

Figure 3. Modification of the fluorescence intensity (λ_{exc} 421 nm, λ_{em} 648 nm) of $\text{In}_2\text{O}_3\text{-CG}$ (a) and $\sim 8 \times 10^{-10}$ mol/cm² ZnTPP on $\text{In}_2\text{O}_3\text{-CG}$ (b) as the applied potential is scanned from 0.0 to 1.0 V and back. Trace (a) illustrates only the absence of any change in intensity due to the substrate. The dip in (b) represents a loss in intensity of about 20%. The zero of the background trace has been moved for clarity.

evaporating to dryness under a stream of N_2 or by soaking the end of the strip in the solution for several minutes and rinsing off the excess with distilled water.

Fluorescence spectra indicate that the ZnTPP applied to the electrode in this manner does not merely crystallize and adhere to the surface. Excitation and emission spectra of various forms of ZnTPP are shown in Figure 1. Experimental spectra of the solution phase are very comparable to previously reported ones for both absorption²¹⁻²⁴ and fluorescence.^{25,26}

Work with crystalline material is hampered by artifacts caused by full absorption of the excitation beam and reabsorption of emission, but we find that purified crystalline powder dusted onto glass and either immersed in 1 M HCl or left in air shows a long-wavelength emission peak at 658 nm, which is red shifted by about 10 nm from the value observed in toluene or with the electrodes.²⁷

No evidence of demetalation of the ZnTPP is observed, even though demetalation in solution by HCl is a known reaction.²⁸ Our spectra have none of the features distinctive to metal-free porphyrin (H_2TPP), i.e., excitation peaks near 515, 550, 595, and 650 nm and emission peaks at ca. 660 and 720 nm.^{27,28} An authentic sample of H_2TPP applied to the electrodes does show these features.

The ability to observe a fluorescence signal from ZnTPP applied to BPPG as indicated by preliminary experiments is particularly noteworthy. Similar systems are of great interest from a technological standpoint, and a simple monitoring method for adsorbates in operating cells would be valuable to kinetic studies.

Cyclic voltammograms of the adsorbed ZnTPP shown in Figure 2 exhibit two closely spaced oxidation peaks at ca. 820 and 900-1000 mV vs. Ag/AgCl. The two corresponding reduction peaks occur near 700 mV and between 150 and 300 mV. The magnitudes of the peak currents of the two oxidations do not exhibit the same dependences on scan rate, v . The 820-mV peak, which does not shift more than 10 mV as v increases from 100 to 250 mV/s, grows linearly with v . This indicates that the electroactive species is bound to the surface.²⁹ The peak potential of the second oxidation shifts to a more positive value by ca. 60 mV as v changes from 100 to 300 mV/s and exhibits a more complex dependence on v . Previous studies of ZnTPP in aprotic solutions^{43,24} show that successive reversible, one-electron ring oxidations occur at 0.8 and 1.1 V vs. SCE. The difference between

the peak potentials, 0.3 V, is much larger than that observed in the present experiments. Our results could suggest that the electroactive material is undergoing essentially the same electrode process, but in at least two different environments. At present, the precise nature of the electrode process is not clear, and it is not essential to our purpose here to define it. It is chemically reversible since one can run cyclic voltammograms repeatedly with only minor changes in response; however, the splittings between anodic and cathodic peaks show that slow kinetics exist, either in charge transfer or in chemical changes to the molecular structure. Data presented below show that oxidation is fast, but re-reduction is quite slow. The simplest explanation is that a cation radical is formed by oxidation and that it is stabilized by its interaction with the electrode against chemical attack. Other more complicated possibilities involving reversible alteration of the molecular structure may be more likely.

If 8×10^{-10} mol of ZnTPP ($2 \mu\text{L}$) are applied to a 1-cm² portion of the electrode and dried, the amount oxidized during the potential scan is close to 2×10^{-10} equiv (as determined by estimating the area under the anodic peak). If about 1 cm² of the electrode is soaked for ca. 10 min in the solution and the excess is rinsed off with water, then only ca. 6×10^{-11} equiv are oxidized; if the excess is allowed to dry, again 2×10^{-10} equiv are electroactive. The deposition, though, is not irreversible. If the electrode is rinsed well with toluene, the cyclic voltammogram obtained is identical with that of a fresh electrode.

Simultaneous electrochemical and fluorometric experiments provide evidence that at least a portion of the fluorescent material on the surface is also electroactive. The peak fluorescence intensity is diminished as the potential is scanned past the oxidations as shown in Figure 3(b). This attenuation is equal to approximately one-fifth of the original peak intensity, a fraction that correlates well with the ratio of electroactive equivalents estimated from the voltammetric response to the number of moles applied by syringe.^{30,31} After completion of the potential scan, the fluorescence intensity does not revert completely to its initial value in this figure because of slow re-reduction; however, there is some irreversible loss of material with time.

Excitation and emission spectra of the ZnTPP on an electrode being held at 1000 mV show qualitative differences, as well as an overall attenuation of peaks by about one-quarter, from those obtained with the electrode at open circuit.³⁰

On BPPG, the fluorescence intensity of the ZnTPP is also attenuated by oxidation. Further investigation of this system is currently being conducted.

Acknowledgment. We are grateful to the National Science Foundation for supporting this work via Grant CHE-78-00584.

(30) In recent work, we have observed attenuation exceeding 50%. The residual fluorescence may have a contribution from the oxidized form.

(31) Whether the fluorescence observed from the ZnTPP on a substrate is emitted from a layer directly adjacent to the surface is not entirely clear at present. Using a syringe to apply the solution to the electrode does not result in uniform surface coverage, and multilayer regions must exist. However, fluorescence is observed even if the electrode is soaked for several minutes in the ZnTPP solution and rinsed with distilled water, a method which seems to result in greater uniformity and closer to monolayer coverage.

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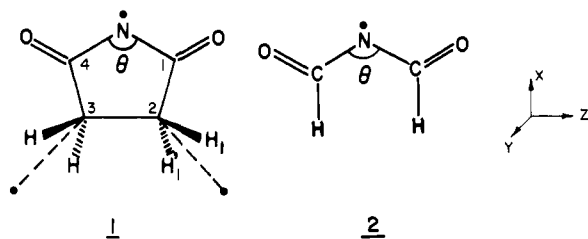
- (21) Rothmund, P.; Menotti, A. R. *J. Am. Chem. Soc.* **1948**, *70*, 1808.
(22) Gouterman, M. *J. Mol. Spectrosc.* **1961**, *6*, 138.
(23) Fajer, J.; Borg, D. C.; Formin, A.; Dolphin, D. H.; Felton, R. H. *J. Am. Chem. Soc.* **1970**, *92*, 3451.
(24) Wolberg, A.; Manassen, J. *J. Am. Chem. Soc.* **1970**, *92*, 2982.
(25) Seybold, P. G.; Gouterman, M. *J. Mol. Spectrosc.* **1969**, *31*, 1.
(26) Quimby, D. J.; Longo, F. R. *J. Am. Chem. Soc.* **1975**, *97*, 5111.
(27) The excitation spectra of surface deposits show a broadening, red shift, and relative attenuation of the Soret band much like that observed in absorption experiments with amorphous, vapor-deposited films. See: Tanimura, K.; Kawai, T.; Sakata, T. *J. Phys. Chem.* **1980**, *84*, 751.
(28) Levanon, H.; Neta, P. *Chem. Phys. Lett.* **1980**, *70*, 100.
(29) Wopschall, R. H.; Shain, I. *Anal. Chem.* **1967**, *39*, 1514.

The Π and Σ_{N} Electronic States of the Succinimidyl Radical. Can Nitrogen-Centered Radicals Have Σ_{N} Ground States? An ab Initio Study

Sir:

The succinimidyl radical **1** was first proposed as an intermediate almost 40 years ago,¹ but its chemical properties remained a

mystery. An important breakthrough, the generation of two



succinimidyl radicals, a ground state and an excited state, with distinct chemical properties, was achieved recently by Skell et al.² This is the first reported generation of an excited-state radical in a thermal chain reaction.² All attempts to observe the two succinimidyl radicals by spectroscopic methods^{2,3} were unsuccessful, leaving their intimate properties poorly characterized.² We report the first ab initio calculations^{4,5} for the ground state and for the first excited state of **1**. We find that the ground state of **1** [${}^2B_1(1\pi)$] is ~ 20 kcal·mol⁻¹ (ΔE) more stable than the first excited state [${}^2A_1(1\sigma)$]. In other imidyl or amidyl radicals, either cyclic or acyclic, ΔE is predicted to be ≥ 20 kcal·mol⁻¹. Smaller ΔE or even Σ_N ground states are predicted for sterically crowded aminyl radicals.

Calculations were carried out with the GAUSSIAN-70^{6a} and GAUSSIAN-76^{6b} series of programs by using the unrestricted Hartree-Fock (UHF) procedure.⁷ Complete geometry optimizations within C_{2v} symmetry were carried out for the ${}^2A_1(1\sigma)$ and the ${}^2B_1(1\pi)$ states of **1** and of the acyclic analogue **2** (i.e., 2σ and 2π), using the STO-3G basis set.^{8a} Single-point calculations with the 4-31G basis set^{8b} followed.^{8c} In 1π and 2π , the unpaired electron is formally delocalized over the entire π framework (Π radical) while in 1σ and 2σ it is formally localized in the sp_x^2 orbital of nitrogen (Σ_N radical).

The optimized structures of 1π and 1σ (or of 2π and 2σ) are similar except for the C=O bond lengths and the CNC angles (Figure 1).⁹ The carbonyl bond lengths are longer in the Π radicals (1.314 and 1.320 Å in 1π and 2π , respectively) than in the Σ_N radicals (1.242 Å in 1σ , 1.253 Å in 2σ), or in succinimide (1.215 Å at STO-3G).¹⁰ The presence of five π electrons in the Π radicals compared with six in the other compounds is probably responsible for this bond lengthening. The C-N bond lengths are similar in 1σ , 1π , 2σ , and 2π (1.431, 1.429, 1.423, and 1.410 Å, respectively), and in succinimide (1.424 Å, STO-3G).¹¹ The CNC bond angle (θ) is smaller in 1π (106.4°) than in 1σ (117.7°) or in succinimide (115.35°, STO-3G).¹⁰ The transformation of the

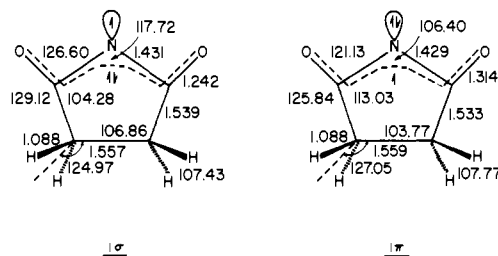


Figure 1. Optimized structures (STO-3G, C_{2v}) of 1π and 1σ .

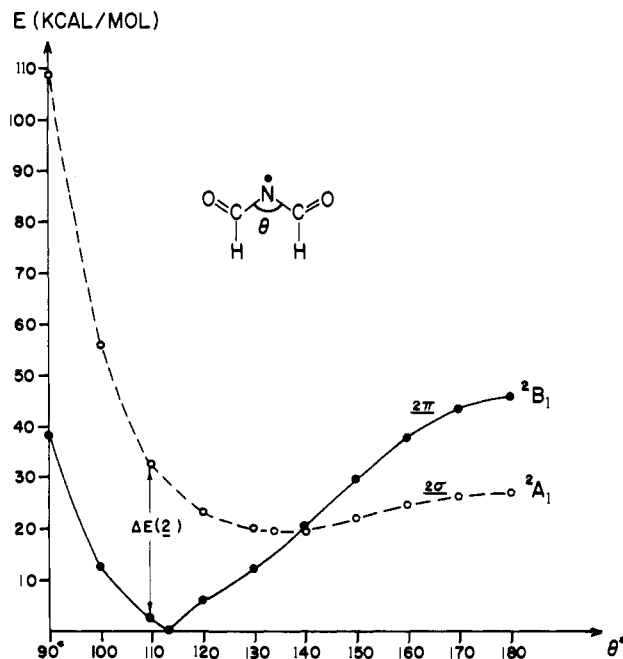


Figure 2. Angular potentials ($\theta \angle \text{CNC}$) for 2σ and 2π .^{23b}

Σ_N state to the Π state involves the transfer of an electron from a π orbital [mainly N($2p_x$)], whose energy is insensitive to changes in θ , to a σ orbital [mainly N(sp_x^2)], which favors strongly small θ angles.¹² In 1σ , ring constraints prevent further broadening of θ ($\theta = 133.6^\circ$ in 2σ and 144° in the 2A_1 state of $\text{H}_2\text{N}^{\cdot}$).¹³

1π is the ground state of the succinimidyl radical, and 1σ is the lowest excited state. The ordering of the states is the same in **2**, in $\text{H}_2\text{N}^{\cdot}$,¹³ and in substituted amidyl radicals.¹⁴ The energy difference between the two states [$\Delta E(1)$] is 55.0 kcal·mol⁻¹ at STO-3G. However, calculations of $\text{H}_2\text{N}^{\cdot}$ [$\Delta E(\text{experimental}) = 29\text{--}32$ kcal·mol⁻¹]^{13a} reveal that at STO-3G ΔE (49.2 kcal·mol⁻¹)^{13b} is overestimated. At 4-31G, however, $\Delta E = 26.4$ kcal·mol⁻¹, only 3–5 kcal·mol⁻¹ smaller than either the experimental or the best theoretical^{13c} estimates. In **2**, $\Delta E = 52.1$ kcal·mol⁻¹ at STO-3G and 19.9 kcal·mol⁻¹ at 4-31G. Assuming that the same correction for the STO-3G deficiencies applies to $\Delta E(2)$ and $\Delta E(1)$,^{8c} we estimate that the $1\pi\text{--}1\sigma$ splitting is 20–25 kcal·mol⁻¹.¹⁵ Analysis of the charge densities reveals that the carbonyl groups are more polarized in 1σ than in 1π , suggesting that $\Delta E(1)$ may be reduced in polar solvents. Both 1σ and 1π are less stable than the corresponding states of $\text{H}_2\text{N}^{\cdot}$ (eq 1);¹⁶ conjugation is apparently less

(12) Buenker, R. J.; Peyerimoff, S. D. *Chem. Rev.* **1974**, *74*, 127.

(13) (a) Johns, J. W. C.; Ramsay, D. A.; Ross, S. C. *Can. J. Phys.* **1976**, *54*, 1804. (b) Lathan, W. A.; Hehre, W. J.; Curtiss, L. A.; Pople, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 6377. (c) Bell, S.; Schaefer, H. F., III *J. Chem. Phys.* **1977**, *67*, 5173.

(14) For experimental determinations, see: Forrester, A. R.; Johansson, E. M.; Thomson, R. H. *J. Chem. Soc., Perkin Trans. 1* **1979**, 1112, and references therein.

(15) (a) ΔE is not expected to change significantly by the use of augmented basis sets.^{13c} (b) A lower splitting of 13.8 kcal·mol⁻¹ was obtained with MNDO.⁵

(1) Ziegler, K.; Späth, A.; Schaaf, E.; Schumann, W.; Winkelmann, E. *Justus Liebig's Ann. Chem.* **1942**, 551, 80.

(2) (a) Skell, P. S.; Day, J. C. *Acc. Chem. Res.* **1978**, *11*, 381, and references therein. (b) *J. Am. Chem. Soc.* **1978**, *100*, 1951. (c) Day, J. C.; Katsaros, M. G.; Kocher, W. D.; Scott, A. E.; Skell, P. S. *Ibid.* **1978**, *100*, 1950. (d) Skell, P. S.; Day, J. C.; Slanga, J. P. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 515.

(3) (a) Davies, A. G.; Roberts, B. P.; Smith, J. M. *J. Chem. Soc., Perkin Trans. 2* **1972**, 2221. (b) Chalfont, G. R.; Perkins, M. J. *J. Chem. Soc. B* **1970**, 401. (c) Hedayat, E.; Hinman, R. L.; Schomaker, V.; Theodoropoulos, S.; Kyle, L. M. *J. Am. Chem. Soc.* **1967**, *89*, 4875.

(4) An INDO study of **1** was reported: Koenig, T.; Wielesek, A. *Tetrahedron Lett.* **1975**, 2007.

(5) A MNDO study of **1** was published when our work was nearly completed: Clark, T. *J. Am. Chem. Soc.* **1979**, *101*, 7746.

(6) (a) Hehre, W. J.; Lathan, W. A.; Ditchfield, R.; Newton, M. D.; Pople, J. A. Program No. 236, QCPE, Indiana University. (b) Program No. 368, QCPE.

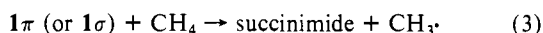
(7) Pople, J. A.; Nesbet, R. K. *J. Chem. Phys.* **1954**, *27*, 571.

(8) (a) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657. (b) Hehre, W. J.; Pople, J. A. *Ibid.* **1972**, *56*, 4233. (c) Convergence for **1** could not be achieved at 4-31G.

(9) The calculated total energies (STO-3G) are -353.39506 and -353.30734 hartrees for 1π and 1σ , respectively.

(10) The X-ray structure of succinimide is in good agreement with our optimized STO-3G structure: Mason, R. *Acta Crystallogr.* **1961**, *14*, 720.

(11) The bond length alternation that is found in 1π is probably not an artifact of the calculations: (Y. A., unpublished results.) Baird, N. C.; Gupta, R. R.; Taylor, K. F. *J. Am. Chem. Soc.* **1979**, *101*, 4531. Yamaguchi, K.; Fueno, T. *Chem. Phys. Lett.* **1976**, *38*, 47, 52. Yamaguchi, K. *Chem. Phys.* **1977**, *25*, 215.



important in the radicals than in succinimide. As eq 2 is nearly thermoneutral,^{17a} the reactions of 1π and 1σ with methane (eq 3) are calculated to be exothermic by ~ 15 and $35 \text{ kcal}\cdot\text{mol}^{-1}$, respectively. The high exothermicity of hydrogen abstraction by 1σ is consistent with the observed low selectivity.² As the dissociation energies of N-Cl bonds are by $\sim 30 \text{ kcal}\cdot\text{mol}^{-1}$ smaller than those of C-Cl bonds,^{17b,c} we conclude that the generation of 1σ [from $\text{CH}_3\cdot + N\text{-chlorosuccinimide (NCS)}]$ is endothermic by $\sim 5 \text{ kcal}\cdot\text{mol}^{-1}$.^{18a} The generation of 1π from $\text{Cl}\cdot + \text{NCS}$ is endothermic by $\sim 12 \text{ kcal}\cdot\text{mol}^{-1}$.^{18b,c} These conclusions are different from the qualitative energetic scheme suggested by Skell.²¹⁸

PMO theory¹⁹ provides a basis for explaining the different chemistries of the two states. For example, 1π is more selective than 1σ in hydrogen abstraction reactions² because its SOMO (-12.10 eV in 1π ; -13.22 eV in 1σ)^{20,21} and the HOMO of the alkane (-12.52 eV in ethane)²⁰ are closer in energy and therefore interact more strongly.¹⁹ Aromatic compounds, on the other hand, react preferably with 1σ ^{2c} which possess a lower LUMO than 1π .²² The lower $k(\text{neopentane})/k(\text{CH}_2\text{Cl}_2)$ ratios observed for 1π ^{2b} can be rationalized similarly.

The experimental study of Σ_N radicals could be greatly facilitated if additional systems with small $\Pi-\Sigma_N$ splittings or preferably with Σ_N ground states were available.^{23a} A search for such radicals can be carried out computationally. Figure 2^{23b} shows that the $2\pi-2\sigma$ energy difference, $\Delta E(2)$, is dependent on the CNC bond angle (θ). Thus, $\Delta E(2)$ increases sharply at $\theta < 110^\circ$; e.g., at $\theta = 90^\circ$, $\Delta E(2) \sim 70 \text{ kcal}\cdot\text{mol}^{-1}$ (Figure 2). Widening of θ , on the other hand, reduces $\Delta E(2)$. At $\theta > 140^\circ$, 2 is predicted to be a Σ_N ground state. Experimentally, it is simpler, however, to design systems with small CNC angles than to constrain θ to angles $> 140^\circ$. Examples include glutarimidyl, phthalimidyl, maleimidyl, and the malonimidyl radicals where θ is smaller (or similar) than in 1 , and ΔE is therefore $\geq 20 \text{ kcal}\cdot\text{mol}^{-1}$. Cyclic imines with $\theta > 130^\circ$, where the corresponding Π and Σ_N imidyl radicals are expected to be nearly degenerate (Figure 2), are unknown. Steric repulsions between bulky substituents (B strain) can produce considerable widening of bond angles. However, the application of this idea to acyclic iminyl radicals (e.g., 2 , H substituted by *t*-Bu) will probably fail because the steric interactions can be relieved in a *E,Z* or *Z,Z*, or in intermediate twisted conformations.²⁴ The same considerations apply to RCONR'.²⁵

(16) At STO-3G, the energies of reaction 1 are similar with either 1 or 2 and we assume that this holds at 4-31G.^{8c} At 4-31G, reaction 1 is estimated to be endothermic by 11 and 16 $\text{kcal}\cdot\text{mol}^{-1}$ for 1σ and 1π , respectively.

(17) (a) Franklin, J. L.; Dillard, J. D.; Rosenstock, H. M.; Herron, Y. T.; Draxl, K.; Field, F. M. *Natl. Stand. Ref. Data Ser. (U.S., Natl. Bur. Stand.)* **1969**, No. 26. (b) Benson, S. W. *J. Chem. Educ.* **1965**, *42*, 502. (c) Howard, P. B.; Skinner, H. A. *J. Chem. Soc. A* **1966**, 1536.

(18) (a) Exothermic by $0.8 \text{ kcal}\cdot\text{mol}^{-1}$, according to MNDO.⁵ (b) Exothermic by $14.6 \text{ kcal}\cdot\text{mol}^{-1}$, according to MNDO.⁵ (c) The MNDO energetic scheme⁵ is inconsistent with available thermodynamic data. ΔH_f° of $\text{CH}_3\cdot$ is $5 \text{ kcal}\cdot\text{mol}^{-1}$ higher than ΔH_f° of $\text{Cl}\cdot$ and ΔH_f° of CH_3Cl is $20.6 \text{ kcal}\cdot\text{mol}^{-1}$ lower than ΔH_f° of Cl_2 .^{17b} If 1π is more stable than 1σ by only $13.8 \text{ kcal}\cdot\text{mol}^{-1}$, then the energy of $1\pi + \text{Cl}_2$ must be higher (by $\sim 7 \text{ kcal}\cdot\text{mol}^{-1}$) than that of $1\sigma + \text{CH}_3\text{Cl}$, contrary to the MNDO predictions.^{5,18a,b}

(19) Fleming, I. "Frontier Orbitals and Organic Chemical Reactions", Wiley: New York, 1976; Chapter 5.

(20) STO-3G orbital energies correlate well with experimental ionization potentials; see, for example: Domelsmith, L. N.; Houk, K. N.; Regenhart, C. R.; Paquette, L. A. *J. Am. Chem. Soc.* **1978**, *100*, 100.

(21) In $\text{H}_2\text{N}\cdot$, the SOMO of the Π and Σ_N states are very close in energy (-12.27 eV , STO-3G).

(22) The HOMO(radical)-HOMO(arene) separations are large ($\sim 5 \text{ eV}$), so that these three-electron interactions are destabilizing (more strongly for 1π), supporting the same conclusion. See: Bernardi, F.; Cherry, W.; Shaik, S.; Epitotis, N. D. *J. Am. Chem. Soc.* **1978**, *100*, 1352.

(23) (a) $\text{O}_2\text{N}\cdot$ is a ground-state Σ_N radical; see: Atkins, P. W.; Symons, M. C. R. "The Structure of Inorganic Radicals", Elsevier: New York, 1967; p 131. (b) The potential curves are based on STO-3G calculations (bond lengths and bond angles except θ are held constant). The curve for 2σ is corrected for the overestimation of the $\Pi-\Sigma_N$ splitting by STO-3G (see text). A complete 4-31G potential curve is too expensive but several representative points at 4-31G fit Figure 2.

(24) See, for example: Noe, E. A.; Raban, M. *J. Am. Chem. Soc.* **1975**, *97*, 5811.

In amino radicals $\text{RR}'\text{N}\cdot$, however, steric repulsions can be minimized only by the widening of the CNC angle. Widening of θ (in the region $120-170^\circ$) results in a small change in the energy of the Σ_N radical (Figure 2).²⁵ We suggest, therefore, the use of crowded haloamines (several are known) as convenient precursors to ground state Σ_N radicals. Our predictions call for experimental verification.

Note Added in Proof: Two recent ESR studies have provided definitive proof for π ground state configurations in *N*-alkyl-carboxamidyl and sulfonamidyl radicals. See: Lessard, J.; Griller, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1980**, *102*, 3262; Dannen, W. C.; Gellert, R. W. *Ibid.* **1980**, *102*, 3264, respectively.

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(25) Plots which are similar to Figure 2 are obtained also for HCONH and $\cdot\text{NH}_2$. For similar INDO calculations, see: Koenig, T.; Hoobler, J. A.; Klopfenstein, C. E.; Hedden, G.; Sunderman, F.; Russell, B. R. *J. Am. Chem. Soc.* **1974**, *96*, 4573.

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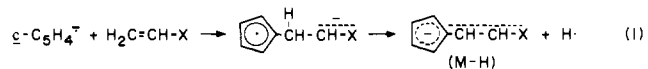
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Identification of Nucleophilic 1,2- and 1,4-Addition Processes with α,β -Unsaturated Molecules in the Gas Phase¹

Sir:

The ability to observe and largely control 1,2- vs. 1,4-addition processes of various nucleophiles to α,β -unsaturated compounds allows these reactions to be useful in synthetic organic chemistry. Gas-phase studies of such nucleophilic addition reactions have met with limited success with "naked" nucleophiles² but appear to be more promising with the nucleophile solvated.³ We report certain related gas-phase results with hypovalent anion radicals which allow both 1,2- and 1,4-addition reactions to be observed.

Our studies were carried out in a flowing afterglow apparatus (298 K , $v = 80 \text{ m s}^{-1}$, $P_{\text{He}} = 0.5 \text{ torr}$). Cyclopentadienylidene anion radical ($c\text{-C}_5\text{H}_4\cdot^-$)⁴ was produced from diazocyclopentadiene by dissociative electron attachment. From the reactions of $c\text{-C}_5\text{H}_4\cdot^-$ with acrylonitrile and methyl acrylate, the delocalized M-H adducts were produced.⁵ The magnitude of substituent effects in $\text{H}_2\text{C}=\text{CHX}$, where $\text{X} = \text{CN}$, CO_2CH_3 , and H , on the rate constants for addition by $c\text{-C}_5\text{H}_4\cdot^-$ (Table I) requires a nucleophilic (not radical) addition mechanism.⁶ That this simple addition/fragmentation process (eq 1) is a special function of the



(1) Paper 8 in the series "Hypovalent Radicals"; for paper 7, see: McDonald, R. N.; Chowdhury, A. K. *J. Am. Chem. Soc.* **1980**, *102*, 5118.

(2) Bowie, J. H. *Acc. Chem. Res.* **1980**, *13*, 76, and references therein.

(3) Bartmess, J. E. *J. Am. Chem. Soc.* **1980**, *102*, 2483.

(4) Cyclic structure and electronic configuration ($\sigma^1\pi^2$) of $c\text{-C}_5\text{H}_4\cdot^-$; Pa-($c\text{-C}_5\text{H}_4\cdot^-$) = $377 \pm 2 \text{ kcal}\cdot\text{mol}^{-1}$, $D^\circ(c\text{-C}_5\text{H}_4\text{-H}^-) = 104 \pm 5 \text{ kcal}\cdot\text{mol}^{-1}$; McDonald, R. N.; Chowdhury, A. K.; Setser, D. W. *J. Am. Chem. Soc.*, in press.

(5) Addition of O^- to acrylonitrile followed by loss of $\text{H}\cdot$ gave the M-H adduct as a minor reaction channel: Dawson, J. H. J.; Nibbering, N. M. M. *Int. J. Mass Spectrum. Ion Phys.* **1980**, *33*, 3.

(6) Kerr, J. A.; Parsonage, M. J. "Evaluated Kinetic Data on Gas Phase Addition Reactions", Butterworths: London, 1972.