

Table VIII. Calculated Activation Energies and Relative Rates for the Deprotonation of the C₂ and C₅ Atoms in 1,3-Azolium Systems

	ΔE_a^a au	E_a^b au	rel k_{calcd}^c	rel k_{exptl}^d
1,3-imidazolium C ₂	0.1203	0.7503	<<1	1
1,3-oxazolium C ₂	0.1139	0.6872	2.0×10^5	$10^{5.5}$
1,3-thiazolium C ₂	0.0731	0.6923	1.0×10^3	$10^{3.5}$
1,3-phosphazolium C ₂	0.1010	0.7441	<1	
1,3-imidazolium C ₅	0.2191	0.8936	<1	1
1,3-oxazolium C ₅	0.2316	0.8646	10^5	$10^{5.4}$
1,3-thiazolium C ₅	0.2022	0.8708	2.5×10^2	$10^{3.0}$
1,3-phosphazolium C ₅	0.2172	0.8975	<1	

^a Energy difference between π HOMO and appropriate σ MO in cation. ^b Activation energy: $E_a = \Delta E + \Delta E_r$ (ΔE_r , see Table I).

^c Relative rates, calculated from the activation energies ($T = 33^\circ\text{C}$).

^d Relative rates as measured by Haake et al.^{2a,b} (pH 4–5, $T = 33^\circ\text{C}$).

has the most negative energy value with respect to the other 1,3-azolium cations. This means that decarboxylation will occur most rapidly with thiamin pyrophosphate as catalyst.

Conclusion

This study shows that 3d orbitals of sulfur and phosphorus have no effect on the formation and acidity properties of carbanions adjacent to these heteroatoms. The 1,3-thiazolium conjugate base is stabilized with respect to the other conjugate bases by the greater polarizability of the sulfur atom. The relatively faster H–D exchange rate of the 1,3-thiazolium cation can be explained by the small amount of energy this cation needs to utilize the appropriate σ MO with respect to the other cations.

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On the Thermal Rearrangement of Cyclobutylidene to Methylene-cyclopropane. Intermediacy of a Novel Nonclassical Carbene¹

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Abstract: The reaction of cyclobutylidene to methylenecyclopropane represents a ring contraction rearrangement in which a three-membered ring is generated from a four-membered ring. The quantum-mechanical investigation of its singlet state ($^1\sigma^2$) by the MINDO/3 method reveals that the reaction is initiated by an electrophilic attack of the empty p AO at the carbene site C₁ to the CH₂ group C₃. Thus it takes up a bicyclobutane-like structure. In this species, which corresponds to a nonclassical carbene, electron density is shifted toward the carbene site. In a second step it can easily undergo rearrangement to methylenecyclopropane. In this process the bond fission is controlled by orbital symmetry. For the total reaction an activation enthalpy of 8 kcal/mol is computed. When correction terms for the ring strain are added, this represents an upper limit for the reaction.

Cyclobutylidene (**1**, X = CH₂) derived from the thermal cleavage of cyclobutanone tosylhydrazone² rearranges to methylenecyclopropane (**2**). To a minor extent cyclobutene (**3**) is formed by hydrogen shift from C₂ (or C₄) to C₁. Subsequent ring opening in **3** yields the butadiene **4**. The ring-contraction reaction has been used as a synthetic route to ho-

mofulvenes.³ The rearrangement has also been observed in the reaction of cyclobutylidene derivatives containing heteroatoms, such as X = SO₂⁴ and X = O, NH.⁵

No details are yet known for the mechanism of the very common ring-contraction reaction, **1** to **2**. In order to reveal a mechanistic concept and to examine the experimental ob-

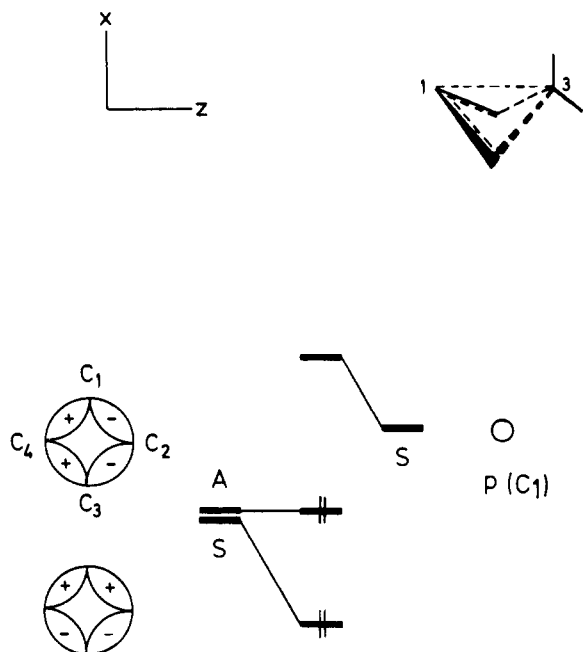
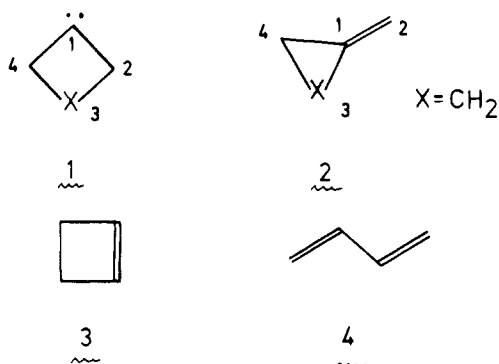


Figure 1. Interaction diagram for the formation of a bond between C_1 and C_3 in **1**, of the empty p AO at C_1 with the set of bonding valence orbitals of the cyclobutane moiety. The x,z plane bisects the angle between the planes $C_1C_2C_3$ and $C_1C_4C_3$.



servations more closely, we have carried out a quantum-mechanical study to determine the electronic hypersurface directing the reaction path from **1** to **2** for $X = CH_2$.

Methods

We performed calculations at a semiempirical level of sophistication utilizing the MINDO/3 approximation.^{6,7} All calculated geometries were optimized with respect to the total energy. On this basis a two-dimensional contour map for the electronic hypersurface was constructed from a series of optimized geometries, each of which was varied in 22 dimensions (including bond lengths, bond angles, and torsional angles) until the minimum energy was achieved. For the optimization a gradient search was employed, the gradient being derived by the method of finite differences.⁸

Results and Discussion

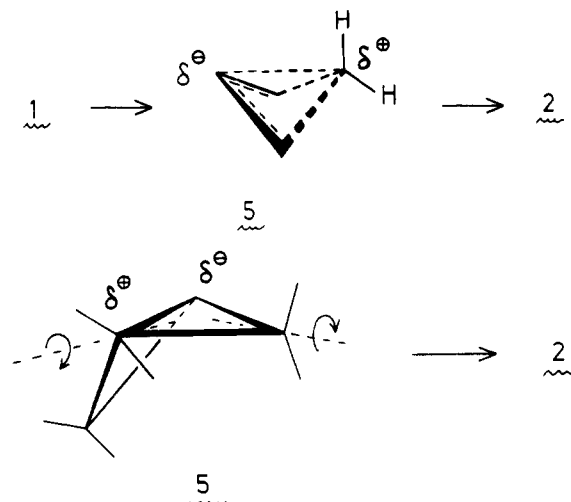
There are two orbitals at the carbene site of C_1 of **1**, one in the plane formed by the atoms $C_1C_2C_3(C_4)$ and the other orthogonal to this plane. These orbitals may be denoted as σ type or p type as previously introduced by Hoffmann and co-workers.⁹

Four different electronic configurations of importance can be constructed: the singlet states $^1(\sigma^2)$, $^1(\sigma^1p^1)$, and $^1(p^2)$ and the triplet state $^3(\sigma^1p^1)$. MINDO/2 calculations including 3

$\times 3$ configuration interaction¹⁰ place the triplet state $^3(\sigma^1p^1)$ below the singlet state. The energy gap between these two configurations is 8.9 kcal/mol. It may well be affected by more sophisticated quantum-mechanical procedures.^{7,11}

1. The Intermediate Nonclassical Carbene. Because most of the reactions of carbenes are believed to occur mainly from their singlet ground states,¹² we will restrict the following considerations to the properties of the singlet state lowest in energy, $^1(\sigma^2)$.

To proceed on the reaction coordinate from **1** to **2** it is necessary to form a carbon-carbon bond between C_1 and C_3 and to break one bond, either between the carbon atoms C_2 and C_3 or between C_3 and C_4 . This can occur in either of two ways: (a) in a one-step process with simultaneous bond formation (between C_1 and C_3) and bond cleavage (between C_2C_3 or C_3C_4); (b) alternatively, in a two-step process, with a bond forming first between C_1 and C_3 as indicated in **5**. In this structure



partial bonding between the atoms C_1 and C_3 would be achieved. In a second step **5** then could undergo cleavage of one of the bonds, C_2C_3 or C_3C_4 , to the final product **2**.

The electronic properties of **5** will now be analyzed in more detail. Our study begins with an investigation of the process of forming a bond between C_1 and C_3 . The electrophilic attack of the empty p AO at the carbene site C_1 can be viewed as the interaction of the p AO with the highest energy bonding set of Walsh orbitals.¹³⁻¹⁵ This is illustrated in Figure 1. With respect to a symmetry plane (x,z plane) the orbitals of the cyclobutane moiety and the p AO are symmetric (S) or antisymmetric (A). According to perturbation theory¹⁶ the symmetric orbitals interact and introduce bonding^{17,18} between the atoms C_1 and C_3 .

The stabilization energy which emerges from the formation of **5** from **1** will now be estimated from the optimized SCF calculations. In order to substantiate the previously derived arguments, we have computed a contour diagram for the electronic energy as a function of the two reaction parameters, the distances C_1C_3 and C_2C_3 . All other geometrical parameters, such as bond lengths and bond angles, were varied until the minimum total energy was achieved. The computed contour map for the electronic energy is plotted in Figure 2.

According to the calculations there are three energy minima on the hypersurface presented in Figure 2, educt **1**, product **2**,

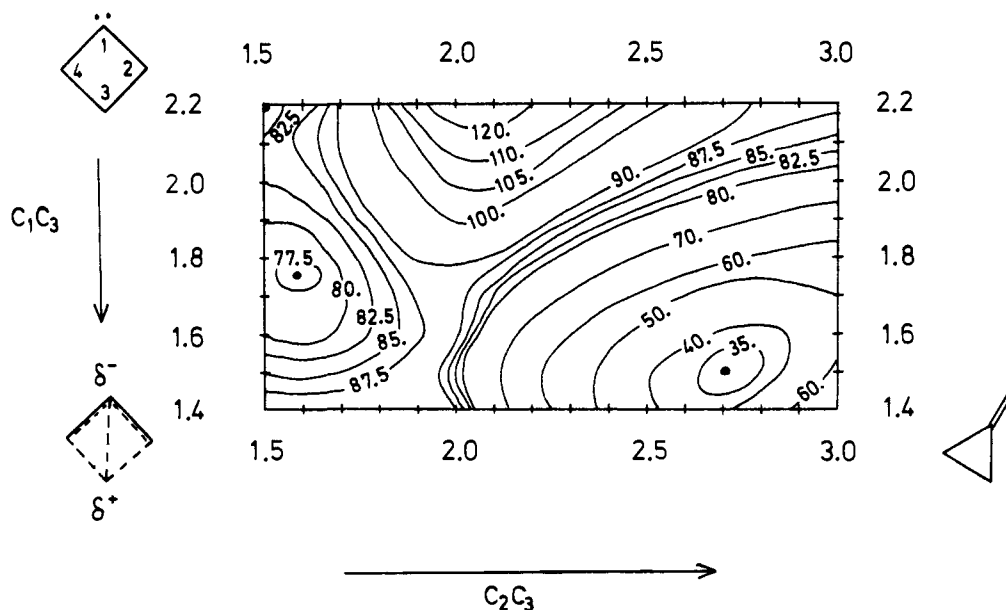


Figure 2. Energy contour diagram for the reaction of **1** to **2** as a function of the bond distances C_1C_3 and C_2C_3 . The energy contours are in kcal/mol.

Table I. Valence Charge Densities for the Energy Optimized Structures **5** and **1** and the Transition State TS Leading from **5** to **2**

position	5	1	TS
C ₁	-0.188	-0.007	-0.326
C ₂	0.125	0.009	0.294
C ₃	0.139	0.067	0.174
C ₄	0.125	0.009	0.122
H(C ₂) _{endo}	-0.058		-0.098
		0.001	
H(C ₂) _{exo}	-0.026		-0.038
H(C ₃) _{endo}	-0.001		-0.028
		-0.041	
H(C ₃) _{exo}	-0.032		-0.026
H(C ₄) _{endo}	-0.058		-0.058
		0.001	
H(C ₄) _{exo}	-0.026		-0.017

and the nonclassical species **5**. The bonding parameters for **5** are reported in Figure 3. The corresponding charge densities are collected in Table I. For comparison we also included in Figure 3 and Table I the parameters for **1** and for the transition state TS for the reaction leading from **5** to **2** (which will be discussed later).

An analysis of the charge densities of the nonclassical species **5** (Table I) reveals its dipolar nature. Electron density is shifted considerably from the methylene group at C₂ into the empty p AO at C₁. At the same time the carbon positions C₂ and C₄ become more positive.

2. Ring Opening from 5 to 2. Next to the formation of a nonclassical carbene we will now discuss the reaction from **5** to the final product **2**. This process involves the bond fission of C₂C₃ or alternatively C₃C₄. According to the rules of orbital symmetry¹⁹ the opening of one three-membered ring in **5** can be viewed as a concerted process including the participation of four electrons (two electrons from the HOMO plus two electrons from the breaking σ bond C₂C₃ or C₃C₄). On the basis of these considerations a conrotatory ring opening is predicted and obtained. The hydrogen atom at C₂, endo with respect to the bicyclobutane structure, turns away from the methylene group at C₃.

A representation of the activation enthalpy as a function of

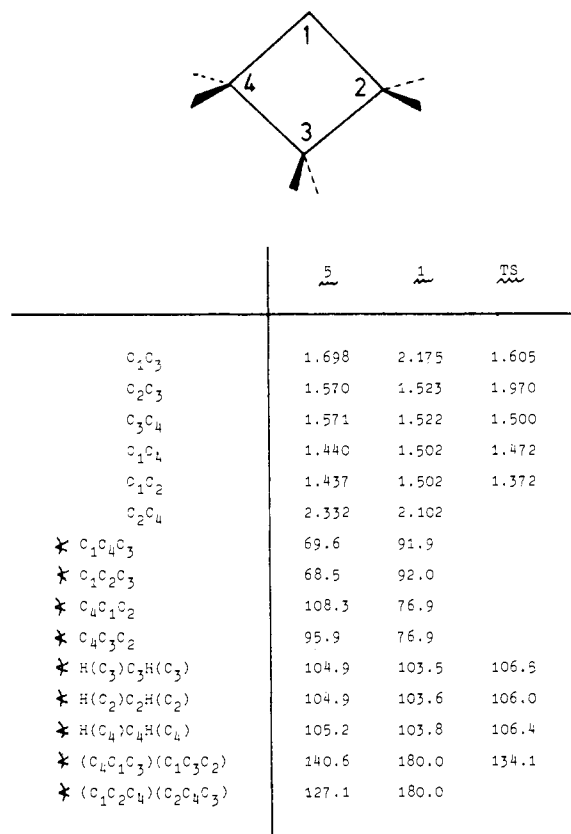


Figure 3. Optimized geometries for the structures **5**, **1**, and the transition state TS for the reaction leading from **5** to **2** (see Figure 4).

the bond distance C₂C₃ is provided in Figure 4. The structural parameters for the corresponding transition state (here denoted as TS) are collected in Figure 3 and its valence charges in Table I. According to Figure 3 the bond C₂C₃ is strongly loosened in TS. In contrast the bond C₃C₄ is shortened. In other words, the three-membered ring C₁C₃C₄ is already formed. An analysis of the valence charge densities (Table I) reveals additional insight into the bonding nature. Compared with **5** negative charge density is concentrated at C₁ and positive charge is attenuated at C₂.

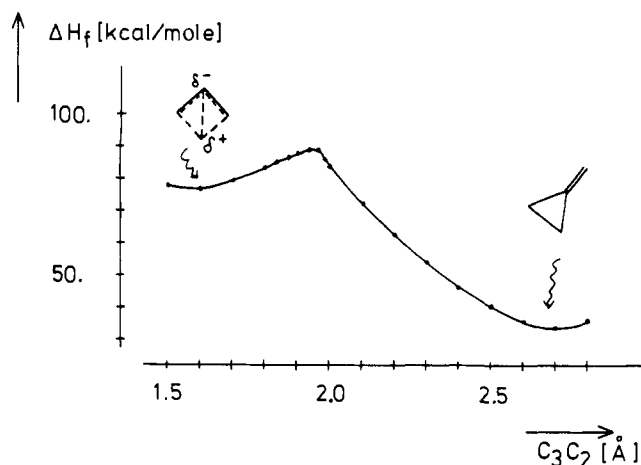
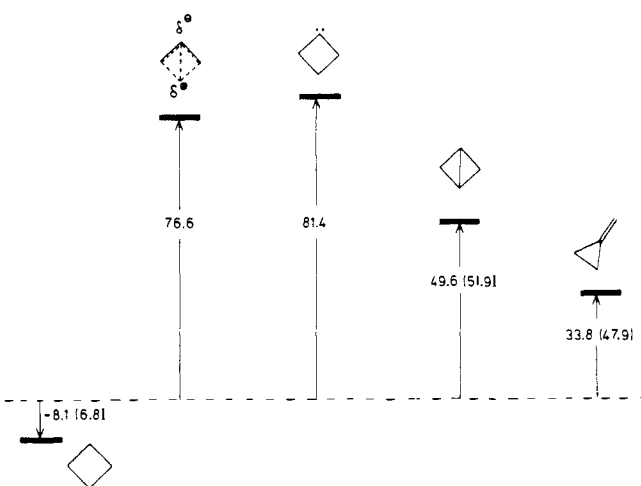


Figure 4. Heats of formation (kcal/mol) for the reaction of **5** to **2** as a function of the bond distance C_2C_3 (Å).

Scheme I



A stringent test of the validity of our quantum-mechanical investigations into the ring-contraction reaction is provided by a comparison of different points of the computed electronic hypersurface with experimentally known heats of formation for these species. The values in parentheses in Scheme I refer to heats of formation known from experiment (see Table I, ref 6b). The semiempirical MINDO/3 method overestimates the stability of cyclobutane by 14.9 kcal/mol.²⁰ On this basis **1** is overestimated in its stability by at least the same amount. In contrast, the deviation from experiment is much smaller for bicyclobutane. Here the neglect of strain amounts to 2.3 kcal/mol.²¹ Therefore one is tempted to conclude that **1** is too low in energy compared to TS (which resembles more a distorted bicyclobutane). Although this test reveals the lack of semiempirical methods regarding their numerical accuracy,⁷ it does not invalidate the mechanistic conclusions of our theoretical investigations.²²

Conclusion and Consequences

We have presented a quantum-mechanical investigation of the ring-contraction reaction of cyclobutylidene (**1**) to methylenecyclopropane (**2**) for its singlet state lowest in energy. The results of our investigations can be summarized as follows:

(1) The extremely facile reaction of **1** to **2** is initiated by formation of a nonclassical carbene.

(2) In the initially formed **5** electron density is shifted to C_1 , thus forming a dipolar species. This ylide is stabilized by withdrawing electron density from the peripheral ring bonds to the central bond C_1C_3 . Hence electron-donating substituents

at C_3 and to a smaller extent at C_2 and C_4 should promote the formation of **5**.

(3) The ring opening of **5** to **2** is controlled by orbital symmetry. It should occur in a conrotatory mode (relative to the residue). Since there is strong separation of charge in the transition state TS, electron-donating substituents at C_4 and/or C_2 should enhance the rate of the reaction.

The calculations suggest an activation enthalpy of 8 kcal/mol for the reaction. The easy formation of **2** can be attributed to the simultaneous formation (C_1C_3) and breakage (C_2C_3 or C_3C_4) of a carbon-carbon bond. It is very likely that our optimized SCF calculations suffer from a well-known deficiency of semiempirical methods: the overestimation of bonding in **1**. Thus the energy of **1** results as too low compared to the rest of the calculation. This should also apply to the transition state, but to a lesser extent. On this basis the computed activation enthalpy should represent an upper limit for the ring-contraction reaction.

The here presented investigations reveal a new nonclassical carbene structure. Our conclusions reached are also of importance for the interconversion of the cyclobutyl-cyclopropylcarbinyl cation, which will be discussed in a forthcoming publication.

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- (21) The calculated (1) and experimentally (2) determined heats of formation follow: (1) 49.6 ; (2) 51.9 kcal/mol.
- (22) Configuration interaction between the ground state and the doubly excited configuration has no effect on energy minima and maxima of the computed electronic hypersurface. This is in agreement with previous recognitions on carbene reactions.¹

Estimation of Excited-State Redox Potentials by Electron-Transfer Quenching. Application of Electron-Transfer Theory to Excited-State Redox Processes

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Abstract: Rate constants for electron-transfer quenching of $\text{Ru}(\text{bpy})_3^{2+*}$ (bpy is 2,2'-bipyridine) by a series of organic quenchers have been determined in acetonitrile ($\mu = 0.1$ M) at 22 ± 2 °C. The reactions studied were based on three different series of structurally related quenchers having varying redox potentials. They include oxidative quenching both by a series of nitroaromatics (ArNO_2) and by a series of bipyridinium ions (P^{2+}) and reductive quenching by a series of aromatic amines (R_2NAr). After corrections for diffusional effects, the quenching rate constant (k_q') data fall into two classes both of which can be treated successfully using Marcus-Hush theory. For case I, which includes the data for oxidative quenching by P^{2+} and reductive quenching by R_2NAr , $RT \ln k_q'$ varies as $\Delta G_{23}/2$ where $|\Delta G_{23}| \ll \lambda/2$. ΔG_{23} is the free energy change for electron-transfer quenching within an association complex between the quencher and excited state and λ is the vibrational contribution to the activation barrier to electron transfer. The experimental data are also consistent with Marcus-Hush theory over a more extended range in ΔG_{23} where the free energy dependence includes a quadratic term. For case II, which includes quenching by several of the nitroaromatics, $RT \ln k_q'$ varies as ΔG_{23} and evidence is obtained from the remainder of the data for a transition in behavior from case II to case I. The microscopic distinction between the two cases lies in competitive electron transfer to give either ground- or excited-state products following the electron-transfer quenching step. For case II, back-electron transfer (k_{32}) to give the excited state, e.g., $\text{Ru}(\text{bpy})_3^{3+}, \text{ArNO}_2^- \rightarrow \text{Ru}(\text{bpy})_3^{2+*}, \text{ArNO}_2$, is more rapid than electron transfer to give the ground state (k_{30}), e.g., $\text{Ru}(\text{bpy})_3^{3+}, \text{ArNO}_2^- \rightarrow \text{Ru}(\text{bpy})_3^{2+}, \text{ArNO}_2$. For case I, electron transfer to give the ground state is more rapid. The different behaviors are understandable using electron-transfer theory when account is taken of the fact that k_{30} is a radiationless decay rate constant, and the electron-transfer process involved occurs in the abnormal free-energy region where $-\Delta G_{23} > \lambda$. An appropriate kinetic treatment of the quenching rate data allows estimates to be made of redox potentials for couples involving the excited state. Formal reduction potentials in CH_3CN ($\mu = 0.1$ M) at 22 ± 2 °C are $E(\text{RuB}_3^{3+/2+*}) = -0.81 \pm 0.07$ V and $E(\text{RuB}_3^{2+*/+}) = +0.77 \pm 0.07$ V. Comparisons between ground- and excited-state potentials show that the oxidizing and reducing properties of the $\text{Ru}(\text{bpy})_3^{2+}$ system are enhanced in the excited state by the excited-state energy, that the excited state is unstable with respect to disproportionation into $\text{Ru}(\text{bpy})_3^{3+}$ and $\text{Ru}(\text{bpy})_3^{3+*}$, and that the excited state is thermodynamically capable of both oxidizing and reducing water at pH 7. A comparison between the estimated 0-0 energy of the excited state and the energy of emission suggests that there may be only slight differences in vibrational structure between the ground and excited states.

Introduction

Molecular excited states which are sufficiently long lived to be in thermal equilibrium with their surroundings are distinct entities having characteristic chemical and physical properties of their own.¹ An excited-state property which is potentially exploitable in net light to chemical energy conversion processes is the enhanced ability of excited states to function as both oxidants and reductants compared with the ground state.^{2,3} Mataga and Weller and their co-workers have shown that electron transfer can be a common reaction for organic excited states^{4,5} and more recent work has demonstrated the same reactivity for metal complex excited states, the most notable example being the emitting charge transfer (CT) excited state of $\text{Ru}(\text{bpy})_3^{2+}$ (bpy is 2,2'-bipyridine).^{2,6}

Perhaps the most fundamental properties associated with electron-transfer reactivity are redox potentials. In earlier communications⁷ we reported an experimental approach to the estimation of a reduction potential for the excited-state couple $\text{Ru}(\text{bpy})_3^{3+/2+*}$. The approach was based on rate studies for the quenching of $\text{Ru}(\text{bpy})_3^{2+*}$ by a series of nitroaromatics having varying strengths as oxidants. The analysis of the data was based on a kinetic scheme used by Rehm and Weller for electron-transfer quenching of fluorescence from a series of aromatic compounds.⁵ Since our initial report, additional quenching studies on $\text{Ru}(\text{bpy})_3^{2+*}$ and other excited states have given similar results.⁸⁻¹⁰

We have now completed studies of the oxidative quenching of $\text{Ru}(\text{bpy})_3^{2+*}$ by a series of dipyrindinium ions like paraquat