

Carbonyl exchange in solid $\text{Fe}_3(\text{CO})_{12}$ is a result of rotation of the Fe_3 triangle while the carbonyl ligands remain fixed in the crystal lattice.^{5,21} Several cyclooctatetraene derivatives of metal carbonyls, e.g., $(\text{COT})_2\text{Ru}_3(\text{CO})_4$, have been investigated by solid-state NMR.^{22,23} Exchange in these molecules involves motion of the cyclooctatetraene ring. In other systems where chemical exchange occurs in the solid state, the motion is restricted to a small group, e.g., proton jumping in tropolone⁷ and naphthazarin-B.²⁴

In the nondegenerate Cope rearrangement recently described for solid semibullvalene, the bond-breaking and -forming steps require very little movement of atomic positions.²⁵ The bond-breaking and -forming steps in $\text{Co}_2(\text{CO})_8$ require carbonyl groups to move $\sim 3 \text{ \AA}$ at a jump.

Further mechanistic studies on carbonyl exchange in $\text{Co}_2(\text{CO})_8$ and its derivatives are under way.

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Registry No. Dicobalt octacarbonyl, 10210-68-1.

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Photoinduced Electron-Transfer Reactions. Evidence for Two Different Radical Cations of Hexamethyl(Dewar benzene)

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The photosensitized conversion of hexamethylbicyclo[2.2.0]hexa-2,5-diene [hexamethyl(Dewar benzene) (**1**)] to hexamethylbenzene (**2**) is well established. In nonpolar solvents, **1** quenches the fluorescence of aromatic hydrocarbons and undergoes isomerization to **2**. This conversion is accompanied by a dual exciplex fluorescence.¹ In polar solvents, **1** is converted to **2** with quantum efficiencies far greater than unity.² These results were explained by invoking a radical ion chain reaction initiated by electron transfer from **1** to the photosensitizer. This mechanism requires a highly efficient ring opening of the intermediate cation and raises serious questions as to whether a radical cation of **1** can be an energy minimum. Indeed, a recent nanosecond spectroscopic study failed to reveal any evidence for a radical cation other than the hexamethylbenzene cation.³

Previous experience in many systems⁴⁻⁸ suggested that the

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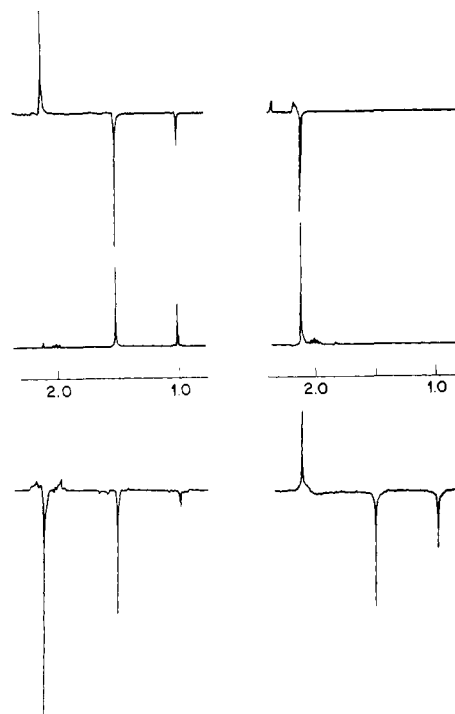
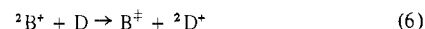
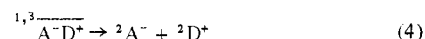


Figure 1. Top: ^1H NMR spectra (90 MHz) observed during UV irradiation of 0.02 M solutions of chloranil in acetone- d_6 containing 0.02 M hexamethyl(Dewar benzene) (left) or hexamethylbenzene (right). Center: ^1H NMR spectra of the same solutions in the dark. Bottom: ^1H NMR spectra observed during UV irradiation of a 0.02 M solution of hexamethyl(Dewar benzene) in acetone- d_6 containing 0.005 M anthraquinone (left) and of a 0.005 M solution of hexamethyl(Dewar benzene) in acetone- d_6 containing 0.02 M acetophenone (right).

Scheme I^a



^a * denotes an excited state; A, D, and B represent the acceptor, hexamethyl(Dewar benzene), and hexamethylbenzene; dagger and double dagger represent nuclear spin polarization of opposite sign.

CIDNP technique is well suited to probe the existence of such a cation and to elucidate its structure. Accordingly, we have studied the photoreactions of strong electron acceptors (e.g., chloranil) with **1** and have examined the nuclear spin polarization effects induced in these reactions: the two methyl signals of **1** appeared in emission whereas the single methyl signal of **2** showed enhanced absorption (Figure 1, top left).

These results can be explained by a mechanism involving electron transfer from **1** to photoexcited (triplet) chloranil (eq 1, Scheme I). The resulting radical ion pair may undergo hyperfine-induced intersystem crossing (eq 2) and recombination (eq 3) or may suffer separation by diffusion (eq 4) and ring opening (eq 5). In essence, the competition between the electron spin dependent reaction (eq 3) and the electron spin independent process (eq 4) causes the generation of nuclear spin polarization

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Table I. Structures, Energies, and Spin Densities of Dewar Benzene and its Radical Cations

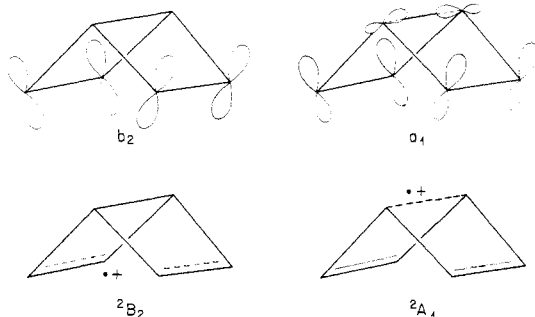
molecule	geometrical parameter, ^a Å		total energy, ^b hartree		relative energy, ^b kcal/mol		carbon spin density ^{b,c}	
	C ₂ -C ₃	C ₁ -C ₄			HF/	MP2/	C ₁ ^d	C ₂ ^e
			HF/6-31G*	MP2/6-31G*	6-31G*	6-31G*		
Dewar benzene	1.331	1.579	-230.56454	-231.32737				
radical cation ² B ₂	1.376	1.583	-230.28411	-231.01716	0	0	-0.051	+0.298
radical cation ² A ₁	1.324	2.085	-230.27805	-231.00446	3.8	8.0	-0.490	+0.001

^a Not all parameters are listed. The geometries were, however, completely optimized with the 6-31G basis. ^b Calculated at the HF/6-31G optimized geometries. ^c Calculated with the 6-31G* basis. ^d Two bridgehead carbons have identical spin densities. ^e Four olefinic carbons have identical spin densities.

in this system. Clearly, electron transfer is preferred over exciplex formation since this reaction is strongly exothermic⁹ and since highly polar media generally favor radical ion formation.

The proposed mechanism implies that a radical cation of **1** exists and that its lifetime is sufficiently long to allow the generation of nuclear spin polarization and longer than the lifetime of the geminate radical ion pairs. These considerations suggest a lifetime of several nanoseconds. The polarization pattern observed for **1** suggests that the intermediate cation has positive spin density on both the olefinic and the bridgehead carbons, a feature that cannot be accommodated readily by a single radical cation.

Ab initio MO calculations were performed on the parent Dewar benzene system in order to have a detailed understanding of the structure and the electronic state of the radical cations involved. These calculations include the effects of polarization functions and electron correlation; the computational details are similar to those employed in the system norbornadiene-quadracyclane.^{11,12} Preliminary inspection of the orbitals of Dewar benzene reveals that the highest occupied orbital has b₂ symmetry and has bonding



character principally between the pairs of olefinic carbons. This assignment is compatible with an analysis of the photoelectron spectra.^{17,18} If an electron were removed from this orbital, the principal feature of the resulting cation (²B₂) would be the elongation of the olefinic bonds. Another low-lying orbital has

a₁ symmetry with significant bonding character across the central bond. Removal of an electron from this orbital would give rise to a cation (²A₁) in which the transannular bond is considerably weakened. These considerations are borne out by detailed calculations (cf. Table I).

The structural changes in the two electronic states of the radical cation are best illustrated by comparison with Dewar benzene, which has olefinic and transannular bond lengths of 1.331 and 1.579 Å, respectively. In the radical cation ²B₂ the olefinic bond length increases to 1.376 Å whereas the transannular bond is changed only slightly, to 1.583 Å. In contrast, the radical cation ²A₁ has slightly shortened olefinic bonds (1.324 Å) whereas the transannular bond is lengthened to 2.085 Å and weakened significantly.

The calculations indicate that ²B₂ is the lower of the two electronic states. When electron correlation effects are included, this state is calculated to be 8 kcal/mol more stable than the ²A₁ state and to lie about 70 kcal/mol higher than the benzene cation.¹⁹ This separation is similar to that calculated between Dewar benzene and benzene (76 kcal/mol). Orbital and state symmetry considerations reveal that both electronic states may have significant barriers for rearrangement to the benzene cation.²⁰

In addition to the structural parameters, we have also calculated the carbon spin-density distribution for the two Dewar benzene cations. The ²B₂ state has most of the spin density in the olefinic positions and low negative spin density on the bridgehead carbons, whereas the ²A₁ state has essentially all its spin density in the two bridgehead positions. The extrapolation from the spin densities calculated for the unsubstituted cations to the CIDNP patterns expected for the hexamethyl derivative is based on two assumptions: that the introduction of methyl substituents on every carbon atom does not significantly distort the spin-density distribution; and that the hyperfine coupling of these methyl groups is proportional to the spin density on the adjacent carbon.

These considerations lead us to expect polarization exclusively for the olefinic methyl groups or exclusively for the bridgehead methyl groups if either cation were involved exclusively. The experimental findings, can be explained by the simultaneous involvement of both species, either in a rapid equilibrium or as two discrete intermediates separated by a significant energy barrier. Theoretical considerations argue against a rapid equilibrium since the two species are structurally very different and have different state symmetries.

Indeed, we have obtained experimental results in support of the intermediacy of two discrete species. The relative rates of generating the two cations and their rates of decay should not be independent of the nature of the acceptor; rather, substantial differences can be expected for different acceptors. These considerations are borne out by the photoreactions of anthraquinone and acetophenone with **1**, which result in substantially different

(9) The free energy of the reaction can be calculated according to¹⁰ $\Delta G = E_{D/D^+} - E_{A-A} - E_T - e^2/\epsilon a$, where E_T (=62 kcal/mol) is the triplet excitation energy of chloranil, E_{D/D^+} (=1.5 V vs. SCE)² is the oxidation potential of **1**, E_{A-A} (=−0.02 V vs. SCE) is the reduction potential of chloranil, and $e^2/\epsilon a$ is a Coulomb term, which accounts for ion pairing; hence $\Delta G = -30$ kcal/mol.

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(20) The ²A₁ state of the Dewar benzene cation does not correlate with either of the Jahn-Teller split states, ²B_{2g} and ²B_{3g}, of the benzene cation. A significant interconversion barrier is expected in such a case. The ²B₂ state of the Dewar benzene cation, on the other hand, correlates with the elongated ²B_{2g} state of the benzene cation but has different orbital occupation. The required orbital crossing would involve an appreciable barrier. We have not, however, attempted to calculate the magnitude of the barrier in either case.

ratios of "olefinic" to bridgehead polarization (Figure 1, bottom). The observed differences are far outside of the experimental limits of reproducibility. These results are incompatible with two rapidly equilibrating cations but can be accommodated readily by two discrete species generated by competing pathways.

The polarization of **2** in these experiments also deserves comment. With acetophenone or chloranil as sensitizer, **2** shows enhanced absorption indicating that it is generated after diffusive separation of the ion pairs. In contrast, the reaction with anthraquinone produces **2** in emission suggesting that it is generated from geminate ion pairs. This change in reaction parameter requires either that the ring opening is accelerated or that the pair lifetime is increased in the anthraquinone reaction.

To our knowledge, hexamethyl(Dewar benzene) is the first system in which two discrete minima on the radical cation surface correspond to a single minimum on the ground-state surface. Further examples of this interesting situation are under study.

Registry No. **1**, 7641-77-2; **1** radical cation, 85293-78-3; chloranil, 118-75-2.

Structure and Dynamic Behavior of a Chiral Alkyl lithium Compound: ^{13}C and ^6Li NMR of *sec*-Butyllithium

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Primary organolithium compounds in hydrocarbon solvents form a variety of aggregates,⁴⁻⁶ $n = 6-9$, whose distribution varies with the temperature and which undergo at equilibrium fast inversion^{7,8} at carbon bonded to lithium, faster interaggregate carbon-lithium bond exchange, and ever faster intraaggregate carbon-lithium bond exchange that is still fast relative to the NMR time scale at -100°C .^{6,8}

We have utilized the existence of scalar coupling between ^{13}C and directly bonded ^6Li ^{9,10} to investigate the nature of the bridge-bonded structure of $(\text{RLi})_n$ aggregates and from its averaging, using NMR line-shape analysis, the dynamics of C, Li bond exchange.⁶ Lithium-6 is used because ^7Li quadrupole-induced relaxation is often fast enough at low temperature to average ^{13}C , ^7Li coupling as well as give broad ^7Li NMR lines.⁶

We have now applied these techniques to study a secondary lithium compound with a chiral center, *sec*-butyllithium.¹⁰ Our results described below provide an unprecedented wealth of structural detail as well as significant insight into dynamic behavior.

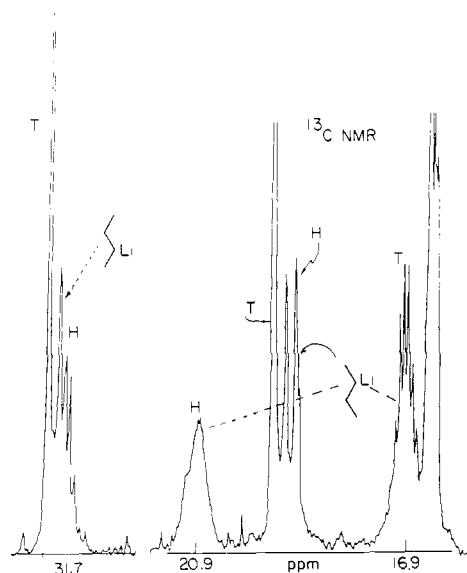


Figure 1. ^{13}C NMR of *sec*-butyllithium 2.0 M in cyclopentane at 232 K, 67.87 MHz.

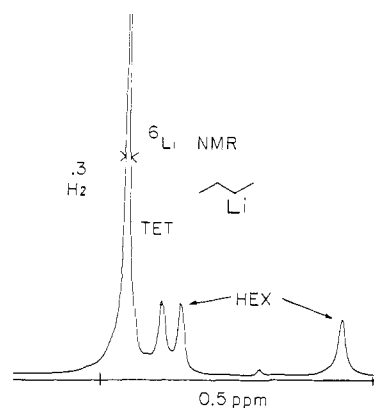


Figure 2. ^6Li NMR of *sec*-butyllithium 2.0 M in cyclopentane at 232 K, 38.73 MHz.

Table I. ^{13}C NMR of *sec*-Butyllithium 2 M in Cyclopentane at 220 K (ppm/ Me_4Si)

	C_1	C_2	C_3	C_4
tet	19.27	16.89	31.69	15.98
hex	19.09	20.91	31.45	15.81
	28.85		31.31	
	18.75		31.22	
			31.11	

The ^{13}C NMR spectrum of a 2 M solution of *sec*-butyllithium^{11,12} in cyclopentane at 232 K shows resonance for C_2 at 20.91 and 16.89 ppm, respectively (Figure 1). The latter is a septet, with relative intensities close to 1:3:6:7:6:3:1, and with splittings of 6.1 Hz, consistent with three lithiums coupled to each $^{13}\text{C}_2$, indicating the existence of nonfluxional or slowly fluxional tetramers; the 20.91 ppm absorption shows poorly resolved splitting of 3.25 Hz, reminiscent of propyllithium hexamer⁶ in cyclopentane, with an overall line width consistent for fluxional hexamer.

With decreasing temperature the hexamer concentrates at the expense of tetramer, and from their respective C_2 peak areas, we derive ΔH and ΔS for the equilibrium

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