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Accurate theoretical predictions for carbonyl diazide molecules: A coupled-cluster study of the potential energy surface and thermochemical properties

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ABSTRACT

Enthalpies of formation (ΔH_f°) of *syn-syn* (C_{2v}), *anti-syn* (C_s), and the newly proposed C_2 isomer of carbonyl diazide, $OC(N_3)_2$, at 298 K have been predicted using CCSD(T) theory in conjunction with a systematic basis set expansion that has been extrapolated to the complete basis set (CBS) limit. The ΔH_f° has been calculated via three independent pathways and 'chemical accuracy' has been obtained. The predicted CCSD(T)/CBS values are (kJ mol^{-1}): *syn-syn* (C_{2v}), 471.5; *anti-syn* (C_s), 479.5; C_2, 517.4. These values deviate by 14.5 kJ mol^{-1} compared to prior G4 approximations. CCSD(T) torsional potential energy scan reveals a previously undiscovered conformer of $OC(N_3)_2$ possessing C_2 symmetry.

1. Introduction

Organic azides have been a popular class of compound since phenyl azide was first synthesized in 1864 [1,2]. Later studies [3,4] in the 1940's and 1950's demonstrated the importance of hydrogen azide's relationship in the rearrangements of acyl azides into their isocyanate counterparts. More recently, studies have exploited capabilities of azides since these compounds interface with materials science, chemical, biological, and pharmaceutical applications [5]. Thus, regarding the biochemical and medicinal relevance, azidonucleosides have been found to be an effective treatment for AIDS and other autoimmune disorders [6–8]. However, the chemistry of many azides and their derivatives has been misunderstood for quite some time [5,9]. This in part because each azido ligand, N_3^-, which is well known for its energy-rich dynamics, adds a considerable 293 kJ mol^{-1} of energy to a potential molecular acceptor [10]. In addition to this, azides and their anions rapidly cause the elimination of N_2. This enormously elevates their shock sensitivity and volatility, making them potentially dangerous, and extremely difficult to study experimentally [10].

Recently, there has been a resurgence of interest and research in the design and synthesis of small polyazides [11,12]. In 2010, Zeng et al. [13], synthesized a new polyazide called carbonyl diazide ($OC(N_3)_2$). It was successfully isolated as a pure compound and fully characterized by spectroscopic techniques. This high-energy and potentially explosive compound was formed from the reaction between FC(O)Cl and NaN_3. Like many other azides [5,10,11,14,15], $OC(N_3)_2$ is extremely dangerous, as it has been labeled as a hazardous toxic material that is intrinsically unstable, and displays high shock sensitivity in the liquid and solid phases. Previously, it had been mentioned as an in situ reagent [16] and had been formed from the hydrolysis of $C(N_3)_4$ [17], but no other experimental or theoretical works have been reported in the literature until recently.

Zeng et al. [13] isolated $OC(N_3)_2$ in the gas and solid phases. X-ray crystallography showed a *syn-syn* conformation of the molecule, while infrared (IR) spectroscopy gave evidence for two conformations, *syn-syn* and *anti-syn* (Figure 1) with equilibrium vapor compositions of 88% and 12%, respectively. These workers also performed theoretical DFT calculations. The calculations revealed: (1) the *syn-syn* conformer is preferred energetically to the *anti-syn* conformer by about 6.9 kJ mol^{-1}; (2) theoretical relative Gibbs free energies give an equilibrium composition that is in fairly good agreement with the IR-derived value; (3) there is fair agreement between the IR data (vapor and Ar matrix) and the calculated data; (4) no other conformers that are local minima were found.

Later in 2011, theoretical work was reported by Ball [18] to obtain a reliable estimate of the (enthalpy of formation) ΔH_f° on the *syn-syn* conformer only. Ball's calculations used the composite G2, G3, and G4 methods. The G2, G3, and G4 values are 465.9, 476.5, and 457.0 kJ mol^{-1}. Another set of G2, G3, and G4 estimates was obtained by considering the reaction $12NH_3 + OC(N_3)_2 \rightarrow NH_2CONH_2 + 8N_2H_4$ (gas phase). The resulting values are 445.9, 440.1, and 451.7 kJ mol^{-1} for G2, G3, and G4, respectively. The results from both reaction paths do not agree very well for G2 and G3.

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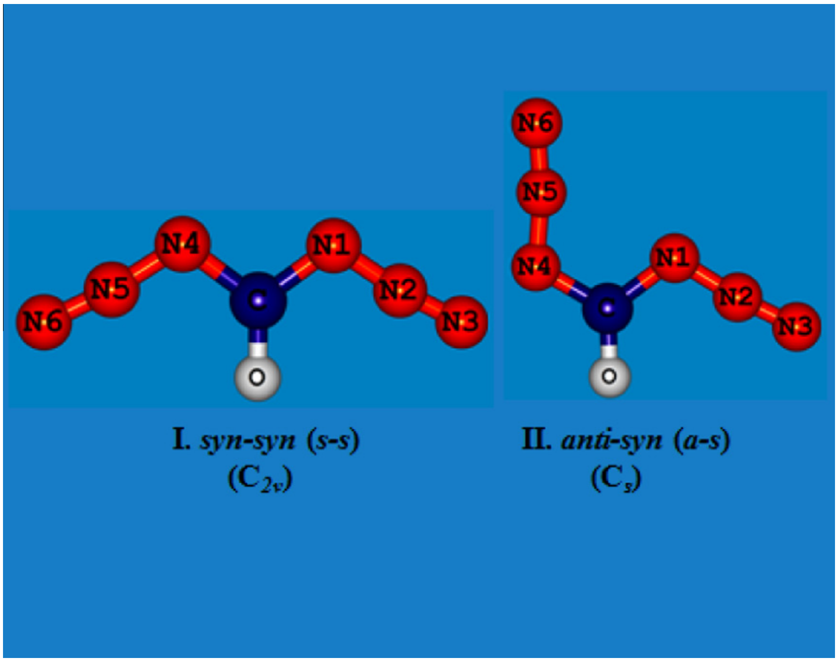

Figure 1. *syn-syn* and *anti-syn* isomers of $OC(N_3)_2$.

At the highest level of theory, G4, the estimate of ΔH_f° for the *syn-syn* isomer is in the range of 451.7–457.0 kJ mol^{-1}.

In this Letter, we report results of calculations on $OC(N_3)_2$ using CCSD(T) and correlation-consistent basis sets. The aims of this Letter include: (1) calculate the ΔH_f° of $OC(N_3)_2$ from several reaction pathways with the CCSD(T) method and extended correlation-consistent basis sets. Using well-established techniques, the results are extrapolated to give complete basis set (CBS) limit results; (2) systematically search the conformational potential energy surface to investigate whether there are local minima other than the established *syn-syn* and *anti-syn* conformers; (3) obtain CCSD(T) geometries and harmonic vibrational frequencies of $OC(N_3)_2$, which is the first time this method has been used to study this eight atom system; (4) calculate theormochemical data using the B3LYP DFT method and critically assess them and previously calculated [13] B3LYP structures and vibrational frequencies by comparison with CCSD(T). Since characterization and isolation of many nitrogen containing HEDMs are extremely difficult, a high level theoretical study such as this is relevant to accurately predict observable properties and benchmark other DFT and GX studies.

2. Computational methods

Calculations were performed using the frozen-core CCSD(T) method [19], which consists of the coupled-cluster singles-and-doubles method followed by a non-iterative (perturbative) treatment of connected triple excitations. CCSD(T) normally provides an accurate value of the correlation energy for a given basis set. The ACES II [20] and Gaussian 03 [21] programs were used. Geometries of $OC(N_3)_2$ were optimized with the 6-311+G(d) [22] and cc-pVTZ [23] basis sets. The latter basis set was used for optimizing geometries for thermochemical calculations. The torsional potential energy scan was performed at the CCSD(T)/6-311G(d) level. CCSD(T) single-point calculations were made at the CCSD(T)/cc-pVTZ geometries using the cc-pVQZ [23], cc-pV5Z [23], aug-cc-pVTZ [24], and aug-cc-pVQZ [24] basis sets. Estimates of core-valence correlation were made with the cc-pwCVTZ [23] basis sets. Basis sets included in ACES II were obtained from the EMSL Basis Set Exchange of the Pacific Northwest National Laboratory [25,26]. The L^{-3} extrapolation technique [27] was applied to estimate CCSD(T)/CBS energies. In addition to the CCSD(T) calculations, some B3LYP [28] calculations were performed with the 6-311+G(3df) basis set [29]. Thermal corrections to the energies to obtain enthalpies at 298.15 K were obtained using structures and harmonic vibrational frequencies from CCSD(T)/cc-pVTZ and B3LYP/6-311+G(3df) calculations.

3. Results and discussion

3.1. Torsional potential energy surface

Multiple conformers of $OC(N_3)_2$ can be obtained by rotation about the C–N1 and C–N4 single bonds. The conformational space is defined by the values of the dihedral angles $\tau_1 = \tau(OCN4N5)$ and $\tau_2 = \tau(OCN1N2)$. Prior work [13] has determined two conformers to be local minima, namely *syn-syn* ($\tau_1 = \tau_2 = 0^o$) and *syn-anti* ($\tau_1 = 0^o$, $\tau_2 = 180^o$). The latter is, of course, equivalent to the *syn-anti* conformer ($\tau_1 = 180^o$, $\tau_2 = 0^o$). To provide a complete view of the conformational space of $OC(N_3)_2$, we have performed a *relaxed* torsional potential energy scan (TPES) in which τ_1 and τ_2 have been independently varied from 0^o to 360^o in 14.4^o intervals, which encompasses a 26×26 grid. This task was completed at the CCSD(T)/6-311G(d) level. For each (τ_1, τ_2) combination, all other geometrical parameters were optimized. The TPES is shown in Figure 2.

Figure 2 clearly shows the *syn-syn*, *anti-syn*, and C_2 minima. The *anti-anti* conformer ($\tau_1 = \tau_2 = 180^o$) is not a local minimum, as noted previously [13]. However, there is a previously unrecognized local minimum of C_2 symmetry (Figure 3) that is quite close to the *anti-anti* conformer. This new minimum has $\tau_1 = \tau_2 \approx 150^o$ (and, equivalently, $\tau_1 = \tau_2 \approx 210^o$). The *anti-anti* conformer is a transition state connecting these equivalent C_2 minima. One can also plot the energy as a function of dihedral angle along the $\tau_1 = \tau_2$ axis. This is shown in Figure 4. The C_2 conformer is approximately 47 kJ mol^{-1} higher in energy than the *syn-syn* conformer (CCSD(T)/6-311G(d)).