Spectroscopic features of the low-lying singlet states of some *N*-alkyl retinylnitrone model systems and their involvement in oxaziridine formation

Supporting Information

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Non-planar B_1 and B_2 geometries from PM3/CI

The planar geometry of S_1 obtained (not shown) at this semiempirical PM3/CI level of treatment has a long C5-N bond. An interesting situation arises as we give an optimization run on this planar excited state geometry using with and without biradical options as the keyword in the input file. In both the cases the geometry deviates from planarity, but in different ways giving two stable non-planar states at lower energy level than the initial planar state. The non-planar forms are characterized by a turn of the N-O bond away from the plane of the molecule; however, there are some differences in the geometries obtained from without biradical (**B_1**) and with biradical (**B_2**) run. In the non-biradical case, there is no significant turn of the C5-H bond, where only the N-terminal part (N-O bond) of the C5=N azomethine bond is found to be rotated by 90^0, while the rest of the system almost remains in the initial plane. The distance between the carbon (C5) and oxygen is quite large in this geometry. On the other hand, in the **B_2** species, simultaneous twists in the C3-C4-C5-N and C4-C5-N-O dihedral angles are noticed, resulting in a shorter C5-O distance (2.28 Å). The above mentioned nature of **B_1** and **B_2** is found to be more or less valid for both the studied systems.

The significant point to be noticed in the ESP-derived atomic charges (Table S1) is the lowering of the negative charge on oxygen as we move from ground state to the planar excited state, which continues to decrease in the **B_1** and **B_2** forms. This initial electronic transfer from oxygen to nitrogen can be noticed in both the systems. A decrease in the size of the non-bonded electron cloud can be seen on oxygen (Figure 3) as we go from HOMO to LUMO in these

systems, which supports this electronic transfer process. The origin of the $\mathbf{B_1}$ form is possibly due to a heterolytic cleavage of the C5-N pi bond leading to an ionic charge separation. On the other hand, the charges on the $\mathbf{B_2}$ species are clearly more in favour of a biradical mechanism. The latter form can be thought of arising due to a homolytic pi bond breaking between the carbon (C5) and nitrogen. The $\mathbf{B_2}$ form is likely to have a lone pair on nitrogen, an odd electron on C5 and a reduced electronic cloud on oxygen.

Table S1. Atomic charges determined from the Electrostatic potential at PM3/CI level

System	Atom	Ground State	Planar excited state	Non-planar $\mathbf{B_1}$ state	Non-planar $\mathbf{B_2}$ state
I	C(5)	-0.5363	-0.5731	-1.1853	-0.3221
	N	0.8584	0.8482	1.2114	0.5141
	C(7)	-0.4954	-0.5026	-0.6119	-0.3269
	O	-0.5248	-0.4695	-0.3691	-0.4458
II	C(5)	-0.5902	-0.6603	-1.1681	-0.3433
	N	0.7609	0.7853	1.1321	0.4731
	C(7)	-0.0173	-0.0558	-0.1660	-0.0093
	O	-0.4987	-0.4372	-0.3446	-0.4338

MOs (described in Sec. 3.2b)

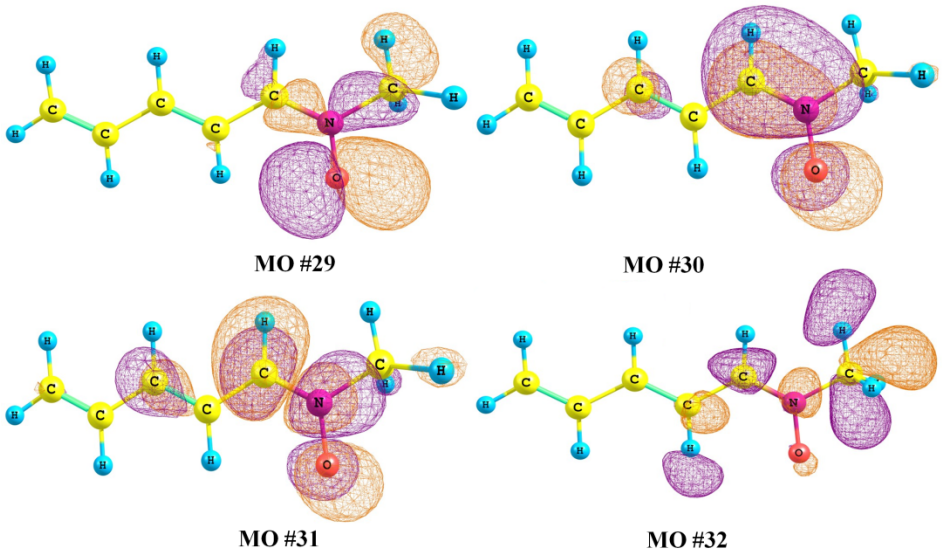
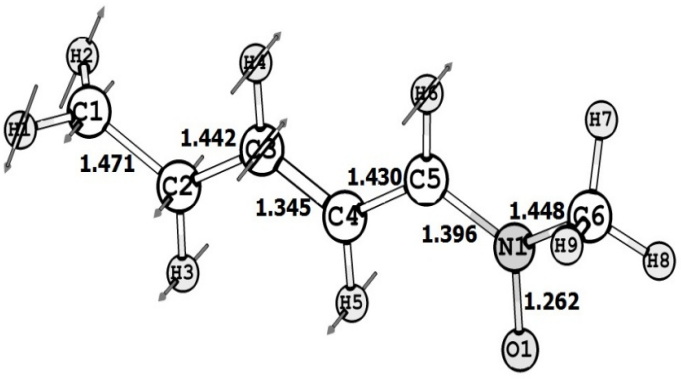


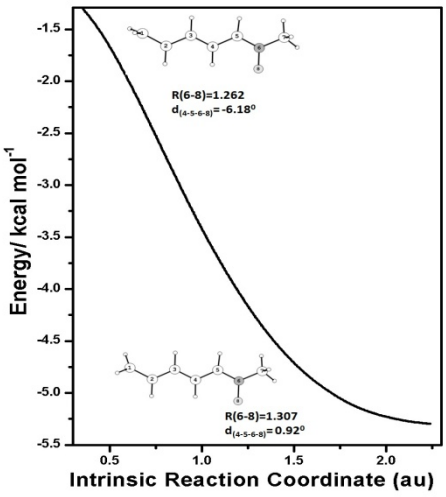
Fig. S1. MOs involved in the (4, 4) active space in CASSCF/6-31G* calculations for the methyl nitrone system

Transition states (TS_1, TS_2, TS_3)

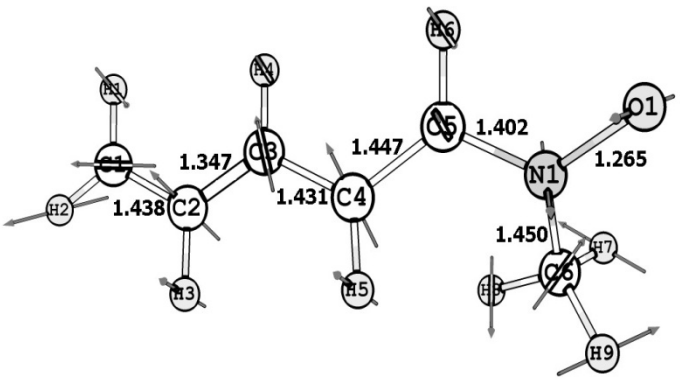
In search of transition states we have initially applied the QST2 optimization using the optimized excited state and the conical intersection geometries. In this method, we have obtained a transition state ($\mathbf{TS_1}$) between the $\mathbf{CI_2}$ and the relaxed excited state (**A**) which resembles the latter geometry (Figure S1a). The initial motion along the transition state is described by the transition vector related to the imaginary vibrational frequency; this frequency corresponds to the intrinsic reaction path. It has been tested that the obtained transition state ($\mathbf{TS_1}$) goes towards the relaxed excited state geometry along the intrinsic reaction coordinate. No transition state has been located between the relaxed excited state and the $\mathbf{CI_1}$/$\mathbf{CI_3}$ geometries in the QST2 method. Two more transition states have been detected on the excited state surface, namely $\mathbf{TS_3}$ and $\mathbf{TS_2}$, by using the normal TS optimization (Figures S1b and S1c) on the relaxed planar excited state (**A**) and slightly non-planar guess geometries, respectively. It is found that in the methyl nitrone system the barrier height from the excited state minimum to $\mathbf{TS_1}$ is 6.7 kcal /mol, while in the case of $\mathbf{TS_2}$, this is roughly 2.5 kcal /mol. The planar $\mathbf{TS_3}$ is very close (0.5 kcal/mol) to the relaxed excited state (**A**) energy.

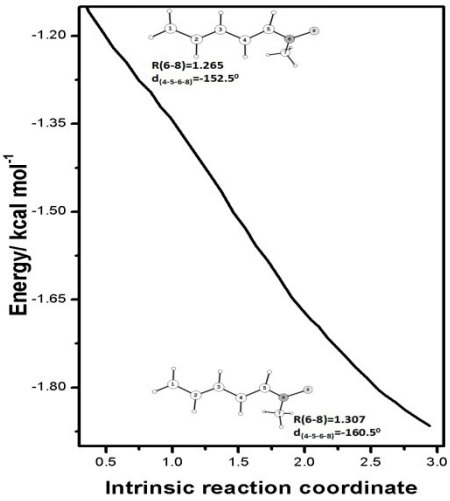
(a) $\mathbf{TS_1}$ with displacement vectors



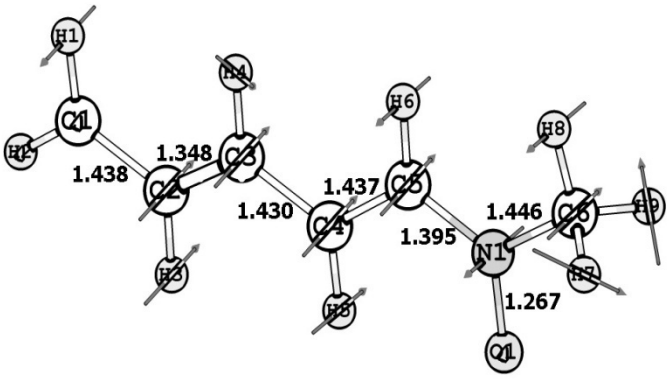


(b) **TS_2** with displacement vectors





(c) **TS_3** with displacement vectors



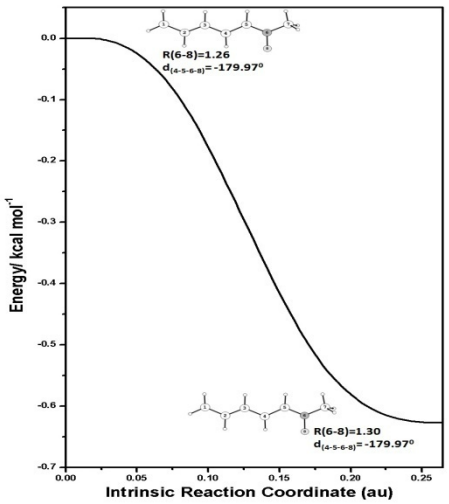


Fig S2. Excited state transition states **(a) TS_1 (b) TS_2 (c) TS_3** of system **I** with the displacement vectors corresponding to their imaginary frequencies and plots of minimum energy path along the intrinsic reaction coordinate from these transition states. [$d_{(4\text{-}5\text{-}6\text{-}8)}$ indicates <C4-C5-N-O torsion angle, R(6-8) indicates N-O bond length]