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Computational Rationalization for the Observed Ground-State Multiplicities of Fluorinated Acylnitrenes

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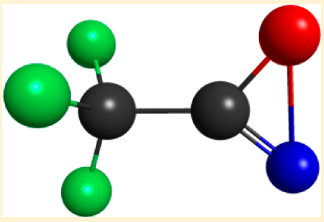
Ⓢ *Supporting Information*

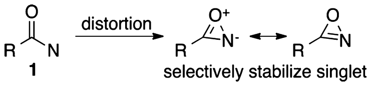
ABSTRACT: Computational methods are used to investigate the mechanism by which fluorination of acetylnitrene reduces the stabilization of the singlet configuration. ΔE_{ST} is made more positive (favoring the triplet state) by 1.9, 1.3, and 0.7 kcal/mol by the addition of the first, second, and third fluorine, respectively, at the CR-CC(2,3)/6-311(3df,2p)//B3LYP/6-31G(d,p) level of theory. Smaller effects observed with substitution of β-fluorines in propanoylnitrene derivatives and examination of molecular geometries and orbitals demonstrate that the effect is due to inductive electron withdrawal by the fluorines, rather than hyperconjugation.



■ INTRODUCTION

The ground-state multiplicities of simple alkyl nitrenes are invariably of triplet multiplicity because of the availability of two approximately degenerate *N*-centered p orbitals. For the parent nitrene, imidogen NH, the singlet−triplet energy gap (ΔE_{ST}) favors the triplet by 36 kcal/mol.[1] By contrast, both experimental and theoretical studies have concluded that acylnitrenes **1**, particularly acetylnitrene and benzoylnitrene, have closed-shell ground states of singlet multiplicity.[2−13] (Early computational studies[14,15] have clearly been superseded by more recent work.)

The singlet configuration is selectively stabilized due to delocalization of the in-plane nonbonding oxygen lone pair into the nominally empty p-type orbital on nitrogen. In fact, computed geometries show that the adjacent carbonyl group further stabilizes the singlet state by bending over in such a way as to maximize this interaction at the expense of increased angle strain.



The geometric distortion of the singlet acylnitrene is sufficiently large that it may be better described as an oxazirene. The analogous interaction between O and N is not available to the triplet acylnitrene because the in-plane N-orbital is half-filled. Optimized geometries of acetylnitrene are illustrated in Figure 1 to demonstrate the geometric distortion associated with this interaction.

By coincidence, the stabilization of $^1CH_3CON$ is just enough to drop its energy below that of $^3CH_3CON$. The singlet−triplet energy gap (ΔE_{ST}) varies with computational method and substituent but is universally no more than a handful of kilocalories per mole.

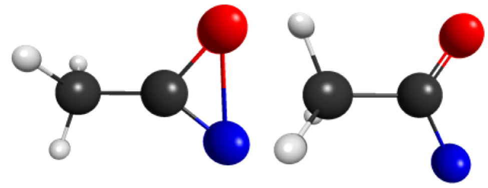
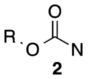


Figure 1. Computed geometries for $^1CH_3CON$ (left) and $^3CH_3CON$. Note the more acute OCN angle for $^1CH_3CON$.

The same principle of selective stabilization of the closed-shell singlet nitrene configuration should apply to other α-substituents with lone pairs, but the stabilization is not always great enough to lower the singlet to below the triplet. For example, alkoxycarbonylnitrenes **2** have been shown to have triplet states because conjugation of the oxygen into the carbonyl (available in the uncyclized triplet nitrene) is more favorable than into the oxazirene by just enough that ^{3}**2** is more stable than ^{1}**2**.[13] α-Sulfonylnitrenes also have triplet ground states.[10,16−22] Thiobenzoylnitrene, however, again has a singlet ground state by formation of the corresponding thiazirene.[23]



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In our previous experimental and computational work,[10] it was noted that both product studies and computations addressing trifluoroacetylnitrene pointed to a triplet ground state, in contrast to nonfluorinated acetylnitrene. In this work, we report a computational investigation into the mechanism of this remote action of the fluorines onto the electronic structure of the acylnitrene moiety.

■ COMPUTATIONAL METHODS

All computations were carried out using the GAMESS suite of programs.[24] Geometries and orbitals were visualized using MacMolPlt.[25] Optimized geometries were obtained at B3LYP/6-31G(d,p), and vibrational matrix calculations confirmed that all stationary points were

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minima. Temperature corrections are all set at 298.15 K. Larger basis sets and higher levels of theory, up through CR-CC(2,3),[26,27] were used in single-point energy calculations as noted. Spherical harmonics were used with the polarization functions. Wiberg bond index and charges based on natural population analysis were obtained with NBO 6.0,[28] as implemented within GAMESS. This version of NBO is not compatible with ROH wave functions for triplets. Therefore, the NBO calculations on the triplet nitrenes were done in UHF mode using the ROHF geometries examined elsewhere in the paper.

■ RESULTS AND DISCUSSION

In order to elucidate whether electronegativity through the σ system or conjugative effects of the fluorine are mainly responsible for the variation in ground-state multiplicity, computational geometries and energies were determined for HCON, FCON, CH_3CON, CH_2FCON, CHF_2CON, CF_3CON, CH_3CH_2CON, CHF_2CH_2CON, CH_3CF_2CON, and CF_3CH_2CON. B3LYP/6-31G(d,p) in RHF and ROHF modes was used to determine geometries for singlets and triplets, respectively.[29−31] Hessians were calculated to verify that all optimized structures were, in fact, minima. Energies were determined at these geometries using several higher levels of theory. Using the precedent of our previous work, CR-CC(2,3)/6-311G(3df,2p)//B3LYP/6-31G(d,p) was used as the most sophisticated calculation, similar to the work of Gritsan and co-workers, who showed that B3LYP/6-31G(d) geometries corresponded well to CCSD(T)/cc-pVTZ for HCON.[5]

In every case, the calculated electrostatic moment was larger for the singlet configuration of a given compound than for the triplet, by approximately 1 D. This implies that addition of solvent would change the observed ΔE_{ST}, with more polar solvents presumably selectively stabilizing the singlet state. The expected effect would be small on an absolute scale, but the states are very close in some instances. We are unaware of data on which to base a firm estimate, but note that Eisenthal and Turro derived a solvent-derived $\Delta\Delta E_{ST}$ of 1.5 kcal/mol for diphenylmethylene from experimental data for methanol vs isooctane.[32] The remainder of the computations discussed here are for gas phase, i.e., without solvent.

HCON and FCON. Results comparing formylnitrene HCON and FCON are given in Table 1. By convention, $\Delta E_{ST} < 0$ implies that the ground state is a singlet. Data are given as ΔH (298.15 K) based on unscaled temperature corrections to the 0 K energies. It is clear from the experimental results for acetylnitrene and benzoylnitrene that ΔE_{ST} is overestimated by the B3LYP/6-31G(d,p) calculations, but we are unaware of any definitive experimental evidence demonstrating its sign for HCON. Extrapolating our previous work on trifluoroacetylnitrene,[10] we believe that the MP2 value for ΔE_{ST} is consistently too negative across all compounds throughout this work.

Table 1. Computed ΔE_{ST} for HCON and FCON at Different Levels of Theory[a]

method	HCON	FCON
B3LYP/6-31G(d,p)	5.6	12.5
B3LYP/6-311G(3df,2p)//B3LYP/6-31G(d,p)	4.0	11.5
MP2/6-311G(3df,2p)//B3LYP/6-31G(d,p)	−4.6	8.7
CR-CC(2,3)/6-311G(3df,2p)//B3LYP/6-31G(d,p)	2.4	10.3

[a] All energies given in kcal/mol as ΔH (298.15 K).

Regardless of whether ^{1}HCON or ^{3}HCON is lower in energy, it is clear that $\Delta E_{ST} > 0$ for FCON. $\Delta\Delta E_{ST}$ for the pair is in the range 10 kcal/mol (7−8 kcal/mol according to three of the methods and 13 by MP2), which is by far the largest effect of any of the comparisons due to fluorination in this paper. This result is consistent with the previous reports regarding hydroxycarbonylnitrene and alkoxycarbonylnitrenes. Like that case, the fluorine in FCON is directly conjugated to the carbonyl group; this is not the case for any other of the fluorinated molecules examined in this paper. Using isodesmic reactions that cannot be applied for FCON, Hadad and Platz concluded that the conjugation by the oxygen lone pair in the alkoxycarbonylnitrenes stabilized the triplet state to a greater extent than it did the singlet.[13] However, the geometric data reported in Table 2 illustrate another worthwhile observation for FCON in particular.

It is well understood that the high polarity of C−F bonds results in opening up of the bond angles between the other substituents (e.g., the H−C−H angles in FCH_3). This is most often attributed to the electronegativity of fluorine causing a rehybridization of the carbon favoring greater p-orbital participation in the C−F bond. Thus, the O−C−N angle in ^{3}HCON is 121.5°, whereas it is 124.1° for ^{3}FCON (Table 2). This suggests that there should be a higher energetic cost associated with squeezing the OCN angle enough to stabilize the singlet configuration in ^{1}FCON than there is for ^{1}HCON. Indeed, the 97.6° OCN angle in ^{1}FCON is the most open of all the singlet nitrenes by a substantial margin.

The same geometric trend is observed for the fluorinated derivatives of acetylnitrene discussed in more detail below. Successive fluorination of the CH_3 to CF_3 increases the net electronegativity of the methyl group and is accompanied by a subtle opening of the OCN bond angle in both the singlet and triplet series.

Table 3 illustrates an approximation of the energy gained by the ^{1}HCON and ^{1}FCON through distorting from the triplet geometry to the cyclized geometry. This quantity, denoted $\Delta E_{\text{S-relax}}$, was obtained by determining the energy of a given nitrene in a singlet configuration at the optimized geometry for the equivalent triplet state molecule. This "singlet energy at triplet geometry" was then compared to the energy of the singlet state nitrene at its optimized geometry. These values are given without vibrational or thermal correction, since the singlets are not at a stationary point. While this energy is a hypothetical quantity in the sense that the singlet does not have a stationary point at the triplet geometry, it reflects the energy that the singlet-state molecule recovers through geometric distortion.

Although the absolute $\Delta E_{\text{S-relax}}$ varies with method, a few observations can be made. First, $-\Delta E_{\text{S-relax}}$ can be taken as a rough estimate of the O−N "bond dissociation energy" in the oxazirene. This BDE is clearly at the low margin of what might be thought of as a covalent bond energy for even HCON. Second, $\Delta E_{\text{S-relax}}$ is about 10 kcal/mol smaller for FCON than it is for HCON, accounting approximately for the $\Delta\Delta E_{ST}$ between the two compounds. A third observation is that the $\Delta E_{\text{S-relax}}$ is consistently much more negative from the MP2 calculations than from other levels of theory, accounting for the much more negative (or less positive) ΔE_{ST} observed for HCON, FCON, and the other compounds in this work (vide infra). MP2 calculations are susceptible to poor results for problems that are not clearly single-reference in nature, e.g., many problems involving biradicals. There were no gross indicators of bad results (e.g., nonsensical orbital occupancies or large spin contamination in UHF) in the MP2 computations.

Table 2. Calculated Geometric and NBO Parameters for Acylnitrene Centers[a]

nitrene	interatomic distance (Å) and (Wiberg bond index) C–O	C–N	O–N	∠OCN (deg)	q_C[b]	q_O	q_N
^{1}HCON	1.31 (1.16)[b]	1.26 (1.78)	1.79 (0.92)	88.2	0.35	−0.41	−0.14
^{3}HCON	1.23 (1.40)	1.38 (1.61)	2.28 (0.28)	121.5	0.18	−0.48	−0.76
^{1}FCON	1.26 (1.29)	1.27 (1.64)	1.90 (0.81)	97.6	0.85	−0.40	−0.15
^{3}FCON	1.20 (1.45)	1.39 (1.43)	2.29 (0.30)	124.1	0.80	−0.29	−0.23
^{1}CH$_{3}$CON	1.31 (1.13)	1.26 (1.75)	1.77 (0.92)	86.9	0.54	−0.43	−0.15
S@T[c]	*(1.53)*	*(1.40)*	*(0.57)*		0.54	*−0.49*	*−0.06*
^{3}CH$_{3}$CON	1.23 (1.67)	1.40 (1.21)	2.25 (0.06)	117.7	0.51	−0.45	−0.06
^{1}CH$_{2}$FCON	1.31 (1.14)	1.26 (1.75)	1.79 (0.91)	87.9	0.48	−0.42	−0.12
S@T	*(1.53)*	*(1.41)*	*(0.57)*		0.49	*−0.49*	*−0.02*
^{3}CH$_{2}$FCON	1.23 (1.66)	1.39 (1.22)	2.26 (0.07)	119.3	0.46	−0.44	−0.03
^{1}CHF$_{2}$CON	1.30 (1.16)	1.26 (1.76)	1.80 (0.92)	89.1	0.44	−0.40	−0.11
S@T	*(1.56)*	*(1.42)*	*(0.54)*		0.47	*−0.49*	0.02
^{3}CHF$_{2}$CON	1.22 (1.68)	1.39 (1.23)	2.27 (0.06)	120.6	0.43	−0.43	−0.02
^{1}CF$_{3}$CON	1.30 (1.17)	1.26 (1.76)	1.81 (0.92)	89.8	0.41	−0.39	−0.09
S@T	*(1.57)*	*(1.42)*	*(0.55)*		0.42	*−0.46*	0.01
^{3}CF$_{3}$CON	1.22 (1.69)	1.39 (1.23)	2.27 (0.07)	121.3	0.40	−0.40	−0.02
^{1}CH$_{3}$CH$_{2}$CON	1.32 (1.12)	1.26 (1.75)	1.77 (0.91)	86.7	0.51	−0.43	−0.15
^{3}CH$_{3}$CH$_{2}$CON	1.23 (1.67)	1.40 (1.20)	2.25 (0.07)	117.9	0.51	−0.46	−0.06
^{1}CH$_{3}$CF$_{2}$CON	1.31 (1.15)	1.26 (1.76)	1.80 (0.91)	89.0	0.46	−0.41	−0.11
^{3}CH$_{3}$CF$_{2}$CON	1.22 (1.68)	1.39 (1.22)	2.27 (0.07)	120.1	0.45	−0.43	−0.02
^{1}CHF$_{2}$CH$_{2}$CON	1.31 (1.13)	1.26 (1.76)	1.78 (0.91)	87.4	0.53	−0.43	−0.13
^{3}CHF$_{2}$CH$_{2}$CON	1.23 (1.67)	1.39 (1.22)	2.26 (0.07)	118.8	0.51	−0.45	−0.04
^{1}CF$_{3}$CH$_{2}$CON	1.31 (1.15)	1.26 (1.76)	1.78 (0.92)	87.7	0.53	−0.41	−0.13
^{3}CF$_{3}$CH$_{2}$CON	1.22 (1.69)	1.40 (1.21)	2.25 (0.07)	118.6	0.51	−0.43	−0.04

[a] Data taken from RHF or UHF B3LYP/6-31G(d,p) computations. Charges taken from natural population analyses. [b] The acylnitrene carbon atom. [c] Singlet configuration at triplet geometry.

Table 3. Computed $\Delta E_{\text{S-relax}}$ of Acylnitrenes at Different Levels of Theory[a]

method	HCON	FCON
B3LYP/6-31G(d,p)	−20.3	−11.7
B3LYP/6-311G(3df,2p)//B3LYP/6-31G(d,p)	−20.6	−11.8
MP2/6-311G(3df,2p)//B3LYP/6-31G(d,p)	−33.5	−21.0
CR-CC(2,3)/6-311G(3df,2p)//B3LYP/6-31G(d,p)	−24.1	−14.5

[a] All data are ΔE (0 K) in kcal/mol. Negative values imply the amount of energy gained by the singlet adopting the distorted geometry over the sp^{2} type geometry seen with the triplet ground state.

However, while consistent, they are outliers in all of these calculations, and they are included in further results only to demonstrate that consistency and for purposes of completeness.

Acylnitrenes and Their Fluorinated Derivatives. The cases of the fluoroalkylcarbonylnitrenes are necessarily more subtle than the comparison between HCON and FCON because the fluorine is no longer directly conjugated to the acylnitrene moiety. The computed ΔE_{ST} (298.15 K) and $\Delta E_{\text{S-relax}}$ for the series CH$_{3}$CON, CH$_{2}$FCON, CHF$_{2}$CON, and CF$_{3}$CON are given in Tables 4 and 5. As reported previously,[10] at the CR-CC(2,3) level of theory, acetylnitrene is predicted to have a singlet ground state, although just barely, and the ΔE_{ST} for trifluoroacetylnitrene is about 4 kcal/mol higher. The experimental results in that paper were also consistent with a triplet ground state for the trifluoro species. As can be seen in Table 4, there is a monotonic increase in ΔE_{ST} as fluorines are added, although the change is smaller with the addition of each additional fluorine.

In order to assess whether this was a straightforward through-bond (inductive) effect or more complex interactions (e.g., interaction between the O–C–N π system and the CF σ^* bonds) were involved, further observations were made. First, in keeping with the work of Liu et al., the energy of isodesmic[33] reaction 1 was obtained for both the singlet and triplet nitrene species in order to show whether the fluorines being moved adjacent to the carbonyl had a significantly different effect in the singlet and triplet states/geometries. At the CR-CC(2,3)/6-311G(3df,2p)//B3LYP/6-31G(d,p) level of theory, ΔH (298.15 K)

Table 4. Computed ΔE_{ST} of Acylnitrenes at Different Levels of Theory[a]

method	CH$_{3}$CON	CH$_{2}$FCON	CHF$_{2}$CON	CF$_{3}$CON
B3LYP/6-31G(d,p)	1.9	4.1	5.4	6.3
B3LYP/6-311G(3df,2p)// B3LYP/6-31G(d,p)	0.3	2.2	3.9	4.7
MP2/6-311G(3df,2p)//B3LYP/6-31G(d,p)	−8.1	−5.6	−4.2	−3.9
CR-CC(2,3)/6-311G(3df,2p)//B3LYP/6-31G(d,p)	−0.2	1.7	3.0	3.7

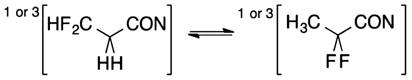
[a] All data are ΔH (298.15 K) in kcal/mol with unscaled temperature corrections from the B3LYP/6-31G(d,p) calculations. Positive values imply a triplet ground state, while negative values imply a singlet ground state.

Table 5. Computed $\Delta E_{\text{S-relax}}$ of Acylnitrenes at Different Levels of Theory and Basis Sets[a]

method	CH_3CON	CH_2FCON	CHF_2CON	CF_3CON
B3LYP/6-31G(d,p)	−20.9	−18.8	−20.3	−19.2
B3LYP/6-311G(3df,2p)//B3LYP/6-31G(d,p)	−21.4	−19.5	−20.7	−19.7
MP2/6-311G(3df,2p)//B3LYP/6-31G(d,p)	−35.8	−32.6	−33.7	−33.7
CR-CC(2,3)/6-311G(3df,2p)//B3LYP/6-31G(d,p)	−23.6	−21.7	−23.3	−22.3

[a] All data are ΔE (0 K) in kcal/mol. Negative values imply the amount of energy gained by the singlet adopting the distorted geometry over the sp^2 type geometry seen with the triplet ground state.

is 1.4 kcal/mol for the singlet (indicating a slight disfavoring of having the fluorines adjacent to the CON) and 0.0 kcal/mol for the triplet nitrene. This difference of 1.4 kcal/mol between the singlet and triplet is considerably smaller than the differences obtained by Liu et al.[13] for conjugation of the α-carbonyl by an oxygen atom. Importantly, however, it points out that the α-fluorines are essentially inconsequential to the stability of the triplet nitrene.



(1)

This result suggested a straightforward through-bond (inductive) basis for the effect of fluorination of the acetylnitrenes, but it was important to consider the geometries of the fluorines, particularly for the mono- and disubstituted cases to solidify this interpretation. For CH_2FCON, a series of constrained optimizations was carried out, holding the F−C−C−O dihedral angles at 20° intervals from 0 through 180° (i.e., carbonyl and CF antiperiplanar). Data are shown in Figure 2, with all energies set relative to the most stable structure at B3LYP/6-31G(d,p). For both $^1CH_2FCON$ and $^3CH_2FCON$, the global minimum is observed at 180°, with a secondary minimum about 0.6 or 1.3 kcal/mol higher with the CO and CF eclipsed. This was confirmed by allowing full optimizations from the same 10 geometries, which all resulted in conformations very near the 0° or 180° structures.

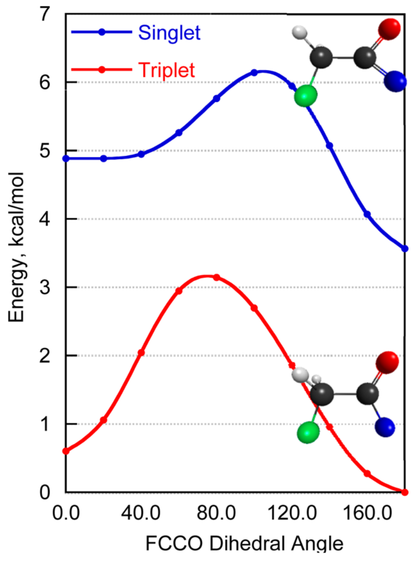


Figure 2. Rotational potential for $^1CH_2FCON$ and $^3CH_2FCON$. Global minima are illustrated adjacent to each curve. No corrections for vibrations are included, since the geometries are not stationary points.

Clearly enough, the C−F in-plane conformations do not imply any complex hyperconjugation; instead they seem to imply conformations in which the CF dipole is aligned in opposition to the CO or CN dipoles. For hyperconjugation, one would expect alignment of the C−F σ^* with a donor orbital (lone pair or π); that is clearly not the case here. An alternative is weak π donation by a fluorine lone pair, but the insulating methyl carbon greatly reduces that potential interaction. Indeed, inspection of the filled orbitals for both the singlet and triplet species did not reveal any significant favorable interaction between the F or CF and the acylnitrene center. (As expected, most of the unpaired spin is assignable to the nitrogen for $^3CH_2FCON$.) NBO calculations also did not indicate any significant π-type interactions between the CF bonds and OCN centers.

The preference for a 180° F−C−C−O dihedral angle in $^1CH_2FCON$ and $^3CH_2FCON$ is consistent with the known preference for an analogous anti conformation (vs syn) for more conventional α-fluoroacetyl carbonyl compounds (amide 7.5 kcal/mol, ester 4.5 kcal/mol, ketone 2.2 kcal/mol).[34,35] As noted in Table 2, the charge associated with O is more negative than that for N in all cases, so a slight preference is expected for the CF to be aligned approximately opposite CO, rather than CN. For the singlet, there may be a slight additional steric preference favoring the global minimum in that the CCN angle is somewhat wider than the CCO angle (142° vs 130°), whereas the difference is much smaller for $^3CH_2FCON$ (122° vs 119°).

Analogous data are illustrated for $^1CHF_2CON$ and $^3CHF_2CON$ in Figure 3. Here, the global minimum for $^3CHF_2CON$ follows the dipole-based preference for the lowest energy conformation

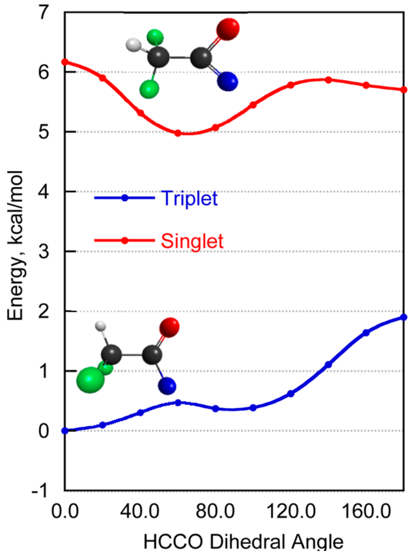


Figure 3. Rotational potential for $^1CHF_2CON$ and $^3CHF_2CON$. Global minima are illustrated adjacent to each curve. No corrections for vibrations are included, since the geometries are not stationary points.

established by $^3CH_2FCON$, in that the net CF_2 dipole opposes the CO dipole, rather than the CN dipole.

The global minimum for $^1CHF_2CON$, however, is entirely different, with a geometry in which the HCCO dihedral angle is near 66°. The fluorine that is closer to the CON plane is on the nitrogen side, where steric interference is smaller (as it was for $^1CH_2FCON$). The conformation in which the CF_2 dipole opposes CO is actually a transition state with respect to the methyl rotation (at HF, MP2, or B3LYP level of theory). As with the other examples, no significant overlap exists between the CF_2 and the CON.

However, precisely teasing out the factors leading to the favored conformation for $^1CHF_2CON$ can be no more than speculative. The total range of energies for the difluoromethyl rotation is just over 1 kcal/mol for $^1CHF_2CON$ (and still shy of 2 kcal/mol for $^3CHF_2CON$); these are numbers comparable to or smaller than those that appear in textbooks regarding even the C−C bond rotation in ethane.

To further elaborate the differences within the fluorinated acetylnitrene series, examination of several structural parameters is worthwhile. The variations are relatively small within each series of a given multiplicity. Baseline Wiberg bond index values for the compounds within each multiplicity series are shown in Figure 4, and specific values are given in Table 2.

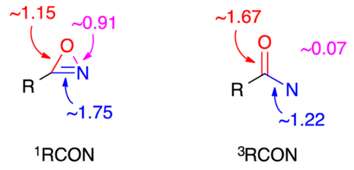


Figure 4. Primary resonance forms and Wiberg bond indices for the singlet and triplet acylnitrenes. Slight bond order drops in C−N bond order and rises in CO bond order with increasing fluorination occurs in the singlet series.

These bond orders should not be taken literally, but their trends and magnitudes are useful. For example, the approximately 0.9 O−N bond index for the singlets stands in stark contrast to the <0.1 value for the triplets. In fact, the bond orders for the CON system of the singlet emphasize the value of the oxazirene resonance form in describing the singlet. Some delocalization of the OCN π system, however, is indicated by the approximately 1.15 and 1.75 O−C and C−N bond orders, respectively. For the triplets, π-delocalization is also observed, but the trend is reversed; it is the C−O bond with a much higher bond index than the C−N.

Table 2 also gives the bond index analogue to the $\Delta E_{\text{S-relax}}$ data by illustrating the bond indexes (and charges) for the acylnitrene singlets at the triplet geometry (notated S@T in Table 2). This parameter is not sensitive to the subtle changes induced by the fluorination. Consistently, geometric relaxation of the singlet increases the C−O bond index by 0.40 and drops the C−N bond index by 0.34, and the O−N bond index increases by about 0.36. A salient observation, however, is that well over half of the O−N "bond" (as indicated by the Wiberg parameter) is formed without allowing the geometric relaxation. This is consistent with the energetic results: the 35 kcal/mol ΔE_{ST} for NH gives a rough idea of how much selective singlet stabilization is required for the singlet and triplet configurations of a nitrene to be approximately degenerate. The $\Delta E_{\text{S-relax}}$ values are only of the order of 20 kcal/mol, which indicates that a great deal of energy has already been recovered by the singlet before the geometry is allowed to distort to maximize that recovery.

Among the relaxed singlet nitrenes, a few small trends are observed with methyl fluorination. Successive fluorinations cause small decreases in the magnitude of the charge on C, O, and N, presumably because the inductive charge withdrawal slightly destabilizes charge separation between C and the more electronegative N and O atoms. Consistent with a very slight relocalization back to the acylnitrene resonance form, the C−O bond index increases slightly, from 1.13 to 1.17, reflective of the slight lengthening of the O−N distance from 1.77 to1.81 Å.

Changes in geometry in the triplet series from $^3CH_3CON$ to $^3CF_3CON$ are even smaller. A slight increase in the O−N distance (2.25 Å to 2.27 Å) and an increase in OCN bond angle (118° to 121°) are the most dramatic changes. As noted previously, this angle change is consistent with known effects of increased electronegativity. Computed orders do not vary systematically within the series of triplet nitrenes. However, with the working hypothesis that a great majority of the variability in ΔE_{ST} among the series of compounds is due to diminishing O−N interaction in the singlets (caused by the fluorination), this is the expected result.

The ΔE_{ST} for the CH_3CON to CF_3CON increases smoothly, regardless of the computational method, with a slightly smaller increase for each additional fluorine atom (Table 4). The total range of change ($\Delta\Delta E_{ST}$) is 3.9−4.4 kcal/mol (i.e., about 4 kcal/mol), regardless of computational method. $^1CH_3CON$ is slightly more apt at making the oxazirene structure, relative to the rest of the series, as evidenced by the coherent changes in energy, bond order, and geometry. We tentatively conclude that the change in ΔE_{ST} is primarily due to inductively induced reduced basicity/nucleophilicity of the oxygen atom with addition of each fluorine. Consistent with this notion is the charge on oxygen, which declines slightly with fluorine substitution.

The trend of a less basic/nucleophilic oxygen atom singlet acylnitrene/oxazirene with each fluorination is consistent with the known gas-phase basicity trend for acetic acid, fluoroacetic acid, and trifluoroacetic acid (179.9, 175.5, 162.7 kcal/mol, respectively)[36] and, of course, the aqueous pK_a's for these acids. Experimental gas-phase basicities are not known for fluorinated acetamides, which are probably a better model for this series, but a couple of computational studies are available.[37,38] As expected, acetamide is more basic than trifluoroacetamide.

At first glance, this conclusion that lower basicity/nucleophilicity due to inductive electron withdrawal causes a systematic decline in the "value" of the O−N interaction would be more convincing if the trend in $\Delta E_{\text{S-relax}}$ was clearer and/or larger. However, it must be recalled that $\Delta E_{\text{S-relax}}$ only represents the portion of singlet stabilization that accompanies the geometric distortion. The S@T bond orders clearly indicate that part of the stabilization occurs without distortion. Moreover, the data in Figure 3 show that methyl rotation contributes a small, but significant portion to ΔE_{ST} in the case of CHF_2CON.

To confirm that the mechanism of fluorine-induced $\Delta\Delta E_{ST}$ is at least predominantly inductive, the ΔE_{ST} values for CH_3CH_2CON, CH_3CF_2CON, CHF_2CH_2CON, and CF_3CH_2CON were obtained. For an effect to be observable from the β-carbon, an inductive mechanism is required. These data are given in Table 6. The effect of β-fluorines is small but clearly real. As expected, a more remote pair of fluorines (CH_3CF_2CON vs CHF_2CH_2CON) provides a smaller, but nonzero, change from the control value based on CH_3CH_2CON. At two levels of theory, the difference between two and three fluorines in the β-position is insignificant. At the MP2 level of theory, the ΔE_{ST} for CF_3CH_2CON is still intermediate between

Table 6. Computed ΔE_{ST} of Propanoylnitrene at Different Levels of Theory[a]

method	CH_3CH_2CON	CHF_2CH_2CON	CF_3CH_2CON	CH_3CF_2CON
B3LYP/6-31G(d,p)	2.7	3.2	3.2	4.9
B3LYP/6-311G(3df,2p)// B3LYP/6-31G(d,p)	1.2	1.8	1.8	3.4
MP2/6-311G(3df,2p)// B3LYP/6-31G(d,p)	−7.3	−6.6	−7.2	−4.6

[a] All data are ΔH (298.15 K) in kcal/mol with unscaled temperature corrections from the B3LYP/6-31G(d,p) calculations. Positive values imply a triplet ground state, while negative values imply a singlet ground state.

CH_3CF_2CON and CH_3CH_2CON but has a counterintuitive change, relative to CHF_2CH_2CON (being slightly more negative, rather than the expected slightly less negative). We have no rationalization for this result, other than that all of these differences are small and another issue (internal dipole interactions?) may contribute. Finally, a β-CF_3 ought to be approximately as potent as an α-F, based on group electronegativities (3.4 vs 4.0, respectively) and Hammet-type inductive parameters (σ_I = 0.45 and 0.50, respectively).[39,40] Comparison of the data in Tables 4 and 6 shows that this comparison is reasonable, if not quantitative; substitution of a single CF_3 for H in CH_3CON makes a slightly smaller change in ΔE_{ST} than does substitution by a single fluorine.

CONCLUSION

The ground-state multiplicity of acetylnitrene is a singlet, while that of trifluoroacetylnitrene is a triplet. This is the result of a coincidence of the substantial stabilization of the closed-shell singlet state by formation of a structure reasonably described as an oxazirene being approximately the same as the ordinary ΔE_{ST} of alkylnitrenes. A small decline in that stabilization, associated with fluorination of the α-carbon, means that the singlet configuration is no longer brought below the triplet nitrene. The mechanism of the reduced stabilization of the singlet does not appear to involve any special hyperconjugative effects but instead derives from straightforward inductive effects of the highly electronegative fluorine atoms reducing the nucleophilicity/basicity of the carbonyl oxygen and widening the O−C−N bond angle. This is deduced from examinations of the preferred conformations of the molecules, a lack of delocalization of the orbitals involving fluorine, and the ability of β-CF_3 and CF_2 groups to affect ΔE_{ST}.

While experimental evidence exists demonstrating that the ground state of trifluoroacetylnitrene is probably a triplet while that of acetylnitrene is a singlet, the precise ΔE_{ST} values are not known. Enough uncertainty exists in all of the computational methods currently available that an accurate prediction of the crossover point in the fluorinated acetylnitrene series (monofluoro or difluoro) cannot be stated with any certainty. However, ΔE_{ST} is surely near zero for the intermediate cases, and its sign may depend on environmental parameters deriving from solvent due to differences in polarity and/or hydrogen bonding by the different species.

ASSOCIATED CONTENT

Supporting Information

Coordinates and absolute energies from computations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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