

a virtually planar Rh<sub>5</sub> pentagon (Rh(1) to Rh(5)),<sup>9</sup> which is capped on one face by a sixth Rh atom Rh(6) and on the other by a *t*-BuAs unit. The five Rh-Rh distances that describe the pentagon are all within the range for Rh-Rh single bonds (see Figure 2) (Rh-Rh min = 2.727 (1), max = 2.930 (1) Å). Rh<sub>6</sub> is also bonded to each of these with an average Rh-Rh distance of 2.799 Å. The *t*-BuAs group on the other face of the pentagon lies somewhat closer to the Rh<sub>5</sub> plane than Rh(6).<sup>9</sup> Minor deviations in planarity for this central Rh<sub>5</sub> unit are sufficient to permit As(3) of this arsinidene unit to be within bonding distance of only three Rh atoms of the ring (Rh(1), Rh(3), and Rh(4)), which are all bent slightly toward it, in addition to Rh(6). The nonbonded Rh atoms, Rh(2) and Rh(5), are bent slightly away from the *t*-BuAs side of the ring. Thus the average As(3)-Rh bonding distance is 2.479 Å while the nonbonded distances average 2.875 Å, and these values compare well with other Rh-As bonding and nonbonding distances in other systems.<sup>10</sup> To our knowledge this geometry is unique, an As-Rh bond passing through a Rh<sub>5</sub> ring which is part of a unique Rh<sub>6</sub> pentagonal pyramid. The cluster with 86 valence shell electrons appears to be in violation of "Wade's rules".

Two di-*tert*-butylarsenido groups bridge two of the Rh-Rh bonds in the Rh<sub>5</sub> pentagon and although they both bridge nearly symmetrically they are bent slightly away from the  $\mu$ -*t*-BuAs face of the ring. There are 11 CO ligands in the structure. Nine are terminally bound with two each to Rh(1), Rh(3), and Rh(4) and one each to Rh(2), Rh(5), and Rh(6). In addition there are two bridging CO's which span the Rh(2)-Rh(6) and Rh(5)-Rh(6) bonds.

The IR spectrum of **1** in the solid state (KBr disc) shows five bands in the CO region while in solution ten are observed. The <sup>1</sup>H NMR in toluene-*d*<sub>8</sub> shows a multiplet consisting of five peaks.<sup>6</sup> Thus, although the solid-state structure has a pseudomirror plane containing As(3), Rh(6), and Rh(1) and passing through the midpoint between Rh(4) and Rh(3), in solution the molecule must exist in a less symmetrical form resulting in the nonequivalence of all five of the *t*-BuAs groups and increasing the number of CO stretches observed in the IR.

The isolation and characterization of **1** suggests that other unusual structures involving metal clusters and R<sub>2</sub>As<sup>-</sup> or RAs<sup>2-</sup> units may shortly be discovered. Further studies are in progress.

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**Supplementary Material Available:** Complete listings of bond lengths, angles, atomic coordinates, thermal parameters, and structure factors (57 pages). Ordering information is given on any current masthead page.

(9) Deviations (Å) from the least-squares plane through the Rh<sub>5</sub> pentagon and As(1) and As(2) are as follows: Rh(1), 0.245 (1); Rh(2), -0.132 (1); Rh(3), 0.263 (1); Rh(4), 0.165 (1); Rh(5), -0.115 (1); As(1), -0.226 (1); As(2), -0.200 (1). Deviations (Å) from this plane for Rh(6) and As(3) are as follows: Rh(6), -1.373 (1); As(3), 1.204 (1). Key bond lengths are given in Figure 3. For convenience key angles (deg) are as follows: Rh(1)-Rh(2)-Rh(3) = 98.89 (2), Rh(2)-Rh(3)-Rh(4) = 109.60 (2), Rh(3)-Rh(4)-Rh(5) = 107.76 (2), Rh(4)-Rh(5)-Rh(1) = 101.12 (2), Rh(5)-Rh(1)-Rh(2) = 118.28 (2), Rh(6)-As(3)-C(300) = 165.9 (2), Rh(3)-As(1)-Rh(2) = 75.46 (2), Rh(4)-As(2)-Rh(5) = 74.19 (2), Rh(1)-As(3)-Rh(3) = 119.18 (3), Rh(1)-As(3)-Rh(4) = 121.28 (3), Rh(1)-Rh(6)-Rh(2) = 58.97 (2), Rh(1)-Rh(6)-Rh(5) = 59.51 (2).

(10) Typical Rh-As bonding distances fall in the range 2.4-2.5 Å; see, for example: Hewitt, T. G.; DeBoer, J. J.; Anzenhofer, K. *Acta Crystallogr., Sect. B* 1970, B26, 1244. Nolte, M. J.; Singleton, E. *Acta Crystallogr., Sect. B* 1975, B31, 2223. Mague, J. T. *Inorg. Chem.* 1973, 12, 2649. We consider Rh-As distances longer than ca. 2.7 Å to be nonbonding; see, for example: Vidal, J. L. *Inorg. Chem.* 1984, 20, 243 and references therein.

(11) Counting the  $\mu$ -*t*-BuAs and  $\mu$ -*i*-BuAs units as four- and three-electron donors, respectively, the Rh<sub>6</sub> cluster has 86 valence shell electrons and should have a "closo" octahedral structure with seven skeletal bonding pairs. Electron counting schemes in which the As atom of the  $\mu$ -*t*-BuAs unit is considered a part of the cluster framework also fail. This approach is also controversial since this unit is not bonded to all the Rh atoms in the Rh<sub>5</sub> plane.

## Evidence for Two Different Radical Cation Types Derived from Methylenecyclopropane

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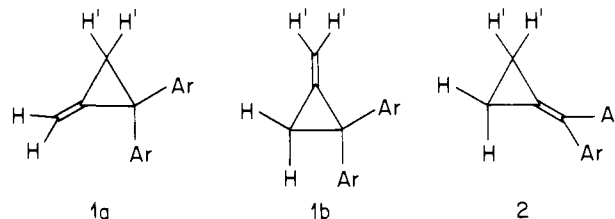
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The photoreactions of quinones with appropriately substituted methylenecyclopropanes, **1** and **2**, give rise to nuclear spin polarization effects supporting the existence of two different radical cation structures, **5** and **6**.

The structure and reactivity of organic radical cations continue to attract much interest and a variety of techniques continue to be employed in their study.<sup>1-6</sup> We are interested especially in the radical cations of strained ring systems because they can assume a variety of interesting structure types.<sup>2,3,7,8</sup> The relative energies of the accessible states are subject to substituent effects, and in selected cases, appropriately chosen substituents can alter the ordering of states.<sup>9,10</sup>

In this paper we describe the application of the CIDNP technique in the photoreactions of quinones with two types of *gem*-diarylmethylenecyclopropanes in order to elucidate the structures of the intermediate radical cations. This work was stimulated by the interesting observation,<sup>3</sup> that two of the *gem*-diarylmethylenecyclopropanes (**1a** and **1b**, H' = D) are readily inter-



converted in the electron-transfer-sensitized reactions with quinones but that the third isomer (**2**) was not formed.

The irradiation of deaerated acetone-*d*<sub>6</sub> solutions of chloranil containing 2,2-dianisyl-1-methylenecyclopropane (**1**, Ar = C<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>, H' = H) gave rise to strong nuclear spin polarization effects for the starting material and for two [3 + 2] cycloadducts, **3** and **4**.<sup>11</sup> These products are formed only in thoroughly deaerated solutions whereas the previously described dioxolanes<sup>3</sup> are formed in oxygen-containing solutions. Similar but weaker effects were observed for the 2,2-ditolyl derivative, whereas no CIDNP results were observed for the 2,2-diphenyl and the 2,2-bis(*p*-chlorophenyl) derivatives.

The structure of the intermediate radical cations can be derived from the observed polarization patterns. Each product shows polarization only for the two CH<sub>2</sub> groups, and in each product

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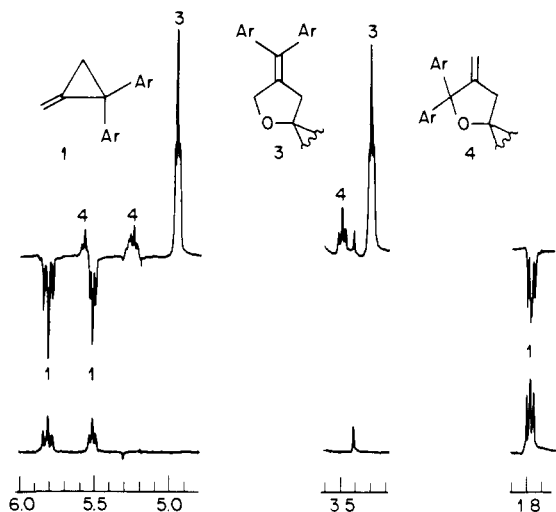
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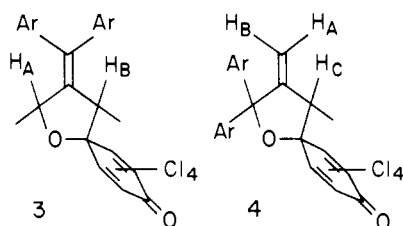
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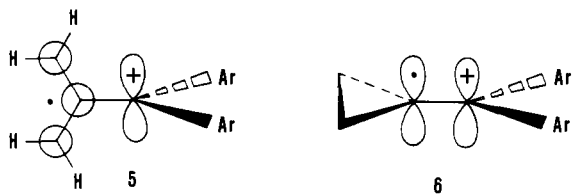
**Figure 1.**  $^1\text{H}$  NMR spectra (90 MHz) of an acetone- $d_6$  solution containing 0.02 M chloranil and 0.02 M 2,2-dianisyl-1-methylenecyclopropane (**1**, Ar =  $\text{C}_6\text{H}_4\text{OCH}_3$ ) in the dark (bottom) and during UV irradiation (top).



the two pairs of protons have the same signal direction and comparable enhancements. This finding suggests a common intermediate for the regeneration of **1** and for the formation of **3** and **4**. On the other hand, the fact that **1** shows emission, whereas **3** and **4** show enhanced absorption (Figure 1), suggests that two different pathways exist between this intermediate and the "products."

Two of the polarization-determining parameters,<sup>12</sup> the initial spin multiplicity of the radical ion pairs ( $\mu > 0$ ) and the relative magnitude of their  $g$  factors ( $\Delta g < 0$ ), can be assigned unambiguously. The observed rearrangement<sup>3</sup> and the polarization suggest that the methylene carbons bear positive spin density and that their protons have negative hyperfine coupling constants ( $a < 0$ ). Given these parameters, the signal direction of the adducts is compatible with singlet recombination ( $\epsilon > 0$ ) of the intermediate radical ion pairs, whereas the starting material most likely is regenerated after separation of the geminate radical ion pairs ( $\epsilon < 0$ ).

On the basis of these considerations, we propose a trimethylenemethane radical cation (**5**) in which the spin density



(11) The adducts are characterized by the following data. **3**: mp 153–155 °C (colorless needles);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.22 (2 H, dd), 3.80 (6 H, s), 4.98 (2 H, dd), 6.81–7.08 (8 H, m); mass spectrum,  $m/e$  (25 eV, 120 °C) 514 ( $M^+ + 2$ , 7.1%), 512 ( $M^+$ , 12.7%), 510 (11.6%), 267 (100%), 251 (17.8%), 235 (35.0%); IR (KBr) 1685, 1600, 1580, 1508, 1280, 1240  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{24}\text{H}_{18}\text{O}_4\text{Cl}_4$ : C, 56.28; H, 3.54. Found: C, 56.46; H, 3.64. **4**: mp 194–196 °C dec (colorless needles);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.40 (2 H, dd), 3.80 (6 H, s), 5.25 (1 H, td), 5.50 (1 H, td), 6.80–7.33 (8 H, m); mass spectrum,  $m/e$  (25 eV, 120 °C), 514 ( $M^+ + 2$ , 31.3%), 512 ( $M^+$ , 55.8%), 510 (49.1%), 405 (26.3%), 267 (100%), 235 (30.8%), 214 (45.9%), 135 (54.9%); IR (KBr) 1680, 1608, 1578, 1508, 1280, 1250  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{24}\text{H}_{18}\text{O}_4\text{Cl}_4$ : C, 56.28; H, 3.54. Found: C, 56.25; H, 3.65.

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is primarily localized in an allyl moiety, whereas the charge is primarily localized in a diarylmethylene group attached in the 2-position.<sup>13</sup> The previously proposed perpendicular (bisected) arrangement<sup>3</sup> of the two  $\pi$  systems is consistent with the apparent localization of spin and charge. This type of intermediate is also favored as the least motion intermediate; its formation requires only rotation of the methylene group and not of the bulkier diphenylmethylene moiety.

Further insight into this system is provided by the photoreaction of chloranil with **2**, which gives rise to strong emission for the cyclopropane singlet but does not result in any phenyl polarization. Moreover, this reaction does not produce any evidence for rearrangement to **1**. For the analysis of this polarization,  $\mu$  ( $> 0$ ) and  $\Delta g$  ( $< 0$ ) once again are unambiguous. The signal direction is then compatible either with singlet recombination ( $\epsilon > 0$ ) and positive hfc's or with triplet recombination ( $\epsilon < 0$ ) and negative hfc's. The latter combination of parameters is unlikely, since negative hfc's are characteristic for the ring-opened trimethylenemethane radical cation **5**, which generates **1** as well as **3** and **4**, none of which are observed. Accordingly, we assign positive hfc's to the intermediate and identify it as belonging to a principally different structure type, **6**, which is in essence a diphenylethylene radical cation. The electron spin is localized principally on the tertiary cyclopropane carbon whereas the charge is localized in the diarylmethyl moiety. The cyclopropane bonds are not involved in delocalizing either charge or spin. This assignment is supported by photoreaction of chloranil with 1,1-diphenyl-2-methylpropene, formally a hydrogenolysis product of **2**. The CIDNP effects observed in this reaction are quite analogous to the results observed for **2**: the allylic (methyl) protons show strong emission, whereas no polarization is observed for the phenyl groups.

The results reported here provide yet another example of two different radical cation structures derived from the same carbon skeleton. The accessibility of the structures is governed by substituent effects. For the radical cation of **2** the geminal pair of aryl substituents restricts spin and charge to the  $\pi$  system, whereas the highly delocalized species **5** results from the interaction of the aromatic  $\pi$  system with the Walsh orbitals of the cyclopropane ring.

(13) This charge distribution shows a similar trend as that derived for the 1,1-diphenylallyl cation (Olah, G. A.; Spear, R. J. *J. Am. Chem. Soc.* 1975, 97, 1539–1546), but **5** shows an even stronger localization of the charge.

## Dependence of Rate Constants for Photoinduced Charge Separation and Dark Charge Recombination on the Free Energy of Reaction in Restricted-Distance Porphyrin–Quinone Molecules

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The primary electron-transfer event of photosynthesis involves oxidation of the lowest excited singlet state of a chlorophyll electron donor by a nearby electron acceptor.<sup>1</sup> The distance between the donor and the acceptor is restricted by the surrounding reaction center protein. We recently prepared a series of restricted-distance porphyrin–quinone donor–acceptor molecules designed to study electron-transfer proceeding from the lowest excited singlet state of the porphyrin (Figure 1).<sup>2</sup> We now report that the rate constants for both radical ion pair formation and recombination in these molecules depend on the exothermicity of the respective

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