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The Structure of Amidyl Radicals. Evidence for the π-Electronic Ground State and for Twist about the Acyl-Nitrogen Bond by Electron Paramagnetic Resonance Spectroscopy[1]

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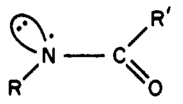
Abstract: The EPR spectroscopic parameters for a number of acyclic *N*-alkylcarboxamidyls, $R\dot{N}C(O)R'$, have been measured over a wide range of temperatures. The results can only be interpreted in terms of a π-electronic configuration in which the unpaired electron resides mainly in an N 2p orbital perpendicular to the RNC plane. Measurements of the ^{13}C hyperfine splittings (hfs) for some $R\dot{N}C(O)^{13}CH_3$ demonstrate that the O and ^{13}C atoms lie in or near the RNC plane except when R is *tert*-butyl, in which case steric forces twist these atoms out of this plane by 20° or more. There is less conjugative delocalization of the unpaired electron from N to O in the $Me_3C\dot{N}C(O)R'$ radicals because they are twisted and hence these radicals have a larger N hfs and a smaller *g* value than amidyls which have R = primary or secondary alkyl. The first cyclic amidyl, 5,5-dimethyl-2-oxopyrrolidin-1-yl, has been detected. This radical has a smaller N hfs (11.2 G) and a higher *g* value (2.0063) than the acyclic radicals.

The nature of the electronic ground state of nitrogen-centered radicals is of considerable interest to theoreticians and to experimentalists since the central nitrogen must accommodate both an unpaired electron and a lone pair of electrons, with the result that either a π- or a σ-electronic ground state is possible.[4] For amidyl radicals[5] (*N*-alkylcarboxamidyls, $R\dot{N}COR'$) both π (**1**) and σ_N (**2**, **3**) states have been suggested.



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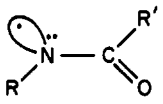

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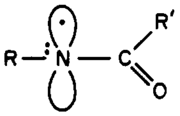

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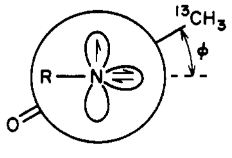
INDO[6] and ab initio[7] calculations on formamidyl supported the π configuration, **1** (R = R' = H). However, INDO calculations on *N*-methylformamidyl[6] gave the best fit with experimental electron paramagnetic resonance (EPR) data for the linear σ_N structure, **3** ($R = CH_3$, R' = H). However, more recent ab initio calculations[8,9] have led Baird[9,10] to conclude that MO theory at anything but the very highest level cannot make meaningful predictions about conjugated radicals of the $R\dot{N}COR'$ type since the theory underestimates the π-bond strength of C═O relative to C═N.

Experimental studies of the chemical reactivities and products of amidyl reactions[5,11] have been interpreted in terms of both the π state, **1** and the bent σ_N state **2**. The π configuration has been favored by a ^{13}C CIDNP experiment.[12] The extremely limited EPR data available before we began our work have also been interpreted in terms of the π configuration.[4,6,13-15]

In a preliminary communication[21] we reported the results of an investigation of four amidyls by variable-temperature EPR spectroscopy which demonstrated that amidyls must have a π-electronic ground state. Both the bent and linear σ_N configurations were ruled out. In the present paper we provide additional evidence supporting these conclusions. However, we have now found that although the electronic ground state for amidyls is π, i.e., the unpaired electron resides in a nitrogen 2p orbital perpendicular to the CNC plane, the simple, planar structure **1** can be misleading since for certain amidyls the R'CO group does not, in fact, lie in the CNR plane. The magnitude of the twist angle, ϕ, between the R'CO and CNR planes has been investigated by measuring ^{13}C hyperfine splittings (hfs) for several ^{13}C-labeled amidyls having the structure $R\dot{N}CO^{13}CH_3$ (**4**). The twist angle is found to



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[4] (a) For a review see: Danen, W. C.; Neugebauer, F. A. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 783. (b) In a π radical the unpaired electron is in a p or π orbital having a nodal plane in the plane of the local molecular framework. In a σ radical the unpaired electron is in an orbital which may or may not have s character but which does not have a nodal plane coinciding with the local molecular plane.

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[14] Five amidyls were known and each had been observed at one temperature: $R' = Me_3C$, R = Me,[13] Et,[4] *i*-Pr;[6] $R = Me_3C$, R' = Me,[6,13] cyclopropyl.[6]

[15] The EPR data on sulfonamidyls, $R\dot{N}SO_2R'$, are more extensive.[16-20] They indicate a π configuration for these radicals.

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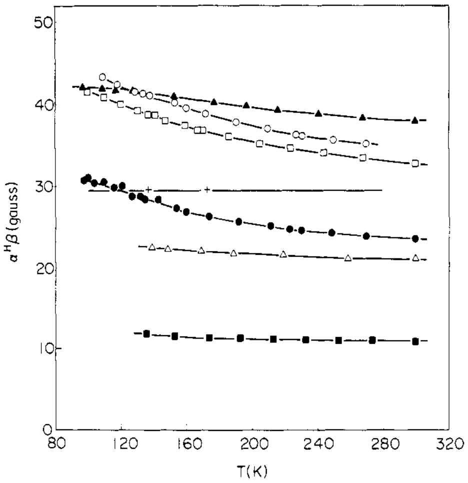

Figure 1. Values of a^{H_β} as a function of temperature for t-BuCH$_2\dot{N}$CO-t-Bu, ▲; Et$\dot{N}$COEt, ○; Et$\dot{N}$CO-t-Bu, □; Me$\dot{N}$COEt, +; i-Pr$\dot{N}$COEt, ●; i-Pr$\dot{N}$CO-t-Bu, △; t-Bu$_2$CH$\dot{N}$COMe, ■.

depend on steric repulsion between R and the carbonyl oxygen. With use of this interpretation, the surprisingly large variations in g factor and in ^{14}N hfs for a series of amidyls with different R groups can be understood in terms of the ease with which the unpaired electron can be delocalized from nitrogen to oxygen. In this paper we also report EPR parameters for the first cyclic carboxamidyl to have been observed in solution.

Experimental Section.

Materials. Amides were prepared from acid chlorides and amines by the usual procedure. Di-*tert*-butylmethylamine was prepared by $LiAlH_4$ reduction of di-*tert*-butylketimine.[22] The ^{13}C-labelled amides were prepared from [2-^{13}C]acetyl chloride (90 at wt % ^{13}C, Merck, Sharp and Dohme), each on about a 5-mmol scale.

The N-chloramides were prepared from the amides with chlorine and aqueous sodium bicarbonate.[23] The corresponding amidyl radicals could only be detected upon photolysis in the cavity of the EPR spectrometer if the N-chloramide was free from residual solvent (methylene chloride) and was colorless. The solvent was removed under vacuum at −78 °C, and yellow colored impurities were removed, when necessary, by careful distillation under vacuum.

N-Chloro-5,5-dimethylpyrrolidin-2-one was prepared from the parent lactam which was a gift from Professor Armin Berndt. The [1,3-^{13}C]-acetone (90 at wt % ^{13}C) was obtained from Merck, Sharp and Dohme.

Radical Generation. Amidyls were generated by UV photolysis of their parent N-chloramides in cyclopropane or, at temperatures below ca. 150 K, in cyclopropane/ethylene as solvent. All samples were very carefully deoxygenated to prevent nitroxide formation. The samples were photolyzed directly in the cavity of a Varian E-104 EPR spectrometer using a 500-W high-pressure mercury-arc lamp. Most of the infrared and much of the visible radiation were removed by passing the light through a quartz filter cell containing an aqueous solution of cobalt and nickel sulfates. The heating effect of the light at the sample was less than 1 °C.

Measurement of EPR Parameters. For most amidyls the EPR parameters were measured at one or two temperatures by Griller and Preston's[24] very accurate procedure which utilizes an NMR field marker and a microwave frequency counter. A least-squares treatment is then used to obtain the best fit for all the measured lines.[24] These calibrated spectra then served as standards for determining the N and H hfs of the amidyl at other temperatures.

Spectral simulation was required to obtain the $^{13}C_\gamma$ hfs in R$\dot{N}$CO^{13}CH$_3$ for R = CH_2CH_2Me, $CHMe_2$, and CH_2CMe_3, because of rather poor signal-to-noise ratios in the EPR spectra of these radicals.

Results and Discussion

The π-Electronic Ground State. The EPR parameters for a large variety of amidyls were measured over the widest possible range of temperatures. The radicals are listed in Table I together with their EPR parameters at one or two specific temperatures. The full experimental data are available as supplementary material. The conclusion that amidyls have a π-electronic ground state comes from consideration of the magnitude and temperature dependence of their H$_\beta$ hfs,[21] i.e., a^{H_β} for $NCH_\beta R''R'''$. Figure 1 shows this temperature dependence for a number of amidyls.

Table I. Selected EPR Parameters for RNCOR′ Radicals[a,b]

R	R′	T, K	g	a^N, G	$a^{H_\beta(R)}$, G	a^{other}, G
Me	Me	151	2.0055	14.9	29.5	1.3_4[c]
Me	Et	137	2.0055	14.9	29.5[d]	
		173	2.0055	14.9	29.5[d]	
Me*	t-Bu	137	2.0054	15.0	29.2	
		173	2.0054	14.9	29.1	
Et*	Et	109	2.0052	14.8	43.3[d]	
		270	2.0052	14.7	35.2[d]	
Et*	t-Bu	148†	2.0051_8	14.8_2	38.0_9[d]	
		238†	2.0052_1	14.8_2	34.5_8[d]	
n-Pr	Me	158†	2.0049_0	14.9_4	39.0_4	1.5_1,[c] 2.4[e]
		201†	2.0050_2	14.7_8	37.2_7	1.6_2,[c] 2.4[e]
n-Pr	Et	160	2.0052	14.8	39.1	
		146	2.0052	14.7	36.9	
t-BuCH$_2$*	Me	138†	2.0051_0	15.0_1	40.2_6	1.4_7,[c] 2.4[e]
		233†	2.0051_1	14.9_3	38.3_1	1.5_2,[c] 2.4[e]
t-BuCH$_2$*	Et	136	2.0053	15.0	41.0	
		300	2.0053	14.8	37.4	
t-BuCH$_2$*	t-Bu	97	2.0053	15.2	42.1[d]	
		300	2.0053	14.9	37.9[d]	
i-Pr*	Me	143	2.0050	14.8	27.5	1.6_3,[c] 2.3[e]
		213	2.0050	14.7	25.1	1.6_1,[c] 2.3[e]
i-Pr*	Et	135	2.0050	14.5	28.4[d]	
		270	2.0050	14.5	23.9[d]	
i-Pr*	t-Bu	138	2.0053_5	14.6	22.5[d]	
		300	2.0053_5	14.5	21.1[d]	
t-Bu$_2$CH*	Me	174†	2.0056	14.6_6	12.3_3[d]	
		300	2.0056		11.9[d]	
t-Bu*	Me	173†	2.0044_3	15.7_6		2.4_3,[c] 4.6,[e] 0.56[f]
		275†	2.0045_4	15.7_7		2.4_8,[c] 4.6,[e] 0.56[f]
t-Bu	Et	169†	2.0044_8	15.6_1		
		221†	2.0045_4	15.6_2		
t-Bu*	t-Bu	143†	2.0049_4	15.7_0		0.63[g]
		283	2.0052_9	15.0		0.63[g]
$O{=}\overline{CCH_2CH_2CMe_2N}\cdot$		209	2.0063	11.2		
		220	2.0063	11.2		

[a] For those amidyls marked with an asterisk hyperfine splittings at other temperatures are available as supplementary material.
[b] Not all measurements of g and of hfs were of equal accuracy. The more reliable data is indicated by the presence of more significant figures and a dagger. In general, data should be reliable to within ±1 in the last number (excluding subscript numbers) except possibly at the very lowest and highest temperatures. [c] 3 H in R′. [d] H$_\beta$ hfs vs. T plotted in Figure 1. [e] ^{13}C in R′. [f] 9 H in R. [g] H from both t-Bu groups. In no other R$\dot{N}$CO-t-Bu radical are the H in the t-Bu group resolved.

The generally accepted relationship between a^{H_β} and θ, the dihedral angle between the C–H$_\beta$ bond and the axis of the semioccupied orbital, is[25]

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

where A and B are constants and A can generally be neglected.[26] In the $CH_3\dot{N}COR'$ radicals the average value of the dihedral angle, $\bar{\theta}$, is 45° at all temperatures. For these radicals, $a^{H_\beta} = 29.5$ G for R′ = Me and Et and ca. 29 G for R′ = t-Bu (see Table I and supplementary material), from which it follows that $B \approx 59$ G.

For all seven $R''CH_2\dot{N}COR'$ radicals (R′ = Me, Et, t-Bu; R″ = Me, Et, t-Bu; see Table I) a^{H_β} is greater than 29.5 G and shows

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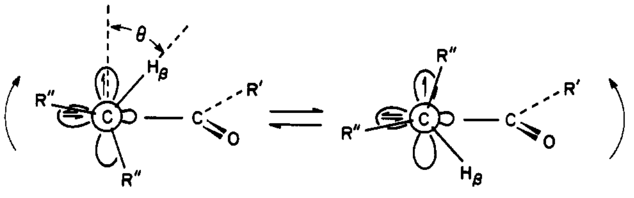
a pronounced temperature coefficient. The magnitude of a^{H_β} decreases with increasing temperature, apparently tending toward the "free rotation" limit of ca. 29.5 G for at least some of these radicals at temperatures above 300 K (see Figure 1). At the lowest temperatures attained (ca. 100 K) the a^{H_β} values for these radicals are ca. 41–44 G which indicates that $\bar{\theta}$ is ca. 30°. This behavior is analogous to that found for alkyl radicals of the type $\mathrm{R''CH_2\dot{C}R_2'}$.[25]

For the four $\mathrm{R_2''CH\dot{N}COR'}$ radicals studied (R′ = Me, Et, *t*-Bu; R″ = Me, *t*-Bu) a^{H_β} is less than 29.5 G at temperatures above ca. 120 K, which means that $\bar{\theta}$ is greater than 45°. The magnitude of a^{H_β} decreases further with increasing temperature which indicates that $\bar{\theta}$ is becoming even larger. The $\mathrm{R_2''CH}$ group in the amidyls, unlike that in alkyls of the type $\mathrm{R_2''CH\dot{C}R_2'}$, does not therefore tend toward "free rotation", at least at temperatures as high as 300 K.

By the arguments presented previously,[21] these observations require the π-radical structure, **1**, for the *N*-alkylamidyls examined in this work. In the $\mathrm{R_2''CH\dot{N}COR'}$ radicals a substantial barrier must exist to full rotation about the $\mathrm{R_2''CH{-}N}$ bond, the $\mathrm{R_2''CH}$ group rocking between two energetically equivalent conformations, **5**. The barrier to interconversion arises from repulsion between the C–H_β and the carbonyl oxygen and should be quite small. Two opposing effects determine $\bar{\theta}$: hyperconjugation to the C–H_β bond which tends to reduce θ toward 0° and steric repulsion between R″ and oxygen which tends to increase θ toward 90°. The rocking motion is subject to a double-minimum potential function,[27-30] and $\bar{\theta}$ increases as the temperature is raised because the slopes of the potential energy profiles are less steep as $\theta \rightarrow 90°$ than as $\theta \rightarrow 0°$ or 180°. As a consequence a^{H_β} decreases with an increase in temperature.[31] The magnitude of a^{H_β} for $t\text{-}\mathrm{Bu_2CH\dot{N}COMe}$ is much smaller than for the $\mathrm{Me_2CH\dot{N}COR'}$ radicals because the greater steric interaction between the *tert*-butyl groups and the oxygen forces the H_β closer to the plane of the radical. If the semioccupied orbital lay in this plane, the magnitudes of a^{H_β} would have been reversed. This rules out both the bent, **2**, and linear, **3**, σ_N configurations.



5 **5**

The "Twist" of Amidyls. In reaching the conclusion that the electronic ground state of amidyls is π, we have *assumed 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 important to our conclusions that amidyls are π radicals. It is based on analogy with the known trans arrangement in carboxamides[32] and in carboxylic esters.[33] The latter assumption is relatively unimportant in the context of the preferred conformation(s) of the $\mathrm{R_2''CH}$ group and the conclusions that arise therefrom since a certain barrier will remain even if the R′CO group were to be partially or fully rotated out of the CNC plane.

The twist angle, φ, between the R′CO and CNR planes (see structure **4**) can, in principle, be estimated from the magnitude of $a^{^{13}\mathrm{C}_\gamma}$ for isotopically labeled $\mathrm{R\dot{N}CO^{13}CH_3}$ radicals. If φ is small $a^{^{13}\mathrm{C}_\gamma}$ will be small and if φ is large $a^{^{13}\mathrm{C}_\gamma}$ will be large. Four ^{13}C-labeled amidyls were examined. The $a^{^{13}\mathrm{C}_\gamma}$ values were found to be 2.3–2.4 G for R = $\mathrm{CH_2CH_2Me}$, $\mathrm{CHMe_2}$, and $\mathrm{CH_2CMe_3}$ and 4.6 G for R = $\mathrm{CMe_3}$ (see Table I and Figure 2).

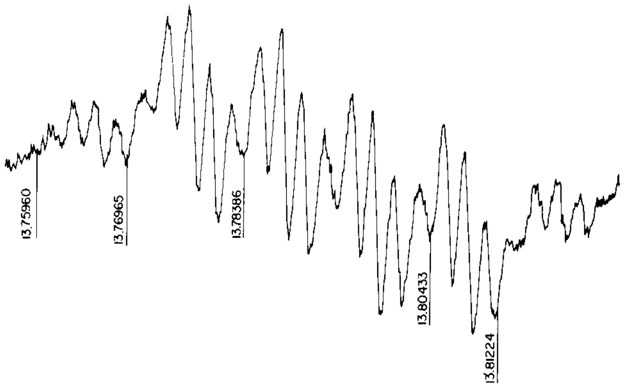


Figure 2. Low-field multiplet for $\mathrm{Me_3C\dot{N}CO^{13}CH_3}$ at 195 K showing $a^{^{13}\mathrm{C}}$ = 4.6 G, a^H(3 H) = 2.45 G, and a^H(9 H) = 0.56 G. Field markers are given in MHz (uncorrected). The average microwave frequency was 9133.80 MHz.

It is immediately obvious from the larger ^{13}C hfs found for $\mathrm{Me_3C\dot{N}CO^{13}CH_3}$ that this radical *must be twisted quite substantially* with respect to the amount of twist (if any) of the other three ^{13}C-labeled amidyls. To decide whether or not these other amidyls are twisted is not easy. Our initial approach was to try to assess indirectly the magnitude of *A′* in the appropriate equation relating $a^{^{13}\mathrm{C}}$ and φ, viz.

$$a^{^{13}\mathrm{C}} = A' + B' \sin^2 \phi$$

The acetonyl radical, $\mathrm{\dot{C}H_2COCH_3}$, seemed to us to be an appropriate model since this is known to be a planar (i.e., φ = 0°), π radical[34] which probably has ca. 85% of the spin density on the α-carbon.[35] Since the magnitude of the appropriate ^{13}C hfs was unknown, it was measured by using $\mathrm{^{13}\dot{C}H_2CO^{13}CH_3}$ which was generated by photolysis of di-*tert*-butyl peroxide in the presence of the labeled acetone. The $^{13}\mathrm{C}_\gamma$ hfs was found to be 0.9 G which, *if* acetonyl is an appropriate model for $\mathrm{R\dot{N}COCH_3}$ radicals, implies that all these amidyls must be twisted. For determination of the approximate angle of twist a model π radical for which φ = 90° is required so that *B′* can be determined. The most appropriate model to suggest itself to us was one of Regenstein and Berndt's[36,37] "perpendicular" allyl radicals for which φ = 90° and the appropriate ^{13}C hfs has been measured at natural abundance, e.g., $\mathrm{(Me_3C)_2\dot{C}C(^*CH_3){=}CH_2}$ for which $a^{^{13}\mathrm{C}_\gamma}$ = 18 G[36] and $\mathrm{(Me_3C)_2\dot{C}C(^*CH_3){=}CHCH_3}$ for which $a^{^{13}\mathrm{C}_\gamma}$ = 16 G.[37] If *B′* is taken to be +17 G and *A′* = +0.9 G, then φ will be 17° for $\mathrm{R\dot{N}COCH_3}$ radicals having R = *n*-propyl, isopropyl, and neopentyl and φ will be 28° for R = *tert*-butyl. However, the possibility that acetonyl is an unsuitable model from which to derive *A′* cannot be ignored. If, instead, it is assumed that the three less hindered amidyls are planar, then *A′* will be 2.3–2.4 G. In this case, if *B′* is still taken as 17 G, then for $\mathrm{Me_3C\dot{N}COCH_3}$, φ = 22°, which means that *this amidyl, at least, is significantly twisted.*

Having demonstrated that $\mathrm{Me_3C\dot{N}COCH_3}$ is twisted, an unusual observation made by Danen and Gellert[13] in the first EPR spectroscopic study of *N*-alkylamidyls (and confirmed by us) can be readily explained. Danen and Gellert found that under their conditions the $\mathrm{Me\dot{N}COCMe_3}$ radical had a^N = 15.00 G and *g*

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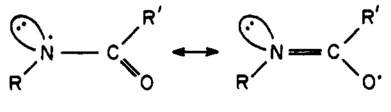
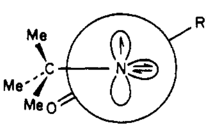
= 2.0053 (T = 173 K) while the $\mathrm{Me_3C\dot{N}COMe}$ radical had a^N = 15.70 G and g = 2.0044 (t = 233 K). The difference in g values for such closely related radicals was commented upon[13] but no explanation was offered. To our knowledge such a change in g is unprecendented, but it follows quite naturally from our conclusion that $\mathrm{Me_3C\dot{N}COMe}$ is more twisted than $\mathrm{Me\dot{N}COCMe_3}$ (the latter radical may of course be planar). That is, twisting in a π amidyl must reduce the extent of delocalization of the unpaired electron from the nitrogen to the oxygen, i.e., the importance of canonical structure **1b** will be reduced relative to **1a** by twisting.


1a **1b**

As structure **1a** becomes more important, the value of a^N will, of course, increase [15.0 ($\mathrm{Me\dot{N}COCMe_3}$) → 15.8 ($\mathrm{Me_3C\dot{N}COMe}$) G]. Furthermore, since oxygen has a larger spin-orbit coupling constant than nitrogen, the value of g might be expected to decrease [2.0054 ($\mathrm{Me\dot{N}COCMe_3}$) → 2.0044 ($\mathrm{Me_3C\dot{N}COMe_3}$)].

Why should $\mathrm{Me_3C\dot{N}COMe}$ be so much more twisted than the other $\mathrm{R\dot{N}COMe}$ amidyls? The answer must be that there is a much greater steric repulsion between oxygen and the $\mathrm{CMe_3}$ group (see **6**) than between oxygen and primary (**7**) or secondary (**8**) N-alkyl groups.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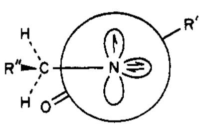
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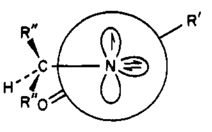
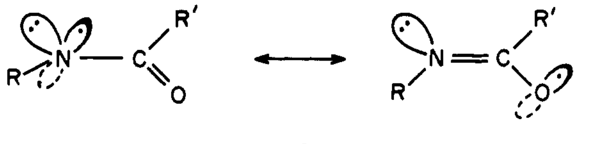

8

Some interesting predictions follow from the conclusion that twist is due to R···O steric repulsion and that twist affects g and a^N. In the first place, to judge by the g values (and the a^N values at the higher temperatures), the $\mathrm{Me_3C\dot{N}COMe}$ radical must be more twisted than $\mathrm{Me_3C\dot{N}COCMe_3}$. This we attribute to a "long-range" steric repulsion between the two *tert*-butyl groups in the latter radical which reduces ϕ relative to its value in the former radical. Following a suggestion by Berndt[38] on the origin of long-range steric effects in hydrazonyl radicals ($\mathrm{R\dot{N}N{=}CR_2'}$), we suggest that the intrinsic barrier to rotation about the amidyl N–COR′ bond is relatively small and, hence, steric effects become significant over surprisingly large distances. The low barrier arises because, although the delocalization energy of the unpaired electron in the ground state, **9**, is lost in the perpendicular transition state for rotation, **10**, this energy is, to some extent, compensated for by the gain in amide-like stabilization due to the nitrogen lone pair. Structure **10** and the linear σ_N structure, **3**, are clearly related.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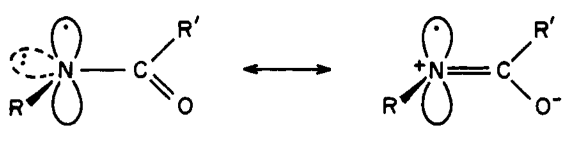
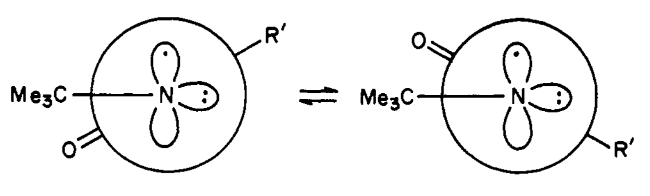

10

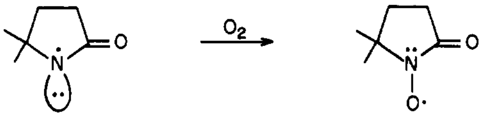
Secondly, it is clear that $\mathrm{Me_3C\dot{N}COR'}$ radicals must have two equivalent conformations, **11**, which will be separated by a small potential barrier at ϕ = 0°. These radicals are therefore subject to rocking within a double-minimum potential function,[27-30] and, as such, their hfs[39] might show a temperature dependence. That is, the usual arguments[27-30] suggest that **11** will become more planar; i.e., ϕ will decrease as the temperature is raised because the slopes of the potential energy function are less steep as $\phi \to 0°$ than as $\phi \to 90°$. The N hfs is therefore expected to decrease as the temperature is raised, and delocalization of the unpaired electron onto oxygen becomes somewhat more important. Such appears to be the case for R′ = $\mathrm{Me_3C}$ (see Table I).[40] On the other hand, if the $\mathrm{R\dot{N}COR'}$ radicals which have R = n-alkyl or *sec*-alkyl have either a single-minimum potential function for rocking about the $\mathrm{R\dot{N}{-}COR'}$ bond (which means they are planar) or a double-minimum potential with a barrier between equivalent conformations which is not much greater than the zero-point energy, then these amidyls should exhibit very little variation in a^N with temperature and this would appear to be the case (see Table I). We therefore conclude that these particular amidyls (which can be characterized as having a^N = ca. 14.5–15.2 G and g = ca. 2.0050–2.0056) either are planar or are slightly twisted with a low barrier between conformers. A more detailed analysis of the differences in a^N and g values found for these radicals seems unwarranted at the present time.


11

In summary, all acyclic N-alkylamidyls are π radicals and they are planar, or nearly so, *except* when the N-alkyl group is *tert*-butyl; in which case the radical will be twisted and the degree of twist can be 20° or larger.

A Cyclic Amidyl. Early attempts to observe by EPR spectroscopy a cyclic amidyl, specifically 5,5-dimethyl-2-oxopyrrolidin-1-yl, **12**, were uniformly unsuccessful,[4,6,16] for reasons which are far from obvious. The hope was that such a radical, being constrained to be planar, would provide unequivocal answers to questions regarding the electronic structure etc. of acyclic amidyls.

Employing the usual procedure (i.e., photolysis of the parent chloramide of **12** in cyclopropane[6,13]), we had no difficulty in observing a radical at 209 K with a^N = 11.2 G, g = 2.0063, and some additional splittings not fully resolved. We assign this radical structure **12**. The low value of a^N and the high value of g, relative to acyclic amidyls, are in full accord with the expected, though not absolutely required, nontwisted (i.e., planar) geometry and imply extensive delocalization of the unpaired electron onto the oxygen (vide supra). Radical **12** is *not* the corresponding nitroxide, **13**, since this species (for which the hfs have been reported previously[41] was formed on admission of air to the sample.


12 **13**

a^N = 11.2 G
g = 2.0063

a^N = 3.2 G; $a^H(2H)$ = 6.4 G
g = 2.0071; T = 239K

The magnitude of a^N for **12** is between 71 and 77% of the a^N values found for acyclic amidyls (see Table I). It is interesting

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[38] Berndt, A. Lecture at EUCHEM Conference on Organic Free Radicals, Cirencester, England, Sept 10–14, 1979.

[39] A small change in g might also be anticipated.

[40] The small increase in g with temperature is probably within our experimental error (which is appreciable at both high and low temperatures for this particular radical). However, the change *is* in the expected direction, i.e., as a^N goes down, g goes up.

[41] (a) Aurich, H. G.; Trösken, J. *Liebigs Ann. Chem.* **1971**, *745*, 159. (b) Aurich, H. G.; Trösken, J. *Chem. Ber.* **1973**, *106*, 3483.

to note that a^N for the nitroxide, **13**, though somewhat solvent dependent,[41a] is also smaller than the a^N values found for acyclic acyl nitroxides (e.g.,[41a] it is 82–87% of the value found for $Me_3CN(\dot{O})COMe$). While ring-strain effects may contribute to the lowering of a^N in the cyclic amidyl and nitroxide, a more important factor would seem to be the improved delocalization of the unpaired electron from N to the carbonyl O in these radicals.

It is interesting to note that cyclic sulfonamidyls have N hfs and g values of 13.1–13.3 G and 2.0040–2.0042, respectively.[16-19] Their EPR parameters are therefore no different from those of acyclic sulfonamidyls (viz., $a^N = 12.9$–13.2 G and $g = 2.0041$–2.0044).[16,17,19]

Attempts to observe other cyclic amidyls (2-oxopyrrolidin-1-yl, 5-methyl-2-oxopyrrolidin-1-yl, and 2-oxopiperidin-1-yl) were frustrated by the poor solubility of the parent chloramides in cyclopropane at low temperatures.

Summary

N-Alkylcarboxamidyl radicals have a π-electronic ground state. Acyclic amidyls are either planar or nearly so when the N group is a primary or secondary alkyl but there is considerable rocking about the preferred conformation. Amidyls having an *N*-*tert*-butyl group are nonplanar, i.e., twisted, because of steric repulsion between the *tert*-butyl and the carbonyl oxygen atom.

Acknowledgment. We are grateful to Professor A. Berndt (Marburg) for his generous gift of 5,5-dimethylpyrrolidin-2-one. We are also pleased to acknowledge some very helpful comments by Drs. B. P. Roberts (London) and S. Glover (Port Elizabeth).

Supplementary Material Available: EPR parameters for amidyls at temperatures other than those listed in Table I (4 pages). Ordering information is given on any current masthead page.

Dehydration and Enolization Rates of Oxalacetate: Catalysis by Tertiary Amines

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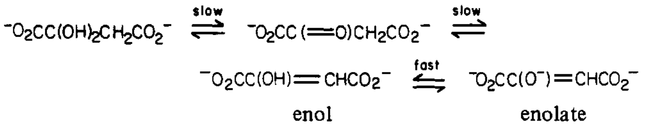
Abstract: The hydration/dehydration and tautomerization rates of oxalacetate are subject to acid and base catalysis. H_2O and OH^- are much more effective for the former process than for the latter, but the opposite holds for tertiary amine catalysis. In buffers comprised of oxyanion bases or unsaturated amines, dehydration is significantly faster than tautomerization and remains so as the buffer concentration is varied. In dilute tertiary amine buffers dehydration rates are also faster, but as the buffer concentration increases, tautomerization rates increase rapidly and eventually surpass those for hydration/dehydration. It is this rate crossover which led earlier workers (ref 9) to propose a carbinolamine mechanism for tertiary amine-catalyzed tautomerization. After the rate crossover is taken into account, enolization is found to show linear rate–buffer concentration behavior with tertiary amines, vitiating the prime evidence cited for the carbinolamine mechanism. However, tertiary amine catalysis likely operates differently in the tautomerization and dehydration reactions.

Oxalacetate (oxac) is an important reactive substance which, because it is an intermediate in a number of crucial biological sequences, has been studied extensively. Fundamental to our understanding of oxac chemistry are the enolization and hydration reactions, shown in Scheme I, which may influence or may be mistaken for other reactions of interest.

While enolization has been investigated for many years,[1-9] relatively little attention has been focused on the solvational reactions. Kokesh[7] has determined the distribution of the components shown in Scheme I as a function of pH (38 °C) by using NMR band area measurements. Pogson and Wolfe[8] studied the rates of the enzymatic reduction of $oxac^{2-}$ at pH 7.4 (20 °C) with the goal of determining the concentrations of the components and their reaction rates. The hydrate content which they found is consistent with that reported by Kokesh,[7] and they established that dehydration rates in tris or phosphate buffers are about 1 order of magnitude faster than enolization rates.

Scheme I



$$^{-}O_2CC(OH)_2CH_2CO_2^{-} \underset{}{\overset{\text{slow}}{\rightleftharpoons}} {}^{-}O_2CC(=O)CH_2CO_2^{-} \overset{\text{slow}}{\rightleftharpoons} \underset{\text{enol}}{^{-}O_2CC(OH)=CHCO_2^{-}} \overset{\text{fast}}{\leftrightharpoons} \underset{\text{enolate}}{^{-}O_2CC(O^{-})=CHCO_2^{-}}$$

A reinvestigation of buffer catalysis on the enolization rates was recently reported by Bruice and Bruice.[9] These authors employed a pH jump technique to determine reaction velocities, and to circumvent interference from the presence of hydrate, which is dominant at low pH, adjusted the initial pH of the oxac solutions to 3.7. While they found normal linear rate vs. buffer concentration plots for catalysis by imidazole, pyridine, and oxyanion buffers, tertiary amines yielded plots showing two linear regions with the limb at higher buffer concentrations having the smaller slope. A multistep mechanism involving the formation of an intermediate carbinolamine was invoked to account for the indicated change in the rate-limiting step.

At the time that the paper by Bruice and Bruice[9] appeared an investigation of the effects of buffers and metal ions on oxac tautomerization rates was under way in our laboratories. Preliminary rate data obtained with *N,N,N′,N′*-tetramethylethylenediamine (tetrameen) buffers containing Mg^{2+} gave no evidence of the two limbed plots. Because complexing metal ions

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