

INDO¹ CONFIGURATIONS FOR SUCCINIMIDYL

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Skell and coworkers² have recently provided experimental evidence which indicates that the selectivity of the succinimidyl radical, in hydrogen atom abstractions, is clearly different from that of bromine atom. These important results rule out the possibility of any fortuitous similarity in the selectivities of the two and strengthen the case³ for the bromine atom as the abstracting species in (normal) heterogeneous Wohl-Ziegler⁴ brominations. The succinimidyl radical, generated under homogeneous conditions, appears to be much less selective than bromine atom.

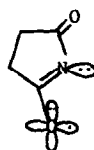
We have been interested⁵ in the description of the electronic structures of such species. The three most likely possibilities are Π (1), Σ_0 (2) and Σ_N (3). Figure 1 shows the results



Π (1)



Σ_N (2)



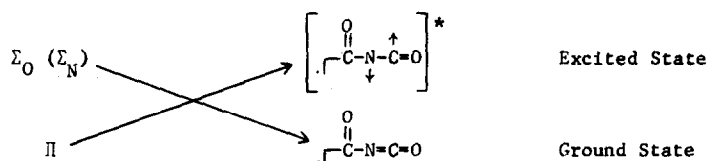
Σ_0 (3)

of a partial geometric optimization of the molecular orbital configurations corresponding to (1)-(3) in the INDO approximation.¹ For C_{2v} symmetry, the lowest structure is Π (1) and the optimized C-N and C-O bond lengths (1.32Å and 1.36Å respectively) are very similar to those found⁵ for Π -formamido. The Σ_0 (3) configuration lies above Σ_N (2) in the C_{2v} geometry which is optimum for the Π (1) configuration.

Distortion away from C_{2v} symmetry, through an antisymmetric change in the C-N and C-O bond lengths, produces a reversal of the Σ_N - Σ_0 energetic ordering. The Σ_0 configuration is strongly stabilized becoming almost degenerate with the optimized C_{2v} Π (1) configuration. The stabili-

zation is due to electron localization which reduces ionic contributions to the total wave function. The Σ_N configuration remains high in energy throughout this antisymmetric displacement. This species would be expected⁵ to be stabilized by large C-N-C bond angles which are opposed by the angle strain in the ring.

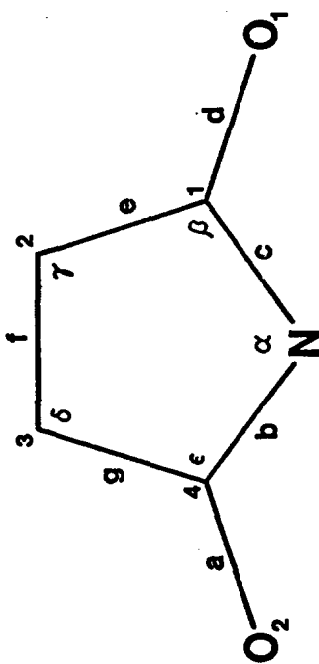
The present results suggest that the adiabatic ground state of the succinimidyl radical may be either Π or Σ_0 . The Σ_0 structure could undergo ring opening⁶ (β -scission) to the electronic ground state of an acyl isocyanate (4) through a transition state which retains the symmetry plane containing the five main atoms. The same nuclear motions for the Π structure leads to an excited state of the isocyanate. The β -scission of the Π radical would thus be expected to be slow. β -Scission of the Σ_N configuration correlates with ground state isocyanate. In fact, the ring opening reaction could be considered to be the end result of the distortion of the Σ_N configuration towards its preferred⁵ large C-N-C bond angle. However, the relatively high (calculated) energy of this configuration suggests that its appearance should be restricted to the most exothermic generating reactions such as photochemical ones.



Abstraction selectivity differences are more difficult to analyze. The selectivity of the Σ_0 intermediate would be expected to resemble tert-butoxy. That of Σ_N would be expected to be much lower than the highly selective bromine atom. However, there are no good analogies for the selectivity of the Π species. Thus any of the three could rationalize the observed² substitution preferences.

Our main purpose here is to point out that all three electronic structures are potential reaction intermediates. Different precursors⁷ or methods⁸ of observation could involve different electronic states. To the extent that INDO is reliable, the Π and Σ_0 intermediates are the most likely from thermal generation while the Σ_N must be considered in photochemical formation.

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Geometry 1 (C_{2v}): $\alpha = 110^\circ, \beta(c) = 111.4^\circ, \gamma(\delta) = 103.6^\circ$

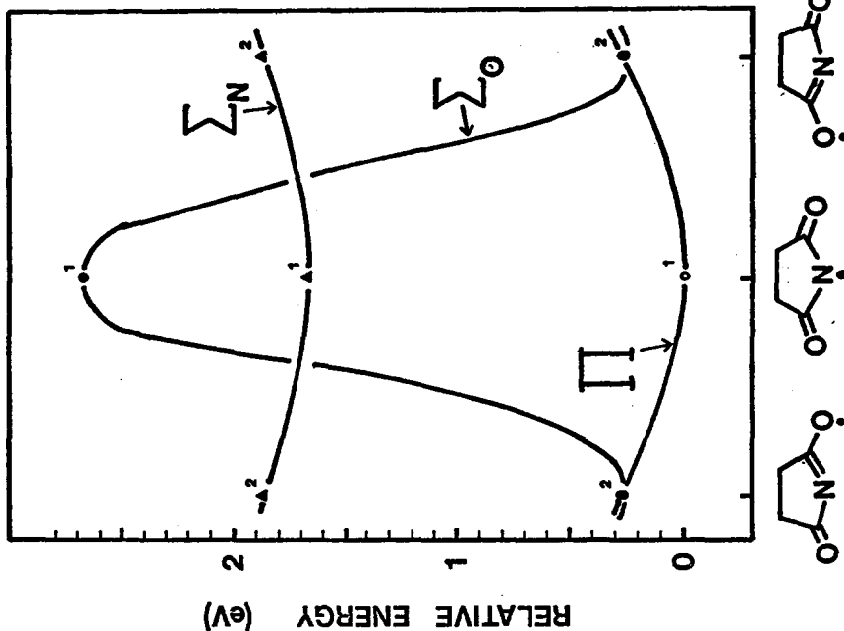
$a=d=1.32\text{\AA}, b=c=1.36\text{\AA}, g=e=1.48\text{\AA}, f=1.54\text{\AA}$

$C-H = 1.09\text{\AA}$ (assumed 109.5° HCH angles)

Geometry 2: $\alpha = 110^\circ, \beta = 111^\circ, \gamma = 103.6^\circ, \delta = 103.4^\circ, \epsilon = 112^\circ$

$a=1.34\text{\AA}, b=1.32\text{\AA}, c=1.40\text{\AA}, d=1.25\text{\AA}, e=1.47\text{\AA}, f=1.535\text{\AA}, g=1.50\text{\AA}$

$C-H = 1.09\text{\AA}$, (HCH angle = 109.5°)



INDO Calculated Results	State	Δ Energy (eV)	a_N^a	a_{O1}^a	a_{O2}^a	a_{C1}^a	a_{C2}^a	a_{C3}^a	a_{C4}^a	$a_{H(C2)}^a$	$a_{H(C3)}^a$	μ^b
1, C_{2v}	Π	0	8.2	11.3	11.3	-23.4	4.9	4.9	-23.4	-19.9	-19.9	3.91
	Σ_N	1.56	42.9	-0.4	-0.4	-2.2	11.4	11.4	-2.2	1.5	1.5	3.96
	Σ_O	2.65	-8.4	6.7	6.7	-11.3	1.3	1.3	-11.3	0.77	0.77	5.67
2	Π	0.273	7.8	7.6	12.8	-15.9	2.9	4.2	-21.8	-13.3	-16.6	4.01
	Σ_N	1.78	41.1	0.16	-0.67	-0.86	9.7	14.8	-6.1	1.2	0.18	4.07
	Σ_O	0.27	-0.36	-0.09	15.6	-0.96	-0.69	8.2	-11.9	0.73	-0.59	5.54

^aEsr hyperfine coupling constant, Gauss.

^bDipole moment, Debyes.

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