aza[3.2]metaparacyclophane **6** was isolated (3%) along with 32% recovered **1** ($n = 2$) and compounds **3-5** ($n = 2$) in 3, 57, and 3.5% yield, respectively.[2] The structure of **6** was supported by the replacement of the characteristic ultraviolet maximum of **1** ($n = 2$) at 302 nm with a broad featureless absorption extending to a maximum at 254 nm (ϵ 5250) in methanol. The pK_a, determined spectroscopically in methanol-water and extrapolated to pure water, was 6.92, significantly higher than 5.06 obtained for *N,N*-dimethylaniline. Both phenomena are in good accord with the expected effect of twisting the amino group out of the plane of the aromatic ring.

The 200-MHz NMR spectrum ($CDCl_3$) of **6** at −60 °C displayed an *N*-methyl peak at δ 2.78 (3 H). The C-9 aromatic proton signal was a triplet at δ 5.33 and the remaining three protons of the meta-substituted ring were centered at δ 6.76 and 7.1 ($J_{6,7} = 7.95$, $J_{5,6} = 6.92$, $J_{5,7} = 1.74$, $J_{7,9} = 1.25$, and $J_{5,9} = 1.78$ Hz). The hydrogens of the para-substituted ring appeared as AB quartets at δ 5.73 and 6.18 ($J = 8$ Hz) and at δ 6.94 and 7.10 ($J = 8$ Hz). At 15 °C the δ 6.18 and 6.94 bands coalesced and at 60 °C were replaced by a broad signal at δ 6.53. The δ 5.73 and 7.10 signals merged into a broad shoulder at δ 6.36 at this temperature. Using the expression[7] $k_c = \pi\Delta\nu\sqrt{2}$, these observations lead to an approximate $\Delta F^{\ddagger}$ for interconversion of 13.5 kcal/mol.

The C-2 and C-3 methylenes protons of **6** at 25 °C appeared as multiplets at δ 3.5 and 2.3. In **6**, C(3)-d_2, which was prepared from the corresponding α-deuterated alcohol **1** ($n = 2$), the C-2 hydrogens appeared at −40 °C as an AB quartet at δ 3.39 and 3.82 ($J = 15$ Hz) which coalesced at 10 °C, $\Delta F^{\ddagger} = 14.0$ kcal/mol. Exchange of the C(2) protons can only be accommodated by flipping of the meta-substituted ring with consequent transformation of the chiral structure **6** to its enantiomer. Although this transformation also results in exchange of the protons of the para-substituted ring, independent rotation of the latter ring could produce the same effect. The 0.5-kcal/mol lower activation energy for exchange of the protons of the para-substituted ring lies close to the sensitivity of the method but suggests that the latter ring may rotate independently and at a similar rate to enantiomeric interconversion.

In analogy to the photochemical condensation of benzyl alcohol with *N,N*-dimethylaniline,[11] the [3.1]metacyclophane **2** is probably formed by cyclization of **7** either before or after internal electron transfer (Scheme I, path a). The formation of the [3.2]metaparacyclophane **6** may occur through proton abstraction by OH^- within the ion pair **7** (Scheme I, path b). Successful competition of this pathway over cyclization to a highly strained [2.1]metacyclophane would not be surprising. Abstraction of a proton from the *N*-methyl in **7** has precedent in the abstraction of protons from amine radical cations by ketone radical anions.[12] While abstraction by anions lacking an unpaired electron does not appear to have been reported, OH^- is a stronger base than the ketyl radical anion[13] and proton transfer to it is energetically reasonable. In agreement with this mechanism the ratio of methyl ether **4** ($n = 2$) to cyclophane **6** increased from ~14 to >62 when the benzyl chloride corresponding to **1** ($n = 2$) was irradiated in place of **1** ($n = 2$) so as to form chloride ion instead of the more basic OH^-. For these experiments short irradiation times were used to avoid secondary photolysis of **4** ($n = 2$) since the latter compound can be converted photochemically into **6** in up to 12% yield (31% based on recovered starting material).

References and Notes

(1) M. Atzmüller and F. Vögtle, *Chem. Ber.*, **111**, 2547 (1978).
(2) Acceptable elemental analyses and spectral data were obtained.
(3) B. M. Wepster, *Recl. Trav. Chim. Pays-Bas*, **71**, 1116 (1952); **72**, 661 (1953); **74**, 161 (1955).
(4) The spectra were measured on a Bruker WH-90 FT NMR spectrometer in $(CDCl_2)_2$ solution using a pulse width of 3.0 μs (4.6 μs = 90°) at 2.0-s intervals. The data were collected in 4096 points, zero filled to 8192 points before Fourier transformation. No digital line broadening function was applied to the FID. The spectral width of 1201 Hz gave a digital resolution of 0.29 Hz.
(5) G. Binch, *Top. Stereochem.*, **3** (1968).
(6) S. Glassstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes", McGraw Hill, New York, 1941, Chapter 1.
(7) J. B. Lambert and S. I. Featherman, *Chem. Rev.*, **75**, 611 (1975).
(8) T. Sato, S. Akabori, M. Kainosho, and K. Hata, *Bull. Chem. Soc. Jpn.*, **39**, 856 (1966); **41**, 218 (1968).
(9) I. Gault, B. J. Price, and I. O. Sutherland, *Chem. Commun.*, 540 (1967).
(10) R. W. Griffin, Jr., and R. A. Coburn, *J. Am. Chem. Soc.*, **89**, 4638 (1967).
(11) C. I. Lin, P. Singh, and E. F. Ullman, *J. Am. Chem. Soc.*, **98**, 6711 (1976).
(12) S. G. Cohen and N. M. Stein, *J. Am. Chem. Soc.*, **93**, 6542 (1971).
(13) G. Porter and F. Wilkinson, *Trans. Faraday Soc.*, **57**, 1686 (1961).
(14) Syntex Corporation, Palo Alto, Calif.

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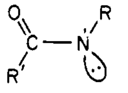
The Structure of Amidyl Radicals. An Investigation by Variable-Temperature Electron Paramagnetic Resonance Spectroscopy[1]

Sir:

There have been many attempts to determine whether amidyl radicals (*N*-alkylcarboxamidyls, $R'CO\dot{N}R$) have a π or σ electronic ground state. Both the π (**1**) and σ_N (**2**) states have been suggested to participate in chemical reactions.[2] The EPR data[3-5]—which is limited in the extreme[6]—has been tentatively interpreted in terms of a π configuration.[3,7] However, bent σ_N (**2**) and linear σ_N (**3**) configurations cannot be excluded.[13]



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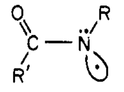

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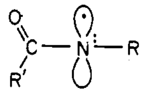

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We have examined the EPR spectra of a variety of amidyls over the widest range of temperatures possible in each case. The amidyls were generated by photolysis of the *N*-chloramides in cyclopropane (cyclopropane–ethylene for the lowest temperatures), which is the procedure pioneered by Danen and Gellert.[3] In this communication we concentrate on just four amidyls and on the magnitude and temperature dependence of their a^{H_β} parameters (the H hyperfine splittings (hfs) of the $NCH_\beta R''R'''$ groups).[14] The experimental results, which are shown in Figure 1, can be interpreted *only* in terms of the π configuration, **1**. Both the bent (**2**) and linear (**3**) σ_N configurations can finally be excluded.

The generally accepted relationship between a^{H_β} and θ, the dihedral angle between the C-H_β bond, and the axis of the semioccupied orbital is[15]

$$a^{H_\beta} = A + B\cos^2\theta$$

where A and B are constants, and A can usually be neglected.[16] In $EtCO\dot{N}CH_3$ the average value of θ is 45° at all temperatures and, since $a^{H_\beta} = 29.5$ G, it follows that $B \approx 59$ G. We have found for $EtCO\dot{N}CH_2Me$, and related radicals,[17] that a^{H_β} is always >29.5 G and that there is a very large variation in a^{H_β} with temperature.[18] The value of a^{H_β} *decreases* with *increasing* temperature and approaches the temperature invariant value found for $EtCO\dot{N}CH_3$. At the lowest temperature attained (109 K), $EtCO\dot{N}CH_2Me$ has $\bar{a}^{H_\beta} = 43.3$ G and hence the *average* value of the dihedral angle, $\bar{\theta}$, is ~30°, while at higher temperatures $\bar{\theta}$ tends toward the "free rotation" value of 45°. This behavior is analogous to that found for alkyl radicals of the type $R_1R_2\dot{C}CH_2R_3$ in which $\bar{\theta}$ also becomes smaller as the temperature is reduced.[15]

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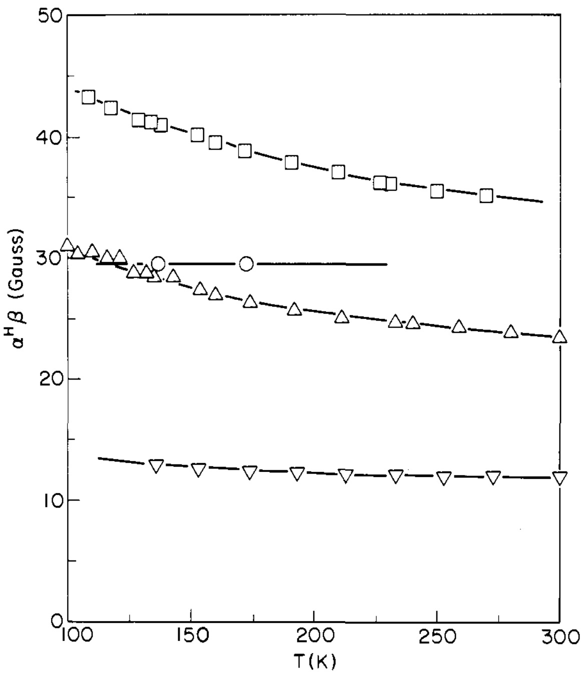
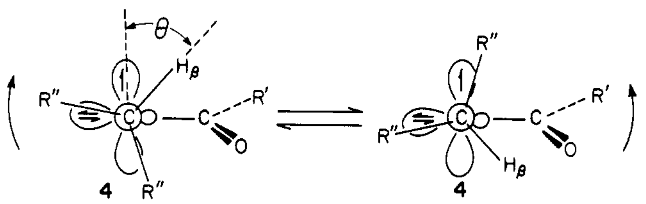


Figure 1. Values of a^{H_β} as a function of temperature: $\mathrm{EtCO\dot{N}CH_3}$, ○; $\mathrm{EtCO\dot{N}CH_2Me}$, □; $\mathrm{EtCO\dot{N}CHMe_2}$, △; $\mathrm{MeCO\dot{N}CH(Bu^t)_2}$, ▽.

In sharp contrast, the value of a^{H_β} for $\mathrm{EtCO\dot{N}CHMe_2}$ is *less* than that for $\mathrm{EtCO\dot{N}CH_3}$ at temperature above ~120 K. Nevertheless, it too *decreases as the temperature increases.* The average value of θ is *not,* therefore, approaching 45° as the temperature is raised, but rather a value >45° and, moreover, θ must be *greater* at high temperatures than at low. This means that the isopropyl group in $\mathrm{EtCO\dot{N}CHMe_2}$, unlike that in alkyl radicals of the type $\mathrm{R_1R_2\dot{C}CHMe_2}$,[15] does *not* tend towards "free rotation" at the highest temperatures attained. The $\mathrm{MeCO\dot{N}CH(Bu^t)_2}$ radical also has an a^{H_β} which decreases with increasing temperature and the absolute magnitude of a^{H_β} is even smaller than that of $\mathrm{EtCO\dot{N}CHMe_2}$.

We can account for the foregoing observations only in terms of the π radical structure, **1.** There must be a substantial barrier to full rotation about the N-CHR″$_2$ bonds, the alkyl group rocking between energetically equivalent conformations, **4.** The situation can be represented as shown in Scheme I. The barrier to interconversion, which arises from the eclipsing of the C-H$_\beta$ bond and the adjacent lone pair on the carbonyl oxygen, should be relatively low. The preferred (low temperature) angle is determined by two opposing effects: hyperconjugation to the C-H$_\beta$ bond which tends to reduce θ toward 0° [15] and steric repulsion between R″ and oxygen which tends to increase θ toward 90°.[16] These effects make the rocking motion subject to a double minimum potential function. The observed negative temperature coefficients for a^{H_β} presumably arise because the slopes of the double-minimum potential energy profiles are less steep as $\theta \rightarrow 90°$ than as $\theta \rightarrow 0$ or 180°. As a consequence, θ increases as the temperature is raised,[19] and a^{H_β} falls.[20] The magnitude of a^{H_β} for $\mathrm{MeCO\dot{N}CH(Bu^t)_2}$ is much smaller than for $\mathrm{EtCO\dot{N}CHMe_2}$ because greater steric interaction between R″ and oxygen forces H$_\beta$ closer to the plane of the radical.[21] *This result rules out the bent* σ_N *configuration,* **2,** *because the magnitudes of* a^{H_β} *would have been reversed in these two species if the semioccupied orbital lay in the plane. For the same reason, the linear* σ_N *configuration,* **3,** *can also be ruled out.* An additional reason for ruling out **3** is that steric effects should be negligible in the linear σ_N configuration. We conclude, therefore, that amidyls must be π radicals. Though the π structure has been generally accepted for some time, the present experimental results put it on a very much firmer base.

Scheme I



In conclusion, we note that implicit in structures **1** and **4** are the assumptions that the R′CO group has a trans arrangement of R′ with respect to R and that it lies in the CNC plane. The former assumption is based on analogy with the known trans arrangement in carboxylic esters[22] and in carboxamides.[23] The latter, fortunately, is relatively unimportant in the context of the preferred conformation(s) of the R″$_2$CH group and the conclusions that arise therefrom. That is, structure **4** shows that the R′CO group provides a steric barrier to rotation of the R″$_2$CH group about its C-N bond. A certain steric barrier will remain even if the R′CO group were to be rotated partly or fully out of the CNC plane. That is, whether amidyls are planar or are "twisted" [24] about their $\mathrm{R'C(O)\text{-}\dot{N}R}$ bonds will not affect the validity of our conclusion that they have a π structure with the unpaired electron in an orbital perpendicular to the CNC plane. Experiments are now in progress to determine whether or not amidyls are "twisted".

Acknowledgment. We thank Professor N. C. Baird for his very helpful comments regarding the value (or otherwise) of MO calculations on amidyl and related radicals.

References and Notes

(1) Issued as N.R.C.C. No. 18159. For a review of amidyl's structure and reactivity see Mackiewicz, P.; Furstoss, R. *Tetrahedron* **1978,** *34,* 3241.

(2) See, e.g.: Joseph, T. C.; Tam, J. N. S.; Kitadani, M.; Chow, Y. L. *Can. J. Chem.* **1976,** *54,* 3517. Glover, S. A.; Goosen, A. *J. Chem. Soc., Perkin Trans. 1* **1977,** 1348; *Prog. Theor. Org. Chem.* **1977,** *2,* 297. Mackiewicz, P.; Furstoss, R.; Waegell, B.; Cote, R.; Lessard, J. *J. Org. Chem.* **1978,** *43,* 3746.

(3) Danen, W. C.; Gellert, R. W. *J. Am. Chem. Soc.* **1972,** *94,* 6853.

(4) Danen, W. C.; Neugebauer, F. A. *Angew. Chem., Int. Ed. Engl.* **1975,** *14,* 783.

(5) Koenig, T.; Hoobler, J. A.; Klopfenstein, C. E.; Hedden, G.; Sunderman, F.; Russell, B. R. *J. Am. Chem. Soc.* **1974,** *96,* 4573.

(6) Five radicals each at one temperature: R′ = $\mathrm{Me_3C}$, R = Me,[3] Et,[4] *i*-Pr;[4] *R* = $\mathrm{Me_3C}$, R′ = Me,[3,5] cyclopropyl.[5]

(7) This configuration is also favored by a ^{13}C CIDNP study[8] and by theoretical calculations on formamidyl,[5,9] $\mathrm{HCO\dot{N}H}$. In contrast, INDO calculations for R′ = H, R = $\mathrm{CH_3}$ give the best fit to experimental hfs for the σ_N structure, **3.**[5] However, more recent ab initio calculations[10,11] have led Baird[12] to conclude that MO theory at anything but the very highest level cannot make meaningful predictions about conjugated radicals of the $\mathrm{R'CO\dot{N}R}$ type.

(8) Brown, C.; Lawson, A. J. *Tetrahedron Lett.* **1975,** 191.

(9) Baird, N. C.; Kathpal, H. B. *J. Am. Chem. Soc.* **1976,** *98,* 7532.

(10) Baird, N. C.; Gupta, R. R.; Taylor, K. F. *J. Am. Chem. Soc.* **1979,** *101,* 4531.

(11) Baird, N. C.; Taylor, K. F. *J. Am. Chem. Soc.*, submitted for publication.

(12) Baird, N. C., private communication.

(13) For all bent structures we have, for simplicity, *assumed* that the R′CO group lies in the CNR plane. This assumption may be incorrect (see text). However, it should be noted that the π configuration, for example, is defined as one in which the unpaired electron resides in an N 2p orbital perpendicular to the CNC plane and this definition is unaffected by the orientation of the R′CO group with respect to this plane.

(14) The a^N and *g* values of these radicals show little or no temperature dependence; their values at ~170 K are 14.9, 14.7, 14.6, and ~14.6 G and 2.0055, 2.0053, 2.0051, and 2.0056 for $\mathrm{EtCO\dot{N}CH_3}$, $\mathrm{EtCO\dot{N}CH_2Me}$, $\mathrm{EtCO\dot{N}CHMe_2}$, and $\mathrm{MeCO\dot{N}CH(Bu^t)_2}$, respectively.

(15) See, e.g., Kochi, J. K. *Adv. Free Radical Chem.* **1975,** *5,* 189.

(16) Griller, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1974,** *96,* 6203. Malatesta, V.; Forrest, D.; Ingold, K. U. *J. Phys. Chem.* **1978,** *82,* 2370.

(17) Unpublished results of J. Lessard.

(18) This temperature dependence, the presence of which does not appear to have been suspected,[3-5] is actually greater than that reported for any other class of radicals having β hydrogens.[15]

(19) For treatments of double-minimum potentials in free radicals see: Krusic, P. J.; Meakin, P. *J. Am. Chem. Soc.* **1976,** *98,* 228. Griller, D.; Ingold, K. U.; Krusic, P. J.; Fischer, H. *Ibid.* **1978,** *100,* 6750.

(20) At still higher temperatures a^{H_β} should again increase.[19]

(21) At 136 K, $\mathrm{MeCO\dot{N}CH(Bu^t)_2}$ and $\mathrm{EtCO\dot{N}CHMe_2}$ have a^{H_β} = 12.9 and 28.3 G, respectively, corresponding to $\theta \sim 62$ and 46°, respectively.

(22) Oki, N.; Nakanishi, H. *Bull. Chem. Soc. Jpn.* **1970**, *44*, 3419. Jones, G. I. L.; Owens, N. L. *J. Mol. Struct.* **1973**, *18*, 1.

(23) Robin, M. B.; Bovey, F. A.; Basch, H. "The Chemistry of Amides", Zabicky, J., Ed.; Wiley: New York, 1970; pp 19–22.

(24) The relatively large magnitude of a^{H_β} for $EtCO\dot{N}CH_3$ compared with other $X\dot{Y}CH_3$ radicals can be interpreted as evidence favoring a twisted structure.

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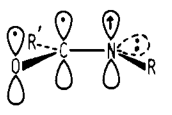
Nitrogen-Centered Free Radicals. 10. Electron Spin Resonance Evidence for a π Ground Electronic Configuration for Sulfonamidyl Radicals[1]

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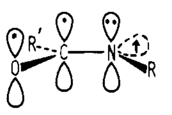
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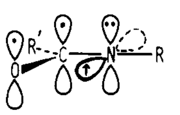
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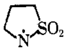
Table I. Electron Spin Resonance Spectral Parameters[a] of Amidyl and Sulfonamidyl Radicals in Cyclopropane

radical	a^N	a^{H_β}	g value	temp, °C
$CH_3SO_2\dot{N}CH_3$	13.4	29.7	2.0041	30
$CH_3SO_2\dot{N}CH_2CH_3$	13.2	35.7	2.0041	30
$CH_3SO_2\dot{N}CH(CH_3)_2$	13.09	8.70[b]	2.0041	0
	13.3	43.4	2.0042	30
$C_6H_5SO_2\dot{N}CH(CH_3)_2$	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
$(CH_3)_3CCO\dot{N}CH_3$	15.00	29.30	2.0053	−100
$(CH_3)_3CCO\dot{N}CH_2CH_3$	14.7	37.8	2.0053	−100
$(CH_3)_3CCO\dot{N}CH(CH_3)_2$	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.

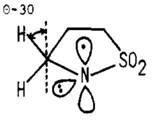
In the accompanying paper, Lessard, Giller, and Ingold[5] provide definitive, variable-temperature ESR data for a π configuration for amidyl radicals. Although sulfonamidyl radicals cannot exist as completely planar species because of the tetrahedral-like arrangement about the sulfur atom and no theoretical 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, $R'SO_2\dot{N}R$, 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.

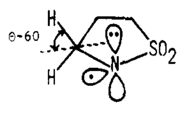
The sulfonamidyl and amidyl radicals were generated by photolysis of the corresponding *N*-chlorosulfonamides[6] or *N*-chloroamides in cyclopropane solution directly in the cavity of the ESR spectrometer.[3] The ESR parameters are summarized in Table I. It is observed that $a^N = 13.2 \pm 0.2$ G and $g = 2.0041 \pm 0.0001$ 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_β} interactions vary widely but systematically for both the sulfonamidyl and amidyl radicals when R is changed from CH_3 to CH_2CH_3 to $CH(CH_3)_2$ as a result of restricted rotation about the N–R bond. The dependence of a^{H_β} 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 $CH_3SO_2\dot{N}CH_3$ 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_2CH_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_β} calculated for a bent σ_N structure



4, π_N



5, σ_N

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

R	$CH_3SO_2\dot{N}R$[b]	θ,[c] deg	$(CH_3)_3CCO\dot{N}R$[d]	θ,[c] deg	$R_2\dot{N}$[e]	θ,[c] deg
CH_3	29.7	45	29.30	45	27.36	45
CH_2CH_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°.

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