Ab Initio Study of Some Persistent Nitroxide Radicals

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Abstract: Stable free radicals have a variety of applications. Particularly, the aminoxyl group is frequently used in spin-labeling experiments. Nitroxides may also exhibit intriguing chiral and magnetic properties, and can be of interest for studies of molecular parity violation. We present results for three different groups of persistent nitroxide radicals: i) acyclic: dimethylaminoxyl (Me_2NO), bis(trifluoromethyl)aminoxyl ($(CF_3)_2NO$), and di-*tert*-butyl nitroxyl [$(Me_3C)_2NO$]; ii) cyclic: aziridine-N-oxyl, azetidine-N-oxyl, pyrrolidine-N-oxyl and piperidine-N-oxyl; and iii) imino nitroxides. We used density functional and *ab initio* (MP2, coupled cluster) methods to obtain insight into the underlying chemistry. The molecular structures, harmonic vibrational frequencies, inversion barriers, and hyperfine coupling constants are reported. The cyclic aziridine-N-oxyl exhibits a considerable inversion barrier of ~hc 3500 cm^{-1} compared to only ~hc 500 cm^{-1} for the other examples. Stable imino nitroxides are theoretically characterized for the first time in our work. We discuss the possibilities that some of the chiral derivatives may be dominated by molecular parity violation in their dynamics.

Keywords: *Ab initio* calculations · Chirality · Inversion barriers · Nitroxide radicals · Parity violation

1. Introduction

The hindered inversion at the pyramidal nitrogen atom is among the classic problems of intramolecular dynamics and in particular tunneling dynamics including the possibility of molecular chirality with appropriate substitution.[1–6] In this context there has been interest in the question, whether chiral (pyramidal) nitrogen compounds may under certain circumstances be dominated by parity violation, if the barrier for inversion is sufficiently high and the effective tunneling mass large.[4,7] This implies that the tunneling splitting for inversion $\Delta E_{\pm}$ in the symmetrical potential is smaller than the parity violating energy difference between enantiomers $\Delta_{pv}E$, a new, intriguing effect, which has not been proven experimentally, so far. For such molecules an experimental scheme has been suggested, which consists in using an intermediate state of well-defined parity,[8] and recent work indicates that an ideal route might be to use infrared excitation to such a state in molecules with modest barriers.[9,10]

In this context we have initiated an *ab initio* study of nitroxide radicals, as their electronic open shell structure may provide additional, possibly favorable aspects compared to closed shell molecules.[11,12] Of course, the stable free nitroxide radicals have also more general, well known chemical interest and application.[13,14] We report here results from *ab initio* calculations for three different groups of persistent nitroxide radicals:

i) acyclic:[15–18] dimethylaminoxyl $(CH_3)_2NO$, bis(trifluoromethyl)aminoxyl $(CF_3)_2NO$, and di-*tert*-butyl nitroxyl [$(Me_3C)_2NO$];
ii) cyclic:[19–21] aziridine-N-oxyl, azetidine-N-oxyl, pyrrolidine-N-oxyl and piperidine-N-oxyl;
iii) imino nitroxides[22] (INN)

The first two classes are relatively well known nitroxide radicals, except for aziridine-N-oxyl, and azetidine-N-oxyl, which have not yet been synthesized. Pyrrolidine-N-oxyl and piperidine-N-oxyl serve as building blocks for numerous NO-radicals. The synthesis of the last mentioned class has been suggested recently, in an attempt to introduce chiral radicals exhibiting special magnetic properties and with the hope to develop materials with the additional magneto-optical effects.[23]

2. Computational Methods

The zeroth-order descriptions of the ground states of the molecules studied were obtained using the one-configuration SCF (unrestricted Hartree-Fock or restricted open-shell Hartree-Fock) wavefunctions. Correlation effects were included employing density functional calculations, MP2[24] methods and coupled cluster theory with singles and doubles (CCSD),[25,26] along with perturbative inclusion of triple excitations [CCSD(T)][27–29] methods. The density functional calculations were performed using the B3LYP density functional, which is a generalized gradient approximation and employs the dynamical correlation functional of Lee, Yang, and Parr[30] in conjunction with the Becke's three-parameter HF/

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DFT hybrid exchange functional (B3).[31] Only the valence electrons were correlated, but all virtual orbitals were included in the theoretical treatments. Series of correlation-consistent (cc-pVDZ, cc-pVTZ) and augmented correlation-consistent (aug-cc-pVDZ, aug-cc-pVTZ) basis sets of Dunning and co-workers[32–34] were used. The so-called EPR II and EPR-III[35] basis sets were used to obtain the hyperfine coupling constants. All computations were performed with the local versions of Gaussian 03[36] and Molpro[37] suite of programs. Using these techniques, the total energies, equilibrium geometries, transition state properties and harmonic vibrational frequencies were determined for the molecules studied.

3. Results and Discussion

The optimized r_e structures of the molecules studied are shown in Fig. 1. No symmetry constraints were assumed prior to the optimizations, but the global minimum found with the MP2 or DFT methods were used as the starting geometries for the relatively expensive optimizations with the CCSD(T) method. No such optimizations were carried out for the imino nitroxides, and for $(CF_3)_2NO$, and $(Me_3C)_2NO$. Table 1 gives a summary of some of the main structural parameters – namely, the lengths r_e of N−O, and C−N bonds; the C-N-C angle; and the C-C-N-O dihedral angle. Further, we include in Table 1 energies of the NO inversion barriers. These were, except for the imino nitronyls, computed as single points at the CCSD(T)/cc-pVTZ level of theory.

The dimethylaminoxyl $[(CF_3)_2NO]$ is found to adopt a pyramidal geometry in its X ^{2}A' ground state with a NO out-of-plane angle τ of 22.3°. The planar structures with C_s or C_{2v} symmetries were confirmed to be the second order saddle point and the transition state. The NO inversion barrier E_{inv} is hc 464 cm^{-1}. The global minimum of the bis(trifluoromethyl)aminoxyl $[(CF_3)_2NO]$ has no symmetry (C_1 point group, and ground state X ^{2}A) when fully optimized at the MP2/cc-pVTZ and aug-cc-pVTZ level of theory, contrary to earlier experimental results which imply[18] the most stable configuration to be planar at the N-atom with C_{2v} symmetry. The NO out-of-plane angle τ is slightly smaller 14.1° than for $(CH_3)_2NO$, but the inversion barrier is substantially reduced (E_{inv} = hc 136 cm^{-1}). However, the experimentally established[18] NO stretching fundamental $\nu(NO)$ = 1397 cm^{-1} compares well with the computed harmonic wavenumber $\omega(NO)$ = 1417 cm^{-1}. The C_s structure (with O, N, two C, and two F atoms in the symmetry plane) is found to be a transition state for the NO inversion, and the structure of C_{2v} symmetry is the second order saddle point. An example
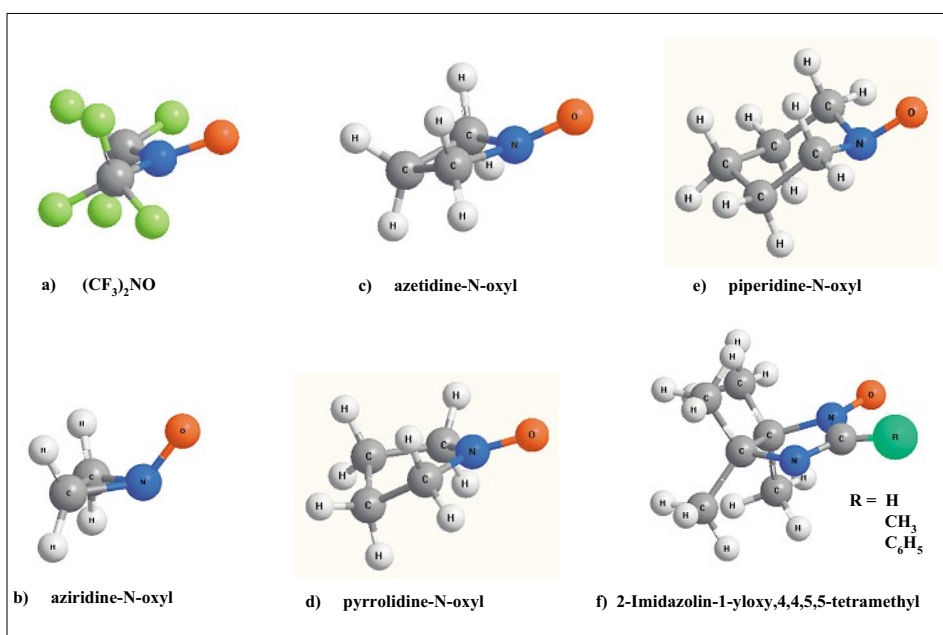

Fig. 1. Scheme of the optimized structures of (a) bis(trifluoromethyl)aminoxyl $(CF_3)_2NO$, (b) aziridine-N-oxyl, (c) azetidine-N-oxyl, (d) pyrrolidine-N-oxyl, (e) piperidine-N-oxyl, (f) imino nitroxide

Table 1. Main geometrical parameters (bond lengths r_e in pm, bond angle α(CNC) and dihedral angle τ(CNCO) in deg) and energy barriers E_{inv} (in hc cm^{-1}) of the nitroxide radicals studied. The structures were optimized at the MP2/cc-pVTZ and CCSD(T)/cc-pVTZ levels of theory

	r_e(NO)	r_e(CN)	α(CNC)	τ(CNCO)	E_{inv}
$(CH_3)_2NO$	126.4	144.6	119.0	22.3	464
$(CF_3)_2NO$	125.2	145.9	120.4	14.1	136
$(Me_3C)_2NO$	128.0	151.6	128.0	19.9	404
aziridine-N-oxyl	127.6	145.5	63.4	63.9	3500
azetidine-N-oxyl	125.6	148.1	94.2	13.8	498
pyrrolidine-N-oxyl	126.5	146.4	113.1	0.0	0
piperidine-N-oxyl	126.9	146.0	117.5	13.3	454
H-INN	126.4	148.5	108.7	8.8	370
CH_3-INN	126.5	149.7	109.3	9.9	345
benzene-INN	126.7	147.0	109.0	9.1	353

for a stable nitroxide radical is di-*tert*-butyl nitroxyl $[(Me_3C)_2NO]$ with X ^{2}A ground state, which exhibits the longest NO bond (r_e = 128.0 pm) and the largest C-N-C angle ($\angle$ CNC = 128.0°) of all molecules studied here as a consequence of adopting a geometry of minimal steric repulsion. The inversion barrier of hc 404 cm^{-1} is comparable to that of $(CH_3)_2NO$. The computed harmonic stretching wavenumber $\omega(NO)$ = 1579 cm^{-1} at the MP2/cc-pVDZ level of theory is well off the measured[15] fundamental $\nu(NO)$ = 1345 cm^{-1}. This might be due to anharmonic effects or a larger basis set has to be employed and the geometry reexamined.

Despite of the numerous experimental studies establishing[38–43] the structure of nitroxide radicals with five-membered

and six-membered rings derived from pyrrolidine-N-oxyl and piperidine-N-oxyl, experimental evidence for the existence of cyclic aziridine-N-oxyl and azetidine-N-oxyl is lacking. We obtained X ^{2}A' ground state of aziridine-N-oxyl with the considerable NO out-of-plane angle τ = 63.9°, and a substantial inversion barrier of hc 3500 cm^{-1}. The NO bond length is slightly longer and the CN bond slightly shorter when compared with the other cyclic aminoxyls. The azetidine-N-oxyl exhibits τ = 13.8°, very similar to the out-of-plane NO angle τ = 13.3° of piperidine-N-oxyl, which has a chair conformation with a pyramidal geometry for the nitrogen atom, and an equatorial NO-bond. The inversion barrier for both species is $E_{inv} \approx$ hc 500 cm^{-1}. The only compound among the cyclic aminoxyls

with a planar equilibrium geometry at the nitrogen atom is the pyrrolidine-N-oxyl. The different structure of the aziridine-N-oxyl compared to the other cyclic aminoxyls is not the only peculiar feature of this molecule. As shown in the Table 2, which lists the adiabatic (AEA) and vertical electron affinities (VEA), and the vertical ionization potentials (VIP), this molecule is the only one to form a stable anion with AEA = 8600 hc cm^{-1} (1.07 eV).

Further, we report some main geometrical parameters (Table 1) of chiral imino nitroxides (see also Fig. 1) with three different substituents on the carbon atom, R= H, CH$_3$, and C$_6$H$_5$. We find for example that the phenyl substituent stays in the N-C-N plane (dihedral angle = 0°), different substituents do not seem to affect the imidazolyl ring. More interestingly, unlike in the case of pyrrolidine-N-oxyl, the NO out-of-plane τ angle is small (τ ≈ 9°), but not zero, with a very small inversion barrier of E$_{inv}$ ≈ hc 350 cm^{-1}. A general trend for all molecules studied has been that with the increase in size of the basis set and the introduction of more highly correlated methods, the NO bond length shortens by ≈ 2 to 3 pm, and the barrier heights of NO inversion are lowered.

Since it appears that the vibrational spectra of nitroxides have not been extensively studied so far, we list the harmonic vibrational frequencies computed for the cyclic aminoxyls in Table 3. Particularly, we point again to the ν(NO) stretching fundamental, which is relatively weak in both the IR and Raman spectra and poorly understood. It is mostly believed (see the results above for the acyclic aminoxyls) that ν(NO) lies between 1310–1380 cm^{-1}. Recently, Rintoul *et al.*[44] reported a band position of 1,1,3,3-tetramethylisoindolin-2-yloxyl (TMIO) to be at 1431 cm^{-1} in the solid phase – outside of the usual range. For the smaller cyclic aminoxyls investigated in our study we found that ω(NO) = 1399 cm^{-1} for aziridine-N-oxyl, ω(NO) = 1661 cm^{-1} for azetidine-N-oxyl, ω(NO) = 1595 cm^{-1} for pyrrolidine-N-oxyl, and ω(NO) = 1587 cm^{-1} for piperidine-N-oxyl. In the case of imino nitroxides, regardless of the substituent, one has ω(NO) = 1460 to 1470 cm^{-1}; namely, for R$_1$ = H, ω(NO) = 1472 cm^{-1} for R$_2$ = CH$_3$, ω(NO) = 1461 cm^{-1}, and for R$_3$ = C$_6$H$_5$, also ω(NO) = 1461 cm^{-1}. Thus, all of the predicted ω(NO) stretching wavenumbers are considerably shifted away from the usually assumed position.

The most frequently used tool to characterize the properties of nitroxide radicals (or free radicals in general), to detect and identify them, is electron paramagnetic resonance (EPR). Therefore, finally, we report the isotropic hyperfine coupling constants (hcc) of the molecules investigated in Table 4 as computed with the B3LYP functional and MP2 method combined with the EPR-II and EPR-III basis sets. Various effects – electronic, geometry, substituents or environment, determining the hyperfine coupling constants, have been extensively discussed in the literature.[45] In a simple picture, the nature of the singly occupied molecular orbital (SOMO), bearing the unpaired electron, and having the largest influence on the magnetic properties of the molecule, and the geometry, suffices to explain the contributions to the hcc values.

Table 2. Adiabatic electron affinities (AEA), vertical electron affinities (VEA), and vertical ionization potential (VIP) in hc cm^{-1} of cyclic aminoxyl radicals computed at CCSD(T)/cc-pVTZ level of theory

	AEA	VEA	VIP
aziridine-N-oxyl	8600	4885	71890
azetidine-N-oxyl	3690	-1010	63580
pyrrolidine-N-oxyl	-4200	-8776	58900
piperidine-N-oxyl	210	-742	60970

Table 3. Harmonic vibrational wavenumbers (in cm^{-1}) of cyclic aminoxyls radicals computed at the MP2/cc-pVTZ level of theory

aziridine-N-oxyl	ω(a') =	[372, 758, 793, 1072, 1136, 1146, 1399, 1505, 3153, 3269]
	ω(a'') =	[480, 883, 1028, 1114, 1174, 1482, 3151, 3258]
azetidine-N-oxyl	ω(a') =	[122, 209, 672, 758, 891, 1006, 1113, 1197, 1300, 1499, 1521, 1661, 3097, 3145, 3165, 3216]
	ω(a'') =	[428, 813, 948, 1056, 1141, 1235, 1267, 1270, 1496, 3093, 3167]
pyrrolidine-N-oxyl	ω(a) =	[178, 265, 335.449, 587, 599, 792, 888, 901, 915, 954, 1001, 1038, 1130, 1185, 1200, 1213, 1253, 1297, 1339, 1356, 1370, 1379, 1515, 1516, 1526, 1536, 1595, 2921, 2923, 2946, 2952, 3003, 3004, 3013, 3020]
piperidine-N-oxyl	ω(a') =	[191, 361, 425, 453, 605, 771, 860, 913, 1029, 1049, 1176, 1297, 1305, 1383, 1401, 1503, 1510, 1521, 1587, 2909, 2931, 2947, 2995, 3004, 3041]
	ω(a'') =	[290, 438, 490, 853, 923, 1000, 1088, 1142, 1184, 1289, 1312, 1367, 1395, 1399, 1502, 1508, 2906, 2947, 3001, 3040]

Table 4.: Nitrogen N hyperfine coupling constants (in MHz), nitrogen and oxygen atomic Mulliken[46] spin densities

	B3LYP/ EPR-II	B3LYP/ EPR-III	MP2/ EPR-II	MP2/ EPR-III	spin density N	spin density O
(CH$_3$)$_2$NO	32.7	36.8	50.6	47.7	0.56	0.41
(CF$_3$)$_2$NO	18.1	19.0	29.0	27.9	0.37	0.62
(CMe$_3$)$_2$NO	33.0	36.9	51.9	51.0	0.41	0.54
aziridine-N-oxyl	81.7	82.2	98.6	99.1	0.42	0.53
azetidine-N-oxyl	34.0	34.8	49.3	46.1	0.51	0.44
pyrrolidine-N-oxyl	23.7	24.8	40.2	36.3	0.54	0.40
piperidine-N-oxyl	34.0	34.8	52.0	49.2	0.55	0.42
H-INN	15.1	16.0	15.1	13.5	0.33	0.48
CH$_3$-INN	16.6	17.4	18.1	14.5	0.33	0.50
benzene-INN	15.9	16.4	15.2	14.9	0.28	0.50

4. Conclusions

We report here exploratory and still preliminary results on dynamical and spectroscopic properties of selected nitroxide radicals. Three different groups of nitroxide radicals were examined and characterized. The study shows a rich variety of properties even within a such small pool of molecules. However, we conclude that very small activation energies are needed for the inversion by out-of-plane motion of the NO group for all of the molecules studied, apart from the aziridine-N-oxyl, which has a relatively high inversion barrier of hc 3500 cm^{-1}. Chiral derivatives of this molecule should be of particular interest for a study of molecular parity violation following the scheme of [8] with infrared excitation above the barrier.[9] While we cannot report at this stage definitive values for the parity violating energy difference of the corresponding enantiomers in relation to the inversion tunneling splittings, one can safely assume by comparison with ClOOCl that also the chirally substituted aziridine-N-oxyls will be dominated by parity violation and thus would be very appropriate candidates for such experiments.

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