

Sulfonamidyls, 4. Ab Initio MO Calculations on Sulfonyl and Carbonyl Substituted Aminyl Radicals

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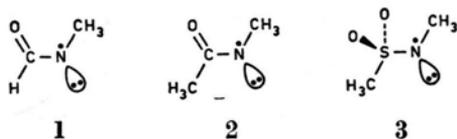
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The relative magnitude of the nitrogen hyperfine splitting constants of sulfonamidyls and carboxamidyls is rationalized in terms of the results of ab initio MO calculations using the "double zeta" basis set of Roos and Siegbahn.

Electron spin resonance spectroscopic data for sulfonamidyls ($R_1SO_2NR_2$) [1–4] as well as for carboxamidyls (R_1CONR_2) [5, 6] are strongly suggestive for π -electronic ground states for these types of amido radicals. However, we noted [2] an intriguing difference between the nitrogen hyperfine splitting constants (A_N): the carboxamidyls possess higher A_N -values (ca. 15 Gauss) than their sulfonyl analogues (A_N ca. 13 Gauss). This is unexpected since in the former type of amidyls the unpaired electron will be delocalized onto the carbonyl group [7] whereas the sulfonyl function will allow little or no spin delocalization [8]. In an attempt to probe the apparently different electronic configurations, we have performed ab initio quantum mechanical MO calculations on the model systems 1–3. The present computations provide a rationale for the differences in A_N between both types of amido



radicals and, in addition, give more insight into the theoretical description of their π and Σ states. Previous MO calculations in the INDO approximation for N-substituted formamido radicals [9] and MO calculations using STO-3G and 4-31G basis sets [10] yielded inconsistent results [11].

The open shell restricted SCF calculations [12] on the Σ_N , Σ_O , π_N , and π_O states of 1 and 2 and on the Σ_N and π_N states of 3 were carried out using the "double zeta" basis set of Roos and Siegbahn [13]. Since preliminary results for 1 and 2 revealed rather similar configurations, the most detailed calculations were carried out on 1 in order to save computer time. The computations on 1 were largely performed on planar structures [14]. Generally, the N-methyl groups were placed in *cis*-position with respect to the carbonyl and sulfonyl group, respectively. This contrasts with previous theoretical studies on the formamido system which only consider the *trans*-isomer. However, our calculations indicate that the *trans* system is 3–5 kcal \cdot mol⁻¹ less favourable in energy than the *cis*-isomer.

Results for geometry optimization [15] for the different configurations of 1 are listed in Table I. The angular potentials ($\angle CNC \equiv \theta$) are shown graphically in Fig. 1. These potentials [16] pertain to the optimized geometry of the π_N configuration except for the C–O distance which was taken as $r_{C-O} = 1.24$ Å. Previous INDO calculations on the formamido radical [9] yielded potentials which are in qualitative agreement with those given in Fig. 1. Optimized structural parameters [17] for sulfonamidyl 3 are also listed in Table I. The calculated S–O and S–N distances accord nicely with those

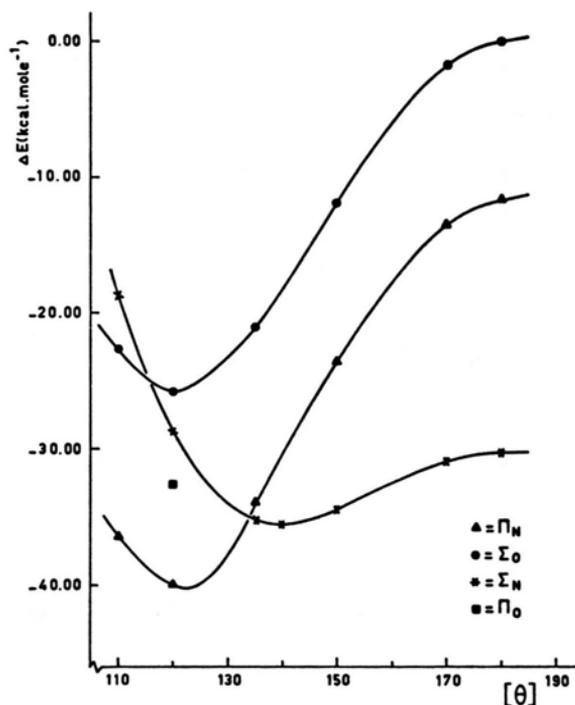


Fig. 1. Angular potentials ($\angle CNC \equiv \theta$) for carboxamidyl 1.

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Table I. Optimized geometries for the radicals **1** and **3**.

Radical 1 :					
State designation	$r_{\text{N-C(=O)}}$ (Å)	$r_{\text{C-O}}$ (Å)	θ (deg)	Energy (au)	Relative energy (kcal · mol ⁻¹)
π_{N}	1.32	1.22	120	-206.99905	0.0
π_{O}	1.26	1.38	120	-206.99938	-0.2
Σ_{N}	1.34	1.24	141	-206.99157	4.7
Σ_{O}	1.24	1.38	120	-206.99865	0.3
Radical 3 ^a :					
State designation	$r_{\text{S-O}}$ (Å)	$r_{\text{S-N}}$ (Å)	θ^{b} (deg)	Energy ^c (au)	Relative energy (kcal · mol ⁻¹)
π_{N}	1.46	1.65	115	-608.27064	0
Σ_{N}	1.46	1.63	140	-680.22691	23.8

^a Geometry with C₁, S, N, and C₂ lying in one plane; ^b interpolated values; ^c calculated for $\angle \text{SNC} = 120^\circ$.

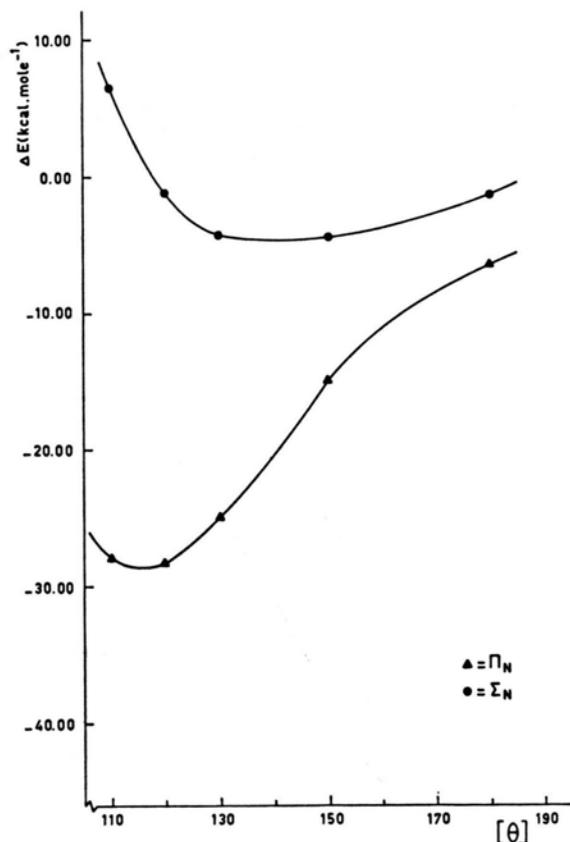


Fig. 2. Angular potentials ($\angle \text{SNC} \equiv \theta$) for sulfonamidyl **3**.

expected on the basis of the corresponding distances in sulfonamides [17]. Fig. 2 portrays the angular potentials ($\angle \text{SNC} \equiv \theta$) for the optimized geometry of the Σ_{N} state. Convergent results could only be obtained for the π_{N} and Σ_{N} states. The π_{O} and Σ_{O} states of **3** probably lie at much higher energies as suggested by calculations using an STO-3G basis set (π_{O} state *ca.* 60 kcal · mol⁻¹ above the π_{N} state).

The following conclusions emerge from the data given in Table I and in Fig. 1 and 2. Firstly, the energies calculated for **1** are not sufficiently separated to allow a definite conclusion about the nature of the electronic ground state. Clearly, further calculations in terms of configuration interaction (including geometry optimization) are necessary [18]. Secondly, it is evident that the situation is much less complicated for sulfonamidyl **3** (Fig. 2). The electronic ground state can now be safely described as a π_{N} state with a geometry close to that given in Table I [19]. The unexpected difference in A_{N} -values between carboxamidyls and sulfonamidyls, as noted above, can now be reasonably accommodated in terms of the quantum mechanical results. Whereas the ground state of the sulfonamidyls is adequately described by a π_{N} configuration, the ground state of the carboxamidyls is a composite of π and Σ configurations. Therefore, the molecular orbital containing the odd electron in the carboxamidyls will have higher s-character, mainly as a result of a contribution of the bent Σ_{N} state. This may well lead [20] to a relative increase in the nitrogen hyperfine splitting constant for the carboxamidyls despite the significant unpaired electron delocalization over the carbonyl function.

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