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MODEL MNDO CALCULATIONS FOR ROTAMERS OF α-ACYLNITROXIDES AND OF N-NITROSONITROXIDES

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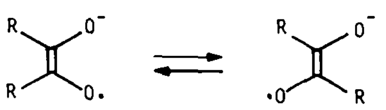
Abstract. Results of MNDO calculations for models of α-acylnitroxides show, in agreement with experiment, that *transoid* conformations *(3B)* have lower energies and higher nitrogen spin densities than *cisoid* conformers *(3A)*. By contrast, N-nitrosonitroxides are found to have lower energy in the cisoid conformation *(4A)* due to the operation of an anomeric effect.

Rotational isomerism is possible in persistent free radicals : in the semidione *1* and hydroxamic acid *2* radical anions, and in the neutral α-acylnitroxide *3* and N-nitrosonitroxide *4* radicals. The ESR coupling constants of *cisoid* and *transoid* rotamers differ markedly. Thus, when only the *cisoid* conformation is possible, as in *3D*, a_N is about 5.7 Gauss.[1] This is appreciably lower than the a_N values of about 7.5 Gauss[2] in acyclic α-acylnitroxides which prefer the *transoid* conformation *3B*. Two possible reasons for the preferred *transoid* conformation are lower steric hindrance between R groups, and favorable dipole-dipole orientation of C=O and N-O bonds.

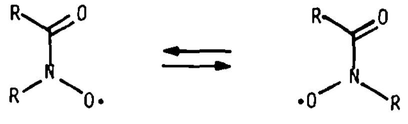
The present note concerns N-aryl-N-nitrosonitroxides *4* (R = phenyl or substituted phenyl groups) which were prepared by several methods, namely by the spin-trapping reaction of nitrosobenzene derivatives with NO, by oxidation of N-nitroso-N-phenylhydroxylamine, its derivatives or its salt (e.g. cupferron), and by decomposition of N-aryl-N-sulphonyl-nitroxides.[3] Their ESR spectra showed that :[3]

$$a_{N-O} = 9.8 - 10.4 \text{ Gauss}, \quad a_{N=O} = 3.4 - 3.8 \text{ Gauss}.$$

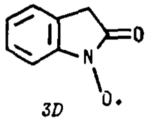


1A *1B*

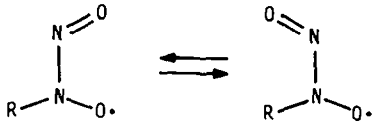
2A *2B*



3A *3B*



3D



4A *4B*

We report here results of half-electron MNDO calculations[4] for model systems *3* (R = H) and *4* (R = H). This method is better suited than unrestricted Hartree-Fock calculations which gave inconclusive results because of spin contamination.[5] In addition to the *cisoid* (*A*, dihedral angle θ = 0°) and *transoid* conformations (*B*, θ = 180°), both belonging to the C_s point group, calculations were also performed for a non-planar orthogonal conformation *C* (θ = 90°), with symmetry C_1.

Table 1 presents data for *3* (R = H) and for *4* (R = H).

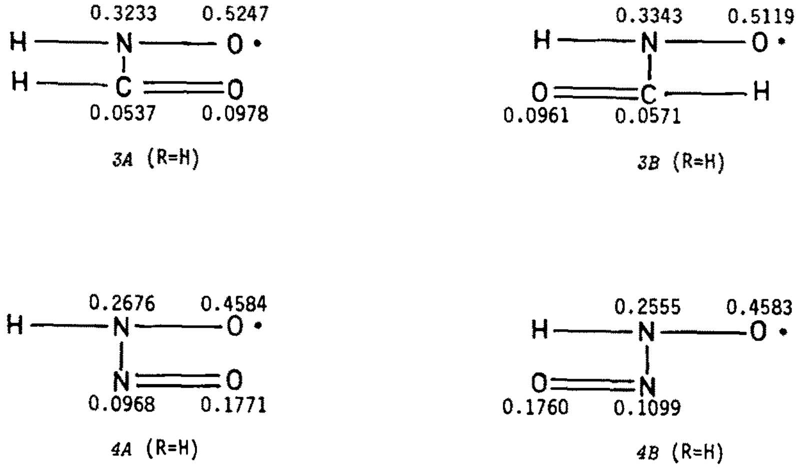
TABLE 1. MNDO results for free radicals $\cdot\overset{1}{O}\text{-}\overset{2}{N}H\text{-}\overset{3}{X}{=}\overset{4}{O}$

Radical	X=CH (*3*, R=H)			X=N (*4*, R=H)		
Conformer / Parameter[a]	*A* θ=0°	*C* θ=90°	*B* θ=180°	*A* θ=0°	*C* θ=90°	*B* θ=180°
$H-N^2$	1.023	1.024	1.024	1.033	1.028	1.039
O^1-N^2	1.228	1.224	1.228	1.221	1.219	1.220
N^2-X^3	1.450	1.447	1.456	1.386	1.434	1.392
X^3-O^4	1.211	1.211	1.214	1.157	1.151	1.159
X^3-H	1.105	1.104	1.103	-	-	-
$H-N^2-O^1$	118.6	118.9	118.7	120.0	121.3	118.9
X^3-N^2-H	117.0	116.5	119.4	114.4	118.9	123.6
$O^4-X^3-N^2$	121.3	120.1	117.7	118.1	115.4	115.1
$H-X^3-N^2$	112.8	112.1	115.0	-	-	-
ΔH_f	-21.41	-20.78	-23.33	14.42	19.77	16.47
E_{rel}	1.92	2.55	0.00	0.00	5.35	2.05
DM	4.48	2.82	0.30	3.52	2.82	2.01

[a] Angles in degrees, distances in Ångstroms, energies (ΔH_f and relative energy E_{rel}) in kcal/mol, dipole moments (DM) in Debye units.

The surprising result is that the lowest energy conformer corresponds to the *transoid* geometry *3B* for α-acylnitroxides and to the *cisoid* geometry *4A* for N-nitrosonitroxides. The energy difference between the two conformers are similar (2±0.1 kcal/mol). In both cases, the orthogonal conformation C_1 has the higest energy ; the energy difference (which should correspond approximately to the rotational barrier) is small for *3* and larger for *4*. Calculated bond lengths and bond angles differ slightly for conformers *A* and *B*, and markedly for the orthogonal conformer. The calculated dipole moment for *3B* is 0.3 D, but with decreasing θ, the dipole moment increases steeply attaining 4.5 D for *3A*. By contrast, there is little difference between calculated dipole moments for *4A* (2.8 D) and *4B* (2.0 D).

Spin densities were calculated from the squared eigenvectors of p_z orbitals (eigenvectors of s orbitals were negligibly small), and are presented in Fig. 1. (No numerical results are presented for orthogonal conformations *C*, because the spin density is practically confined only to the two nitroxidic N and O atoms, in disagreement with experimental data). A slightly smaller spin density for the nitrogen in the *cisoid* conformation *3A* than in the *transoid* one *3B* is indeed found, in qualitative agreement with experimental data. By contrast, the nitroxidic nitrogen has a higher spin density in the *cisoid* conformation *4A* than in the *transoid* one *4B*. There are no experimental data for any *transoid* derivative.



3A (R=H) *3B* (R=H) *4A* (R=H) *4B* (R=H)

Figure 1. Calculated spin densities for model radicals.

One may conclude that unlike acyclic α-acylnitroxides which prefer a *transoid* conformation *3B* in the ground state, N-nitrosonitroxides adopt a *cisoid* conformation *4A*. In confirmation of this conclusion, the experimental ratio between hyperfine coupling constants a_{N-O} / $a_{N=O}$ is 10.2/3.75 = 2.72 for N-(3,5-di-t-butylphenyl)-N-nitrosonitroxide, 10.34/3.78 = = 2.73 for N-phenyl-N-nitrosonitroxide, 10.2/3.8 = 2.68 for N-*p*-tolyl-N-nitrosonitroxide, and 10.3:3.43 = 3.00 for N-*p*-chlorophenyl-N-nitrosonitroxide,[3] in better agreement with the calculated ratio 0.2676 / 0.0968 = 2.76 for *4A* than 0.2555 / 0.1099 = 2.32 for *4B*.

The reasons for the difference in relative energies of the *cisoid* and *transoid* isomers of *3* and *4* seem clear. Isomer *3B* has the lower dipole moment and less electrostatic repulsion than *3A*. While the dipole moment of *4A* is (somewhat) higher than *4B* , the former is more stable because of the generalized anomeric effect ("negative hyperconjugation").[6] The nitrogen lone pair in *4A* engages in a stabilizing hyperconjugative interaction with the *anti* β-N-O bond.

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