An SCF-MO Study of the Relative Barriers to Inversion and to Ring Opening in Three-membered Ring Carbanions

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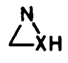
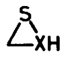
The barriers to inversion of configuration at the centre X and to ring opening in a series of isoelectronic three-membered ring systems (**1**)—(**4**) have been investigated at the single determinantal MNDO and *ab initio* SCF-MO levels of theory. The MNDO-method-predicted barriers to inversion at carbanionic centres are too low compared with experiment and with the *ab initio* calculations. In the specific case of cyclopropyl carbanion, the MNDO method incorrectly predicts the C^- centre to be planar. The two theoretical methods give more comparable results for inversion at nitrogen and oxygen centres. At the highest level of theory employed (RHF-MP4‖6-31+G), loss of configuration in (**1a**)—(**3a**) is predicted to occur *via* ring opening to give an enolate anion, rather than *via* direct inversion at C^-. The reverse is true in cyclopropyl anion (**4**), where direct inversion at the carbon centre has the lower barrier. These results lead to the prediction that oxirane and aziridine anions should be configurationally stable species, whereas thiirane carbanions are predicted to ring-open rapidly to give a thioenol.

It is well established[1] that inversion barriers at nitrogen are substantially increased if the nitrogen atom is part of a three-membered ring. Such barriers are further augmented if an oxygen atom is also present in the ring, as in oxaziridines (**1b**), and indeed the barriers in certain oxaziridine derivatives are sufficiently high to permit resolution of enantiomers.[2] In (**1b**), this high barrier can be attributed[3] to a combination of increased repulsion between the lone-pair electrons on the adjacent nitrogen and oxygen atoms in the transition state for inversion, and the necessarily small C–N–C valance angle in the three-membered ring favouring sp^3 rather than sp^2 hybridisation at the nitrogen atom. This strain effect can also be used to rationalise the configurational stability of cyclopropyl carbanions, which generally undergo reactions with retention of configuration.[4] In contrast, cyclopropyl radicals are generally *not* configurationally stable,[5] and factors other than strain are clearly important in controlling the barrier to inversion in three-membered rings.[1] The configurational stability of other three-membered ring systems such as oxirane carbanion (**1a**) has also been demonstrated.[6] Such species are isoelectronic with oxaziridines and should be expected to display similarly high barriers to ring inversion.

(**1**)

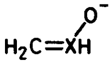


(**2**)

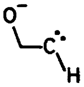


(**3**)


(**4**)



(**5**)



(**6**)

a; $X = C^-$
b; $X = N$
c; $X = O^+$

(**5**) **a**; $X = C$
b; $X = N^+$

In the specific case of three-membered ring systems, alternative reactions involving ring opening are possible, and if reversible would also lead to loss of configuration at the trisubstituted centre. For example, oxaziridines (**1b**) are known to undergo electrocyclic ring-opening under thermal or photochemical conditions to give nitrones (**5b**) by cleavage of the C–O bond[7] and it has been speculated that under favourable circumstances C–N cleavage may also occur, generating carbonyl imines.[8] In oxirane carbanion (**1a**), cleavage of the C–O bond would result in the formation of an enolate anion (**5a**). An apparently less likely alternative is C–O bond cleavage giving the oxyanion carbene (**6**).

Although a number of quantitative SCF-MO calculations have been carried out for oxaziridines, aziridines, and cyclopropyl systems, no study of (**1a**) has been reported, and in particular no comparative study of the barriers to inversion and to ring opening has been made. We report here such a theoretical study of the systems (**1**)—(**4**) using both the MNDO[9] and *ab initio*[10] SCF-MO procedures. The present study is restricted to unsolvated models for the reactions, no attempt having been made at this stage to include counter-ions such as Li^+.

Computational Procedure.—Initial calculations were carried out using the MNDO SCF-MO method[9] using a standard *s*/*p* valence basis set. Two types of reaction co-ordinate were defined; R_1, the bond corresponding to cleavage of the ring to give either the enol anion or the carbene and R_2, corresponding to the dihedral angle giving the degree of co-planarity of the XH component with the three-membered ring (Figure 1). Enthalpies of formation were calculated at fixed values of R_1 and R_2, with full optimisation of the remaining $3N - 8$ geometrical variables, and used to construct a contour map. Approximate transition states were located either as saddle points on these contour maps, or from one-dimensional plots in which only R_1 was varied. These approximate geometries were then located exactly by minimising the sum of the squared scalar gradients[11] and characterised as transition states by calculating the cartesian force constant matrix[12] and showing that this had only one negative eigenvalue with the correct form for the eigenvectors. Initial estimates of the *ab initio* energies were obtained using a 3-21G* basis set at these MNDO geometries, employing the GAUSSIAN 82 program system.[10] For the ring substituent $X = C^-$, major differences in the calculated MNDO and 3-21G* activation energies for inversion and ring opening were obtained by this procedure. In the case of (**4**),

Figure 1. Reaction co-ordinate system for (**1a**)—(**4**): (a) defining ring opening and (b) Newman projection defining the dihedral angle for inversion at the C^- atom. R_1 in Å, refers to the length of the cleaving C–O bond, R_2 in degrees

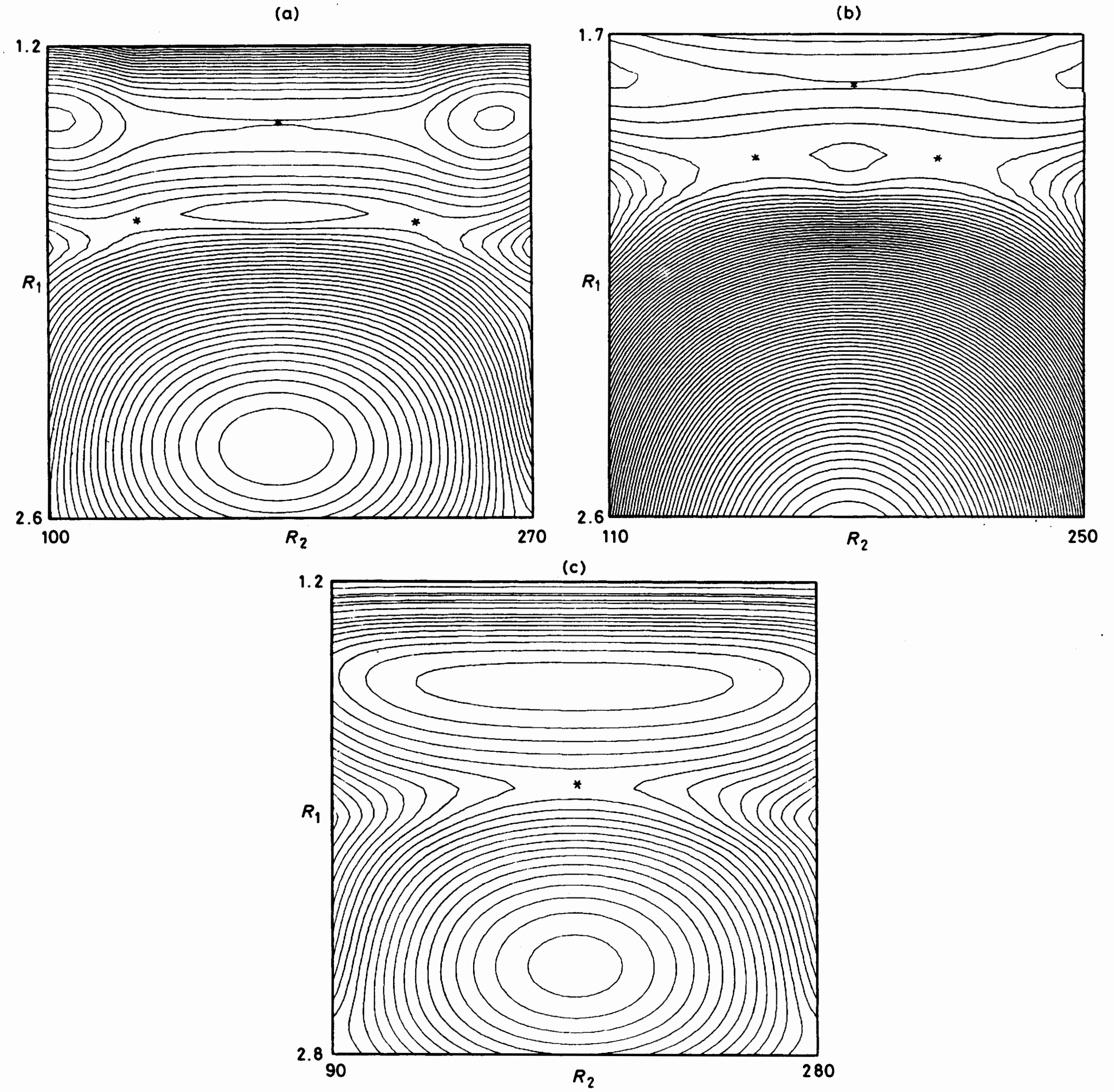


Figure 2. Energy-contour map as a function of the two reaction co-ordinates R_1 and R_2 for (a) (**1a**). The separation between the contour levels is 2.8 kcal mol^{-1}. (b) (**3a**). The separation between the contour levels is 0.8 kcal mol^{-1}. (c) (**4a**). The separation between the contour levels is 3.5 kcal mol^{-1}. The transition states are indicated with an asterisk

the MNDO ground-state geometry appeared qualitatively incorrect. Accordingly, the stationary points were reoptimised at the 3-21G* level using the method reported by Schlegel,[13] and again characterised by inspection of the calculated Hessian matrix. Further corrections to the *ab initio* energies were made at these geometries by either including a zero-point energy correction, obtained from the normal vibrational frequencies calculated from the Hessian matrix, or by including electron-correlation corrections up to the RMP4 level.[6] Since C$^-$ species have been shown [14] to require the addition of diffuse *p* functions to reproduce inversion barriers correctly, a further set of calculations using the 6-31+G augmented basis set were carried out, again with reoptimisation of the geometries and inclusion of RMP4 correlation corrections.

Results and Discussion

Loss of configuration at the C$^-$ centre in (**1a**) could proceed in three ways, (*i*) by direct inversion at this atom, (*ii*) by ring opening to give (**5a**), or (*iii*) by formation of the carbene (**6**). The relative characteristics of (*i*) and (*ii*) are shown in an MNDO energy-contour map (Figure 2), which clearly shows two distinct pathways, the lower of which corresponds to inversion (Table 1). A reaction-path calculation using only R_1 as a reaction co-ordinate shows that formation of carbene anion (**6**) is a relatively high-energy pathway ($\Delta H^{\ddagger}$ 33.7 kcal mol^{-1}) and is significantly endothermic (ΔH +28.7 kcal mol^{-1}), compared with the enol anion (**5a**) which is formed exothermically (ΔH −61.5 kcal mol^{-1}). We do note however that elements such as lithium can stabilise carbenoid systems[15] and hence that the

Table 1. Calculated barriers to inversion (in kcal mol^{-1}) at the centre X in compounds (**1**)—(**3**)

	X = C^{-}	Barrier	X = N	Barrier	X = O^{+}	Barrier
MNDO	(**1**)	9.17	(**1**)	31.96	(**1**)	~14^{c}
3-21G*‖MNDO		42.03		28.79		
MNDO	(**2**)	1.38^{b}	(**2**)	22.28,^{a} 28.45^{b}	(**2**)	16.91^{b}
3-21G*‖MNDO		27.46^{b}		17.84,^{a} 26.99^{b}		16.35^{b}
MNDO	(**3**)	1.03	(**3**)	23.32	(**3**)	9.24
3-21G*‖MNDO		19.76		15.65		5.21

^{a} *cis*. ^{b} *trans*. ^{c} O–O Distance not optimised.

Table 2. Calculated barriers for inversion at centre X and for ring opening to (**5**) for compounds (**1**)—(**4**)

	(**1**)		(**2**)		(**3**)		(**4**)	
X = C^{-}	inv^{b}	ro^{c}	inv^{b}	ro^{c}	inv^{b}	ro^{c}	inv^{b}	ro^{c}
MNDO	9.17	25.39	1.38	13.79	1.03	3.58	0	18.58
3-21G*	45.00	44.50	37.69	43.57	36.08	16.22	20.78	38.54
RMP4/3-21G*	46.66	26.94	36.54	26.11	34.22	9.31	19.38	26.89
ZPE/3-21G*	−1.19	−1.79	−1.47	0.41	−1.21	−0.35	−1.12	−2.15
6-31+G	36.16	34.71	31.46	39.39	34.11	11.80	17.65	35.34
RMP4/6-31+G	35.18	18.23	29.52	23.98	30.15	3.52	16.54	25.36
$\Delta S^{\ddagger a}$/3-21G*	−0.68	0.66	−0.14	0.22	−0.36	0.20	−0.88	−0.87

^{a} $\Delta S^{\ddagger}_{298}$ In cal K^{-1} mol^{-1}. ^{b} Transition-state barrier for inversion at atom X in kcal mol^{-1}. ^{c} Transition-state barrier for ring opening to give (**5**) in kcal mol^{-1}.

Table 3. Reactant energies for X = C^{-} in compounds (**1**)—(**4**)

Reactant X = C^{-}	(**1**)	(**2**)	(**3**)	(**4**)
MNDO^{c}	25.538	66.837^{a}	45.502	56.927
		67.757^{b}		
3-21G*^{d}	−151.312 97	−131.580 07^{a}	−472.599 06	−115.686 42
	−151.630 53	−131.572 38^{b}		
RMP4/3-21G*^{d}	0.044 28	−131.890 48^{b}	−472.923 18	−115.984 94
ZPE/3-21G*^{d}	−152.125 34	0.057 71^{a}	0.042 80	0.069 26
6-31+G^{d}	−152.469 41	−132.293 22^{a}	−474.844 25	−116.317 65
RMP4/6-31+G^{d}		−132.626 52^{a}	−475.105 14	−116.635 34

^{a} *trans*. ^{b} *cis*. ^{c} kcal mol^{-1}. ^{d} Atomic units, 1 atomic unit = 627.52 kcal mol^{-1}.

Table 4. Charges on the carbon at the X = C^{-} centre in compounds (**1**)—(**4**)

	(**1**)		(**2**)		(**3**)		(**4**)	
X = C^{-}	*q*	inv^{a}	*q*	inv^{a}	*q*	inv^{a}	*q*	inv^{a}
MNDO	−0.78	9.17	−0.78	1.38	−0.73	1.03		0
3-21G*	−0.48	45.00	−0.49	37.69	−0.65	36.08	−0.60	20.78
6-31+G	−0.91	36.16	−1.05	31.46	−0.73	34.11	−1.08	19.38

q = charge on C at inverting centre.

^{a} Barrier to inversion in kcal mol^{-1}.

presence of a Li^{+} counter-ion may make the formation of species such as (**6**) more favourable.

In the related aziridine (**2a**), the barrier to inversion at carbon was even lower. For the sulphur system (**3a**), the energy-contour map shows that the transition states for both inversion and cleavage to the thioenol are very reactant-like (Figure 2b) and both barriers are very small. In the case of (**4**), MNDO predicts the C^{-} centre to be planar, and the energy-contour map (Figure 2c) is clearly qualitatively different from that for either (**1a**) or (**2a**). This last result is particularly surprising, since numerous derivatives of cyclopropane carbanion have been experimentally demonstrated to be configurationally stable.[4] To investigate how the *ab initio* method reproduces the barriers, energy calculations were initially carried out on a range of systems (**1**)—(**4**), at the fully optimised MNDO geometries, using a 3-21G* basis set (Table 1). The results clearly establish that a qualitative difference between the two methods is predicted only for C^{-} systems. Basis set quality is known to be particularly important in such negatively charged systems, and it is possible that the minimal valence basis set employed in MNDO has serious deficiencies in calculations for such carbanions. Indeed, it has been previously noted[16] that the electron affinities of C^{-} systems can be seriously in error if the negative charge is localised predominantly on one carbon.

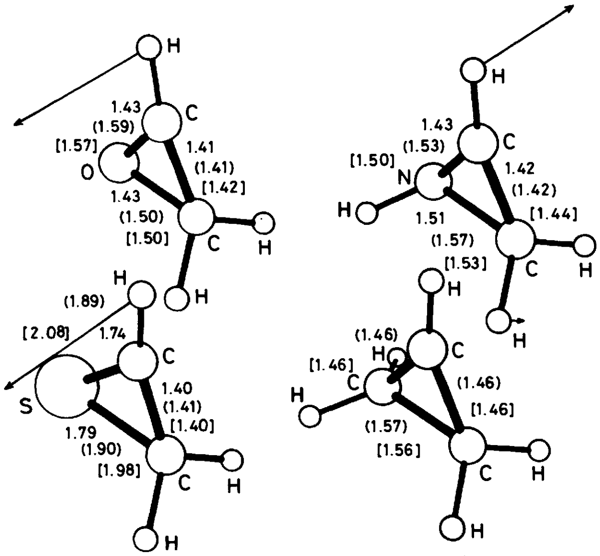


Figure 3. Transition-state geometries for inversion at atom X in (**1**)—(**4**). Bond lengths (in Å) optimised at the MNDO (3-21G*) [6-31 + G] levels. Arrows indicate the calculated MNDO displacement co-ordinates for the imaginary frequency

Geometry optimisation at the single determinantal *ab initio* level was carried out at the 3-21 G* and (6-31 + G)[13] basis set level. The absolute energies so obtained are shown in Table 2, and the activation energies for inversion at X and for ring opening to the enol (**5**) in Table 3. The two basis sets yield similar transition-state structures for inversion (Figure 3) and for ring opening (Figure 4). However, significant differences between the MNDO and the *ab initio* structures are found. In particular, the carbanionic centre in (**4**) is correctly predicted to be non-planar at the 3-21G* and 6-31 + G levels. The other major difference is in the calculated lengths of the cleaving bonds at the transition state for ring opening, for which the MNDO values are consistently shorter than the *ab initio* ones (Figure 4). We note in this context that the *ab initio* geometries are obtained at the non-correlated RHF SCF level, whereas MNDO in principle includes electron correlation effects at the parametric level. It is possible therefore that geometry re-optimisation at the *ab initio* RMP4 level would give more comparable results, although the computer resources currently required to do this are prohibitive. It is also known[17] that the MNDO method overestimates non-bonded nuclear repulsion terms at internuclear distances of *ca.* 2.0 Å. This tends to result in an overestimation of bond lengths in transition states. This particular failing (apparently corrected at the AM1 level,[17] a reparameterised version of MNDO) does not explain the present differences between the two methods. In (**3a**) particularly, the MNDO C–S bond length for ring opening is predicted to be much shorter than the *ab initio* result. The correlated RMP4/6-31 + G and MNDO methods do however agree in predicting very small barriers to ring opening in (**3a**).

There are no significant differences in the calculated geometries between the 3-21G* basis, which includes polarisation functions, and the 6-31G + G basis set, which is augmented with a set of diffuse *p* functions. In particular, it is unlikely that *d*-type functions play a major geometric role in the sulphur system (**3a**). The larger 6-31 + G basis does however result in lower absolute energies, and in lower barriers to inversion and to ring opening.

Both the MNDO and the *ab initio* methods predict electrocyclic ring opening of cyclopropyl carbanion to proceed with conrotation, giving an allyl carbanion. This is consistent with the Woodward–Hoffmann rules, and is similar to the result previously found for the ring opening of oxaziridine to give a carbonyl imine.[4] Although the transition state corresponds to conrotation, it does *not* have the C_2 axis of symmetry associated with this mode. The strongly pyramidal nature of the C^- atom in (**1a**) means that the only element of symmetry common to both reactant and product is the plane bisecting this atom. This precludes C_2 symmetry, and since the selection rules disfavour C_s symmetry, the transition state can only have C_1 symmetry. Indeed, when C_2 symmetry is imposed, a stationary point with *two* negative roots in the force constant matrix is located, the second such root corresponding to out-of-plane motion of the central hydrogen atom.

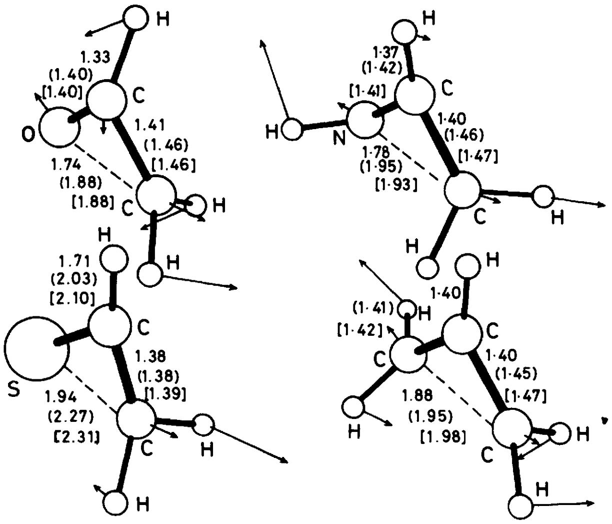


Figure 4. Transition-state geometries for ring opening in (**1**)—(**4**). Bond lengths (in Å) optimised at the MNDO (3-21G*) [6-31 + G] levels. Arrows indicate the calculated MNDO displacement co-ordinates for the imaginary frequency

In contrast to the geometries and energies given by the semiempirical and *ab initio* procedures, the calculated charge densities (Table 4) are similar for both methods. For (**1**), (**2a**), and (**4**), the calculated charge at the C^- centre *increases* for inversion and *decreases* for ring opening to an allylic system. In the former case, the lone pair on carbon becomes orthogonal to the C–C framework and hence more localised, whereas in the latter case the charge migrates to the two terminal atoms of the allylic system. The one exception is the thiirane (**3a**), for which both MNDO and the *ab initio* methods predict an *increase* in charge on the carbon at the transition state for allylic ring opening. In this aspect, as in several others, the thiirane is anomalous.

Several types of correction to the calculated *ab initio* energies were also investigated. (i) The calculated correction to the barriers for zero-point energy terms was very similar for both inversion and ring opening (Table 3). (ii) The entropies of activation for the two types of reaction are both small, indicating that $\Delta H^\ddagger$ and $\Delta G^\ddagger$ will be very similar (Table 3). There does appear to be a systematic difference between the entropy of activation for inversion, which is slightly negative, and ring opening, which tends to be positive. The only exception is (**4**), where both entropies are negative. (iii) Electron-correlation corrections carried out to the RMP4 level reduce the barriers to inversion significantly less than the barriers to ring opening. This is to be expected, since the former process involves no bond breaking, whereas the latter involves significant electronic reorganisation from the σ to the π network.

At the highest level of theory (RMP4/6-31 + G‖6-31 + G) the barrier to ring opening of (**1**; X = C^-) is clearly lower in energy than inversion at carbon. This result applies of course to the gas phase. In solution, it is highly probable that the C^- centre will be associated with the positive counter-ion. This is likely to increase the barrier to inversion, and to decrease the barrier to ring opening by preferentially stabilising the enol anion product. Whereas in (**1a**) the barrier to ring opening to give (**5a**) is likely to be sufficiently large for the species to have a significant lifetime at low temperatures in solution, the calculations predict a very low barrier for the sulphur analogue (**3a**). If this result is correct, (**3a**) is most unlikely to have a significant lifetime in solution.

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