An Accurate Estimate of the Relative Energetics of the π- and σ-Succinimidyl Radicals

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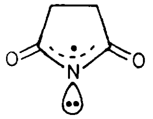
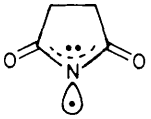
Ab initio calculations of the relative energetics of the π- and σ-states of the succinimidyl radical including geometry optimization and electron correlation result in the following relative energies (in kJ mol^{-1}): S_π, 0.0; S_σ(N), 21.5; S_σ(O), 168.9.

Radical-chain reactions in systems containing *N*-bromosuccinimide involve the succinimidyl radical as the chain carrier. Skell and coworkers[1—3] have shown that two radicals having distinctive properties were produced, which were suggested to be the π (S_π) and σ (S_σ) radicals, (I) and (II), respectively. Kinetic data suggested that the ground state of the succinimidyl radical was S_π, with an upper bound of 75 kJ mol^{-1} for the enthalpy difference been (I) and (II).[3] A further species which needs consideration is the σ-radical with the spin density localized on a *single* oxygen atom, leading to a distortion from C_{2v} to C_s symmetry. We refer to the two possible σ-radicals as S_σ(N) and S_σ(O) being $^2A_1$ and $^2A'$ states in C_{2v} and C_s symmetry, respectively. The S_π radical is a $^2B_1$ state in C_{2v} symmetry.

In the absence of accurate experimental geometries for these three species, theoretical calculations including geometry optimization are needed. Estimates of the energetics of these species have, to date, been confined to the use of semiempirical and minimal basis, *ab initio* methods. INDO,[4] MNDO,[5] and minimal basis UHF[6] calculations predict S_π to be the ground state. The INDO method predicts S_σ(O) to be the second state, 26 kJ mol^{-1} from S_π, whilst MNDO predicts



(I)



(II)

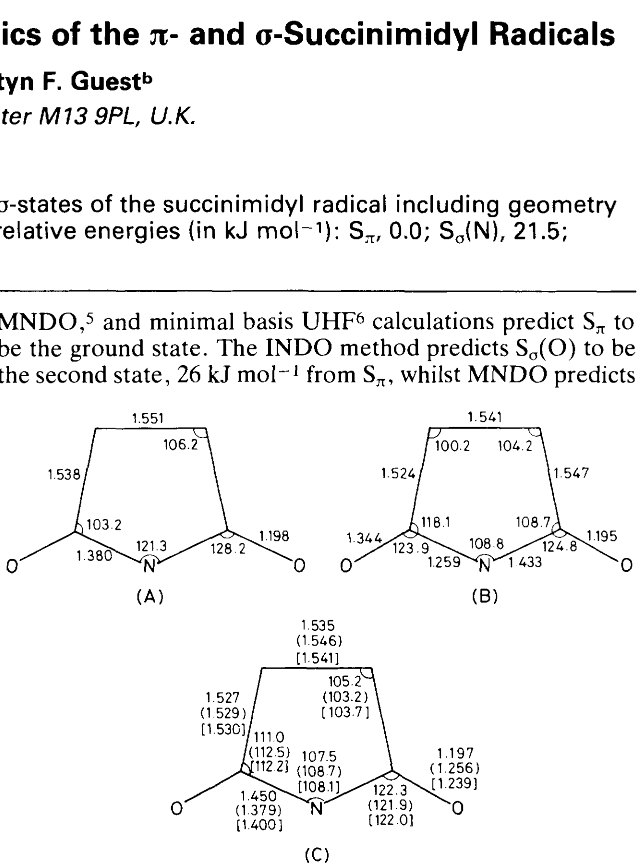


Figure 1. Optimized geometries, distances in Å and angles in degrees, of the three states of the succinimidyl radical using 3-21G basis: (A), S_σ(N) ($^2A_1$); (B), S_σ(O) ($^2A'$); (C), S_π ($^2B_1$). Results are for RHF calculations, except for S_π where UHF and CASSCF results are given in round and square brackets respectively.

Table 1. Relative energies (kJ mol^{-1}) of the $^2A_1$, $^2B_1$, and $^2A'$ states of the succinimidyl radical.

	RHF/3-21G[a]	UHF/3-21G[b]	CI/6-31G*[c]
$^2A_1$	26.5	71.7	7.4 (21.5)
$^2B_1$	27.2	0.0	0.0 (0.0)
$^2A'$	0.0	47.1	170.3 (168.9)

[a] Relative energies and optimized geometries obtained using 3-21G basis and RHF wavefunctions. [b] Relative energies and optimized geometries obtained using 3-21G basis and UHF wavefunctions. [c] Relative energies obtained from SDCI calculations using 6-31G* basis and RHF wavefunctions. The optimized geometries were obtained using a 3-21G basis, with RHF wavefunctions for the $^2A_1$ and $^2A'$ states and a CASSCF wavefunction for the $^2B_1$ state. The values in parentheses include Davidson's correction for higher order excitations.

$S_\sigma(N)$ to be the second state, 61 kJ mol^{-1} from S_π. The UHF calculation predicts a S_π–$S_\sigma(N)$ separation of 230 kJ mol^{-1}.

To provide more accurate estimates of the structures and energetics of these species we here present the results of *ab initio* calculations, including full geometry optimization in an extended valence basis (3-21G)[7] of the three species S_π, $S_\sigma(N)$, and $S_\sigma(O)$. It is well known that such a basis is needed to predict accurate geometries of organic molecules.[8] Both restricted and unrestricted Hartree–Fock calculations were carried out. For the two σ-radicals both methods gave essentially identical optimized geometries (to within 0.002 Å). However, for the π-radical, bond lengths obtained from the two methods differed by up to 0.05 Å owing to the importance of correlation effects involving the partially and doubly occupied π orbitals, which are included in the UHF method. However, the UHF method yielded a wavefunction for S_π ($^2B_1$) heavily contaminated with higher-spin components, so that a multiconfiguration SCF method (CASSCF)[9] which included π-electron correlation (involving the seven π-orbitals) and avoided such contamination was used to obtain an accurate molecular geometry of S_π ($^2B_1$). The geometries of the three states of the succinimidyl radical thus calculated are shown in Figure 1 and their relative energies are given in Table 1. Of particular interest are the considerably different geometries obtained for S_π by the three methods used, with the CASSCF structure differing significantly from the RHF structure, and the result that at the RHF level $^2A'$ is predicted to be the lowest state, whereas at the UHF level the ground state is predicted to be $^2B_1$. To obtain the relative energies of the three radicals as accurately as possible and taking into account a uniform treatment of electron correlation throughout the three species, the following strategy was adopted. Firstly, RHF calculations were carried out at the optimal RHF [for $S_\sigma(N)$ and $S_\sigma(O)$] and CASSCF (for S_π) geometries using a larger atomic basis including polarization functions (6-31G*).[10] The resulting molecular orbitals were then used as a basis for configuration interaction calculations[11] which included all single and double excitations (SDCI) from the filled valence orbitals of the RHF configuration to the first 46 virtual orbitals. The calculations resulted in ~230 000 configurations for the S_π and $S_\sigma(N)$ species and ~460 000 configurations for $S_\sigma(O)$. The resulting relative energetics (in kJ mol^{-1}) for the three species are: S_π, 0.0; $S_\sigma(N)$, 7.4; $S_\sigma(O)$, 170.3. Estimates of the importance of higher (than double) excitations were obtained by the use of Davidson's correction,[12] yielding the following relative energetics (in kJ mol^{-1}): S_π, 0.0; $S_\sigma(N)$, 21.5; $S_\sigma(O)$, 168.9.

These *ab initio* calculations thus predict that the ground state of the succinimidyl radical is S_π, in agreement with experimental conclusions, with the $S_\sigma(N)$ state having a small energy separation from it. These findings differ from previous semiempirical results which place S_π and $S_\sigma(O)$ close in energy,[4] or predict a considerable energy separation between S_π and $S_\sigma(N)$.[5]

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