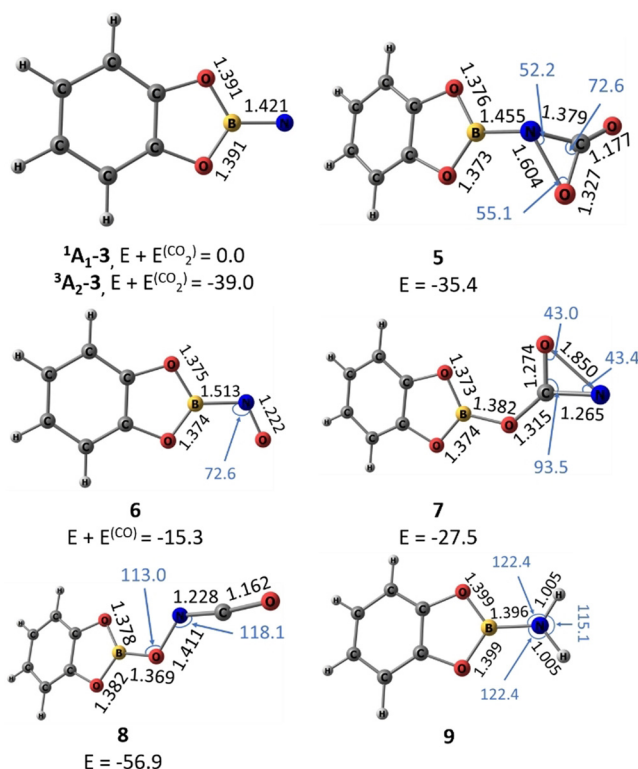


Figure 2. Geometrical parameters (black font: bond lengths in Å; blue font: bond angles in degrees) and relative energies (in $kcal\ mol^{-1}$) of 1A_1 -**3** and various possible photoproducts that can be formed as the result of the reaction between **3** and CO_2 .

The computed ^{18}O isotopic shift of 33 cm^{-1} is in good agreement with the observation. The other signals assigned to **5** hardly undergo any shift upon ^{18}O substitution (see Figure 3 and Table S2). This is in agreement with harmonic vibrational computations that suggest that only the in-plane deformation mode of the three-membered ring (for $^{12}C(^{16}O)_2$, exp.: 1019 cm^{-1} and calc.: 1008 cm^{-1}) should show a significant

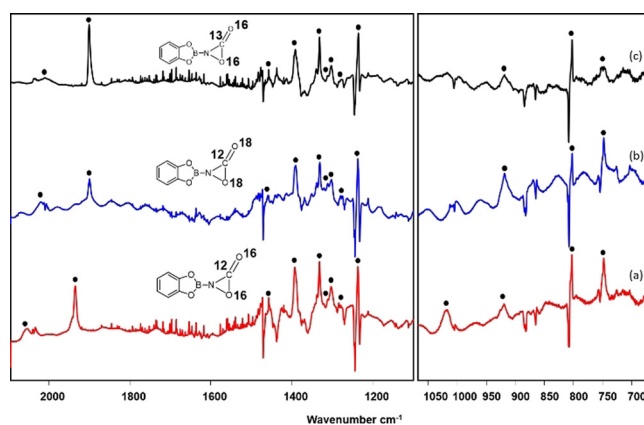


Figure 3. Difference spectra obtained after irradiation of N_2 matrix with $\lambda > 550$ nm (following the irradiation with $\lambda = 254$ nm) in the presence of a) $^{12}C(^{16}O)_2$, after 100 min, b) $^{12}C(^{18}O)_2$, after 90 min, c) $^{13}C(^{16}O)_2$, after 60 min in solid N_2 at 10 K. ● correspond to the fundamental and overtone/combination bands in three of the isotopologues of **5**.

isotopic shift (15 cm^{-1}). The associated band could, however, not be detected in ^{13}C and ^{18}O isotopologues of **5**.

The ^{13}C isotopic shift is 34 cm^{-1} . This is very similar to the ^{18}O isotopic shift, and smaller than expected based on our harmonic vibrational computations at B3LYP/6-311++G(2d,p) (53.0 cm^{-1}) and comparison with **2** (53.1 cm^{-1}).^[34] Note that Sander considered the ^{13}C isotopic shift of 53 cm^{-1} to be larger than expected, but our computations for **2** at B3LYP/6-311++G(2d,p) arrive at isotopic shifts of 51 cm^{-1} and 32 cm^{-1} for ^{13}C and ^{18}O , respectively, in a very good agreement with Sander's experimental data.^[34] Similar to the ^{18}O isotopologue, no other signals assigned to **5** show a significant shift upon ^{13}C substitution, in agreement with the computed vibrational spectra (see Figure S2).

To shed light on the vibrational properties of the 3-oxaziridinone system, we computed the cubic force field for **5** (see Table S4). For a system like **5**, such computations are a formidable task as two second derivative calculations are required for each of the 45 normal modes of each of the three isotopologues. We chose the MP2/6-311++G(2d,p) level of theory as numerical noise resulting from DFT grids is then avoided. The analysis reveals that for all isotopologues, the C=O stretching frequency (ν_5) is involved in Fermi resonances with the first overtone of ν_{19} ($2\nu_{19}$) in the case of $^{12}\text{C}(^{16}\text{O})_2$ isotopologue and with the first overtone of ν_{20} ($2\nu_{20}$) in case of $^{13}\text{C}(^{16}\text{O})_2$ and $^{12}\text{C}(^{18}\text{O})_2$ isotopologues (see Table S4). For the $^{13}\text{C}(^{16}\text{O})_2$ isotopologue, additional Fermi resonances of ν_5 with the $\nu_{24} + \nu_{18}$ and $\nu_{24} + \nu_{20}$ combination bands can be identified while only the $\nu_{24} + \nu_{18}$ combination band was found to be in Fermi resonance with ν_5 of $^{12}\text{C}(^{18}\text{O})_2$. The vibrational deperturbation analysis (Table S5) places ν_5 at 1951 cm^{-1} and 1907 cm^{-1} for the $^{12}\text{C}(^{16}\text{O})_2$ and $^{12}\text{C}(^{18}\text{O})_2$ isotopologues, respectively. The Fermi resonances then resulted in a shift of ν_5 to 1906 and 1859 cm^{-1} , respectively. Compared to the experiment, the Fermi resonance seems to be too strong and the shift of ν_5 thus too pronounced. The ^{18}O isotopic shift, 47 cm^{-1} , is higher than that of the experimental value (35 cm^{-1}). For the ^{13}C isotopologue, the deperturbation analysis arrived at a value of 1888 cm^{-1} for ν_5 which was shifted to 1863 cm^{-1} after Fermi resonance. This explains the occurrence of ν_5 at nearly the same position in the experimental IR spectra of ^{13}C and ^{18}O isotopologues (which are at 1900 cm^{-1} and 1899 cm^{-1} respectively). Hence, the Fermi resonances explain the unexpectedly small isotopic shift for ν_5 of the ^{13}C isotopologue relative to ν_5 of the ^{18}O isotopologue.

The reaction of **3** with CO_2 does not proceed thermally in accord with our previous experience that the reaction of **3** with closed-shell molecules (N_2 , CO , CH_4 , H_2 , or D_2) requires photoexcitation.^[38-40] The small kinetic isotope effect measured for the insertion of the closely related pinBN (pin = pinacolato) derivative into a CH bond of cyclohexane suggests that the singlet nitrene is undergoing the reaction.^[35] The singlet nitrene $^1\text{A}_1$ -**3** inserts into dihydrogen with a very low barrier according to previous computations,^[38] while its cycloaddition to CO_2 is without potential energy barrier. A relaxed potential energy surface scan computed at B3LYP/6-311++G(2d,p) starting from a large distance between one of the oxygen atoms and the nitrogen atom of $^1\text{A}_1$ -**3** results in barrierless potential energy curve that reaches species **5** as

minimum (Figure S5). A TS can be located at the CASSCF-(14,14)/def2-SV(P) level, but its energy drops below that of reactants after considering dynamic correlation with NEVPT2//CASSCF and B3LYP//CASSCF single point evaluations, suggesting that the reaction between $^1\text{A}_1$ -**3** and CO_2 can proceed without a potential energy barrier.

The oxaziridinone **5** (see Figure 2) has a pyramidal nitrogen atom (sum of bond angles: 292.0°) that is characteristic of aziridines, but contrasts the planar coordination in the aminoborane CatBNH₂ (**9**, sum of bond angles: 359.9° Figure 2). Compared to the nitrogen center in the latter, the pyramidal nitrogen atom is a poorer electron donor towards boron as evidenced by NBO^[63] analysis (Figure S6a). This results in a longer BN bond with a smaller Wiberg bond index (WBI) than in **9** (Figure S6b). The nitrogen and oxygen lone pairs of the three-membered ring donate electron density into the π^* orbital of the CO double bond according to second order perturbation analysis to a degree that is similar to carbamic acid (see Figure S6a). The NO distance in **5** is quite long (1.604 \AA) compared to that in hydroxylamine (exp. 1.453 \AA , calc. 1.446 \AA).^[58,64] The NBO analysis revealed that the NO natural bond orbital is comprised of natural atomic hybrids (NAH) on both nitrogen and oxygen atoms with p character of 96% each. The high percentage of p and a low percentage of s (4% on each NAHs) character of the NAH explains the unusually long NO bond in **5**. On the other hand, the NC and the endocyclic CO distances are quite short, 1.379 \AA and 1.327 \AA , respectively. Also, the exocyclic CO distance is quite short (1.177 \AA) compared to typical CO double bonds of carboxylic acid derivatives (1.202 – 1.229 \AA).^[65-67] It appears that the inherently weak NO bond can "adjust" in length to minimize strain of the system and at the same time maximize the bonding to carbon (larger s character of N and O) by employing p orbitals for the N–O bond. Note that there exists a diradicaloid isomer of **5** with a significantly stretched NO bond (2.272 \AA) and high spin density on the N and O atoms (see Figure S7). This is higher in energy than **5** by 3.6 kcal mol^{-1} and collapses to **5** with a barrier of 2.8 kcal mol^{-1} . This suggests that the NO bond is quite weak and that its description as a dative bond is inappropriate. This is in agreement with the atoms in molecules analysis that found no N–O bond critical point for the parent oxaziridinone.^[58] We could not observe any indication for formation of this higher energy isomer of **5** or for ring opening to the more stable isocyanatoxy borane **8**. The latter rearrangement is associated with a sizeable barrier (see Figure S8).

As the unusual three-membered heterocycle of **5** is unknown experimentally, we also estimate its strain energy. Using Liebman's method of combination with cyclopropane or similar three-member ring compounds (Figure S9),^[68-71] we arrived at a strain energy of $36.7\text{ kcal mol}^{-1}$ for **5** at the CBS-QB3^[72] level of theory. The value is larger than that computed for aziridine ($27.0\text{ kcal mol}^{-1}$), but smaller than that of α -lactone ($47.0\text{ kcal mol}^{-1}$) and α -lactam ($55.0\text{ kcal mol}^{-1}$).^[73,74] The reduced strain of oxaziridinone **5** is in agreement with the conclusions of Bach et al. that insertion of two hetero atoms decreases the strain of a three-membered ring.^[73]

In summary, we here report the first example of the cycloaddition reaction between a nitrene and carbon dioxide. This cycloaddition reaction proceeds after photoexcitation of the triplet nitrene and its intersystem crossing to the singlet nitrene without barrier and produces the strained oxaziridinone system that has never been observed before. The three-membered heterocycle shows Fermi resonance between the CO stretching frequency and overtones of ring deformation modes causing unexpected isotope shifts for the ^{13}C and ^{18}O isotopologues of CO_2 . The strain of this ring system amounts to almost 40 kcal mol^{-1} , which is smaller than that of α -lactones and α -lactams presumably due to the long N–O bond.

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Conflict of Interest

The authors declare no conflict of interest.

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