Finally we note that the CNDO/2-NO-CI parametric scheme does a pretty good job of estimating rotational barriers in small molecules. The INDO-NO-CI results are less good and the CNDO/S parameters are not useful for calculating rotational barriers (Table VI). In cases where the SCF process very nearly produces the dominant configuration, the CNDO/2-NO-CI will offer little improvement, but where alternate low-energy configurations are available (delocalization) the natural orbital CI should offer improved electronic structure interpretations.

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Nonempirical Calculations on the Conformation and Hyperfine Structure of the Nitroxide and Ketyl Groups. Consequences of Out-of-Plane Bending on Hyperfine Interactions

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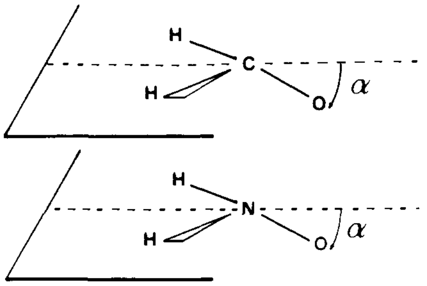
Abstract: Nonempirical calculations of the ground-state energy and hyperfine coupling constants of the isoelectronic H_2NO and H_2CO^- radicals are performed using the spin-restricted SCF method and first-order perturbation theory. It is shown that the nitroxide functional group does not possess a well-defined intrinsic geometry, in agreement with experiment. The equilibrium geometry found for the ketyl is nonplanar, with an out-of-plane angle of 24-27° and close to that of the excited $(n-\pi^*)$ neutral molecule. The nitrogen and carbon-13 splittings are positive and increase with the out-of-plane torsion at the radical site.

Nitroxides are one of the most remarkable series of free radicals,[2a] the interest of which has grown in recent years as a consequence of their extensive use for biological studies. Esr measurements in spin-label experiments[2b] are generally interpreted on the assumption of a planar radical site in spite of the fact that the nitroxide group is known to exist in both planar[3] $(\alpha = 0^\circ)$ and bent[4] $(\alpha \neq 0^\circ)$ geometries. On the other hand, the question of the geometry around the radical carbon in the isoelectronic ketyl series has recently been the object of both experimental[5] and theoretical[6] investigations.



This prompted us to investigate the conformation and hyperfine structure of the nitroxide and ketyl groups in the simple H_2NO and H_2CO^- radicals using *ab initio* quantum mechanical methods. The calculation of the ground-state electronic wave function, energy, and hyperfine splittings was performed using the spin-restricted LCAO-SCF method of Roothaan.[7,8] A configuration interaction including all spin-adapted monoexcited configurations with three uncoupled electrons was then carried out using perturbation theory.[9] Under those conditions, the total energy is given by

$$E = E_{\mathrm{SCF}} + E_{\mathrm{sp}} \tag{1}$$

with

$$E_{\mathrm{sp}} = \sum_{\mathrm{d}}\sum_{\mathrm{v}^*}\frac{3}{2}\frac{\langle\phi_{\mathrm{d}}\phi_{\mathrm{u}}/\phi_{\mathrm{u}}\phi_{\mathrm{v}^*}\rangle^2}{E_0 - E_{\mathrm{d}\to\mathrm{v}^*}} \tag{2}$$

The total hyperfine splitting of nucleus M is

$$a_{\mathrm{M}} = a_{\mathrm{d}} + a_{\mathrm{sp}} = (8\pi/3)(g_{\mathrm{e}}/g_0)g_{\mathrm{M}}\beta_{\mathrm{M}}(\rho_{\mathrm{d}} + \rho_{\mathrm{sp}}) \tag{3}$$

with

$$\rho_{\mathrm{d}} = |\phi_{\mathrm{u}}(\mathbf{r}_{\mathrm{M}})|^2$$

$$\rho_{\mathrm{sp}} = \sum_{\mathrm{d}}\sum_{\mathrm{v}^*} - 2\frac{\langle\phi_{\mathrm{d}}\phi_{\mathrm{u}}/\phi_{\mathrm{u}}\phi_{\mathrm{v}^*}\rangle}{E_0 - E_{\mathrm{d}\to\mathrm{v}^*}}\,\phi_{\mathrm{d}}(\mathbf{r}_{\mathrm{M}})\phi_{\mathrm{v}^*}(\mathbf{r}_{\mathrm{M}}) \tag{4}$$

In these equations, E_{sp} and ρ_{sp} are the energy correction and spin density arising from spin-polarization effects respectively. The ϕ_{d} are the doubly occupied MO's of the ground-state, the ϕ_{v^*} are the associated virtual MO's, and ϕ_{u} is the singly occupied orbital, responsible for the delocalization spin density ρ_{d}.

Two basis sets of Gaussian-type orbitals were used. Basis I was composed of (7s,3p/3s) functions[10] contracted to (3s,2p/1s). Basis II was built from basis I by adjunction of d orbitals on first-row atoms (C, N, O) and p orbitals on hydrogens[11] (3s,2p,1d/1s,1p).

Basis I. H_2NO. Starting with an approximate geometry,[12] the bond lengths (NO,NH) and bond angle (HNH) were successively varied in a cyclic procedure until a minimum in energy was located for the planar form (NO = 1.34 Å; NH = 1.00 Å; HNH = 123°). The introduction of out-of-plane geometrical parameters confirmed the stability of the planar structure. However, there is only a 0.6 kcal difference between α = 0 and 30° (Table I).

H_2CO^-. The initial geometry was adapted from the parent neutral molecule[13] except for the CO bond length which has been taken as 1.34 Å by analogy with H_2NO. The bond length and bond angles were varied in turn using the same cyclic procedure until the total energy was minimized. This point was achieved for a pyramidal structure (CO = 1.33 Å; CH = 1.09 Å; HCH = 117°5′; α = 24°). The computed inversion barrier is 0.446 kcal (156 cm^{-1}) as shown in Table II.

Basis II. H_2NO. Starting with the above geometry, the same process of optimization led to a pyramidal equilibrium form (NO = 1.27 Å; NH = 1.00 Å; HNH = 123°; α = 17°). The inversion barrier is then 0.064 kcal (22 cm^{-1}).

Table I. Total Energies of H_2NO (au)

	α, deg	E_{SCF}	$E_{\mathrm{SCF}} + E_{\mathrm{sp}}$
Basis I	0	−130.027677	−130.035687
	30	−130.026646	−130.034443
Basis II	0	−130.125392	−130.140818
	17	−130.125494	−130.140843
Basis III	0	−126.59425	
	26°22′	−126.59477	
		−126.5973[a]	

[a] UHF calculation.

Table II. Total Energies of H_2CO^- (au)

	α, deg	E_{SCF}	$E_{\mathrm{SCF}} + E_{\mathrm{sp}}$
Basis I	0	−113.465440	−113.475202
	24	−113.466150	−113.475691
Basis II	0	−113.531012	−113.544414
	27	−113.532407	−113.546823

At this stage, it is of interest to mention (Table I) that a previous unrestricted SCF calculation[14] of H_2NO using a noncontracted basis of a rather limited size (3s,2s,2p) led to a pyramidal equilibrium geometry (NO = 1.32 Å; NH = 0.99 Å; HNH = 116°25′; α = 26°22′). Using the same basis set (basis III) in the present restricted SCF formalism, we found that, all other parameters unchanged, their pyramidal form was lower than the planar one by 0.326 kcal (114 cm^{-1}). Therefore, the structure found for the radical site is independent of the UHF or RHF formalism but highly sensitive to the basis. The NO bond length of 1.34 Å (basis I, RHF) or 1.32 Å (basis III, UHF) reduces to a value of 1.27 Å (basis II, RHF) in fair agreement with experiment.[3,4] This suggests that polarization functions which spread far from the NO axis give a better description of the singly occupied antibonding orbital and consequently of the nitroxide group.

H_2CO^-. Starting with the above geometry, reoptimization of bond lengths and angles has led to a quite similar pyramidal form (CO = 1.30 Å; CH = 1.09 Å; HCH = 116°5′; α = 27°). The inversion barrier is then 0.875 kcal (306 cm^{-1}).

The preceding results are not significantly modified when adding the energetical corrections given by the first-order perturbation treatment[15] to the SCF values (Tables I and II). Introduction of polarization functions leads to a small shortening in the CO bond length, the structure found for the radical site being much less sensitive to the basis in the ketyl than in the nitroxide.

In either event, the potential energy curve is very flattened around the α = 0° position for the nitroxide and the inversion barrier, if any, is undoubtedly of the same order of magnitude as the zero point vibrational energy of the out-of-plane vibration. Therefore, a precise determination of α in H_2NO appears to be somewhat speculative. By contrast, the depth of the energetical well for the ketyl and the related inversion barrier are more significant, so that a pyramidal structure can be reasonably expected for H_2CO^-.

Both radicals, in their pyramidal forms, are described by the electron configuration

$$(1a')^2(2a')^2(3a')^2(4a')^2(1a'')^2(5a')^2(6a')^2(2a'')^2(7a')\ (C_s)$$

It should be added that there is only one more electron in the 2a″ level, essentially nonbonding at the oxygen, compared with the lowest excited (n-π*) singlet or triplet states of formaldehyde. Interestingly, the geometrical parameters and inversion barrier determined here for H_2CO^- are in close concordance with experimental findings[16] and theoretical calculations[17] on excited H_2CO. This is in agreement with Walsh predictions on H_2AB molecules[18] and supports

Subra et al. / Conformation and Hyperfine Structure of H_2NO and H_3CO^- Radicals

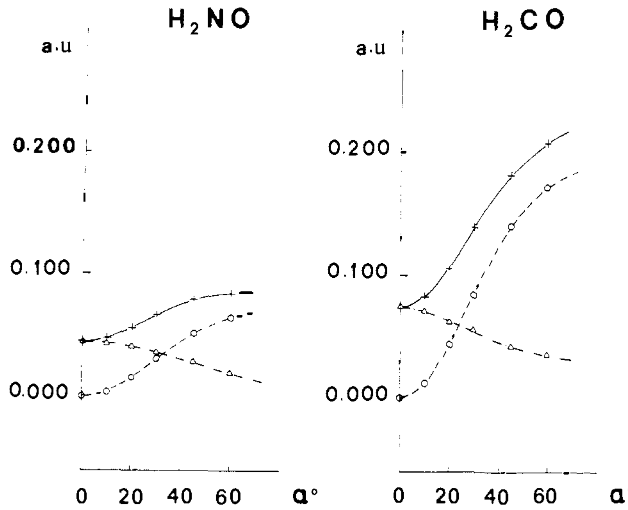


Figure 1. Nitrogen and carbon-13 spin densities; a_N (G) = 115.3ρ (au), a_C (G) = 401ρ (au); delocalization contribution (O), spin-polarization contribution (△), total spin density (+).

the common assumption according which n electrons have a minor influence on the molecular geometry.

For the equilibrium geometries, the computed splittings (basis II) are $a_N = +6.09$ G, $a_O = -41.70$ G, $a_H = -8.94$ G for H$_2$NO, the experimental values being[19] $|a_N| = |a_H| = 11.9$ G, and $a_C = 51.31$ G, $a_O = -17.30$ G, $a_H = -11.27$ G for H_2CO^-, the experimental values being[5g] $|a_C| = 37.68$ G, $|a_H| = 14.26$ G.

All our results are correct in sign, as compared to available experimental data.[5d,20] They are in good agreement with the observed values, especially for H_2CO^-, if one considers the high sensitivity of a_C to out-of-plane distorsions as illustrated by the variation of spin densities reported below. In assessing the quality of agreement with experiment, it should be kept in mind that a large basis set and rather extensive configuration interaction are required in order to obtain convergence of the hyperfine splittings,[21] especially for nitrogen.[22]

Nevertheless, the comparative evolution of the nitrogen and carbon-13 hyperfine splittings with α is illuminating (see Figure 1).

Both direct and indirect spin densities are positive. The net lowering of spin polarization as α increases is completely overwhelmed by the delocalization contribution. The most striking feature of these curves is the higher amplitude of the variation of a_C compared with that of a_N. This can be simply apprehended by inspecting the distribution of spin populations, which are often identical with spin densities ρ^π in semiempirical estimations, in the equilibrium geometries of H$_2$NO ($\rho_N{}^\pi = 0.24$; $\rho_O{}^\pi = 0.76$) and H_2CO^- ($\rho_C{}^\pi = 0.63$; $\rho_O{}^\pi = 0.33$).[23] The difference between these two isoelectronic compounds is that the unpaired electron is mainly located on the central atom in the ketyl group, contrary to the nitroxide group. This is responsible for the strong sensitivity of a_C to geometrical changes at the radical site. Thus we would anticipate an increase in a_N and a_C with the out-of-plane bending.

These *ab initio* calculations clearly show the similarity of the isoelectronic ketyl and nitroxide radicals. They throw some light on the large variety of geometries and a_N found in nitroxides. They clearly show that the nitroxide functional group does not possess a well-defined intrinsic geometry, as the rigid carbonyl group does, for instance. So, the conformation at the radical site, the inversion barrier, and the nitrogen coupling will be critically dependent on the molecular framework.[24] Nitrogen inversion studies in closed shell molecules have provided similar conclusions.[25] They also suggest that the ketyl functional group should be nonplanar. The value of the out-of-plane distorsion at the radical site, the inversion barrier, and, of course, the a_C coupling constant would be expected to depend to some extent on surrounding interactions.

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(23) Spin populations are normalized to unity. The deviation to unity appearing for H_2CO^- represents the delocalization on the two hydrogens.

(24) See, for example, 2,2,6,6-tetramethyl-4-piperidone-1-oxyl[3a] (CNC =

123°5′; α = 0°; a_N = 15.15 G), 2,2,6,6-tetramethyl-4-piperidinol-1-oxyl[4a] (CNC = 125°4′; α = 15°8′; a_N = 16.05 G), 2,2,6,6-tetramethylpiperidine-1-oxyl[4b] (CNC = 125°5′; α = 19°4; a_N = 16.30 G), *cf.* R. Briere, H. Lemaire, and A. Rassat, *Bull. Soc. Chim. Fr.*, 3273 (1965); 2,2,5,5-tetramethyl-3-pyrrolidone-1-oxyl azine[3c] (CNC = 112°; α = 0°; a_N = 14.27 G), *cf.* R. M. Dupeyre and A. Rassat, *J. Amer. Chem. Soc.*, **87,** 3771 (1965); 9-aza-bicyclo[3.3.1]nonan-3-one-1-oxyl (CNC = 114°2′; α = 30°1′, a_N = 17.55 G), *cf.* R. M. Dupeyre and A. Rassat, *J. Amer. Chem. Soc.*, **88,** 3180 (1966).

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On Avoided Surface Crossings

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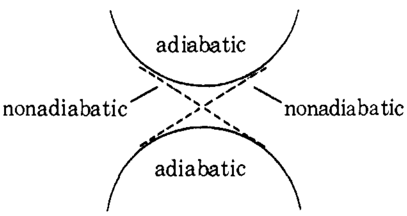
Abstract: A classification of avoided surface crossings relevant to organic chemistry is proposed. Four different types (A, B, C, and D) are defined. An "intermediate" Hamiltonian technique is introduced for describing appropriately the avoided-crossing region between a closed-shell surface and an open-shell surface. The gap size for avoided crossings near a symmetry-allowed crossing is shown to be proportional to the transition force between the two neighboring states.

Surface crossings, whether real or intended, are playing an increasingly important role in the interpretation of organic phenomena. It is well known that in Woodward–Hoffmann thermally forbidden reactions, there is an intended crossing between the ground-state surface and the surface for the doubly-excited state.[3] More recently the photochemical Norrish type II process has been shown to involve an intersection between the energy surface for excited reactant and that for ground reactant.[4] A similar surface crossing occurs in other major photochemical reactions.[4] Certain organic transients have two neighboring singlet surfaces with intersections and near-intersecting regions.[5] Our purpose here is not to deal with rigorously allowed intersections between electronic states. The theory of these crossings is well established.[6] Our intention is to bring to light the different types of "intended" or "avoided" crossings between states of the same spin multiplicity. In certain instances the avoided crossing occurs near a real crossing. In other cases the "intention" to cross is unknown to the real surfaces; the crossings are due to an approximate starting description of the wave functions for the two neighboring surfaces.

The first part of this paper contains a classification of the different types of avoided crossings which are known. In the second part of our work we introduce a method which allows for proper calculation of the neighboring surfaces in an avoided crossing region. Finally, in the third section, we demonstrate a simple law for the energy gap when a rigorously allowed crossing is destroyed concomitant to the destruction of a symmetry plane. The manner in which this gap varies with nuclear geometry is emphasized.

A Classification of Avoided Surface Crossings

A useful study of certain avoided crossings and of the appropriate terminology has been given by O'Malley.[7] The familiar distinction is made between stationary *adiabatic* states, which diagonalize the electronic Hamiltonian, and whose surfaces would be followed by slowly moving nuclei, and *nonadiabatic* (or diabatic) states for which the total electronic Hamiltonian is not diagonal. An avoided-crossing situation arises when the nonadiabatic surfaces intersect but when this intersection disappears by inclusion of the remaining off-diagonal terms



We have been able to distinguish between four types of avoided surface crossings, The first type (A) occurs *in the neighborhood of a true crossing of electronic states.* The other types (B, C, D) originate from "incorrect," nonadiabatic starting electronic wave functions, which are useful in that they are a good initial basis for discussing the "correct," adiabatic, surfaces. *In these cases a physical crossing never occurs.*

In the first case the previously *adiabatic* states and surfaces, which described correctly a physically correct intersection in one region of multidimensional space (C_s symmetry), become *nonadiabatic* when they are carried over into those regions of multidimensional space where the crossing is forbidden (C_1 symmetry). However, they again serve as a useful starting point for the study of the new, avoiding, adiabatic states in this region of space.

Type A. Neighborhood of a Symmetry-Allowed Crossing (Destruction of the Symmetry Element). The first type of avoided crossing is encountered for molecular geometries close to, but not identical with, a symmetrical geometry in which a crossing occurs rigorously between two electronic states. A common case will be the crossing between a symmetric A′ state and an antisymmetric A″ state for a molecular system with a plane of symmetry. Such interactions have been called "accidental" [6d] but are quite common. Examples of such crossings in organic chemistry include σ,π bitopic reactions[4b] (such as hydrogen abstraction by ketones), certain $\sigma(\sigma,\pi)$ tritopic reactions[4b] (coplanar α cleavage of hexadienones), etc. In the former family, one surface leads to a zwitterion, the other to a diradical; in the second family, the two surfaces lead to diradicals of different symmetry. If one or several nuclei are displaced slightly so as to destroy the symmetry plane, the crossing becomes forbidden since the adiabatic states must now have the same symmetry. Its intended character, however, shows up clearly for displacements which are not too large. Such a type A avoided crossing is illustrated in Figure 1.

Salem et al. / On Avoided Surface Crossings