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Nitrogen-Centered Free Radicals. 10. Electron Spin Resonance Evidence for a π Ground Electronic Configuration for Sulfonamidyl Radicals[1]

Sir:

Amidyl radicals have been the subject of considerable controversy because of the possibility of such species existing in either a π or σ electronic ground state.[2] In an earlier report[3] we published the first unequivocal identification of two simple amidyl radicals and interpreted the a^N, $a^{H\beta}$, and g values in terms of a π electronic configuration, **1**, although the possibility of a bent σ_N (**2**) or linear σ_N (**3**) configuration could not be rigorously excluded. Theoretical calculations have not been
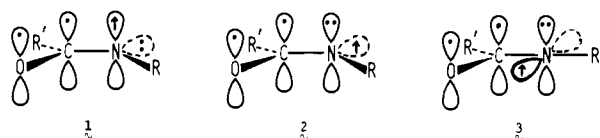
definitive. Semiempirical INDO calculations predict a π state with a CNH angle ∼114–120° for formamidyl but the available ESR data were best correlated with a σ_N configuration.[2c]

Table I. Electron Spin Resonance Spectral Parameters[a] of Amidyl and Sulfonamidyl Radicals in Cyclopropane

radical	a^N	$a^{H\beta}$	g value	temp, °C
CH$_3$SO$_2$ṄCH$_3$	13.4	29.7	2.0041	30
CH$_3$SO$_2$ṄCH$_2$CH$_3$	13.2	35.7	2.0041	30
CH$_3$SO$_2$ṄCH(CH$_3$)$_2$	13.09	8.70[b]	2.0041	0
⟨◯⟩SO$_2$ (N)	13.3	43.4	2.0042	30
C$_6$H$_5$SO$_2$ṄCH(CH$_3$)$_2$	13.07	8.82[c]	2.0042	0
		7.36		−80
		7.36		−60
		8.00		−40
		8.51		−20
		9.43		20
		10.01		40
		10.91		60
(CH$_3$)$_3$CCOṄCH$_3$	15.00	29.30	2.0053	−100
(CH$_3$)$_3$CCOṄCH$_2$CH$_3$	14.7	37.8	2.0053	−100
(CH$_3$)$_3$CCOṄCH(CH$_3$)$_2$	14.85	22.10	2.0053	−100

[a] Hyperfine splitting constants reported in gauss. [b] $a^{H\gamma} = 0.92$ G (6 H). [c] $a^{H\gamma} = 0.98$ G (6 H).

Recent ab initio calculations (STO-3G and 4-31G basis sets including configuration interaction), however, indicate that molecular orbital calculations at even this level cannot give reliable conclusions concerning the ground electronic configuration of formamidyl.[4] The results do suggest that an oxygen-centered configuration ($\dot{O}$—CR′=NR, π_O or σ_O) should probably not be excluded from consideration.
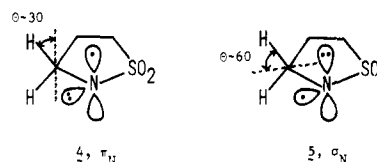
In the accompanying paper, Lessard, Giller, and Ingold[5] provide definitive, variable-temperature ESR data for a π configuration for amidyl radicals. Although sulfonamidyl radicals cannot exist as completely planar species because of the tetrahedral-like arrangement about the sulfur atom and no theoretical calculations have been reported, similar questions can be raised concerning the preferred electronic configuration of this class of radicals.

We now report ESR data for sulfonamidyl radicals, R′-SO$_2$ṄR, which necessitate a π configuration for such species. A π electronic ground state is defined as that electronic configuration in which the unpaired electron on nitrogen resides in the nitrogen 2p orbital perpendicular to the SNC plane.

The sulfonamidyl and amidyl radicals were generated by photolysis of the corresponding *N*-chlorosulfonamides[6] or *N*-chloroamides in cyclopropane solution directly in the cavity of the ESR spectrometer.[3] The ESR parameters are summarized in Table I. It is observed that $a^N = 13.2 \pm 0.2$ G and $g = 2.0041 \pm 0.0001$ for the five sulfonamidyl radicals and $a^N = 14.9 \pm 0.2$ G and $g = 2.0053$ for the three amidyl radicals. These values are similar to those reported for other nitrogen-centered π radicals[2,7,8] and strongly mitigate against a π_O, σ_O, or a bent σ_N configuration, the latter of which would be expected to exhibit a much greater a^N value since the unpaired electron would reside in an orbital with significant s character.

In contrast to the similar a^N values, the $a^{H\beta}$ interactions vary widely but systematically for both the sulfonamidyl and amidyl radicals when R is changed from CH$_3$ to CH$_2$CH$_3$ to CH(CH$_3$)$_2$ as a result of restricted rotation about the N–R bond. The dependence of $a^{H\beta}$ on the dihedral angle θ between the β hydrogen and the p orbital of the radical center is well documented and exhibits a relationship $a^{H\beta} = A + B \cos^2 \theta$ where $A \sim 0.9$ Since $a^{H\beta} = 29.7$ G for CH$_3$SO$_2$NCH$_3$ and a freely rotating methyl group exhibits $\theta = 45°$, $B = 59.4$ G for sulfonamidyl radicals; $B = 58.6$ G for the amidyl radicals. From these B values the time-averaged dihedral angles given in Table II may be calculated for the cases in which R = CH$_2$CH$_3$ and CH(CH$_3$)$_2$.

The ESR results for the relatively rigid cyclic sulfonamidyl radical listed in Table I definitely require a π electronic configuration since such a species cannot possibly exist as a linear σ_N radical.[10] Furthermore, θ is calculated to be 31° which matches almost precisely the ∼30° dihedral angle anticipated from structural considerations for a π configuration as depicted for **4**. The magnitude of $a^{H\beta}$ calculated for a bent σ_N structure

Table II. Comparison of β-Hydrogen Hyperfine Splittings and Time-Averaged Dihedral Angles for Related Nitrogen-Centered π Radicals[a]

R	CH$_3$SO$_2$ṄR[b]	θ,[c] deg	(CH$_3$)$_3$CCOṄR[d]	θ,[c] deg	R$_2$Ṅ[e]	θ,[c] deg
CH$_3$	29.7	45	29.30	45	27.36	45
CH$_2$CH$_3$	35.7	39	37.8	37	36.90	35
CH(CH$_3$)$_2$	8.70[f]	68	22.10	52	14.31	59

[a] Hyperfine splittings in gauss. [b] 30° except where noted. [c] See text. [d] −100°. [e] Reference 7, −90°. [f] 0°.

such as **5** is ~15 G which is not at all consistent with the observed $a^{H\beta}$ of 43.4 G.[12] The similarities in a^N and g value for both the cyclic and acyclic sulfonamidyl radicals and the variation and temperature dependence in $a^{H\beta}$ for R = CH_2CH_3 and $CH(CH_3)_2$ reported in Table I for the acyclic sulfonamidyl radicals strongly suggest that these species, likewise, exist in π ground electronic state configurations.

The correspondence in ESR parameters, particularly the $a^{H\beta}$ values for similar R groups, in the aminyl, sulfonamidyl, and amidyl radicals reported in Table II lend considerable support for π ground states for all three types of radicals. Although the CH_3 groups in these radicals are essentially freely rotating, the CH_2CH_3 and $CH(CH_3)_2$ groups attempt to adapt those conformations which minimize steric interactions.[13] As a result of symmetry, there must be an oscillatory motion as discussed in the accompanying paper[5] which is rapid on the ESR time scale so as to render the two β hydrogens of the *N*-ethyl radicals equivalent. Compared with the carbonyl group in amidyl radicals, the bulkier SO_2 group in sulfonamidyl radicals induces an even stronger repulsive interaction in $CH_3SO_2\dot{N}CH(CH_3)_2$ and $C_6H_5SO_2\dot{N}CH(CH_3)_2$ resulting in small $a^{H\beta}$ couplings. Even at $+60°$, $a^{H\beta}$ is only 10.91 G for the latter radical which is far from the free rotation limit of ~30 G.

In conclusion, the data reported herein, coupled with the variable-temperature studies described in the accompanying paper,[5] should lay to rest any controversy surrounding the ground electronic configuration of sulfonamidyl or amidyl radicals.

References and Notes

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(6) Zomer, G.; Engberts, J. B. F. N. (*Tetrahedron Lett.* **1977**, 3901) were unable to generate sulfonamidyl radicals from the corresponding *N*-chlorosulfonamides, the sulfonyl nitroxides being obtained instead; they utilized *N*-bromosulfonamides successfully. We encountered no difficulty in cleanly generating the sulfonamidyl radicals from the *N*-chlorosulfonamides provided that oxygen was rigorously excluded. With traces of oxygen, the more persistent sulfonyl nitroxides were produced as anticipated.
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(10) We have been unsuccessful in generating analogous cyclic amidyl radicals either by photolysis in solution or X-ray irradiation in an adamantane matrix.[11]
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(12) This reasoning assumes that the relationship $a^{H\beta} = 59.4 \cos^2 \theta$ applies to such a σ radical. Since hyperconjugation is expected to be less important for a σ radical, the ~15 G value predicted for **5** is probably a maximum value.
(13) The actual conformation adapted is presumably determined by a relatively complex interplay of steric and electronic effects, the latter including unpaired electron π delocalization and hyperconjugation and lone-pair-bond-pair repulsions; steric effects predominate.

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Stereoselective Syntheses via a Photochemical Template Effect

Sir:

Contemporary interest in the use of synthesized polymers in chemical processes has led to many important new developments in solid-phase synthesis.[1-3] Most of the successful applications have used already synthesized polymers as handles in the preparation or separation of organic compounds.[1]

As part of a program designed to take advantage of the properties of polymers in organic processes,[5] we have been investigating the synthesis of polymeric materials which maintain a recognizable macrostructure throughout subsequent photochemical processes. In this communication we describe model studies toward this end and report the synthesis of a series of styrene-divinylbenzene copolymers which not only *recognize their origins*, but which are also able to guide a subsequent photochemical reaction in a specific stereochemical direction. We believe this the first example of a "photochemical template effect".

In principle, the work is based on that of Dickey[6] who demonstrated that silica gel, prepared from sodium silicate and acetic acid in the presence of methyl orange, had a specific affinity for methyl orange in the presence of the ethyl, *n*-propyl and *n*-butyl isomers. More recent work, first by Wulff[7] and later by Shea,[8] has shown that a macromolecule may develop molecular pattern recognitions during its construction based on the monomers from which the macromolecule was constructed—even though the specific molecules of construction no longer remain.

Our goal was to build a polymer with cavities specific for one particular configuration as designated by the three-dimensional structure of an appended small molecule. The question was, would a photochemical reaction carried out in the cavity left after the appended small molecule has been removed from the synthetic polymer lead to a photoproduct with the same geometry as existed in the model compound?[9]

As an example reaction we chose the extensively studied solid-state photodimerization of *trans*-cinnamic acid, the stable crystalline form (α) of which gives α-truxillic acid and the metastable (β) form of which produces β-truxinic acid.[10]

Using methods developed previously[11] to build cavities of specific structure, stereoisomeric α-truxillic, β-truxinic, or δ-truxinic acids were converted into polymerizable monomers. These were then copolymerized with appropriate excesses of styrene and divinylbenzene to form highly cross-linked polymers. Removal of the truxillate or truxinate esters by acidic hydrolysis in methanol left two benzyl alcohol groups in the cavity (Table I, Scheme I).[11]

Treatment of the hydrolyzed polymers **1** with an excess of *trans*-cinnamoyl chloride yielded the polymers **2** (Scheme I). Irradiation of these polymers in degassed benzene suspension[12] produced mixtures of photodimers which could be released from the polymer by acid hydrolysis.

From Table II it is apparent that 53% of the cavities in ⓟ$_\beta$-**2** specifically synthesize β-truxinic acid when *trans*-cinnamate is irradiated in a ⓟ$_\beta$ cavity. Thus, using a polymer synthesized from bis(vinylbenzyl) β-truxinate the irradiation of the *trans*-cinnamate ester gives 53% β-truxinate, *even though a randomly synthesized polymer cinnamate ester* would give rise only to α-truxillate under identical conditions.[14] The other 47% of the cavities of ⓟ$_\beta$-**2** give nonspecific direction and hence the formation of α-truxillic acid—the expected random product—is observed. α-Truxillic acid forms exclusively in ⓟ$_\alpha$-**2** as is expected since polymeric cinnamate esters,[14] when irradiated in solution, give only α-truxillic acid derivatives.

The generality of the concept of the photochemical template effect is demonstrated with a polymer synthesized with bis(vinylbenzyl) δ-truxinate **3**. δ-Truxinic acid[15] is *never*