Accurate Calculations of the Structure and Energy of the π- and σ-Succinimidyl Radicals: an *Ab initio* Study including Electron Correlation

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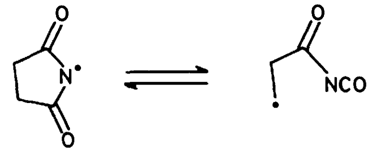
Ab initio calculations of the structure and energies of the π and σ states of the succinimidyl radical have been carried out including electron correlation. The results are found to be extremely sensitive both to basis set size and to the degree of electron correlation included. With molecular geometries obtained using a multiconfiguration SCF wavefunction where appropriate, a 6-31G* basis and large scale CI calculations resulted in the following relative energies (in kJ mol^{-1}); S_π, 0.0; S_σ(N), 21.5; S_σ(O), 168.9.

Following the recognition that radical chain reactions in systems containing *N*-bromosuccinimide involve the succinimidyl radical as the chain carrier,[1,2] Skell and co-workers reported evidence for the participation of two succinimidyl radicals, which they assigned to the π and σ states.[3,4] A major focus of experimental studies has been on the competitive bromination of methylene dichloride and neopentane in the presence and absence of free bromine.[4,5] Without bromine, the ring-opening reaction was identified, and on symmetry grounds

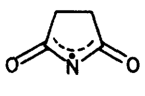


was attributed to a so-called σ radical (S_σ). The recognition that the presence of Br_2 largely eliminated the ring-opening reaction was taken by Skell *et al.* to suggest that a second imidyl radical (S_π) was involved. However, a recent re-examination of the role of succinimidyl radicals in chain reactions by Skell *et al.*[6] has led to the conclusion that the evidence for the species previously labelled 'π' is not definitive. The experimental results which were attributed to the 'σ' radical stand without modification, although the identification of this intermediate as a spectroscopic σ state is not settled.

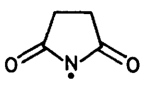
In view of these uncertainties accurate calculations of the structure and the energetics of the various possible succinimidyl radicals are of value, and are presented in this paper.

Koenig and Wielesek[7] proposed three valence-bond structures for these radicals:

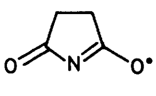
π_N



σ_N



σ_O



An asymmetric π_O form can also be envisaged. From these structures and using symmetry arguments alone S_π can be equated with π_N or π_O and S_σ with σ_N or σ_O. The energy differences between the radicals determined from INDO calculations, with partial optimisation of the molecular geometries,[7] predict the symmetric π_N radical to be the most stable. This result is supported by the calculations of Dewar *et al.*[8] and of Apeloig and Schreiber.[9] Both fully optimised the radicals of C_{2v} symmetry only, the former using the UMNDO semiempirical MO method and the latter *ab initio* unrestricted Hartree–Fock (UHF) calculations with a minimal STO-3G basis. The relative energies of the various states of the succinimidyl radical given by these calculations are summarised in Table 1.

Table 1. Relative energies of the succinimidyl radicals

	Relative energy (kJ mol^{-1})		
State	INDO[7]	MNDO[8]	STO-3G[9]
σ_N	150.5	60.9	230.0
π_O	26.3		
σ_O	26.1		
π_N	0.0	0.0	0.0

Tlumak *et al.*[5] estimate an upper limit of about 75 kJ mol^{-1} for the π − σ energy separation from their experimental work.

Our aims in the present study are to determine the relative stabilities of the radical forms with greater accuracy than previously known, using state-of-the-art *ab initio* MO techniques.

Computational Methods and Results

In order to carry out *ab initio* MO calculations on the radicals it was necessary to reformulate the valence-bond structures given above. The succinimidyl ring was taken to be coplanar with the attached carbonyl oxygens. This makes the symmetric and asymmetric radicals of C_{2v} and C_s symmetry respectively and means there are six states available for study; $^2A_1$, $^2A_2$, $^2B_1$, $^2B_2$, $^2A'$, and $^2A''$. The VB/MO equivalences are roughly:

$$\sigma_N - {}^2A_1, {}^2B_2 \qquad \sigma_O - {}^2A'$$
$$\pi_N - {}^2B_1 \qquad \pi_O - {}^2A_2, {}^2A''$$

The $^2A_2$ state was found to be of much higher energy than the others and so was not considered further.

A variety of theoretical techniques was employed because, as will become apparent, the radical states are not satisfactorily described by straightforward restricted Hartree–Fock (RHF) or UHF wavefunctions. For that reason the details of the calculations and their results will be given together as the need arises. All geometry optimisations were performed with the program GAMESS[10] employing analytic gradient methods.

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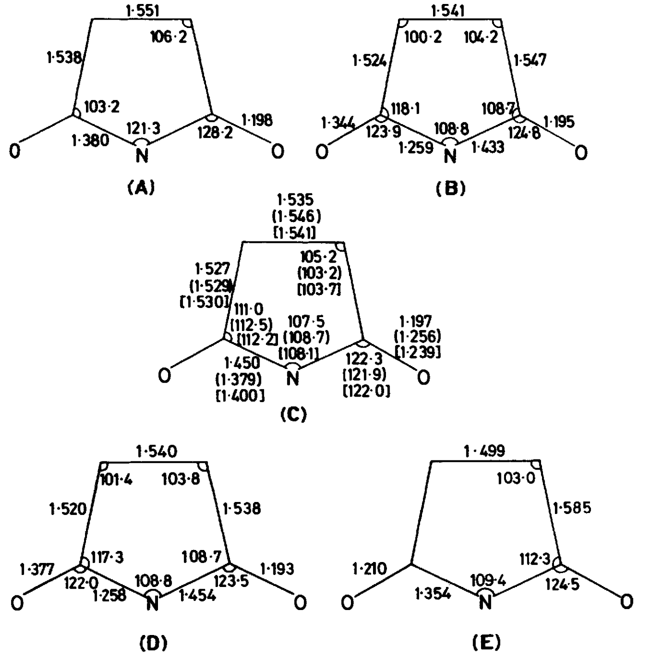


Figure 1. RHF-optimised geometries of the succinimidyl radical using a 3-21G basis set. The UHF- and CASSCF-optimised geometries are given for the $^2B_1$ state in round and square brackets respectively. Bond lengths are in angstroms and angles in degrees

(A)	C_{2v}	$^2A_1$ state
(B)	C_s	$^2A'$ state
(C)	C_{2v}	$^2B_1$ state
(D)	C_s	$^2A''$ state
(E)	C_{2v}	$^2B_2$ state

Note: the RHF and UHF geometries of the σ radicals are essentially the same whilst the $^2A''$ state has a UHF-optimised geometry the same as that for the $^2B_1$ state.

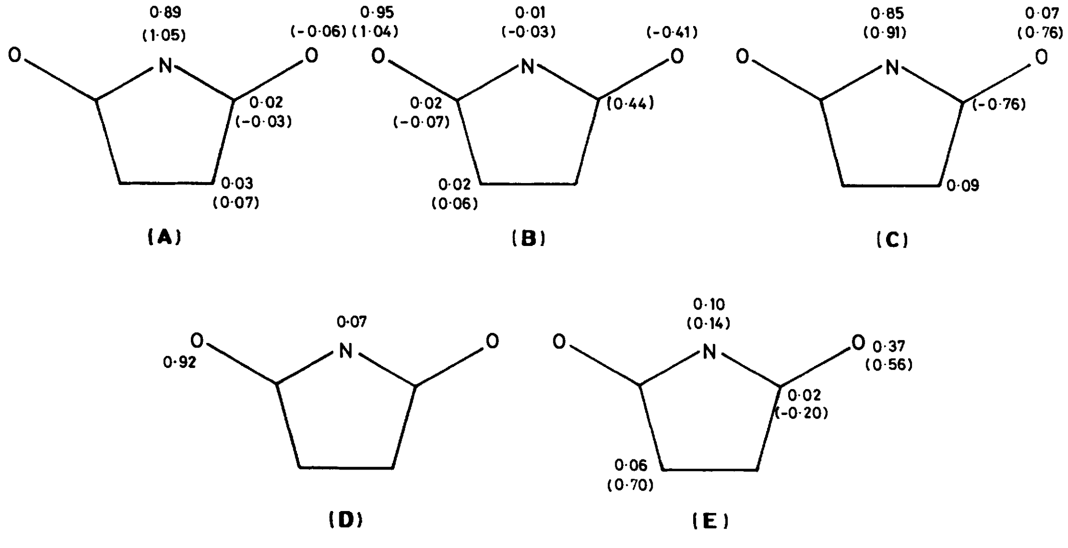


Figure 2. RHF and UHF atomic spin populations for the succinimidyl radical using a 3-21G basis set. The UHF results are in parentheses

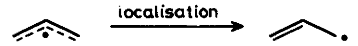
(A)	C_{2v}	$^2A_1$ state
(B)	C_s	$^2A'$ state
(C)	C_{2v}	$^2B_1$ state
(D)	C_s	$^2A''$ state
(E)	C_{2v}	$^2B_2$ state

The configuration interaction (CI) calculations were carried out using the direct CI method within the ATMOL system.[11]

Step 1.—Full geometry optimisations, within the C_{2v} or C_s symmetry constraints, were done on the five radical states under study using an open-shell RHF single-determinant wavefunction and the 3-21G split valence basis set.[12] The geometries of the optimised structures are given in Figure 1, the spin populations (excess α over β spin) in Figure 2, and the energies in Table 2.

The atomic orbital spin populations show that the radicals conform to the valence-bond pictures given above except for the $^2B_2$ structure in which the odd electron is concentrated mainly on the two oxygen atoms and not in the nitrogen *p*-orbital. The presence of an extra electron in the π system in the σ states is found to make the C–N bonds involved shorter because it occupies a slightly bonding π-orbital rather than a non-bonding σ-orbital as in the π states. This effect is especially marked for the $^2A_1$ state in which the switch of an electron from the nitrogen lone pair orbital in the $^2B_1$ species to the π system decreases the C–N bond lengths by 0.07 Å and, because of the greatly reduced lone pair–bond pair repulsions, increases the C–N–C bond angle by about 14°.

In contrast to previous predictions both the $^2A_1$ and $^2A'$ σ radicals are lower in energy than the π radicals, with the C_s forms being lower than those of C_{2v} symmetry within each type. Such a situation is reminiscent of the doublet instability problem. It is well known that RHF wavefunctions are often inadequate to describe doublet states.[13] For example, for the C_{2v} $^2A_2$ allyl radical, it is found that, in order to minimise repulsion between the π electrons of unlike spins, a localisation of the electron density is produced which means that if the C_{2v} symmetry restrictions are relaxed a lower-energy, non-physical, C_s form results. In addition a more stable C_s wavefunction occurs even at C_{2v} geometries so a non-analyticity exists in the potential surface at these points.



To counteract this effect the optimisations were repeated but using a spin-unrestricted HF single-determinant wavefunction. By allowing electrons of different spins to occupy different orbitals the UHF method permits some correlation of the unpaired electron and the paired electrons of opposite spin in the lower bonding orbitals thereby reducing the likelihood of

Table 2. SCF energies[a] of the succinimidyl radical in 3-21G basis

State	RHF energy	RHF relative energy	UHF energy	UHF relative energy	UHF spin [s(s + 1)]
$^2A_1$	−355.912 499	26.5	−355.915 140	71.7	0.766
$^2B_1$	−355.912 231	27.2	−355.942 457	0.0	1.290
$^2B_2$	−355.851 549	185.6	−355.854 830	230.0	0.803
$^2A'$	−355.922 604	0.0	−355.924 525	47.1	0.760
$^2A''$	−355.912 303	27.0	−355.942 461	0.0	1.288
$^2B_1$ (UHF)	−355.898 529	63.2	—	—	—
$^2B_1$ (CAS)	−355.905 327	45.4	—	—	—

[a] In this, and subsequent tables, absolute energies are in a.u., and relative energies are in kJ mol^{-1}.

Table 3. CI energies of the succinimidyl radical in 3-21G basis

State	CI energy	CI relative energy	Correlation energy	Davidson's correction	Revised energies
$^2A_1$	−356.124 940	43.9	557.8	64.3	50.0
$^2B_1$	−356.136 009	14.8	587.5	75.9	9.3
$^2B_2$	—	—	—	—	—
$^2A'$	−356.141 665	0.0	575.2	70.4	0.0
$^2A''$	−356.137 948	9.7	592.4	79.3	0.8
$^2B_1$ (UHF)	−356.134 808	18.0	620.4	88.3	0.1
$^2B_1$ (CAS)	−356.137 425	11.1	609.4	84.3	−2.8

localisation. The results of these calculations are given in Figures 1 and 2 and Table 2.

The most striking feature of the results is that the $^2A''$ structure converges to the symmetric $^2B_1$ state and that this geometry has the lowest energy of all the radicals. The spin populations for the $^2B_1$ UHF geometry show that there is a very large 'static' polarisation effect;[14] that is, the electron with spin in the non-bonding b_1 orbital polarises the electrons in other orbitals so that electrons of parallel spin tend to be in similar regions of space. This minimises the coulombic repulsion between electrons of unlike spin in different orbitals while maximising the exchange interaction between electrons of like spin. In this case the increased delocalisation of the non-bonding π electron caused by the inclusion of the polarisation effect prevents the formation of a $^2A''$ minimum and equalises the π system bond lengths making the C–O bonds longer and the C–N bonds shorter than in the RHF structure.

A relatively large spin polarisation within the C–O bonds is also evident for the $^2B_2$ and $^2A'$ species but its presence does not affect their geometries or energies to any marked extent. The geometry and energy of the $^2A_1$ structure are essentially unchanged from the RHF values.

Although the above discussion suggests that the existence of a stable $^2A''$ species is an artefact of the RHF approximation the UHF results are unsatisfactory in two ways. First, the expectation value of the spin squared [s(s + 1)] for the π radical wavefunction is high, about 1.3 compared with the doublet value of 0.75. Such a large degree of non-doublet instability casts doubt upon whether the delocalisation effect actually occurs for a true doublet wavefunction or is due to the higher spin components introduced by the UHF method. Indeed, spin contamination in UHF wavefunctions generally leads to poor geometry predictions.[15] Second, the size of the 'static' polarisation effect is extremely large and indicates that the UHF description is itself inadequate.[14,16] To overcome these problems by including correlation effects by the CI method, small CI calculations were performed for all radicals, except the $^2B_2$ state of the highest energy, at their RHF optimised geometries. The CI expansion included all single and double excitations [CI(SD)] of the valence electrons from the single RHF root configuration to the virtual minimal basis set orbitals, giving expansions of about 19 000 and 38 000 for the C_{2v} and C_s radicals respectively. An additional calculation was done on the $^2B_1$ radical using an RHF wavefunction but at the UHF-optimised geometry. The 3-21G energies (both uncorrected and corrected for the effect of higher excitations)[17] are given in Table 3.

The uncorrected CI energies give essentially the same energy ordering for the radicals as the RHF results. When the Davidson correction is included to allow for the effect of higher excitations, the two C_s radicals become almost degenerate whilst the $^2B_1$ − $^2A'$ energy gap also decreases. The $^2B_1$ state at the UHF geometry has a corrected energy equal to that of the $^2A'$ radical because of a very large correlation energy. That it is so big (about 30 kJ mol^{-1} greater than for any of the other geometries) may not be surprising as the UHF procedure itself selects a minimum-energy configuration where the amount of correlation of the type it allows is maximised. These results indicate that the π radical surface is a very flat one but unfortunately tell us little about the nature of the $^2A''$ state.

Step 2.—As the UHF and CI results were inconclusive it was decided to try and show directly that the $^2A''$ state was not a minimum on the true potential surface. Two approaches were adopted. First, a search was carried out for the existence of a non-analyticity in the RHF $^2B_1$ surface to prove that a doublet instability was occurring and, second, geometry optimisations were performed on the $^2A''$ and $^2B_1$ states with correlated wavefunctions which should be sufficiently flexible to avoid the localisation problem of the RHF method.

As previously mentioned, for the allyl radical a lower-energy symmetry-broken wavefunction exists at certain symmetric geometries.[13] That this is so can be determined, most generally by showing that the second-derivative matrix of the energy with respect to orbital mixing is not positive definite[18] (a condition due to Thouless)[19] or by showing that such a symmetry-broken solution exists. For the larger succinimidyl systems,* both σ and

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* It is to be noted that, for the semiempirical Pariser–Parr–Pople model, Paldus and Cizek proved that radicals with (4*n* + 1) electrons are *always* doublet stable.[20]

π, a number of lower-energy C_s wavefunctions were taken and used as starting points for the RHF procedure at the symmetric C_{2v} geometries but without the appropriate symmetry constraints.[21] The asymmetric wavefunctions converged to *their symmetric* counterparts in all cases. However, because of the increased number of degrees of freedom in these radicals it may be that the wavefunctions for the optimised C_{2v} geometries are not doublet unstable but that an instability occurs at other geometries (*cf.* Paldus and Veillard).[13]

A multiconfiguration SCF (CASSCF) wavefunction[22,23] in a 3-21G basis was chosen for the additional optimisations of the π radicals thus allowing for the most important correlation effects. Further corrections to gain more of the correlation energy can then be applied *via* CI calculations, if desired. For the π radicals it was felt that although a multireference CI calculation could have been performed the difficulty to optimise at this level, due to our lack of a CI gradient code, made the CASSCF method preferable.

From simple arguments and the previous CI calculations it was evident that correlation within the π-orbitals was going to be the most important. The active space selected for the $^2B_1$ state, therefore, consisted of the three b_1 and two a_2 orbitals of the pentadienyl-like O–C–N–C–O π system and the occupied a_2 and unoccupied b_1 orbitals contributed by the π-like orbitals on the CH_2–CH_2 fragment of the molecule, giving 392 configurations in total. The optimised geometry is shown in Figure 1 and the CASSCF wavefunction is summarised in Table 4. For the $^2A''$ state the active space was reduced in size to six a″ orbitals or 210 configurations in all. This was done because the decrease in symmetry would have made the full seven-orbital active space calculation prohibitively time consuming and because the configurations involving excitations amongst the lowest- and highest-energy active space orbitals in the $^2B_1$ calculation were found to contribute little to the wavefunction. The highest unoccupied a″ orbital was the one removed. The $^2A''$ optimisation converged to give the $^2B_1$ CASSCF geometry [hereafter referred to as $^2B_1$ (CAS)] with the energies of the final structures being identical so that the reduction in the π space had no effect. The $^2A'' - {}^2B_1$ energy separation of the RHF structures at the CASSCF level was 23.4 kJ mol^{-1} with the $^2B_1$ state most stable.

From Figure 1, it can be seen that the $^2B_1$ geometry optimised at the CASSCF level is intermediate between those found using the RHF and UHF procedures but closer to the UHF geometry. The increase in bond lengths can be understood to be due to the inclusion of configurations that involve $\pi \longrightarrow \pi^*$ and $\pi_0 \longrightarrow \pi^*$ excitation in the CASSCF wavefunction. Similarly, from Table 4 it can be seen that configurations involving three or even five unpaired electrons make a substantial contribution to the determinantal expansion indicating why, if configurations of this type but with the incorrect spin couplings were part of the UHF wavefunction, it had such a large spin contamination. A direct comparison between the configuration coefficients for the CI and CASSCF wavefunctions is difficult because the expansions are of different lengths and so the contributions from each configuration should be less for the CI case. However, it is apparent that the root configuration is less dominant in the $^2B_1$ CASSCF wave function. It should also be noted that the CASSCF method will include the effects of higher excitations, within the active space orbitals, than our CI expansion will allow.

A CI calculation, comparable to those described earlier, was

Table 4. Important configurations in CI or CASSCF wavefunction of the succinimidyl radical (3-21G basis)

	Orbital[a] and occupancies					
State	a_2	b_1	b_1	a_2	b_1	Coefficients
$^2B_1$	2	2	1	0	0	0.933
(CI calculation	2	1	1	0	1	−0.063
at RHF-optimised	2	1	2	0	0	0.061
geometry)	1	1	1	1	1	−0.055
$^2B_1$	2	2	1	0	0	0.926
(CI calculation	2	1	1	0	1	0.082
at UHF-optimised	1	2	1	1	0	0.081
geometry)	2	1	2	0	0	−0.076
	1	1	1	1	1	0.060
	0	2	1	2	0	−0.055
$^2B_1$	2	2	1	0	0	0.928
(CI calculation	2	1	1	0	1	−0.077
at CASSCF-optimised	2	1	2	0	0	−0.073
geometry)	1	2	1	1	0	−0.070
	1	1	1	1	1	0.060
	a″	a″	a″	a″	a″	
$^2A''$	2	2	1	0	0	0.931
(CI calculation	2	1	1	1	0	0.067
at RHF-optimised	2	0	1	2	0	−0.067
geometry)	2	1	2	0	0	0.054
	a_2	b_1	b_1	a_2	b_1	
$^2B_1$	2	2	1	0	0	0.923 (0.940)
(CASSCF-calculation	1	2	1	1	0	0.191 (0.134)
at CAS optimised	2	1	1	0	1	−0.173 (−0.140)
geometry and at RHF-	1	1	1	1	1	−0.159 (−0.165)
optimised geometry in	0	2	1	2	0	0.125 (0.110)
brackets)	1	1	2	1	0	−0.080 (−0.075)
	2	0	1	2	0	0.075 (0.075)
	2	0	1	0	2	0.075 (0.082)
	0	2	1	0	2	0.068 (0.075)
	0	2	2	0	1	0.067 (0.058)
	1	2	0	1	1	0.057 (0.053)
	a″	a″	a″	a″	a″	
$^2A''$	2	2	1	0	0	0.939
(CASSCF calculation	2	1	1	1	0	−0.177
at RHF-optimised	1	1	1	1	1	−0.155
geometry)	2	0	1	2	0	−0.129
	0	2	1	0	2	−0.088
	0	2	1	2	0	−0.070
	1	2	1	0	1	−0.069
	2	0	1	0	2	−0.068
	1	2	1	1	0	0.062
	2	1	1	0	1	0.061

[a] The orbitals are the five π-MOs of the O–C–N–C–O system.

Table 5. Energies of the succinimidyl radical in 6-31G* basis

State	RHF energy	RHF relative energy	CI energy	CI relative energy	Correlation energy	Davidson's correction	Revised energies
$^2A_1$	−357.922 542	0.0	−358.493 939	7.4	1 500.2	416.7	21.5
$^2B_1$	−357.914 964	19.9	−358.496 764	0.0	1 527.5	430.8	0.0
$^2A'$	−357.851 503	186.5	−358.431 884	170.3	1 523.8	432.2	168.9
$^2A''$	−357.915 205	19.3					

carried out at the $^2B_1$ (CAS)-optimised geometry. The final corrected energy is the lowest of all the results (Table 3), showing the improved geometry produced by the CASSCF method. That the $^2B_1$ energy surface is quite flat is suggested by the small differences in the final revised energies of Table 3, obtained at the RHF-, UHF-, and CAS-optimized geometries.

Step 3.—In an attempt to obtain the most accurate relative energy separation for all the radicals it was decided to perform single-point RHF and CI (SD) calculations with a 6-31G* basis[24] at the optimised 3-21G geometries for the $^2A_1$, $^2A'$, and $^2B_1$ states. The σ RHF/UHF and $^2B_1$ (CAS) structures were used. The CI wavefunctions included all configurations generated from excitations from an internal valence space of 19 orbitals to an external space of 46 orbitals leading to expansion lengths of about 230 000 and 460 000 for C_{2v} and C_s symmetry respectively. An RHF calculation was also done for the $^2A''$ state to test the validity of this approach. The results with the larger basis are given in Table 5.

The relative energies differ markedly from those in the 3-21G basis. At the RHF level the symmetric σ or $^2A_1$ state is lowest in energy with the unsymmetric $^2A'$ much higher than either it or the $^2B_1$ radical. The uncorrected CI energies reverse the stability of the $^2A_1$ and $^2B_1$ states whilst leaving the $^2A'$ radical still about 170 kJ mol^{-1} above them. The addition of Davidson's correction[17] serves to increase the $^2A_1/^2B_1$ separation to 21.5 kJ mol^{-1}. The same configurations were important in the CI expansions as before, although, because of their larger size, there were no secondary coefficients with a magnitude greater than 0.04.

Discussion of the Computational Results

The reason for embarking on this study was to gain accurate energy differences for the proposed species of succinimidyl radicals. It has emerged from the work described in this paper that to obtain a balanced wavefunction for the π radical surface is not straightforward and raises the question as to the accuracy of the calculated σ − π state energy differences, and whether the σ radicals are as straightforward as they seem.

The π Radicals.—We have shown fairly conclusively that if a wavefunction of sufficient flexibility is chosen to describe the π potential energy surface then the most stable doublet succinimidyl radical is of $^2B_1$ symmetry. The $^2A''$ state is a minimum only for the RHF method in which to reduce interelectronic repulsion a localisation of electron density occurs on opposite sides of the molecule; that is, the symmetric solutions are doublet unstable.[13]

Given this, how can an accurate energy be best obtained? The ideal solution would be to select the most important configurations from the CASSCF wavefunction and use these with the CASSCF MOs as the basis for a multireference CI (SD) calculation. This procedure is computationally prohibitive, so is a large single-reference CI (SD) calculation using RHF MOs sufficiently accurate?

At the RHF level both 3-21G and 6-31G* wavefunctions give lower energy $^2A''$ than $^2B_1$ states. However, the $^2B_1$ (CAS) state is the lowest-energy species from the 3-21G CI results which means that the RHF/CI methodology employed here seems to produce energies that mimic at least partially the behaviour of the CASSCF surface. It is to be noted too that whereas the 3-21G RHF π potential surface is very flat, the $^2A''/^2B_1$ energies differing by less than 1 kJ mol^{-1}, on the CASSCF surface the differences have increased in favour of the $^2B_1$ state to 18.1 and 31.7 kJ mol^{-1} for the $^2A''$ (RHF geometry)/$^2B_1$ (RHF geometry) and $^2A''$ (RHF geometry)/$^2B_1$ (CAS geometry) energy differences respectively. Thus, the trend in the CASSCF energy surface is reproduced by the CI calculations.

The σ Radicals.—The σ radical results raise a number of questions: (*i*) For all the 3-21G basis set calculations, the $^2A'$ is more stable than the $^2A_1$ state, suggesting that a doublet instability-type problem may be occurring.

(*ii*) If (*i*) is true, why do the UHF energies not differ significantly from the RHF ones?[16] In that case, the σ radicals would show only a doublet instability and not a non-doublet instability as well, as do the π radicals.[21]

(*iii*) At the 6-31G* level the C_s form is greatly destabilised with respect to the C_{2v} form. Is this because polarisation functions have been added or is it due to non-optimisation of the geometries in the new basis set?

Dealing with each point in turn. (*i*) There is no evidence for a doublet instability in either the π or σ radical RHF wavefunctions. However, at the 3-21G RHF level the π state wavefunctions are not sufficiently flexible to describe the correct minimum-energy geometry, exhibiting an instability with respect to C_{2v} to C_s nuclear geometry distortions if not to C_{2v} to C_s variations in the molecular orbital coefficients. That this could be occurring for the σ radicals is possible but the evidence is less conclusive. For CASSCF single-point calculations performed at the RHF/UHF $^2A_1$ and $^2A'$ optimised geometries the σ radical energy difference increases to 64 kJ mol^{-1} with the C_s form more stable whereas for the π radicals the $^2B_1$ state is clearly favoured.

(*ii*) The doublet and non-doublet instabilities are different phenomena such that a wavefunction is unstable to variations that do and do not maintain double occupancy and a single-determinant wavefunction respectively. So, if a wavefunction displays one behaviour it does not have to display the other (although all doublet wavefunctions should show a small non-doublet instability, at least).[21] The spin polarisation in the $^2A_1$ radical is small presumably because its propagation from an a_1 orbital is difficult (it would be easier *via* a b_2, for example).[14] The effect for the $^2A'$ state is larger, although, as for the C_{2v} radical, the energy lowering is very small.

(*iii*) The destabilisation of the C_s σ radical with the 6-31G* basis set seems due to the introduction of *d* functions[25] rather than the lack of geometry optimisation where the size of the change would not be expected to be so great. The addition of polarisation functions produces, for all states, a movement of electron density from oxygen and nitrogen to the carbons in the π system of 0.07, 0.12, 0.04, and 0.04 electrons per carbon for the $^2A_1$, $^2A'$, $^2B_1$, and $^2A''$ states respectively. The increased delocalisation of charge seems to favour the symmetric σ state over the asymmetric form.

Relative Energies.—To obtain accurate relative energies all species must be treated with an equivalent level of theory which must be sufficient to allow an adequate description of the true wavefunction. The π and σ state energies have been calculated throughout using the same techniques so they should be comparable. The validity of the π radical results has been discussed and it is decided that the $^2A''$ minimum is an artefact of the RHF method and can be discarded. For the σ radicals it appears that the addition of polarisation functions is essential for the correct description of the C_s and C_{2v} forms.

In summary, the final $^2B_1$ − $^2A_1$ energy difference obtained was 21.5 kJ mol^{-1} with the π state more stable.

Conclusions

In this study an attempt to calculate the relative energies of the π and σ succinimidyl radicals has been made. The final $^2B_1$ − $^2A_1$ state energy separation is 21.5 kJ mol^{-1}. This value is likely to be an underestimate due to the difficulties in obtaining the π radical wavefunction. Our value is substantially smaller than the 230 kJ mol^{-1} calculated directly at the STO-3G level.[9] However, when this value is modified in the light of higher-level calculations for related smaller radicals a value of 85—100 kJ mol^{-1} is obtained, more in line with the value we calculate.

As noted by Skell *et al.*[6] calculations which predict the ground state to be S_π pose a dilemma. If ring opening is assigned as a ground-state property, then it is occurring from a π state which should not undergo this reaction based on orbital symmetry and MNDO/3[26] arguments. Thus, if these arguments *are* valid, most of the currently known imidyl chemistry is that of an excited state, S_σ, and few ground-state reaction properties are known at the present.

However, these calculations emphasise the care that is required in applying *ab initio* techniques to many molecular species to produce meaningful results and illustrate the great attention to detail, and an awareness of the limitations of the techniques used, which are needed to obtain a minimum qualitative description of a potential-energy surface.

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