

the binding of the ester group or thought of these esters as inverted substrates, though many studies have been done with active esters since then.

### Concluding Remarks and Further Applicability of Inverse Substrates

The most striking characteristic of inverse substrates is the generation of acyl enzymes with little restriction on the structure of the acyl moiety. As a result, a wide variety of acyl groups can be introduced specifically into an enzyme active site. The new approach to thrombolytic therapy reported by Smith et al.<sup>25</sup> succeeded by exploring this characteristic feature of inverse substrates. A further type of application was exemplified recently by the report on photoactivatable acylated thrombin.<sup>39</sup>

Esters derived from *p*-(aminomethyl)phenol and *p*-guanidinophenol have also been effective as substrates for trypsin and trypsin-like enzymes,<sup>15b,40</sup> and (tri-

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methylamino)butanoic acid *p*-nitrophenyl ester is an inverse substrate for butyrylcholinesterase.<sup>41</sup> Application of the inverse concept to thiol enzymes has also been successful: *p*-amidinophenyl esters are substrates for clostripain,<sup>15a</sup> a thiol enzyme with trypsin-like specificity. Although not every hydrolytic enzyme may act on inverse substrates, this concept should be useful with many enzymes for both research and clinical applications.

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## Organic Radical Cations in Fluid Solution: Unusual Structures and Rearrangements

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Organic radical ions are important intermediates in a wide variety of chemical processes, and they also command attention because of a multitude of unusual structure types and a variety of interesting reactions.<sup>1-4</sup> Several techniques have been applied to probe various aspects of radical ion chemistry. Fast, time-resolved optical spectroscopy is a useful tool to derive information about the kinetics of formation and decay but usually provides little or no information concerning the identity or structure of the transient.<sup>5-7</sup> Electron spin resonance (ESR) allows insight into the structure of radical ions by probing their unpaired spin density distributions and has proved invaluable for a large variety of radical ions.<sup>8-10</sup> Its application is usually limited to species with lifetimes well above the millisecond range, although selected hydrocarbon cation radicals have been studied on the nanosecond time scale.<sup>10</sup> A large number of radical cations have been studied by matrix isolation optical or EPR spectroscopy.<sup>4</sup> However, the relatively high energy ( $\sim 1$  MeV) of the  $\gamma$ - or X-irradiation employed for the generation of the radical cations combined with the relatively slow dissipation of excess energy in rigid matrices constitutes a potential

drawback of this method of study. Since the barriers to radical cation rearrangements are considerably lower than those on the parent energy surfaces, a number of the most interesting radical cations, e.g., those of strained-ring hydrocarbons such as quadricyclane,<sup>11</sup> Dewar benzene,<sup>12</sup> or benzvalene, have eluded this technique because of rapid rearrangements under the conditions of their generation. Clearly, a milder method of generation and a faster method of observation would be useful.<sup>13-15</sup>

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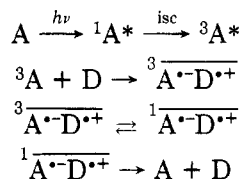
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Heinz D. Roth was born in the Lower Rhine region of Germany and studied chemistry at the Universities of Karlsruhe and Köln where he received a Dr. rer. nat. degree (with Emmanuel Vogel). After 2 years as a postdoctoral fellow in William Doering's laboratory at Yale University, he joined the Organic Chemistry Research and Development Department of AT&T Bell Laboratories. His research interests include mechanisms of light-induced and thermal reactions; structure and reactivity of short-lived reaction intermediates, particularly carbenes, free radicals, and radical ions; electron donor-acceptor interactions, and photoinduced electron transfer.

### Photoinduced Electron Transfer

A mild and versatile method for the generation of radical cation-radical anion pairs in solution is based on photoinduced electron transfer (PIET). This method utilizes the fact that the oxidative power of an acceptor and the reductive power of a donor are substantially enhanced by photoexcitation. Thus, even for donor-acceptor pairs with weak interactions in the ground state, electronic excitation of either reactant may lead to the generation of radical ion pairs via electron transfer. We have used this method to generate many radical cations derived from strained-ring hydrocarbon donors. The resulting radical ions have limited lifetimes, since the pairs readily undergo intersystem crossing and recombination. Furthermore, the exothermicity of the electron-transfer reaction can be adjusted by variation of the solvent (polarity) and of the acceptor (reduction potential, excited-state energy).

#### Scheme I

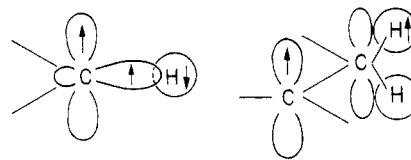


Two competing reactions pose potential drawbacks to the PIET method. First, the triplet states of typical electron acceptors (ketones, quinones) abstract hydrogen atoms with formation of neutral radicals. Second, radical cations are potential proton donors and radical anions are comparably strong bases. Accordingly, proton transfer in geminate radical ion pairs may produce neutral radicals, and the sequential involvement of two or more reactions may introduce mechanistic ambiguities.

### The CIDNP Method

Radical cations generated by photoinduced electron transfer can be studied conveniently by an indirect method complementary to ESR, which has been developed since 1967. Chemically induced dynamic nuclear polarization (CIDNP) is based on transient enhanced NMR signals, in absorption (A) or emission (E), shown by some products of radical reactions.<sup>16,17</sup> The potential of CIDNP effects as a mechanistic tool for radical pair reactions was soon recognized, and we were able to extend their application to radical ion pairs.<sup>18</sup>

The theory underlying this effect depends on two selection principles: the nuclear spin dependence of intersystem crossing in a radical pair and the electron spin dependence of the rates of radical pair reactions. Combined, these selection principles cause a "sorting" of nuclear spin states into different products and result in characteristic nonequilibrium populations in the nuclear spin levels of geminate reaction products (whose formation is spin forbidden for triplet pairs) and in complementary nonequilibrium populations in free-radical ("escape") products (whose formation is electron spin independent). The transitions between these levels



**Figure 1.** (a, left) Preferred configuration of electron spins in the  $\sigma$  orbital connecting a hydrogen atom to an  $sp^2$ -hybridized carbon atom bearing unpaired  $\pi$  spin density. (b, right) "Molecular  $\pi$  orbital" consisting of two carbon  $p_z$  orbitals and an  $H_2$  "group orbital" generated by hyperconjugative interaction of an  $sp^2$ -hybridized C atom bearing unpaired spin with a  $CH_2$ -R group.

will be in the direction toward the normal Boltzmann population; their intensities will depend on the extent of nonequilibrium population. The observed effects are optimal for radical pairs with lifetimes in the nanosecond range. On a shorter time scale, hyperfine induced intersystem crossing is negligible, whereas on a longer time scale, the spin polarization decays due to spin-lattice relaxation in the radicals.

The quantitative theory of CIDNP<sup>19-22</sup> allows the simulation of CIDNP intensity ratios from reaction and relaxation rates and characteristic parameters of the radical pair (initial spin multiplicity), the individual radicals (electron  $g$  factors, hyperfine coupling constants), and the products (spin-spin coupling constants). Conversely, the patterns of signal directions and intensities observed for different nuclei of a reaction product can be interpreted in terms of the hyperfine coupling constants of the same nuclei in the radical cation intermediate.

The  $^1H$  hfc's are related to carbon spin densities by different mechanisms of interaction. For  $\pi$  radicals, there are two principal mechanisms involving either an exchange interaction or hyperconjugation. Protons attached directly to carbon atoms bearing positive spin density have negative hfc's because of the preferred exchange interaction between the unpaired  $\pi$  spin density and the carbon  $\sigma$  electron (Figure 1a). Positive hfc's, on the other hand, are usually observed for protons which are one C-C bond removed from a carbon bearing positive spin density. The positive sign is due to a hyperconjugative interaction which delocalizes the  $\pi$  spin density on carbon into an  $H_2$  "group orbital" (cf. Figure 1b).

In summary, the patterns of CIDNP signal directions and intensities observed for diamagnetic products can be related to signs and magnitudes of  $^1H$  hfc's of paramagnetic intermediates. The hfc's, in turn, can be interpreted in terms of carbon spin densities, and these reveal important structural features of the intermediates. In the following sections we introduce unusual structures that had eluded other techniques, we discuss (unimolecular) rearrangements and (bimolecular) cycloadditions of radical cations, and we consider factors that determine radical cation structures or guide their rearrangements.

### Radical Cations of Cyclopropane and Bicyclobutane Derivatives

In order to deduce the structure of a radical cation, it is useful to consider the nature of the highest occu-

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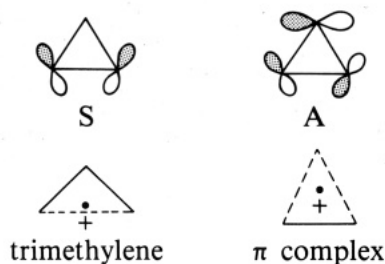
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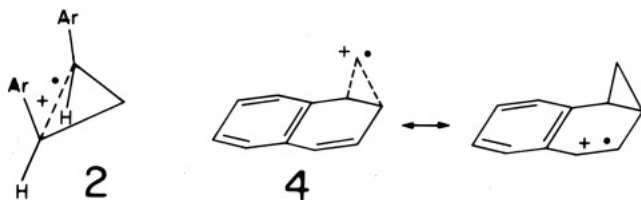
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piated molecular orbital (HOMO) of the parent molecule, from which an electron is removed when the cation is formed. For cyclopropane two structure types must be considered, which formally are derived from a pair of degenerate HOMO's. A radical cation with a symmetric (S) singly occupied (SO) MO would have a weakened



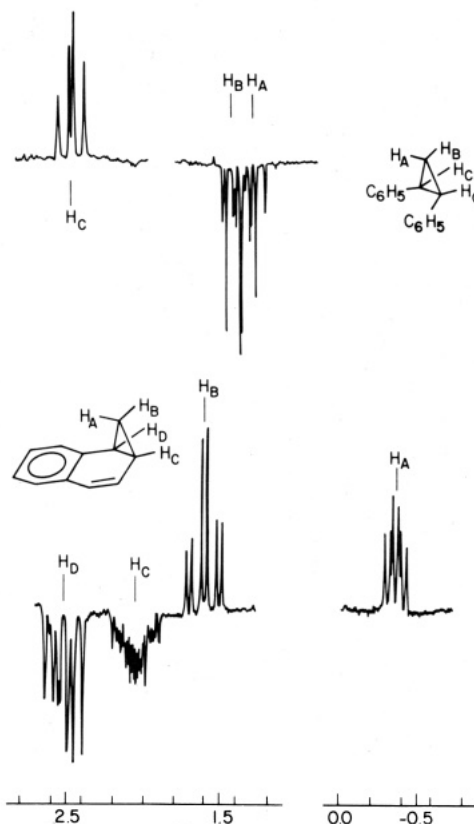
(and lengthened) bond between one pair of carbons; it could be described as a trimethylene species with a one-electron bond between the terminal methylene groups. On the other hand, a radical cation with an antisymmetric (A) orbital as SOMO could be described as a  $\pi$  complex between ethylene and a methylene cation. Two of its carbon-carbon bonds would be weakened (and lengthened), whereas the third would be strengthened (and shortened).<sup>23</sup>

Appropriate substitution of the cyclopropane system will lift the degeneracy and favor one of the radical cation structures. In many cases the predominant structure type can be rationalized on the basis of the frontier MO/perturbation MO theory of homoconjugation.<sup>24</sup> For example, the CIDNP results (Figure 2, top) observed during the reaction of triplet excited chloranil with *cis*- or *trans*-1,2-diphenylcyclopropane (1) suggest positive spin density in the phenyl groups and on the benzylic carbons. These features can be accommodated only by structure 2 (and the corre-



sponding *trans* isomer), in which the bond joining the benzylic carbons is weakened. However, no geometric isomerization is observed under these reaction conditions. Apparently, a degree of bonding sufficient to retain the initial molecular geometry remains between the benzylic carbon atoms on the time scale of the PIET experiment.<sup>25</sup> In contrast, cyclopropane radical cations may undergo geometric isomerization under conditions favoring more extended lifetimes.<sup>26</sup>

The reaction of chloranil with benzenorcaradiene (3) gives rise to a completely different polarization pattern (Figure 2, bottom): the geminal cyclopropane protons ( $H_A$ ,  $H_B$ ) show the same signal directions as the aromatic and olefinic protons (not shown), indicating positive spin density in all these positions. Based on these results, the benzenorcaradiene radical cation is



**Figure 2.**  $^1\text{H}$  CIDNP spectra observed during the photoreaction of chloranil with *cis*-1,2-diphenylcyclopropane (top) and with benzenorcaradiene (bottom). Only the resonances of the cyclopropane protons are shown. The opposite signal directions observed for analogous protons in the two compounds constitute evidence that the two radical cations belong to two different structure types.

best represented as a resonance hybrid of several structures, including one (4) derived from the second structure type considered for cyclopropane radical cations.<sup>27</sup>

The HOMO of the bicyclobutane system is bonding primarily in the transannular bond, whereas the next lower MO's are bonding in the perimeter bonds. We have generated the radical cations of a series of bicyclobutane systems, which are constrained by a bridging moiety, for example a trimethylene chain, as in tricyclo[4.1.0.0<sup>2,7</sup>]heptane (5). The radical cation of 5 can be generated by PIET in solution, and trapping experiments have provided evidence for structure 6, in which the transannular bond ( $C_1$ - $C_3$ ) is broken or weakened.<sup>28</sup> CIDNP results obtained during the reaction of several quinones with 5 provide evidence for the same structure, with positive spin density on the bridgehead carbons ( $C_1$ ,  $C_3$ ) and with negative hfc's for the bridgehead protons and positive hfc's for the adjacent protons.<sup>29</sup>

Introduction of a symmetrical unsaturated bridging unit changes the character of the HOMO and the nature of the intermediate radical cation. CIDNP results

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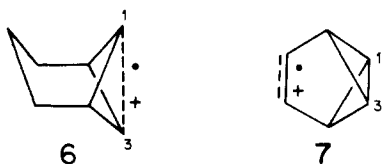
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indicate that benzvalene and naphthalene form radical cations (e.g., 7) in which the spin density is located



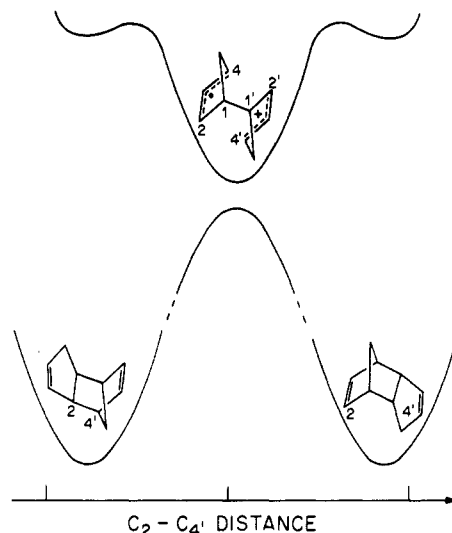
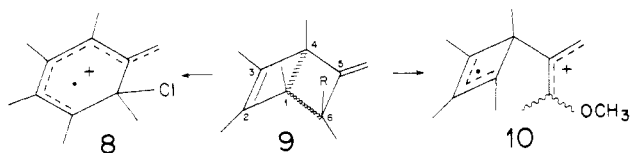
largely in the unsaturated moieties.<sup>15</sup> The olefinic (or aromatic) protons have negative hfc's, whereas the bridgehead protons ( $H_1$ ,  $H_3$ ) have positive hfc's due to a strong homohyperconjugative interaction. This assignment is in keeping with the conclusions of photoelectron spectroscopic (PES) studies, which have identified pure  $\pi$  orbitals as the HOMO's of these substrates.<sup>23</sup> The PES results also imply a strong interaction between the unsaturated moieties and the bicyclobutane system. Our results support an interaction but preclude that it leads to positive spin density on the bridgehead carbons,  $C_1$  and  $C_3$ , and to a weakening of the bond between them. The character of the bicyclobutane moieties in 6 and 7 is fundamentally different.

### Nonvertical Radical Cations

The radical cations discussed so far have SOMO's closely resembling the HOMO's of their parent molecules. Since the SOMO's are bonding or antibonding in a limited number of bonds, limited changes occur in the pattern of bond lengths and angles characteristic of the parent. For example, the radical cations of diphenylcyclopropane<sup>25</sup> (2) or several bicyclobutanes<sup>15,29</sup> (6) have one lengthened (one-electron) single bond. Moreover, all bonds of the parent molecules remain bonding to a significant degree and no major increases in bond order are observed.

Other systems may undergo significant changes upon one-electron oxidation. The resulting radical cations assume structures decidedly different from the parent molecules or any of their isomers with paired spins and charges. One C-C bond of the parent is broken (or a bonding interaction uncoupled) completely, the adjacent carbon atoms are rehybridized, and other bonds may have significantly increased bond orders. These structures may be similar to the transition states for the thermal isomerization of the parent molecules, or they may resemble biradicals or zwitterions. Because of the pronounced dissimilarity between radical cation and parent structures, which documents a remarkable reversal of relative stabilities (Figure 3), we call these radical cations nonvertical.

We emphasize the difference between merely rearranged and nonvertical radical cations, as illustrated by two species derived from 6-chloro- and 6-methoxy-5-methylene-1,2,3,4,6-pentamethylbicyclo[2.2.0]hexene (9). Oxidation of the chloro derivative (9, R = Cl)

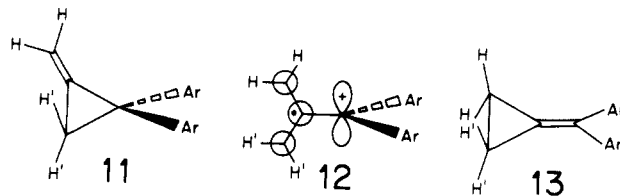


**Figure 3.** Schematic energy surfaces for dicyclopentadiene and its radical cation (14). The geometry of the radical cation corresponds to a saddle point or a shallow local minimum on the potential energy surface of its neutral diamagnetic precursor.

produces a ring-opened radical cation (8) that is directly related to a methylenecyclohexadiene derivative, a lower energy isomer of 9. In contrast, oxidation of the methoxy derivative (9, R = OCH<sub>3</sub>) gives rise to the unusual radical cation (10), in which the doubly allylic perimeter bond is broken; the spin density is localized largely in the cyclobutenyl moiety and the charge in the methoxyallyl group.<sup>30</sup> Structure 10 corresponds to a saddle point or a high-lying minimum on the energy surface of 9.

These examples illustrate two factors favoring the formation of nonvertical (as well as rearranged) radical cations: relief of ring strain and resonance stabilization. The ring strain inherent in a parent molecule may be relieved, partially or completely, by rupture of a strategic bond. The formation of nonvertical species is favored, when the spin and charge of a localized radical cation can be delocalized into two separate extended  $\pi$  systems, as in 10. This formation of a nonvertical (bifunctional) radical cation is analogous to the fragmentation of a radical cation into a cation and a free radical.

Another example of the separation of spin and charge is observed in geminal diarylmethylenecyclopropanes, 11. One-electron oxidation leads to rapid equilibration of two isomeric forms, 11a and 11b, whereas the third isomer, 13, is not formed.<sup>31</sup> These findings were in-



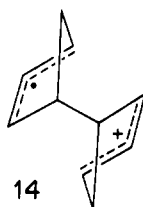
terpreted as evidence for a ring-opened trimethylenemethane radical cation (12). CIDNP results observed during the reaction of quinones with 2,2-diaryl-1-methylenecyclopropane suggest that spin and charge

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are localized in two different  $\pi$  systems, the spin in an allyl group and the charge in a diarylmethylene moiety.<sup>32</sup> To explain the lack of any polarization in the aromatic rings, and thus the absence of any substantial spin density, we postulate that the two conjugated systems are perpendicular to each other.

Dicyclopentadiene gives rise to a radical cation, 14,



in which the doubly allylic link between the two monomer units is broken,<sup>33</sup> two (bridgehead) carbons are rehybridized, and spin and charge are separated into two conjugated systems. This structure corresponds to a saddle point or a shallow, high-lying minimum on the parent potential energy surface. Interestingly, this radical cation is of the general structure type considered by Woodward and Katz for the thermal rearrangement of dicyclopentadiene derivatives<sup>34</sup> (cf. Figure 3).

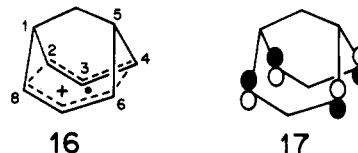
#### Radical Cations with Homoaromatic Structures

Of the factors favoring one radical cation structure over another, the release of strain is recognized as a general driving force for the reactions of ground states and intermediates alike. In contrast, the extension of conjugated systems is subject to restrictions. For example, bifunctional structures (zwitterions, biradicals) are generally less stable on the parent energy surface than alternative structures in which spins and charges are paired. Yet, several radical cation energy surfaces have bifunctional structures as minima. A similar divergence is found between the relative stabilities of homoaromatic structures in neutral diamagnetic systems and in radical cations.

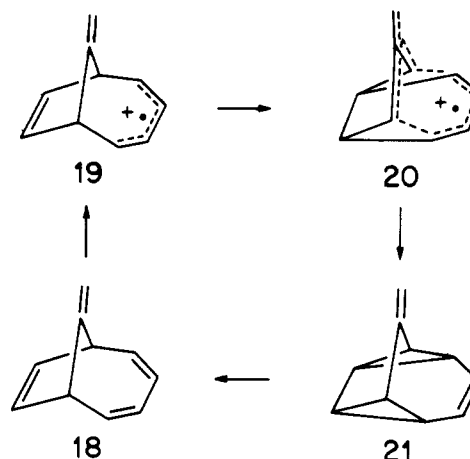
The concept of homoaromaticity was introduced by Winstein<sup>35</sup> to account for the relative stability of molecules in which the cyclic conjugation of  $\pi$  orbitals is interrupted by an aliphatic fragment, but the "gap" is bridged by a through-space interaction. Homoaromatic stabilization appears to be more significant for some cations than for most neutral diamagnetic systems. However, even the homotropenylium cation, the paradigm of homoaromaticity, enjoys only modest stabilization, which can be negated by substituent effects, as shown by the different structures of 1- and 2-methoxyhomotropenylium cations.<sup>36</sup> We have found several systems that give rise to radical cations with cyclic conjugated, bishomoaromatic structures. Since the parent molecules clearly have structures with less extended conjugation, our results suggest an astonishing reversal of relative stabilities.

For example, barbaralane, 15, and related systems have double-well potentials and undergo rapid degenerate Cope rearrangements,<sup>37</sup> which may be fast even

at  $-150\text{ }^{\circ}\text{C}$ .<sup>38</sup> In contrast, CIDNP results indicate that their radical cations, 16, assume structures with a single minimum,<sup>39</sup> at least on the time scale of the CIDNP experiment ( $\leq 10^{-8}$  s). The spin density resides primarily on the termini ( $\text{C}_{2,4,6,8}$ ) of the twin allyl moieties, whereas the internal carbons ( $\text{C}_3, \text{C}_7$ ) of the  $5\pi$  electron perimeter have negative spin density. This spin density distribution reflects the coefficients of orbital 17, the HOMO of a bishomoaromatic structure.<sup>40</sup>



Another bishomoaromatic radical cation is obtained upon one-electron oxidation of 9-methylenebicyclo[4.2.1]nonatriene (18). Because of the nature of its HOMO, it is reasonable to assume that this system initially forms a radical cation, 19, with spin and charge restricted to the butadiene moiety. This intermediate undergoes rapid intramolecular cycloaddition to generate a bishomoheptafulvene radical cation (20) formally derived from a highly strained tetracyclic structure, 21. The cyclization of 19 must be fast even at  $-50$



$^{\circ}\text{C}$ ; the barrier is estimated at  $\sim 5$  kcal/mol. The existence of 20 is all the more remarkable as the parent hydrocarbon can be detected by NMR only at  $-50\text{ }^{\circ}\text{C}$ ; at temperatures as low as  $-20\text{ }^{\circ}\text{C}$  it rearranges within seconds to 18 with a barrier of  $\leq 15$  kcal/mol.<sup>41</sup> We ascribe the increased stability of 20 to its cyclic conjugated nature and to the fact that the increase in strain energy relative to 19 is minimized, as the two pivotal cyclopropane bonds are only partially formed.<sup>41</sup> We emphasize that the bishomoaromatic character of 20 cannot be rationalized exclusively as that of a bishomotropenylium cation bearing a methylene group with an unpaired spin. This structure is precluded because of the high spin density indicated for  $\text{C}_3$  and  $\text{C}_4$ .

Homoaromatic structures clearly are more important for some radical cations than for their neutral dia-

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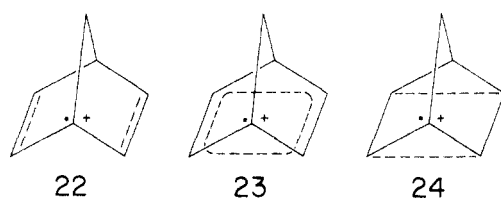
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magnetic precursors. This trend is evident in the equilibrium  $19 \rightleftharpoons 20$ , which is substantially shifted relative to the parent hydrocarbons.<sup>41</sup> For the barbalane system the homoaromatic structure is a transition state on the parent energy surface but is a minimum on the radical cation energy surface.<sup>39</sup>

### Rearrangements of Radical Cations

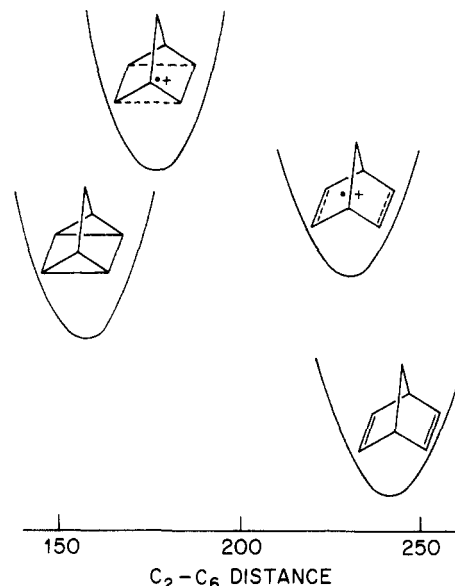
The study of electron donor-acceptor systems in solution has brought to light numerous electron-transfer-induced rearrangements belonging to a variety of reaction types: electrocyclic reactions, geometric isomerizations, sigmatropic shifts, and intramolecular cycloadditions. In this Account we are concerned mainly with thermal rearrangements of organic radical cations at ambient temperature within up to several microseconds. These reactions often lead to "one-way" isomerizations, typically the generation of a less strained radical ion; some have exceedingly low barriers so that only rearranged radical cations are observed. We have mentioned the failure of matrix isolation UV spectroscopy to provide evidence for several highly strained radical cations, which can be characterized by CIDNP results. Alas, some intermediates rearrange too rapidly even for detection by CIDNP. For example, the radical cations 10 and 12 derived from methylenecyclopropane and methylenebicyclo[2.2.0]hex-2-ene systems, respectively, are rearrangement products of more highly strained radical cations.<sup>30,32</sup> In general, the nonvertical and homoaromatic radical cations discussed in the preceding sections require significant changes in the carbon skeleton of the parent molecule. Their formation implies the rapid rearrangement of more localized and more highly strained radical cations.

A somewhat slower rearrangement is observed for the intramolecular cycloreversion that converts the radical cation of quadricyclane to that of norbornadiene. While other methods had failed to provide evidence for more than one radical cation on this energy surface, CIDNP results dispelled any notion of a single minimum, 23,



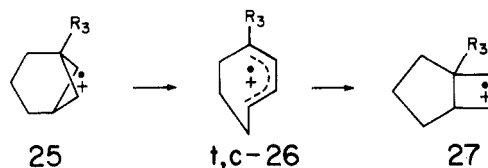
and furnished clear-cut evidence for two distinct transients, each corresponding to one of the precursors. These studies also showed that 22 has no tendency to rearrange to 24, whereas 24 rearranges to 22, though on a slower time scale than that of intersystem crossing and recombination.<sup>13</sup> These results are in keeping with the substantial energy difference and a nonnegligible barrier between the isomeric radical cations (cf. Figure 4).

A different type of cycloreversion is observed for bicyclobutane systems. For example, the radical cations of benzvalene and naphthvalene undergo ring opening to the corresponding benzenoid aromatics. These rearrangements must have appreciable energy barriers since they can be suppressed at  $-40^\circ\text{C}$ .<sup>15</sup> Other bicyclobutane derivatives undergo electron-transfer-induced rearrangements to cyclobutene derivatives.<sup>42</sup>

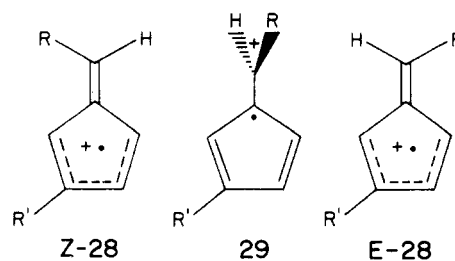


**Figure 4.** Schematic energy diagram for norbornadiene, quadricyclane, and their radical cations. Each minimum on the radical cation potential energy surface corresponds to a minimum on the energy surface of the neutral diamagnetic precursor, with characteristic changes in bond lengths and angles.

Since this reorganization is analogous to the thermal reaction of the parent hydrocarbon, it is tempting to postulate an analogous mechanism: conrotatory cycloreversion ( $25 \rightarrow 26$ ) followed by conrotatory ring closure ( $\rightarrow 27$ ). The role of orbital symmetry control in radical cation reactions has been considered.<sup>43,44</sup> We suggest the ring opening of appropriate bicyclobutane systems and the stereochemistry of the cyclobutene  $\rightleftharpoons$  butadiene interconversion as test cases to evaluate the importance of orbital symmetry control in radical cation reactions.<sup>45</sup>



Geometric isomers of olefins are separated by substantial energy barriers. In the corresponding radical cations these barriers are much reduced, and cases of rapid isomerization are well documented;<sup>3,4</sup> they proceed in both directions, even though the equilibrium concentration of the cis isomer may be quite low.<sup>3</sup> The geometric isomers of disubstituted fulvenes are of particular interest because of the potential involvement of structure 29, in which a stabilized cation is held or-



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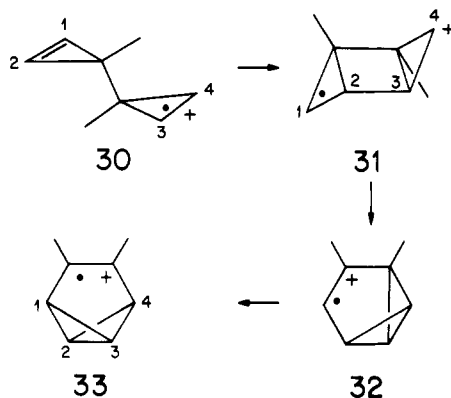
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thogonal to a cyclopentadienyl radical.<sup>46</sup> The isomeric (dimethylamino)-*tert*-butylfulvenes [R = N(CH<sub>3</sub>)<sub>2</sub>; R' = *t*-C<sub>4</sub>H<sub>9</sub>] are interconverted readily upon one-electron oxidation, suggesting that the radical cations **28** have a low barrier to rotation, possibly due to the separation of spin and charge. However, the orthogonal structure (**29**) can be ruled out as the main intermediate;<sup>46</sup> this structure is either a saddle point or, at best, a shallow minimum.

A somewhat surprising rearrangement without parallel on the parent energy surface converts the radical cation of dimethylbicyclopentenyl (**30**) to that of dimethylbenzvalene (**33**). The key step in this conversion is a [1 + 2] intramolecular cycloaddition to generate the highly strained intermediate **31**, in which spin and charge are separated but not delocalized. An alkyl shift concurrent with cleavage of an internal cyclopropane bond then forms a benzvalene radical cation (**32**) which is converted by a 1,3 sigmatropic shift to its isomer **33**. Of nine conceivable dimethylbenzvalene isomers, only that derived from the presumably most stable radical cation (**33**) is observed.<sup>47</sup>



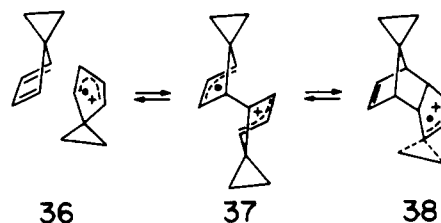
An intramolecular cycloaddition of the [3 + 2] type is involved in the formation of the bishomoheptafulvene species (**20**) discussed above.<sup>41</sup> It is interesting to note that both the [1 + 2] and the [3 + 2] additions are orbital symmetry forbidden, yet they occur with apparent ease. The detailed mechanism of these reactions is of obvious interest, but the intramolecular cycloadditions fail to provide mechanistic clues. This leads us to discuss intermolecular cycloadditions and the potential role of orbital symmetry in this reaction type.

### Cycloadditions and Cycloreversions

The electron-transfer-induced dimerization of olefins to form [2 + 2] cycloadducts and the fragmentation of the latter (cycloreversion) are well-documented. The application of the CIDNP technique in this area has led to the discovery of new reaction types and the elucidation of mechanistic details. For example, one-electron oxidation of the dimethylindene dimer gave rise to effects indicating the involvement of a singly linked intermediate and suggesting a two-step cycloreversion,<sup>48</sup>

whereas other cleavage reactions proceed without evidence for a stepwise mechanism.<sup>18,49</sup>

More recently, much attention has been focused on the so-called radical cation Diels–Alder reaction,<sup>50–52</sup> which results in [4 + 2] cycloadducts. Is the addition stepwise or concerted? Does the radical cation serve as the “diene” component ([3 + 2] cycloaddition) or as dienophile ([4 + 1] cycloaddition)? We have identified a system in which a stepwise cycloaddition component is clearly established. Spiro[2.4]heptadiene (**34**), upon one-electron oxidation, undergoes rapid cyclo-dimerization, and the [4 + 2] dimer **35**, under similar conditions, suffers rapid cycloreversions. CIDNP effects observed during CW irradiation provide evidence for a monomer radical cation, **36**, and a doubly linked dimer radical cation, **38**, in which spin and charge are localized in the fragment originating as the dienophile.<sup>53,54</sup>



Significantly, pulsed laser excitation of an acceptor in solutions containing high concentrations of **34** produced evidence for an additional radical cation, the singly linked species, **37**. These reaction conditions minimize accumulation of **36** and **38** due to their rapid bimolecular reactions with **34**. As a result, the overall polarization is dominated by effects induced in **37**, whose lifetime is unaffected by the high monomer concentration, as its reduction by **34** is endergonic. Aside from establishing an interesting mechanistic detail for one radical cation cycloaddition, the implication of **37** as an intermediate suggests greater mechanistic variety for such cycloadditions than was previously considered.<sup>53,54</sup>

### Perspective

The application of CIDNP in photoinduced electron-transfer reactions has brought to light a variety of unusual structures and interesting mechanistic details. These results are observed because of the exclusive features of the PIET–CIDNP approach: formation of short-lived radical ion pairs in a medium permitting rapid dissipation of excess energy and interpretation of the unique information content inherent in the CIDNP spectra of appropriately chosen substrates. These interesting structures await further investigation and evaluation under different reaction conditions, in different media, and by different techniques. Interesting challenges remain in the determination of actual

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barrier heights for radical cation interconversions and in the detailed characterization of the photochemical interconversions.

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## Monte Carlo Studies of the Long-Time Dynamics of Dense Polymer Systems. The Failure of the Reptation Model

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### Introduction

Imagine a very large bowl of overcooked spaghetti that is subject to constant random jiggling. Suppose one picks a given spaghetti strand. How on average does this strand move across the bowl? The strand sees a matrix comprised of the other spaghetti strands which it cannot cross. Thus, one has in principle a very complicated many-body (many-strand) problem. This is a simple realization of the problem that has over the past 15 years occupied a central position in the study of concentrated polymer solutions (analogous to a bowl of spaghetti with tomato sauce) and melts (analogous to a bowl of spaghetti drained of all other liquids).<sup>1-4</sup> Namely, what is the microscopic mechanism by which a highly entangled collection of polymers moves? The answer to this question has practical applications to, among other areas, polymer rheology, polymer adhesion, and polymer failure.

Any successful theory of polymer melt motion must be able to rationalize the following experimental results.<sup>1-6</sup> For a linear polymer composed of  $n$  bonds, the center-of-mass self-diffusion coefficient of the polymer,  $D$ , behaves like

$$D \sim n^{-1} \quad \text{if } n < n_c \quad (1a)$$

$$D \sim n^{-2} \quad \text{if } n > n_c \quad (1b)$$

with  $n_c$  a critical degree of polymerization, although recently other exponents  $\alpha$  in  $D \sim n^{-\alpha}$  have also been

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Table I.  
Compilation of Parameters

parameter	definition
$n$	degree of polymerization, i.e., the number of beads (monomer units) per polymer chain
$n_c$	degree of polymerization above which $D$ is proportional to $n^{-2}$
$n'_c$	degree of polymerization above which the shear viscosity is proportional to $n^{3.4}$
$N$	number of polymers in the Monte Carlo box
$n_M$	degree of polymerization of the larger volume fraction (matrix) component in a bidisperse melt
$n_P$	degree of polymerization of the smaller volume fraction (probe) component in a bidisperse melt
$n_B$	average number of monomers down a given chain in the melt where the excluded-volume effect is screened out
$n_e$	the average distance between dynamic entanglements
$n_b$	number of beads in the subchain or blob used in the averaging process to construct the equivalent path
$\tau_R$	terminal or longest relaxation time of the end-to-end vector

reported.<sup>7</sup> Furthermore, the zero-frequency shear viscosity  $\eta$  scales like

$$\eta \sim n \quad \text{if } n < n'_c \quad (2a)$$

$$\eta \sim n^{3.4} \quad \text{if } n > n'_c \quad (2b)$$

with  $n_c > n'_c$ .<sup>5,6</sup> The source of the difference between  $n_c$  and  $n'_c$  is not at all understood.<sup>8</sup> (For the convenience of the reader a compilation of various parameters employed in this article may be found in Table I.) The above experimental behavior indicates that as the molecular weights of the chains increase, entanglements between the chains become important. Thus, another important feature of a successful theory is to elucidate the nature of these intermolecular entanglements.

One of the most striking consequences of the experimental observations embodied in eq 1 and 2 is that for

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