The unique property of the DTBQ-Re(CO)₄ (and other related ketone–rhenium complexes) radical is its extraordinary thermal stability. Even at high temperatures up to 80 °C, the radical complexes do not decay significantly. Planned experiments include both X-ray and ¹³C NMR characterization of these interesting quinone–rhenium radical complexes.

Finally, the results also shed some light on the mechanism of the photoreaction of quinone and the rhenium carbonyl. If the benzene solution containing both reactants was irradiated at the n,n*- band of the o-quinone at 395 nm, no reaction was observed. However, if the photolysis was carried out at 310 nm, which is associated with the α,π* band of the Re₂(CO)₁₀, the solution immediately turned red with the formation of the DTBQ-Re(CO)₄ radical complex. This is consistent with the following reaction mechanism:

\[
\text{Re}_2\text{(CO)}_{10} + \text{DTBQ} \rightarrow \text{DTBQ-Re(CO)}_4 + \text{CO} \tag{3}
\]

The escape of CO from the solution during photolysis was also observable. In the present system, a photochemical charge transfer mechanism between Re₂(CO)₁₀ and DTBQ is unlikely, as quinone is not the photoreactive reactant here and the quinone radical anion was not observed during the reaction.

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An NMR Technique for Tracing Out the Carbon Skeleton of an Organic Molecule

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We propose a new method of establishing the connectivity of the carbon skeleton of an organic molecule, the first and most important step in a complete structural determination. The technique is based on an earlier NMR experiment¹ for studying carbon-13–carbon-13 spin–spin coupling which uses the motley creation of double-quantum coherence² to suppress the strong signals from isolated carbon-13 spins and reveal the weak carbon-13 satellite spectrum. If the magnitudes of the coupling constants are sufficiently well differentiated, they may be assigned to specific pairs of carbon resonances simply by picking out the repeated splittings. Adjacent carbon sites are thus identified directly. However, in many cases the molecular framework is too complex for this simple method to be applicable—each carbon site can have up to four directly bonded neighbors, and the carbon–carbon splittings may be close in magnitude or not clearly resolved. Consequently an independent method of assignment is needed.

¹ On leave from the Delft University of Technology, Delft, The Netherlands.


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345 and 705 nm. This suggests that the planarity of the quinone moiety has been retained in the radical complex. As a comparison, the UV spectrum of the parent DTBQ has band centers at 335 and 665 nm.

Comparison of the IR spectrum of the DTBQ-Re(CO)₄ radical complex with those of the starting compounds (in KBr pellets) suggests that the carbonyl groups of the o-quinone have been drastically altered, whereas the carbonyl groups originally complexed to the rhenium retain much of their original character upon radical formation. This is inferred from the observation that the carbonyl stretch of the quinone at 1650 cm⁻¹ completely disappears from the IR spectrum of the radical, while the carbonyl absorption region of Re₂(CO)₁₀ at ~2000 cm⁻¹ changes very little. The C–H stretching region is very similar in both the parent quinone and the rhenium–quinone radical complex, which supports the assignment of the DTBQ-Re(CO)₄ radical as having a planar quinone moiety with the Re complexing symmetrically to the two quinone oxygen atoms.

The first-derivative ESR spectrum of the radical complex at various temperatures is shown in Figure 2. The second-derivative spectrum at 60 °C, also shown in Figure 2, clearly exhibits the proton hyperfine splitting of 3.46 G, which by analogy to the uranyl–DTBQ complex⁴ assigned to the proton between the two tert-butyl groups on the quinone ring. The g factor of the DTBQ-Re(CO)₄ radical complex was measured to be 2.003. The "average" Re hyperfine coupling constant is 28.2 G; the two isotopes of ¹⁸⁵Re (37.05%, I = ⁵/₂) and ¹⁸⁷Re (62.93%, I = ⁵/₂) could not be resolved, as their magnetic moments differ only by 1%. The low g factor of the radical complex is expected and is probably due to the large spin–orbit coupling of the Re atom.

A number of related diketone–rhenium carbonyl radical complexes have also been prepared and studied in our laboratory. These include the furil–rhenium carbonyl, the o-naphthoquinone–rhenium carbonyl, the tetrachloro-o-quinone–rhenium carbonyl, the tetrabromo-o-quinone–rhenium carbonyl, and the di-tert-butyl azodicarboxylate–rhenium carbonyl radical complexes. Two unusual features common to the ESR spectra of the rhenium radical complexes are the symmetrical broadening of the pair of lines corresponding to m_I = ⁵/₂ and the slightly unequal spacings among the rhenium lines, with the splittings at the high-field half being about 5% greater than the corresponding low-field half. These features are due to second-order effects, including both nuclear hyperfine and quadrupole coupling effects. A detailed ESR investigation of the rhenium-quinone radical complexes and other group 7B metal–ketone radical complexes is in progress.

Figure 2. (a) First-derivative ESR spectra of the DTBQ-Re(CO)₄ radical complexes in toluene at various temperatures; (b) second-derivative ESR spectrum of the same radical complex at 60 °C.

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Communications to the Editor

Table I. Comparison of the Observed and Predicted Double-Quantum Frequencies of 5α-Androstane

<table>
<thead>
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<th>carbon site</th>
<th>obsd freq, Hz</th>
<th>pred freq, Hz</th>
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<tr>
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<td>564, 1091</td>
<td>+565, +1089, +1335</td>
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<tr>
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</tr>
<tr>
<td>17</td>
<td>403</td>
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\(^a\) Signs not determined.

Examination of several possible methods of identifying coupled carbon-13 spins suggests that the procedure which promises the highest sensitivity is one which uses the frequency of the double-quantum coherence itself as the criterion for connectivity. In natural-abundance samples, the carbon-13 satellite spectra are carbon-13 satellite lines in the respect to the transmitter frequency.

A two-dimensional Fourier transform experiment is performed in which both A and X carry information about the double-quantum frequency, thus identifying them as part of the same coupled spin system. The double-quantum frequency occurs at the transmitter frequency near the center of the conventional spectrum, using quadrature detection.

Directly coupled carbon-13 resonances are identified by the fact that they generate the same double-quantum frequency. Figure 1 shows a series of F1 traces extracted from the two-dimensional spectrum of 5α-androstan (I). This spectrum was obtained in

![Figure 1](image-url)

Figure 1. Traces extracted from the two-dimensional carbon-13 spectrum of 5α-androstanone, showing the double-quantum transitions in the F1 dimension and their relationship to the resonances of the conventional spectrum (left-hand edge). A common frequency of 545 Hz may be observed in traces from sites C12 and C13; three other examples are shown, linking sites C1 and C2, C3 and C4, and C5 and C7. Sensitivity was too low to detect the double-quantum transition from the methyl groups C18 and C19. The resulting assignment is in agreement with that of Eggert and Djerassi.

(11) Bax, A.; Freeman, R.; Frenkel, T. A.; Levitt, M. H., to be submitted for publication.
The Principle of Cooperativity in Asymmetric Induction: A Demanding Test for Concertedness

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The requirement for orbital symmetry conservation in concerted reactions is such a powerful and general one ("Violations. There are none")\(^1\) that its scope has been extended through topological considerations to a host of systems which lack formal symmetry but whose stereochemistry indicates concert.\(^2\) More recently, the existence of concertedness at all has been questioned by a revisionist school which has invoked instead a relative rate effect which produces the stereospecific fingerprint of concertedness only through the fast collapse of intermediate biradicals.\(^3\) Attempts to resolve this controversy have relied largely on a test case, the Diels–Alder reaction and demonstrate that the cooperativity in asymmetric induction achieved is a direct result of the concertedness of the reaction.

Controversy surrounding the Diels–Alder reaction hinges on whether the incipient $\pi$ bonds are formed simultaneously or sequentially. The essential distinguishing feature of the two mechanisms is the nonequivalence of the two ends of the dienophile for the nonconcerted mechanism and the equivalence of the two ends for the concerted mechanism. Our approach was to probe the geometry of the transition state by using one or two chiral groups with an 1-bornyl group. First, for the concerted reaction leading to enantiodifferentiation of replacing one, then two, methyl groups with an 1-bornyl group, for exo singly substituted transition states. Since the principle of cooperativity in asymmetric induction holds rigorously in such cases.

Conversely, the entropy contribution, which is often more important in determining asymmetric induction,\(^4\) will be given by $R \ln (P_{\text{endo}}/P_{\text{exo}})$, where $P_{\text{endo}}$ are the probabilities for enantiodifferentiation for exo and endo singly substituted transition states. Since the entropic effects will also be additive, we have the important result that the difference in activation free energies themselves will be additive and the relative rate of enantiomer formation $k_\alpha/k_\beta$ in the presence of two chiral groups will be the product of the rates in the presence of one chiral group (see eq 1).

$$\frac{k_\alpha}{k_\beta} = \frac{k_{\alpha1}}{k_{\beta1}} = \frac{k_{\alpha2}}{k_{\beta2}} \tag{1}$$

concerted reaction, moreover, the lack of equivalence of the two ends implies that their energy effects on asymmetric induction will be nonadditive. We call this linear free energy relationship the principle of cooperativity in asymmetric induction. This concept is similar to the cumulative effects observed for methyl substitution on solvolytic reactions involving symmetric transition states.\(^5\) However, severe steric and electronic interactions introduce second-order effects which may prevent this relationship from holding rigorously in such cases.

The reaction of dimethyl fumarate with 1,3-diphenylisobenzofuran produced the Diels–Alder product 1 in quantitative yield. The reaction of dibornyl fumarate produced both diastereomers 2a and 2b in a 67:33 ratio, while the reaction of methyl bornyl fumarate gave a mixture of all four possible diastereomers 3 (see Figure 2). Fortunately, it was possible to relate the pair

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