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Research paper

Difluorodiazirine (CF_2N_2): A comparative quantum mechanical study of the first triplet and first singlet excited states

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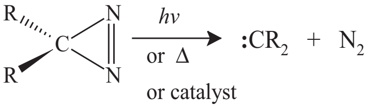
ABSTRACT

3,3′-Difluorodiazirine is a precursor of difluorocarbene radical (:CF_2) which is used in organic synthesis and photo affinity labelling. This molecule possesses no dipole moment in the ground electronic state (S_0) but has a significant dipole moment (of magnitude ~0.97 D) in both its first (triplet, T_1) and second (singlet S_1) excited states. These equal dipole moments are shown to originate from widely differing atomic polarization and inter-atomic charge transfer terms (defined by the Quantum Theory of Atoms in Molecules (QTAIM)). The calculated vertical/adiabatic excitation energies for the T_1 and S_1 states are 2.81/2.63 and 3.99/3.78 eV, respectively. Geometries, vibrational frequencies, atomic charges and spin populations, and the localization–delocalization matrices (LDMs) (Matta, J. Comput. Chem. **35** (2014) 1165) of the excited states are compared with those of the ground state. All calculations have been conducted at the (U)QCISD/aug-cc-pVTZ level of theory.

1. Introduction

Diazirines (R_2CN_2) are organic compounds that contain a three-membered CNN ($R_2\overline{C-N{=}N}$) ring. A representative of this class of compounds, 3,3′-difluorodiazirine (F_2CN_2 or DFD), was first synthesized in the mid-1960s [1–7]. (The numerical prefix will be dropped for simplicity in the remainder of this Letter). An important use of diazirines is to generate di-substituted carbene radicals (:CR_2) intended for use in stereospecific organic synthesis [3–5] and in macromolecular photoaffinity labelling experiments [8–12]. The carbene radical (:CR_2) can be formed in the gas phase via thermolysis or UV photolysis following the electronic excitation of the corresponding diazirine (Scheme (1)) [13], which provides the impetus for the study of the common representative of these molecules, DFD, in its two lowest electronic excited states.



(1)

A third route for dissociation is the deposition of diazirine on transition metal surfaces [14–16]. The deposition on Pd(110) surfaces can catalyze either the C—N (as in Scheme (1)) or the N=N bond cleavage on the surface of the metal depending on the geometry of adsorption on the surface as revealed by X-ray photoelectron spectroscopy (XPS) and thermal-programmed desorption (TPD) measurements [15,16]. It has also been found that deposition on Cu(110) surface selectively catalyzes the cleavage and the dissociative adsorption of the N=N bond [14].

Given the importance of DFD, in particular as a precursor for the carbene radical intermediate, its structure in the ground electronic state (singlet S_0 state) has been reported using high-resolution rotationally-resolved Fourier transform-IR spectroscopy [17], conventional IR spectroscopy [5], Raman spectroscopy [5,18], and gas-phase electron diffraction [19]. An analysis of microwave spectroscopic rotational centrifugal distortion constants was used to elucidate the structure of the first singlet excited state of DFD (S_1) [20]. More recently, the structures of the ground and low lying excited states have also been explored at post Hartree–Fock levels of quantum chemical theory [21,22].

DFD has a point group symmetry of C_{2v} with a central carbon bonded to two nitrogen atoms and two fluorine atoms, which curiously has a vanishing dipole moment in the ground state. On excitation, however, the molecule acquires a significant dipole moment

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in its first singlet excited state (S_1) [exptl., microwave spectroscopy [7]: 1.5 ± 0.2 Debye (D); theor., QCISD//aug-cc-pVTZ [22]: 0.969 D] and, as will be seen below, also in its first triplet (T_1) excited state.

The vanishing dipole moment in the ground state is unexpected on the basis of a spherical atomic model due to the great electronegativity difference between nitrogen and fluorine [22]. The considerable dipole moment acquired by DFD on excitation to the S_1 state can be traced to its atomic origins in the 'real-space' topography of the total electron density distribution [22]. The advantage of the real-space approach is that it rationalizes the observed dipole moment in terms of observable features of the electron density *without any reference to particular orbital contribution(s)*, since there are no privileged sets of molecular orbitals given that all sets yielding the same total electron density are inter-convertible by unitary transformations [23].

The vanishing dipole moment of S_0 is the result of a balance between an *inter*-atomic charge transfer contribution and an *intra*-atomic polarization contribution that reflects the departure of an atom-in-a-molecule from spherical symmetry [22]. The latter contribution arises from the lack of coincidence between the center of the negative electronic charge distribution of an atom-in-a-molecule and its center of positive charge (the nuclear position). The balance of these two contributions is altered upon excitation to the S_1 state [22].

In accordance with Hund's first rule [24], the S_1 state is not predicted to be the lowest excited state of DFD but rather that should be a triplet (T_1) state. These predictions are confirmed by our calculations, which yield vertical excitation energies for the T_1 and the S_1 states of 2.81 eV and 3.99 eV, respectively [22]. The S_0 state exhibits a calculated dipole moment magnitude of 0.05 D, which changes to 0.973 and 0.969 D for the adiabatically excited states T_1 and S_1, respectively, with all three dipole moments pointing their negative end toward the nitrogen atoms [22].

Our former investigation [22] focused primarily on the changes in the topography of the electron density, the Laplacian of the electron density, and the electrostatic potential on excitation to the S_1 level. In the present study, the characteristics of the S_1 excited state will be compared and contrasted with those of the T_1 state, which was not examined in detail previously. A benchmarking comparison of various electronic structure theory methods determined that (U)QCISD/aug-cc-pVTZ basis is an adequate level of theory for treating the ground and excited states of DFD [22] and hence will be used here without further justification.

2. Computational methods

Electronic structure calculations were conducted at the (unrestricted) quadratic configuration interaction with single and double excitations ((U)QCISD) [25] under the frozen core variant (FC) with an aug-cc-pVTZ correlation-consistent Dunning triple-zeta basis set augmented with diffuse functions [26] in conjunction with a linear response approach to obtain the excited state densities [27]. The same computational protocol described previously [22] is followed in the present work.

Electronic structure calculations, geometry optimizations, and vibrational frequency calculations were performed using Gaussian 09 [27]. Wavefunctions and electron densities were analyzed with AIMAll/AIMStudio [28]. Atomic Lagrangians never exceed 10^{-4} a.u. and the differences between the sums of atomic populations and the total number of electrons ($N = 38\ e^-$) are always below 10^{-6} e. The UQCISD singlet/triplet excited state calculations (both vertical and adiabatic) result in $\langle S^2 \rangle = s(s+1)$ to four decimals (0.000/2.000), indicating practically no spin contamination.

3. Results and discussion

3.1. Electronic excitation energies

Table 1 shows the adiabatic and vertical excitation energies for the first triplet and the first singlet excited states along with available literature reference values. The vertical energies were corrected by the subtraction of the zero point vibrational energy (ZPE) of the ground state from the transition energy. It is important to note that in Ref. [22], we have mistakenly *added* rather than *subtracted* the ZPE to the vertical excitation calculations in Table 2 of that reference. A corrigendum has been submitted for publication to correct for this mistake which now has resulted in a significantly better (actually excellent) agreement between calculated excitation energies and experiment (0.02 eV discrepancy at the level of theory used in the present work).

Our (U)QCISD/aug-cc-pVTZ calculations yield a vertical ($T_1 \leftarrow S_0$) excitation energy of 2.38 eV in excellent agreement with the value obtained at the GVVPT2/cc-pVTZ of 2.25 eV by Hoffmann et al. [21]. Our calculated vertical ($S_1 \leftarrow S_0$) excitation energy is 3.54 eV, only 0.02 eV higher than the experimental value (3.52 eV) [20,29] and in reasonable agreement with the calculations of Hoffmann et al. (2.95 eV) [21]. Adiabatic excitation energies show less agreement with the values of Hoffmann et al. [21] as can be seen from Table 1, but there are no reversal of the energetic ordering of the excited states upon geometry optimization in both our calculations and those of Hoffmann et al.

3.2. Changes of geometrics parameters upon excitation

The optimized geometries of the ground state along with available experimental data [19] and the corresponding values in the excited states (and changes upon excitation) are listed in the Table 2 and the optimized geometries of the three electronic states are displayed in Fig. 1. The average absolute deviations for inter-atomic distances between our calculations and the experimental values for the ground state is 0.016 Å and for the available two angles is 1.25°, indicating a reasonable general agreement.

Upon excitation, both the N—C and the N=N bonds become longer in both excited states. The d(N—C) is longer by 0.043 Å

Table 1
Excitation energies of difluorodiazirine (CF_2N_2) calculated at the (U)QCISD/aug-cc-pVTZ level of theory.[a]

Transition	Vertical[b]				Adiabatic[b]	
	$\Delta E_{vert(raw)}$	E_{ZPE}	$\Delta E_{vert(corr)}$	dev[c]	ΔE_{ad}	dev[c]
$T_1 \leftarrow S_0$	2.81	0.43	2.38 2.25[d]	0.13	2.63 2.19[d]	0.26
$S_1 \leftarrow S_0$	3.99	0.45	3.54 2.95[d](3.52)[e]	0.59(0.02)	3.78 2.86[d]	0.74

[a] All energies entered in the table are in electron volts (eV).

[b] Calculated adiabatic energy differences (ΔE_{ad}) do not include zero-point vibrational energy (ZPE) corrections (*i.e.*, bottom-of-the-well differences). Vertical excitation energies ($\Delta E_{vert(raw)}$) are the raw differences between the excited state total energy calculated at the optimized geometry of the ground state and the total energy of the ground state, and $\Delta E_{vert(corr)} = \Delta E - E_{ZPE}$ is a corrected vertical transition energy in which the ZPE correction is included for the ground state only. (In Ref. [22] the ZPE has been mistakenly *added* rather than *subtracted* to the vertical excitation calculations, this error will be corrected in a published corrigendum).

[c] Deviation (dev) is defined as the calculated minus the reference value.

[d] The reference values for excitation energies were calculated at the GVVPT2/cc-pVTZ levels of theory and were obtained from Ref. [21].

[e] The experimental reference value (in parentheses) was obtained from Refs. [20,29].