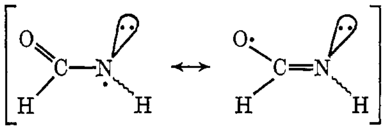
Electronic Configurations of Amido Radicals[1a]

**T. Koenig,*[1b] J. A. Hoobler,[1b] C. E. Klopfenstein,[1b] G. Hedden,[1b,2]
F. Sunderman,[1b] and B. R. Russell[1c]**

*Contribution from the Departments of Chemistry, University of Oregon,
Eugene, Oregon 97403, and the North Texas State University,
Denton, Texas 76203. Received October 12, 1973*

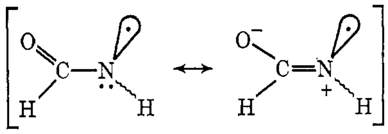
Abstract: The C–N–H angular (θ) potentials for cis-planar formamido, *N*-hydroxyformamido, and *N*-methylformamido radicals in the Π, Σ_N, and Σ_O electronic configurations have been calculated using the Hartree–Fock SCF method in the INDO approximation. The lowest states are predicted to be Π with $\theta \sim 114$–$120°$ with the possible exception of the *N*-methyl compound. Standard "aufbau" population methods give the Σ_O configuration. The results are compared with observed esr spectra for several systems. The chemical implications of the theoretical results are discussed.

We wish to discuss the results of our studies of the configurations of amido radicals through esr experiments which are compared with the predictions of the INDO[3] method. Our primary concern is the energetic dependence of the Π (**1a** and **1b**) and Σ_N (**2a** and **2b**) configurations on the C–N–R (θ) angle. This preoccupation with the θ coordinate is due to its connection with expectations of the esr hyperfine coupling to nitrogen. A considerably larger coupling to the ^{14}N nucleus is expected for the Σ_N configuration for $\theta < 180°$ because of the increased nitrogen 2s character of the spin density function which accompanies the deviation from $\theta = 180°$. For $\theta = 180°$, the vacancy center is p with respect to the nitrogen atom in both the Π and Σ_N configurations. The esr criterion would be less definitive in cases where $\theta = 180°$ is favored.



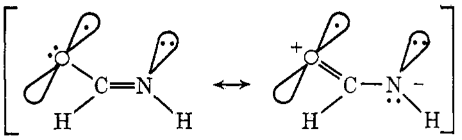
1a **1b**

Π



2a **2b**

Σ_N



3a **3b**

Σ_O

Application of even simple methods reveals the importance of the θ coordinate. Using the structure representation model of Simpson[4] and the experimental[5] potential energy surface of the simple amidogen ($NH_2\cdot$) radical (Figure 1) predicts the formamido ground state to be Σ_N at $180° > \theta > 140°$ but Π for $\theta = 105°$. This follows from the relative electronic stabilization factors for formation of the amide (RSA $\simeq$ 20 kcal/mol)[4] *vs.* (Π) amido radical electron groups (RSAR < 11 kcal/mol).[6]

An alternative is to use the equation of Hedaya and coworkers[8] which was derived from Hückel theory (eq 1). The α terms are the Hückel Coulomb integrals

$$\Delta E_{\Sigma}^{\Pi} = {}^1\!/_2(\alpha_C^{\Pi} + \alpha_N^{\Pi}) - \alpha_N^{\sigma} \qquad (1)$$

and ΔE_{Σ}^{Π} is the difference in the energies of the Σ and Π states, respectively. Treating $NH_2\cdot$ as a one-center Hückel problem allows the extraction of the angular dependence of the two Coulombic terms for nitrogen from the curves in Figure 1. Thus at 180°, for $(-\alpha_O^{\Pi} >$

$$\alpha_N^{\Pi,180°} = \alpha_N^{\sigma,180°} = \alpha_N$$

$$\alpha_N^{\Pi,103°} = \alpha_N - \beta$$

$$\alpha_N^{\sigma,103°} = \alpha_N + 1.5\beta \quad (\beta = -19 \text{ kcal/mol})$$

$\alpha_N^{\Pi})$, eq 1 predicts a Σ_N ground state (**2**) as suggested by Hedaya. However, at 103° a σ ground state requires $(\alpha_N - \alpha_O^{\Pi}) > (-4\beta)$ which is too large a difference to be reasonable. Thus, this method also makes the *strong prediction* of a Π ground state with a small C–N–H angle (θ) though these workers favored a σ species.

Though the simple methods agree rather well in their predictions, calculations with all valence electron methods would be more convincing. The EHT[9] method predicts a σ ground state for formamido at all geometries. This conflicting result is not too surprising since this method fails to predict the form of the known $NH_2\cdot$ surface (Figure 1) giving the Π state only slightly lower that the Σ state at all $\theta°$. The deep minimum in the *observed* Π configuration surface for $NH_2\cdot$, which

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(1) (a) Taken in part from the B.S. Thesis of G. Hedden (Honors College, University of Oregon, 1969) and the Ph.D. Thesis of J. A. Hoobler (University of Oregon, 1971). (b) University of Oregon. (c) North Texas State University.

(2) National Science Foundation Undergraduate Research Participant, 1966–1968.

(3) J. A. Pople, D. A. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967).

(4) W. T. Simpson, *J. Amer. Chem. Soc.*, **75**, 597 (1953); E. J. Rosa and W. T. Simpson in "Physical Processes in Radiation Biology," L. G. Augenstein, Ed., Academic Press, New York, N. Y., 1964, pp 43–49.

(5) R. N. Dixon, *Mol. Phys.*, **9**, 357 (1965); K. Dressler and D. A. Ramsay, *Phil. Trans. Roy. Soc. London, Ser. A*, **251**, 553 (1959).

(6) The value should be less than an allylic[7] radical.

(7) R. Crawford and R. Tagaki, *J. Amer. Chem. Soc.*, **95**, 4507 (1973).

(8) E. Hedaya, R. L. Hinman, V. Schomaker, S. Theodoropulos, and L. M. Kyle, *J. Amer. Chem. Soc.*, **89**, 4875 (1967).

(9) R. Hoffmann, *J. Chem. Phys.*, **34**, 1379 (1963).

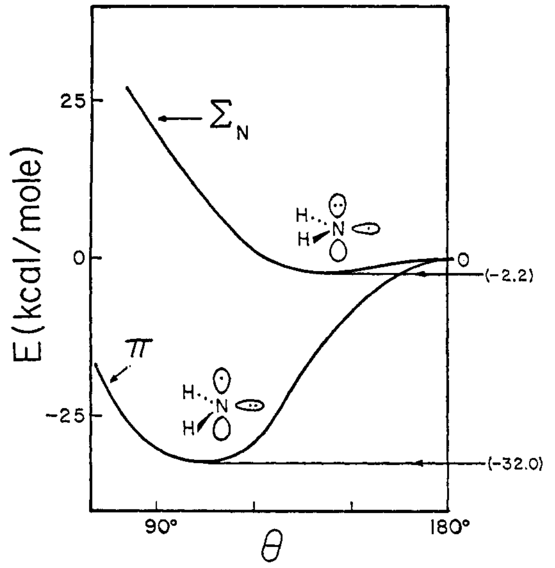


Figure 1. Angular potentials for amidogen ($NH_2\cdot$, after Dixon).

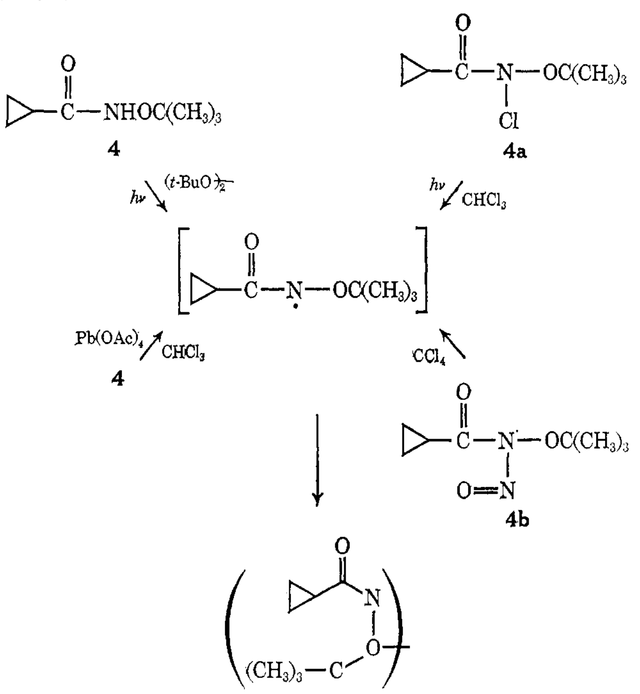
EHT misses, may be due to the electron-electron repulsion balance rather than fraction S or H-H bonding character. The EHT method would then give unreliable results for the amido systems because of the neglect of repulsions.

The INDO method is the simplest version of SCF calculations which does take repulsion into account. During the course of this work a study of INDO results was published[10] for formamido which gave Σ_O (3). The present results are quite different in demonstrating that the configuration which is converged on in the standard program is not the one of lowest energy.

Esr Results

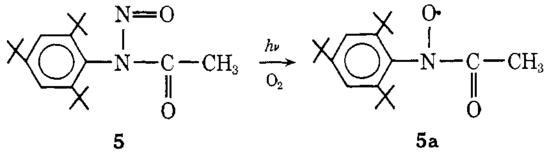
An earlier report[11] gave our results on the formation of a number of *N-tert*-butoxyamido radicals which are easily formed from the amide (**4**) or its *N*-chloro (**4a**) or *N*-nitroso (**4b**) derivatives. For the cyclopropanecarbonyl derivative (**4**), the same species was observed from four independent reactions (Scheme I). Furthermore, the products of treatment of *N*-alkoxyamides with lead tetraacetate are the corresponding hydrazine dimers (**4c**).[12] A preparative scale reaction was run in which **4c** was isolated and characterized, and aliquots from this reaction showed the presence of the same radical as that observed by the other methods.

Scheme I



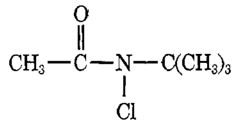
4c

Our previous attempts at generating the amido species from photolysis of **5** failed to give signals attributable to the desired intermediate though four distinct nitrogen containing species were detected, among which was the corresponding acyl nitroxide (**5a**). The major product of the photolysis of **5** in benzene was the parent amide. As indicated by Danen and Gellert,[13] the signals observed from photolysis of simpler nitrosoamides[14] are certainly due to such acyl nitroxides.[15]

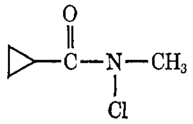


5 **5a**

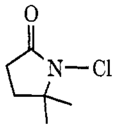
More recent low-temperature photolyses of **6** and **7** were successful in producing signals which we assign to the corresponding amido systems. No signal was observed during photolysis of the *N*-chloro-γ-lactam (**8**) under the same conditions. The *N*-chloro-β-lactam (**9**) did produce a very weak three-line signal suggestive of coupling to a single nitrogen-14 nucleus. The low intensity of this signal prevents us from making a definite assignment of its origin. The acyl nitroxides corresponding to **6** and **7** were easily observed when oxygen was present but no such signals could be obtained from **8** or **9**. Table I summarizes our esr results.



6



7



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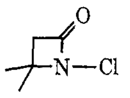

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INDO Results

The INDO[3] method of Pople and coworkers gives calculated results for $NH_2\cdot$ which are quite close to the experimental ones represented in Figure 1. Straightforward application of this method to the formamido

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[10] E. Evleth, P. Horowitz, and T. Lee, *J. Amer. Chem. Soc.*, **95**, 7948 (1973).

[11] T. Koenig, J. A. Hoobler, and W. R. Mabey, *J. Amer. Chem. Soc.*, **94**, 2514 (1972).

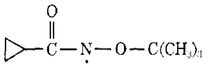
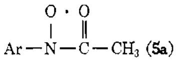
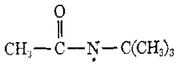
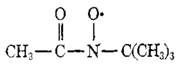
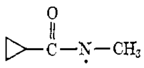
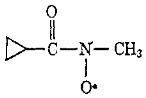
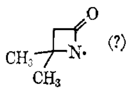
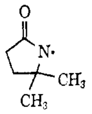
[12] J. H. Cooley, M. Mosher, and M. A. Khan, *J. Amer. Chem. Soc.*, **90**, 1867 (1968).

[13] W. C. Danen and R. W. Gellert, *J. Amer. Chem. Soc.*, **94**, 6853 (1972).

[14] P. Tordo, E. Flesia, and J. Surzur, *Tetrahedron Lett.*, 183 (1972); P. Tordo, E. Flesia, G. Labrot, and J. Surzur, *ibid.*, 1413 (1972).

[15] A. Mackor, Th. Wajor, and Th. deBoer, *Tetrahedron*, **24**, 1623 (1968); A. Vasserman, Y. Basicakov, and A. L. Buchachenko, *J. Struct. Chem.*, **10**, 620 (1969).

Table I. Esr Results

Radical	Source	Solvent	Temp, °C[a]	a_N, G	a_{CH_3}, G
	**4** + $Pb(OAc)_4$	$CHCl_3$	RT	10.40	
	4 + $(t\text{-}BuO\text{-})_2$	t-BuOH	RT	10.35	
	4a	$CHCl_3$	RT	10.30	
	4b	CCl_4	RT	10.50	
 $Ar-N(O\cdot)-C(=O)-CH_3$ (**5a**)	**5** + O_2	Benzene	RT	7.50	
 $CH_3-C(=O)-\dot{N}-C(CH_3)_3$	**6**	Cyclopropane	−70	15.70	2.71
 $CH_3-C(=O)-N(O\cdot)-C(CH_3)_3$	**6** + O_2	Cyclopropane	−70	7.58	
	6 + O_2	CCl_4	RT	7.58	
	**7**	Cyclopropane	−70	14.9	29.8
	**7** + O_2		−70	7.6	8.4
 (?)	**9**	Cyclopropane	−70	(13)	
	**8**	Cyclopropane	−70	No signal	

[a] RT, room temperature.

problem, using the microwave geometry[16] for formamide except for the C–N–H angle (θ), gives the Σ_N configuration for $\theta = 180°$ as expected. At $\theta = 105°$ the configuration of convergence is Σ_O (**3**).

The latter result was viewed with some circumspection since it is not clear that the configuration which happens to be converged upon, by repetitions of "aufbau" population schemes during the SCF cycles, necessarily corresponds to the lowest one.[17] We thus modified the INDO population scheme so that several configurations could be examined. This was accomplished by specifying the configuration to be calculated after the first (Hückel) diagonalization. The α spin eigenvector, to be unpaired in the β-spin set, was found using the maximum of the dot product of the original vacancy eigenvector with entire set, generated by each interaction, as the criterion. Figure 2 shows the angular potentials of the three configurations (using the microwave geometry[16] of formamide). The forms and the relative positions of the curves for Π and Σ_N are in good agreement with the predictions of the simple structure representation method present above.

The next question is the effect of an N-methyl substituent. The skeletal geometry for the N-methyl compound was assumed to be the same as for formamido. The $N-CH_3$ bond length was 1.40 Å. At $\theta = 180°$, the relative energies of the three configurations were hardly different than those for the parent system. However, the energy minima for both Π and Σ_N configurations was near $\theta = 180°$. These results would suggest a change in ground state from Π ($\theta = 115°$) to Σ_N ($\theta = 180°$) on N-methyl substitution.

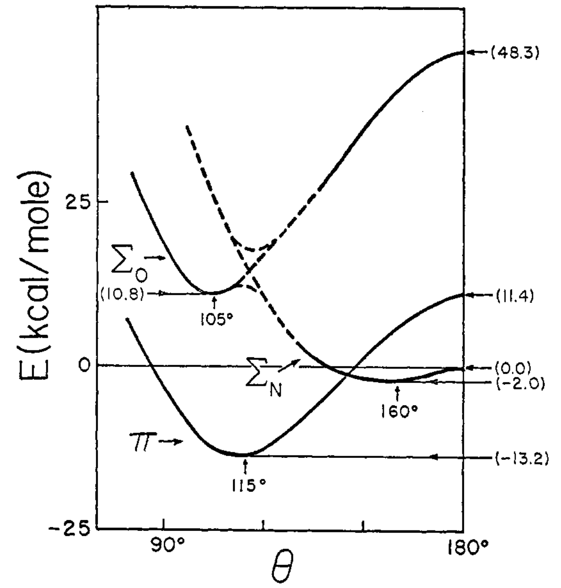


Figure 2. INDO angular (C–N–H) potentials for formamido radical (cis-planar formamide geometry). The dashed portions were not calculated due to convergence difficulties.

Inspection of the structure (**3**), representing Σ_O, suggests a relatively short C–N distance and a relatively long C–O distance. To investigate this structural feature, calculations were carried out varying R_{C-O}, R_{C-N}, and θ holding the other internal coordinates fixed at standard values.[18] The results of optimization over these three variables are summarized in Table II along with the dipole moments and hyperfine coupling

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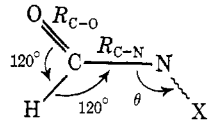
(16) C. C. Costain and J. N. Dowling, *J. Chem. Phys.*, **32**, 158 (1960).

(17) R. E. Stanton, *J. Chem. Phys.*, **48**, 257 (1968); H. F. King and R. E. Stanton, *ibid.*, **50**, 3789 (1969); W. H. Adams, *Phys. Rev.*, **127**, 1650 (1962).

(18) The formyl group angles were taken as 120° and the CO–H bond length was held at 1.10 Å.

Table II. INDO Results Optimized in R_{C-N}, R_{C-O}, and θ



X	Configuration	θ, deg	R_{C-O}, Å	R_{C-N}, Å	E_{rel}, kcal/mol	a_N[a]	a_{H_x}[a]	a_H[a]	μ[b]
H	Σ_N	180	1.27	1.33	(0.00)	19.8	−24.3	68.6	4.14
H	Σ_N	158	1.27	1.33	−0.6	28.3	−10.6	64.8	4.42
H	Σ_O	114	1.34	1.29	−25.1	0.7	−2.1	41.7	3.20
H	Π	114	1.32	1.32	−27.0	8.6	−12.9	5.74	3.18
CH_3[c]	Σ_N	180	1.32	1.32	(0.0)	17.8	30.3[d]	46.0	4.68
CH_3[c]	Σ_O	165	1.32	1.32	+5.1	5.8	−0.6[d]	37.9	2.85
CH_3[c]	Π	120	1.32	1.32	−16.1	10.20	16.9[d]	6.1	3.43
OH[e]	Σ_N	180	1.21	1.30	(0.00)	18.92	54.68	44.35	2.17
OH[e]	Π	120	1.21	1.30	−30.9	9.56	−4.69	2.39	2.81
OH[e]	Σ_O	120	1.21	1.30	+0.9	−1.32	3.63	87.03	1.18

[a] Gauss, unprojected. [b] Dipole moment, Debyes. [c] R_{N-CH_3} = 1.40 Å, optimized in θ only. [d] Average coupling to three methyl hydrogen nuclei. [e] R_{C-H} = 1.09 Å, R_{C-N} = 1.30 Å, $R_{C=O}$ = 1.21 Å, R_{N-OH} = 1.26 Å, R_{O-H} = 0.96 Å, O–C–N angle = 124°, H–C–N angle = 112°, and N–O–H angle = 108°. Optimized in θ only.

constants calculated for each configuration. The most important result of the bond length minimization is with respect to **3** which becomes nearly degenerate with the Π configuration. The *N*-methyl compound was recalculated at θ = 180 and 120° using the minimized values of R_{C-N} and R_{C-O} for the Π configuration of formamido. This gave the Π configuration with θ = 120° being the lower state though the stabilization with respect to θ = 180° was only 16 kcal/mol.

The skeletal geometry[19] for the *N*-hydroxy derivative was chosen from different models. The assumed C–O bond length was 1.21 Å and the C–N bond length was 1.30 Å. At 180°, the Σ_N configuration was only slightly favored over the Π configuration (<1 kcal/mol). The Π configuration was strongly favored at smaller θ and the energy minimum was near 120°. These results are given in Table II.

Discussion

A complete energy–structure optimization for each configuration of each particular amido radical would be necessary before the INDO answer to the question of the ground electronic states could be obtained. The expense of such an undertaking is presently beyond our reach. In addition, the approximate way in which the electron–electron repulsion integrals are treated, within the INDO formalism, means the reliability of the energetic results would be open to question. The spherical averaging, required to maintain invariance when differential overlap is neglected,[20] is particularly suspect for repulsions between lone pairs. The partial minimization presented here serves our purpose which is to focus on the problems associated with the geometry and multiple electronic possibilities. It is hoped that this focus will stimulate the application of better theoretical models to this system.

The problem of the relevance of the configuration converged upon by "aufbau" population schemes is clearly demonstrated by the present results. For example, in Figure 2 for $\theta \sim 120°$ the standard method gives the Σ_O configuration which is 1 eV above the Π configuration. This general problem has been recognized[17] in principle but examinations of the SCF energies of more than one configuration are rare. Such an examination is necessary whenever configurational energy differences are small. Other examples which are similar to the present one in having near degeneracy of Σ and Π configurations include aryl[21] and vinyl[22] radicals and cations[23] and radical cations of aromatic heterocycles.[23]

The present results suggest several conclusions about the electronic energies of the amido system. The first is that the Σ_N configuration is very high in energy for small values of θ. The INDO results thus give strong support to the deductions about the relative ordering of Π and Σ_N for small θ, made on the basis of the simple models. The second is that the lowest Σ configuration for $\theta \sim 120°$ is Σ_O rather than Σ_N. The angular dependence of this stabilization (Figure 2 Σ_O, Σ_N crossing) is consistent with the conclusion mentioned in connection with eq 1 that the effective value of $\alpha_N^{\sigma,103°}$ was lower in energy than $\alpha_N^{180°}$ by $\sim$38 kcal/mol. The value of α_N^{σ} could thus fall below the effective Coulomb integral of the oxygen lone pair as θ decreases. This qualitative ordering of the Σ_O and Σ_N configurations is thus not entirely unexpected.

The fact that the Σ_O configuration was so near the Π configuration when the geometry was optimized in θ, R_{C-O}, and R_{C-N} was more surprising. The direction of the changes in R_{C-O} and R_{C-N}, which are necessary for this result, indicates a small β_{C-O} and a large β_{C-N} for the four Π electrons of the Σ_O configuration. Inspection of structure **3b** reveals how this may connect. The Π interaction of the oxygen lone pair (in **3a**) with the C=N Π bond produces positive charge on oxygen (with a σ vacancy). The repulsions would tend to reverse the charge polarization. The lengthened C–O bond and shortened C–N bond minimize this Π interaction. The localization of the Π electrons, in this case, stabilizes the system (Σ_O).

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(19) The assumed bond lengths and bond angles were taken from *Chem. Soc., Spec. Publ., Suppl.*, **No. 18** (1963). The N–O bond length was taken to be the same as that used by W. C. Danen and C. T. West, *J. Amer. Chem. Soc.*, **93**, 5582 (1971).

(20) G. Klopman and B. O'Leary, *Fortschr. Chem. Forsch.*, **15**, 445 (1971).

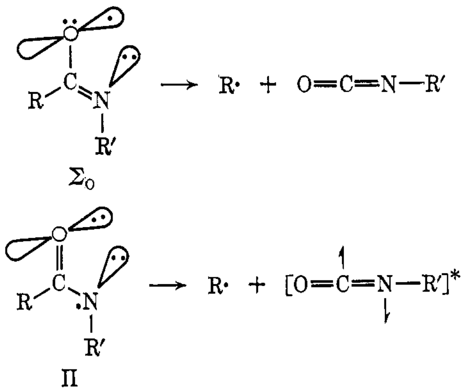
(21) P. Kasai, P. Clark, and E. Whipple, *J. Amer. Chem. Soc.*, **92**, 2640 (1970).

(22) J. Kochi and P. Krusic, *J. Amer. Chem. Soc.*, **92**, 4110 (1970).

(23) E. Evleth and P. Horowitz, *J. Amer. Chem. Soc.*, **94**, 5636 (1972).

This near degeneracy has important chemical implications. The Σ_O configurations should have abstraction rates like alkoxy radicals. In addition, the β scission of the Σ_O configuration correlates with the ground state of the isocyanate with no symmetry imposed barrier. The Π configuration correlates with an electronic excited state of the isocyanate (Scheme II).

Scheme II



A rapid interconversion of Π and Σ_O could thus lead to decreased steady-state concentration of the Π ground state by either H-atom transfer or β scission. The Σ_O species could also be formed initially in the photolysis if the excitation were of the carbonyl $n-\pi^*$ type. This could *rationalize* the fact that we were not able to observe esr spectra for the cyclic compounds which are restricted to the geometry where the Σ_O configuration is of low energy. The products and wavelength dependence of the photolysis of **8** and **9** could provide some insight into this problem.

A third suggestion concerns the effect of N-methylation. The results with either the formamido or optimized bond lengths indicate a smaller stabilization of the Π configuration at $\theta \sim 120°$ compared to $\theta \sim 180°$ for the *N*-methyl *vs.* the N–H compounds. This is a result of nuclear repulsion differences since the electronic energy changes for the N–H and $N-CH_3$ compounds are similar at the two values of θ. The reduced preference of the Π configuration for small θ on N-methylation can thus be described as a steric effect and suggests that the ground states of amido radicals could change due to repulsions between large groups. The observed hyperfine coupling to the nitrogen-14 nuclei is between those calculated for these two possibilities (Table I). The observed spectra are for compounds in which steric effects should be enhanced with respect to the model. If the argument presented above, concerning the shape of the θ dependence for the *N*-methyl compound has validity, then the larger steric effect could lead to a situation where Σ_N with $\theta = 180°$ is preferred. The experimental coupling to the *N*-methyl protons of the *N*-methylcyclopropanecarboxamido (Table I, 29.8 G) and the *N*-methylpivalamido (ref 13, 29.3 G) radicals are closest to those calculated for Σ_N with $\theta = 180°$ (Table II, 30.3 G) and much higher than those calculated for Π in any geometry (the maximum value for the Π configuration was 20.4 G). The best fit with the INDO wave functions, insofar as we have taken them, is Σ_N with $\theta = 180°$. This is essentially the same conclusion as reached by Danen and Gellert[13] when the value of θ is taken into account.

The results for the *N*-alkoxy systems present little difficulty in structural assignment. The standard calculations for the *N*-hydroxy model give the Π configuration and the modified method demonstrates that the Σ_N and Σ_O configurations are of higher energy using the assumed geometry. More importantly, the calculated hyperfine coupling constant to the nitrogen-14 atom is in reasonable agreement with the observed values in the case of the Π configuration only. The chemistry is also indicative of a stabilized radical in that formation is facile and the product is the hydrazine dimer (Scheme I) rather than an abstraction or fragmentation product. All criteria point to a Π configuration for the ground state of the *N*-oxy substituted species.

Experimental Section

The esr spectra were recorded using a Varian-E3 spectrometer and a focused 100-W high-pressure mercury lamp in quartz sample tubes. The *N*-chloroamides were prepared from the corresponding amides using *tert*-butyl hypochlorite in carbon tetrachloride in the presence of potassium carbonate. Their purity was judged by the liberation of iodine in the presence of potassium iodide and by the absence of the N–H stretching band in the infrared ($\sim$3400 cm^{-1}). The *N*-nitroso compounds were prepared by nitrosation of the corresponding amides using nitrosyl chloride and pyridine. These compounds were too unstable to isolate in pure form but solutions showed the N–NO band in the infrared near 1530 cm^{-1} and the N–H stretching band in the 3400-cm^{-1} region was absent. The amides were prepared by literature procedures (**6**,[24] **8**,[25] **9**,[26]); melting points: 2,4,6-tri-*t*-butylacetanilide, 266–267°; *N*-*tert*-butoxycyclopropanecarboxamide, 136–138°; *N*-methylcyclopropanecarboxamide, 63–64°; and *N*,*N*′-dicyclopropanecarbonyl-*N*,-*N*′-di-*tert*-butoxyhydrazine, 65–68°. The hydrazine (**4c**) was obtained in quantitative yield by treatment of the corresponding *N*-chloro compound (**4a**) with the sodium salt of the amide (**4**) in tetrahydrofuran solution.

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(24) R. Neale, N. Marcus, and R. Schepers, *J. Amer. Chem. Soc.*, **88**, 3051 (1966).

(25) R. Moffet, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 357.

(26) R. Graf, *Justus Liebigs Ann. Chem.*, **661**, 111 (1963).