Stable Triplet States of Some Cyclopentadienyl Cations[1a]

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Abstract: A number of cyclopentadienyl cations have been prepared in solution, and for all of them a triplet state has been detected. This is the ground state for the pentachloro cation (V), a low-lying excited state for the pentaphenyl cation (IIa), and a somewhat higher state for less symmetrical cations (IIb–f). The methods used for detection include esr spectra of frozen solutions, magnetic susceptibility determinations, and an nmr method.

As we have emphasized previously,[2] one of the most interesting predictions of molecular orbital theory is the possibility that certain symmetrical derivatives of cyclic 4n π-electron systems may have triplet ground states. This prediction is not unambiguous, since it is based simply on the proposition that the lowest electronic state of a symmetrical conformation of such a molecule should be the triplet state. Real molecules are free to adopt the conformation of lowest energy, which may not be the symmetrical one; this is especially a problem since the Jahn–Teller principle states that the singlet states of such molecules as cyclobutadiene may be stabilized by distortion away from perfect (in this case, square) symmetry. Thus, even if it is true that for such molecules the symmetrical triplet is more stable than the symmetrical singlet, the unsymmetrical singlet might be still more stable. This is apparently the case in heptaphenylcycloheptatrienyl anion.[2] The conformation with perfect D_{7h} symmetry is predicted to have a ground triplet state, but no triplet could be detected. Furthermore, both the tetrapotassium salt of tetrahydroxybenzoquinone[3] and also coronene dianion[4] are predicted by simple standard calculations to have open-shell electronic configurations in their symmetric conformations and thus to be ground-state triplet molecules; neither of these species is in fact a triplet in its lowest state.

The energetic advantage of a triplet state over the corresponding singlet increases in smaller molecules, since it derives from interaction of the two electrons whose spins are either paired or unpaired, and this interaction becomes larger in small molecules. Accordingly, it was not unexpected that we observed a thermally accessible triplet state of pentaphenylcyclopentadienyl cation in equilibrium with the singlet state,[5] and that in the still smaller pentachlorocyclopentadienyl cation the triplet is the ground state.[6] Hoijtink has also observed stable triplet states of triphenylbenzene dianion and of decacyclene dianion.[7] In this paper we wish to report the details of our studies on the cyclopentadienyl cations.

Results and Discussion

Formation of Cations. As we have reported elsewhere,[8] treatment of pentaphenylcyclopentadienol (Ia) with strong acids at room temperature leads to rapid rearrangement. However, when solutions of I are treated at −60 to −70° with BF₃, a deep blue solution of pentaphenylcyclopentadienyl cation (IIa) is rapidly formed. Spectroscopic measurements on solutions in methylene chloride, handled at low temperature (−65°) throughout, show a broad band with λ_{max} 650 mμ (ϵ 50,000) with shoulders at 550 and 750 mμ. This spectrum is unchanged up to −40°, but above that temperature the shoulder at 550 mμ increases irreversibly so this shoulder may be due in part to decomposition products.

The cold solution of the cation II in methylene chloride affords 90% of the expected product, the methyl ether (III), on quenching in methanol at low temperature and essentially the same yield if it is allowed to stand for 1 hr at −60° before quenching. Although it is thus apparently stable at low temperature, it is destroyed rapidly at higher temperatures, as the ultraviolet studies also indicate. Quenching the methylene chloride solution of the cation after warming to room temperature affords a mixture of products. Thin layer chromatography shows that the major path of decomposition is not that reported previously for solutions of cation IIa in sulfuric acid, in which a cyclopentenophenanthrene was found,[8] but instead unidentified fluorinated materials are formed. However, none of the methyl ether III could be detected.

The cation solution at low temperature was also quenched by hydride transfer from excess cycloheptatriene, affording a 98% yield of pentaphenylcyclopentadiene[9] (IV). In a similar fashion to the above, cation solutions at low temperature were prepared from p-anisyltetraphenylcyclopentadienol (Ib), p-chlorophenyltetraphenylcyclopentadienol (Ic), methyltetraphenylcyclopentadienol (Id), β-naphthyltetraphenylcyclopentadienol (Ie), and p-tolyltetraphenylcyclopentadienol (If). Hydride transfer to the resulting cations (IIb–d) generally afforded good yields of a cyclopentadiene mixture, from which apparently a single major isomer could be separated. However, in the case of the methyl cation (IId) there was visible evidence of decomposition even at low temperatures, and only 22% of a cyclopentadiene could be isolated from the hydride transfer. Presum-

(1) (a) Partial support of this work by the National Science Foundation and the National Institutes of Health is gratefully acknowledged; (b) Columbia University; (c) Bell Laboratories.

(2) R. Breslow and H. W. Chang, *J. Am. Chem. Soc.*, **87**, 2200 (1965).

(3) R. West and H. Y. Niu, *ibid.*, **84**, 1324 (1962).

(4) G. J. Hoijtink, *Mol. Phys.*, **2**, 85 (1959).

(5) R. Breslow, H. W. Chang, and W. A. Yager, *J. Am. Chem. Soc.*, **85**, 2033 (1963).

(6) R. Breslow, R. Hill, and E. Wasserman, *ibid.*, **86**, 5349 (1964).

(7) R. Jesse, P. Biloen, R. Prins, J. van Voorst, and G. Hoijtink, *Mol. Phys.*, **6**, 633 (1963).

(8) R. Breslow and H. W. Chang, *J. Am. Chem. Soc.*, **83**, 3272 (1961).

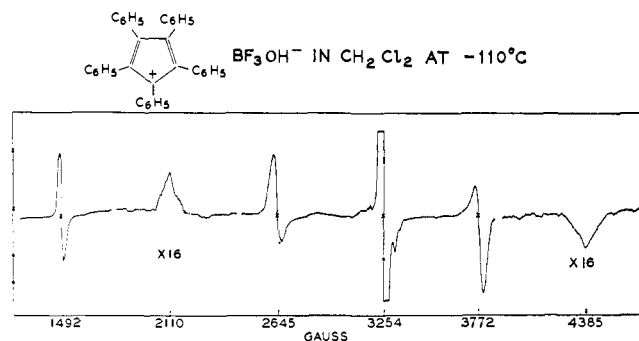(9) K. Ziegler and B. Schnell, *Ann.*, **445**, 266 (1925).

Figure 1. Esr of IIa·BF$_3$OH$^-$ in CH$_2$Cl$_2$ at $-110°$.

Figure 2. Dipolar field due to electron of moment μ_e.

ably the methyl cation decomposes by deprotonation to a fulvene and subsequent reactions.

The structures of these compounds (IVa–d) have been written as tetraphenylbutadienes, with the fifth group on the saturated carbon, since in the ultraviolet they are all rather similar.

Compound	Longest wavelength, λ_{max}, mμ
IVa	338
IVb	347
IVc	343
IVd	337

Furthermore, in the nmr spectrum of IVd the methyl group is split by the ring proton, although J is only 2 cps. However, the various tautomers of IVb–d should be easily equilibrated, and the spectroscopic data are not strongly supportive of the tautomeric structures shown. Accordingly, the question of which tautomer predominates in IVb–d is left open.

I II
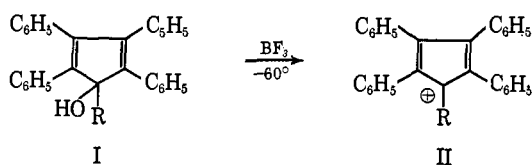
a, R = C$_6$H$_5$
b, R = p-CH$_3$OC$_6$H$_4$
c, R = p-ClC$_6$H$_4$
d, R = CH$_3$
e, R = β-naphthyl
f, R = p-CH$_3$C$_6$H$_4$

III

IV a–d
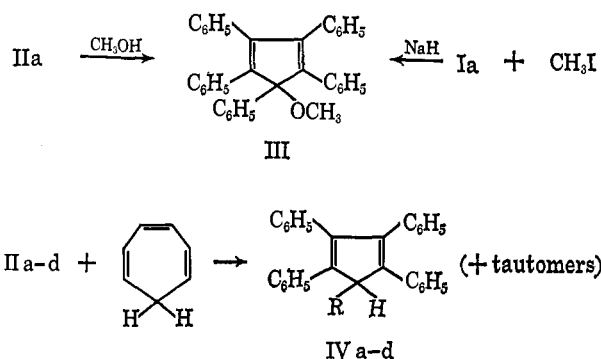
Esr. The electron spin resonance spectra of cations IIa–f were examined by freezing the solutions to liquid nitrogen temperature so as to utilize the frozen solution technique[10,11] for obtaining triplet esr spectra.

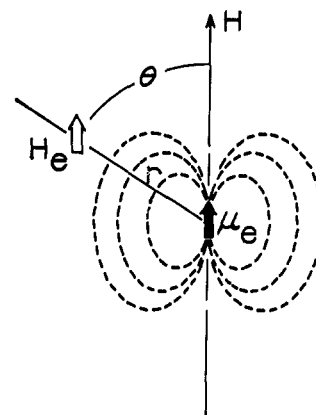(10) M. S. deGroot and J. H. van der Waals, *Mol. Phys.*, **3**, 190 (1960).

All of the cations showed an esr signal near 3200 gauss, due to some monoradical impurities. In addition to this, cations IIa, c, d, and f showed typical[11] triplet esr spectra (*cf.* Figure 1), while IIb and e did not show a triplet spectrum at any temperature. Thus the first derivative spectrum of pentaphenylcyclopentadienyl cation (IIa) in Figure 1 has detectable signals at 1492, 2110, 2645, 3772, and 4385 gauss.

One may view the extension of the triplet spectrum over several thousand gauss as a consequence of the magnetic field of the second electron. Usually, organic monoradicals are found within $\sim$100 gauss of the field for the free-electron resonance, H_0, here near 3200 gauss. We may consider that the unpaired electron in the triplet will undergo a transition at the same total field, which is now composed of the external field of the magnet, H, and the internal field of the second electron. The internal field is that of a dipole and is given by

$$H_e = \frac{\mu_e}{|\vec{r}|^3}(3 \cos^2 \theta - 1)$$

where μ_e is the moment of the electron, $\vec{r}$ is the vector between the two electrons, and θ is the angle between $\vec{r}$ and the external magnetic field (Figure 2). H_e is the component of the dipolar field in the direction of H, with μ_e, on the average, directed parallel or antiparallel to H (up or down). The component of H_e perpendicular to H does not appear in this first-order model for which $H_e \ll H$.

If the triplet system is tumbling freely in the liquid state, $3 \cos^2 \theta - 1$ averages to zero, and resonances may be observed near H_0 in favorable cases. As motion is restricted the spectrum broadens with increasing H_e. The process is the analog of the broadening of nmr spectra on freezing a solution owing to the appearance of dipolar interactions. The main difference is that μ_e is three orders of magnitude larger than the dipole moment of the proton, and the spectral broadening is correspondingly greater in the triplet. The random orientation in the frozen solution yields a continuous distribution of orientations with $\cos^2 \theta$ varying between 0 and 1. The extremes of H_e are determined by these limits, being $2\mu_e/|\vec{r}|^3$ at $\theta = 0°$ and $-\mu_e/|\vec{r}|^3$ at $\theta = 90°$. For those triplets with $\theta = 0°$, the electron undergoing resonance requires an external field of $H_0 - (2\mu_e/|\vec{r}|^3)$; those in which $\theta = 90°$ require $H_0 +$

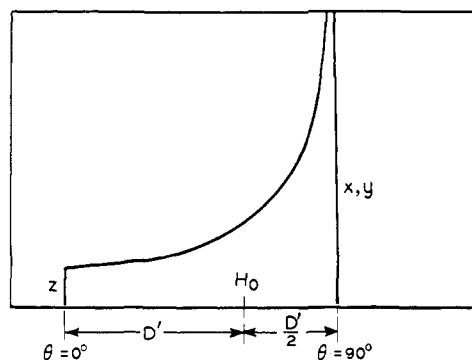(11) E. Wasserman, L. C. Snyder, and W. A. Yager, *J. Chem. Phys.*, **41**, 1763 (1964).

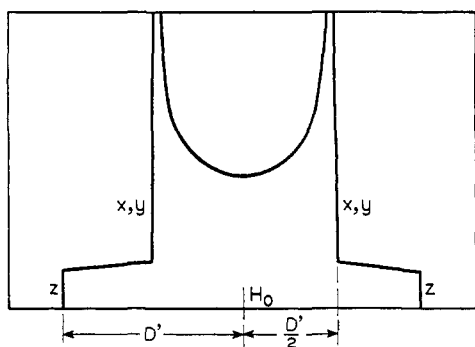Figure 3. Absorption for randomly oriented triplets for a single orientation of μ_e.

Figure 4. Absorption curve for triplets with threefold or higher symmetry.

Figure 5. Model of π-electron triplets in which spins move about the circumference of a circle. The upper figure represents the magnetic field perpendicular to the plane of the molecule; in the lower figure the field lies in the plane.

$(\mu_e/|\vec{r}|^3)$. With D' representing the largest internal field, resonance will vary with increasing θ from $H_0 - D'$ to $H_0 + (D'/2)$ if the second electron is up. Absorption is possible within this range but not outside it. For random orientation the intensity will increase with θ as the number of triplets at a given angle varies as $\sin \theta$. The step characterizing the onset of absorption at $H_0 - D'$ (Figure 3) corresponds to the single orientation of $\vec{r} \parallel \vec{H}$. The infinitely larger cusp at $H_0 + (D'/2)$ corresponds to a direction in the isotropic plane perpendicular to $\vec{r}$ being parallel to $\vec{H}$.

So far, we have only considered one orientation of the second electron. To a good approximation, there is equal probability that it will be up or down. Reversing the spin is equivalent to changing the sign of μ_e and thus that of H_e. The resulting absorption is that of Figure 3 except that it is reflected about H_0. The sum of the two curves is given in Figure 4.

Figure 4 does represent the absorption of a triplet in which one direction $(\vec{r})$ is unique, and the field due to the second electron is the same if $\vec{H}$ lies along any direction in the plane perpendicular to $\vec{r}$. However, the model of two localized spins at fixed positions in space clearly does not correspond to the cyclic π systems, such as II or triplet triphenylene and coronene, in which the electrons are distributed on aromatic rings. We can simulate these by allowing the two spins, separated by a fixed value of $|\vec{r}|$, to move rapidly about a ring with both spins on the circumference at all times (Figure 5). If $\vec{H}$ is perpendicular to the plane of the ring, θ is a constant 90° and the internal field is $-\mu_e/|\vec{r}|^3$. If $\vec{H}$ lies in the plane of the ring, the rotation of $\vec{r}$ in the plane
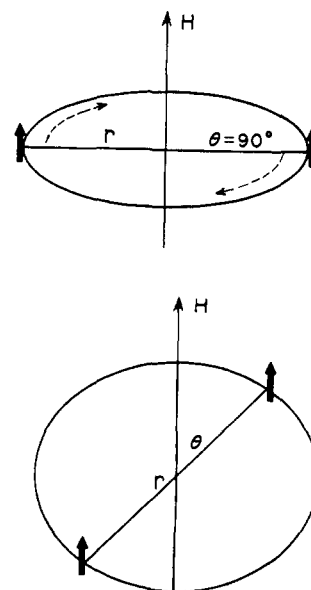
yields all values of θ with equal probability. The average internal field is then given by

$$\frac{1}{2\pi} \frac{\mu_e}{|\vec{r}|^3} \int_0^{2\pi} (3 \cos^2 \theta - 1)\, d\theta = \frac{\mu_e}{2|\vec{r}|^3}$$

With the exception of a factor of 2 in width, the absorption will have the same shape as that for the previous model. There will be a unique orientation in the random sample, here corresponding to molecules in which the $\vec{H}$ is perpendicular to the plane of the molecule $(\vec{H} \parallel z)$. This orientation is still associated with the largest internal field which we continue to represent by D'. Perpendicular to this direction is an isotropic (xy) plane. For the comparatively large number of molecules which are so oriented that $\vec{H}$ lies in the molecular plane, the internal field is $-D'/2$.

For a given direction of μ_e the sign of D' differs in the two models. In the first the unique direction corresponds to $\vec{r} \parallel \vec{H}$, in the second to $\vec{r} \perp \vec{H}$. In describing the internal fields we can either use the value of D' in gauss or, more conventionally, the energy of the first electron in that internal field, D, the spin–spin interaction, or zero-field parameter. For organic species which approximate the free-spin g factor, we use 934.8 gauss = 0.1000 cm^{-1} for conversion.

The characteristic features of the triplet spectra readily appear in a first derivative presentation. The sudden change in absorption corresponding to a principal axis (or plane) being parallel to $\vec{H}$ has a large derivative. In the broad regions between the principal axis fields, the derivative is small and not observed. Only orientations which are important for the determination of D are the ones observed. At the same time, most of the absorption intensity occurs in regions which do *not* give detectable signals. The derivative intensities observed are thus considerably less than those to be expected for the same number of unpaired electrons in isolated monoradical $(S = {}^1/_2)$ species.

The spectrum of IIa is that expected for a triplet in which the molecular (xy) plane is isotropic, a requirement met if the molecule has threefold or higher symmetry, $D = 0.1050$ cm^{-1}. With lower symmetry, each xy line will split into two features separated by $3E'$, a full absorption line corresponding to x-oriented molecules and a half-line for y orientation similar in shape to those observed for the z orientation near 2110 and 4385 gauss. The characteristic shape of the xy line in Figure 1 may be viewed as a superposition of the full-x and half-y lines in the limit that these coincide. In principle, the lower symmetry in IIc, d, and f should yield separate x and y features. However, line broadening obscures the anisotropy in the xy plane and $E' = 0$ within the accuracy of these measurements.

The resonances associated with the flip of a single electron ($\Delta m = 1$ transitions) are not able to explain all of the features of a triplet spectrum. The line at 1492 gauss involves the simultaneous reorientation of both electrons from a down to an up position ($\Delta m = 2$).[10] The transition is allowed by the dipolar interaction. For two spins to absorb together the same amount of energy as taken up by a single spin at H_0, we require a field of $H_0/2$ for resonance. The small downfield displacement of the observed line is due to second-order interactions. The position of the transition is largely independent of the orientation of the triplets; the dipolar interaction remains unchanged as the spins keep the same relative orientation in the transition.

Essentially the same value of D was observed for IIa, c, d, and f. The magnitude is reasonable in comparison with other π-electron triplets, in which the Pauli principle does not allow the two unpaired electrons to be found at the same atom simultaneously, and is much too large to be the result of interaction between two monoradicals. For example, the phosphorescent triplet of 1,3,5-triphenylbenzene has $D = 0.111$ cm^{-1}.[10]

Temperature Dependence. For molecules which have triplet ground states, such as some carbenes and nitrenes, the intensity I of the observed lines turns out[12] to follow the usual Curie law as a function of temperature.

$$IT = \text{constant} \tag{1}$$

On the other hand, if the triplet were not the ground state of the molecule but instead had energy ΔE more than the ground state, then the intensity of the $\Delta m = 2$ transition should also change as the population of the excited state changes.

$$IT = \frac{Ce^{-\Delta E/RT}}{1 + 3e^{-\Delta E/RT}} \tag{2}$$

The weighting factors are as shown since there are three triplet sublevels, one of which is the lower level of the $\Delta m = 2$ transition. If ΔE is zero, this reduces to the Curie law, while for cases in which $3 \exp(-\Delta E/RT) \ll 1$, it becomes

$$\log (IT) = \text{constant} - [\Delta E/2.3RT] \tag{3}$$

(12) (a) R. W. Murray, A. M. Trozzolo, E. Wasserman, and W. A. Yager, *J. Am. Chem. Soc.*, **84**, 3213 (1962); (b) G. Smolinsky, E. Wasserman, and W. A. Yager, *ibid.*, **84**, 3220 (1962); (c) unpublished work, Bell Telephone Laboratories.
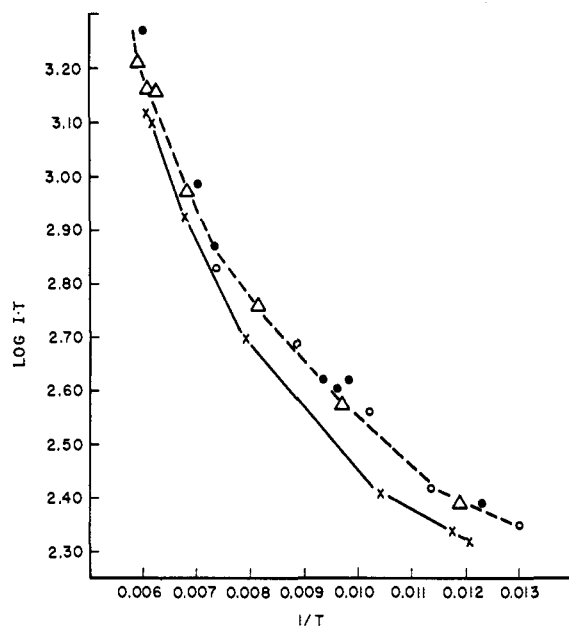

Figure 6. Plot of eq 3: O, IIa·BF$_3$OH$^-$ in CH$_2$Cl$_2$; ●, IIa·BF$_3$OH$^-$ in SO$_2$; △, IIa·AlCl$_3$OH$^-$ in CH$_2$Cl$_2$; ×, IIc·BF$_3$OH$^-$ in CH$_2$Cl$_2$.

In Figure 6 is plotted log (IT) *vs.* $1/T$, where I was measured as the peak-to-peak height of the $\Delta m = 2$ signal. In principle the double integral of this signal should be used, but we find that the width of the signal does not vary with temperature so our procedure is equivalent. The spectra were obtained starting with the lowest temperature, and the change with temperature was fully reversible. Increasing modulation led to a proportionate increase in the signal, ruling out saturation. As Figure 6 shows, essentially the same temperature behavior is obtained when AlCl$_3$ is used instead of BF$_3$ to prepare the cations, and when either CH$_2$Cl$_2$ or SO$_2$ are used as solvents. It is apparent that the triplet signal of the pentaphenylcyclopentadienyl cation (IIa) does not obey the Curie law, so the triplet is an excited state.

From the slope of the curved line in Figure 6, ΔE ranges from 0.35 kcal/mole at 77°K to 1.15 kcal/mole at 170°K. One obvious explanation of this variation is that ΔE may indeed not be a constant over such a large change in absolute temperature. Alternatively, in the frozen solution molecules in different environments may have different ΔE's; it is easy to see that this would lead to the type of curvature observed, in which ΔE seems to increase at higher temperatures. Plots of the data by correction of Figure 6 using eq 2 instead of eq 3 lead to no appreciable change.

In Figure 6 is also plotted the data on IIc. The curvature is still apparent, and ΔE is similar, ranging from 0.30 kcal/mole at 82°K to 1.40 kcal/mole at 174°K. A similar plot of the intensity of the triplet signal from IIf gives ΔE about 1.3 kcal/mole higher than the above, again with curvature over the temperature range. Unfortunately, IId was unstable, and reversible changes in intensity at different temperatures could not be measured. As mentioned before, IIb and IIe gave no detectable triplet signals at any temperature.

Studies in Solution. From the data it seems clear that none of these species is a ground-state triplet. In addition, a measurement of the magnetic suscepti-

bility of IIa of 4°K indicated that <2% of the cation could exist in a triplet state. However, since they are present in a relatively unusual environment, a frozen glass, it seemed desirable to confirm this situation in liquid solution. The triplet esr method is no longer applicable, so bulk magnetic susceptibility measurements were performed. Since our cations must be prepared and maintained at low temperature, the most convenient method is that of Evans[13] in which the magnetic susceptibility of a solute in solution is determined from the nmr shift of the solvent line compared with the signal from a pure solvent. The method was calibrated by examining solutions of diphenylpicrylhydrazyl in methylene chloride; from the difference in the nmr between the solvent line and that of methylene chloride in a capillary, the measured magnetic susceptibility was found to agree with theory within better than 10%, both at room temperature and at $-54.6°$. Then the nmr solvent line shifts were determined for methylene chloride solutions of the alcohols (Ia–c, e, and f) at both room temperature and $-54.6°$, and for the corresponding cations (IIa–c, e, and f) at $-54.6°$. The results are presented in Table I.

Table I. Upfield Shift of the Nmr Signal of Methylene Chloride in Solution Relative to a Solvent Capillary

Compound	Concn, M	Temp, °C	Δf, cps
Ia	0.060	24	1.3 ± 0.1
	0.030	24	0.8 ± 0.1
	0.060	−54.6	2.4 ± 0.1
	0.030	−54.6	1.6 ± 0.1
Ib	0.060	24	1.3 ± 0.1
	0.030	24	0.7 ± 0.1
	0.060	−54.6	2.6 ± 0.1
	0.030	−54.6	1.3 ± 0.1
Ic	0.060	24	1.2 ± 0.1
	0.030	24	0.8 ± 0.1
	0.060	−54.6	1.8 ± 0.1
	0.030	−54.6	1.3 ± 0.1
Ie	0.060	24	1.6 ± 0.1
	0.030	24	0.9 ± 0.1
	0.060	−54.6	2.6 ± 0.1
	0.030	−54.6	1.4 ± 0.1
If	0.060	24	1.5 ± 0.1
	0.030	24	0.8 ± 0.1
	0.060	−54.6	2.2 ± 0.1
	0.030	−54.6	1.6 ± 0.1
IIa	0.060	−54.6	2.4 ± 0.1
	0.030	−54.6	1.3 ± 0.1
IIb	0.060	−54.6	1.6 ± 0.1
	0.030	−54.6	0.9 ± 0.1
IIc	0.060	−54.6	2.0 ± 0.1
	0.030	−54.6	1.0 ± 0.1
IIe	0.060	−54.6	1.6 ± 0.1
	0.030	−54.6	0.9 ± 0.1
IIf	0.060	−54.6	1.6 ± 0.1
	0.030	−54.6	1.0 ± 0.1

Since the effects are small, it is especially important to make an accurate correction for the diamagnetic susceptibility, of both singlets and triplets, in determining the paramagnetic contribution from triplet species. We do this by noting that the diamagnetic effects from pentaphenylcyclopentadienol (Ia) and from p-anisyltetraphenylcyclopentadienol (Ib) are essentially the same, as indeed they are for all the alcohols. Thus we

(13) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

assume that the diamagnetic effects in the corresponding cations would also be the same, and that differences reflect paramagnetic contributions from triplets (quantitative esr measurements on these solutions show that the amount of monoradical impurity present makes a negligible contribution). Our esr studies show that there is no detectable amount of triplet in the anisyl cation (IIb) since it is so unsymmetrical. Thus we assume that the difference in Δf between IIa and IIb (0.8 $\pm$ 0.14 cps at 0.06 M and 0.4 $\pm$ 0.14 cps at 0.03 M) is due to the paramagnetic effect of some triplet in IIa. These data correspond to 2.2 $\pm$ 0.4% triplet for IIa (2.2 $\pm$ 0.8% from the data at 0.03 M). For the p-chloro cation IIc there is 1.1 $\pm$ 0.3% triplet, while no triplet is detected for the others. Thus the esr test, which revealed a triplet signal from the p-tolyl cation (IIf), is more sensitive. This order of relative stabilities of triplets is consistent with that derived from the esr studies, and both are consistent with the expectation that increasing electronic disymmetry will split the degeneracy of the highest potentially occupied orbitals in cyclopentadienyl cations further, and thus increase the singlet–triplet energy gap. The effects of molecular symmetry on the presence or absence of triplet signals also, of course, furnish overwhelming support for our assignment of these signals to the triplet states of the cyclopentadienyl cations.

For comparison, the results of simple Hückel mo calculations on these cations are presented in Table II; the dihedral angle between the five-membered ring and a phenyl ring was taken as 60°, a likely value,[14] and the

Table II. Splitting of the Highest Potentially Occupied Degenerate Pair of mo's in Cyclopentadienyl Cations by Substituents, According to a Hückel Calculation[a]

Compound	Splitting of levels (β's)
IIa	0
IIb[b]	0.017
IId[c]	0.122
IIe	0.086
IIf[d]	0.021

[a] The values listed are for the generally accepted[15] parameters in such calculations: A. Streitwieser, "Molecular Orbital Theory," John Wiley and Sons, Inc., New York, N. Y., 1961, pp 120–123. [b] $\alpha_O = \alpha_C + 2\beta$; $\beta_{CO} = 0.8\beta$. These "standard" parameters are obviously unsuitable, since they grossly underestimate electron donation by the methoxyl group under strong electron demand. [c] Taking the inductive model, with $\alpha_{C-Me} = \alpha_C - 0.5\beta$. The splitting goes to zero with $\alpha_{C-Me} = \alpha_C - 0.1\beta$. [d] Taking $\alpha_{C-Me} = \alpha_C - 0.5\beta_C$.

other parameters are as given. It is apparent that the agreement of these calculations with our results is modest at best. The calculations indicate that a p-tolyl substituent should increase the single–triplet gap by a small amount, in agreement with our data on IIf. The β-naphthyl substituent should increase this gap more, as we have found for IIe. However, with the usual parameters the p-anisyl group should not strongly split the degeneracy, as we observe it does. Such parameters make a p-anisyl group interact less effectively with a cation than a p-tolyl group, in contradiction to general experience. With parameters which imply stronger

(14) From space-filling Courtauld molecular models which correctly indicate the 30° twist in triphenylmethyl derivatives.

electron donation by the methoxyl, the calculated splitting increases. Furthermore, although the instability of cation IId prevents a direct estimate of the singlet–triplet gap, it is obvious from the strong triplet esr signal that this gap is not large; using the inductive model for hyperconjugation, the standard parameters give bad agreement with experiment. We have not calculated the splitting for the p-chloro cation IIc, since the parameters to be used are at least questionable.

The nmr spectra of solutions of IIa show one other important feature in addition to the solvent shifts discussed earlier: no signal can be seen from the protons of IIa itself. This is undoubtedly due to paramagnetic broadening[15] because of the triplet species present. The solvent line also shows some broadening due to the presence of a paramagnetic species in solution, but the effect is much greater in IIa, whose spectrum is completely washed out. Even though only 2% of IIa is present as the triplet, singlet–triplet interconversion is apparently sufficiently rapid that all molecules of IIa pass through the triplet state during the nmr transition time.[16] The same complete washing out of nmr lines is observed for all the cations except the anisyl derivative (IIb), which shows a very broad pattern in the usual aromatic region. Even for IIe, the β-naphthyl cation, the triplet state, which was not detected by our other physical methods, is sufficiently accessible to wipe out the nmr spectrum; apparently this nmr test is more sensitive than the others, and it reveals the presence of nearby triplet states for IIb and e, as well as for the other cations.

Since an appreciable amount of IIa is the triplet, and equilibration is rapid, we have examined the possibility that this species might react with oxygen. When O_2 was bubbled through a solution of IIa at low temperature for 2 min, and then additional BF_3 was added and the reaction mixture was quenched in the usual way, only 30% of the methyl ether (III) could be isolated. When the BF_3 was passed in simultaneously with the O_2, 83% of III could be obtained after 2 min, and only 21% of III after 5 min. While at first sight this seems clear evidence for an oxygen reaction, almost the same results were obtained when pure argon was used in place of oxygen. Thus it seems most likely that the apparent destruction of IIa is not in fact due to chemical reaction with O_2, but is instead the result of a decrease in the partial pressure of BF_3, with consequent decreased saturation of the solution. There does not a priori seem to be a convincing argument that the triplet state of IIa ought to react with O_2, but further work will be needed to clarify the matter.

Pentachlorocyclopentadienyl Cation. With the finding that IIa has a singlet ground state, we decided to examine a smaller pentagonally symmetric cyclopentadienyl cation.[17] As we have discussed elsewhere,[2] a smaller derivative should have a greater triplet energy advantage, as well as fewer opportunities for easy distortion. This was found to be the case for pentachlorocyclopentadienyl cation (V). Treatment of hexachlorocyclopentadiene with antimony pentafluoride afforded
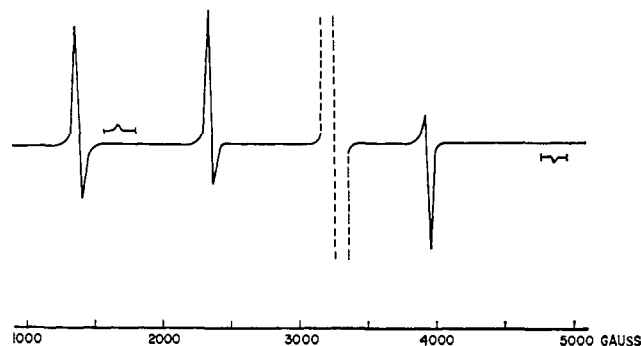

Figure 7. Esr spectrum of $C_5Cl_5^+$ (V). This spectrum shows all the reproducible features of several runs; the very weak z lines are shown at the fields at which they appear with much greater amplification.

a solution which gave a clear triplet esr spectrum (Figure 7) when frozen to a glass. From this spectrum the values of the spectroscopic parameters are $D = 0.1495$ cm^{-1} and $E' < 0.002$ cm^{-1}. The zero value for E is again consistent with a pentagonally symmetric triplet, and the D value is larger than that for IIa, as expected.

V
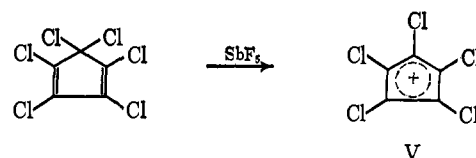
This value of D is in fact within 10% of that calculated[18] for cyclopentadienyl cation itself by an mo method. D is also in close correspondence with that of phosphorescent mesitylene[19] where $D = 0.140$ cm^{-1}. From these data alone there is little doubt that V is the triplet species actually present, but unfortunately under the best conditions most of the hexachlorocyclopentadiene is converted to other materials. Thus quenching in methanol affords only 5% of monomeric products, together with a mixture of dimeric perchlorinated ketones. The monomeric material is mostly recovered hexachlorocyclopentadiene, but approximately 20% (1% over-all) of 1,1-dimethoxytetrachlorocyclopentadiene (VI) can be isolated, identical with an authentic sample[20] in vpc retention time, nmr spectrum, and mass spectrum.

VI
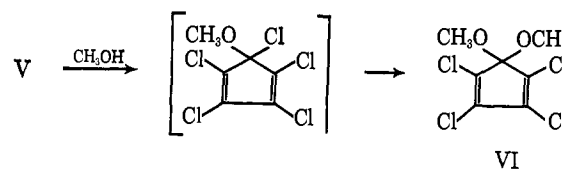
Since such a small fraction of the cyclopentadiene is converted to V, direct determinations of magnetic susceptibility would be useless. However, by observing the intensity of the esr spectrum as a function of temperature, it was found that the Curie law is obeyed. This is shown in Figure 8, where data from two separate runs are plotted down to 77°K. One additional point is also on the line: at 4.2°K (liquid helium) the intensity is 22 times that at 77°K, in good agreement

(15) J. Pople, W. Schneider, and H. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p 207.
(16) This fast equilibration is not surprising since the two species are close in energy and also, presumably, geometry.
(17) For a preliminary report, see ref 6.

(18) M. Karplus and M. Godfrey, unpublished calculations.
(19) M. S. deGroot, I. A. M. Hesselmann, and J. H. van der Waals, Mol. Phys., 10, 9 (1965).
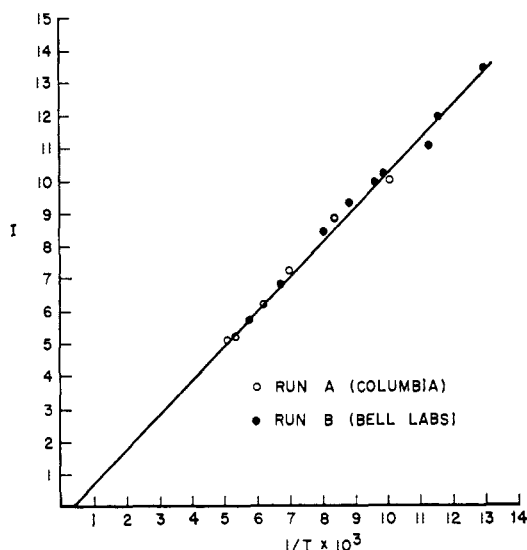(20) J. S. Newcomer and E. T. McBee, J. Am. Chem. Soc., 71, 948 (1949).

Figure 8. Amplitude of the $\Delta m = 2$ signal of V $vs.$ reciprocal temperature.

with eq 1. From this it can be concluded that the ground state of pentachlorocyclopentadienyl cation (V) is a triplet.

Conclusions

Our results indicate that in at least one derivative of cyclopentadienyl cation, the pentachloro compound (V), the ground state is a triplet. This result is predicted if the geometry is assumed to be pentagonal. Simple Hückel calculations combined with Hund's rules make a qualitative prediction, and our more sophisticated calculations on symmetrical cyclopentadienyl cation using Pariser-Parr parameters and interaction with all singly excited configurations also predict that the triplet is more stable. In the pentachloro cation, apparently this advantage outweighs whatever stabilization might result from Jahn-Teller distortion of the singlet.

In pentaphenylcyclopentadienyl cation (IIa), the ground state is by contrast a singlet, although the triplet state lies nearby. In this larger molecule the energetic advantage of electron unpairing is smaller, since the average separation of the two electrons is greater; this is revealed for instance, in the relative values of D for the two triplets of V and of IIa. Thus even in the symmetric configuration the singlet state might now be better since, as our above calculations show, configuration interaction is more important (in an mo calculation) for the singlet than for the triplet state. Furthermore, with a smaller triplet energy advantage Jahn-Teller distortion may now tilt the scale. However, at this point it is possible to make only very general statements about when one or the other factor will dominate. Accordingly, further experimental exploration of various potentially spin-degenerate systems is still needed.

Experimental Section

Pentaphenylcyclopentadienyl Cation (IIa). A solution of 0.2 g of pentaphenylcyclopentadienol[9] (Ia) in 15 ml of methylene chloride was cooled to −70°, and BF₃ was then bubbled in to saturation. A deep blue solution of pentaphenylcyclopentadienyl cation (IIa) resulted. This was quenched by pouring it into 150 ml of well-stirred methanol at −60°, and after 10 min of stirring the solution

was brought to 0°, poured into 200 ml of water, and worked up with benzene and aqueous bicarbonate to yield 0.185 g (90%) of **pentaphenylcyclopentadienyl methyl ether (III)**, mp 192–195° crystallized from benzene-ligroin. Recrystallization afforded the pure ether, mp 197–198°.

$Anal.$ Calcd for $C_{36}H_{28}O$: C, 90.72; H, 5.92. Found: C, 90.60; H, 5.92.

In a control run, the reaction was performed as above except that the pentaphenylcyclopentadienol was added only after the methanol quenching. Pure starting alcohol was isolated, and thin layer chromatography revealed the absence of any of the methyl ether.

A solution of pentaphenylcyclopentadienyl cation was also prepared as above, but in SO₂ solution instead of methylene chloride. Quenching in methanol afforded a 93% yield of the methyl ether, mp 196–198°.

When the methylene chloride solution of the cation was allowed to stand at −60° for 1 hr before quenching, the methyl ether was produced in 87% yield, mp 190–194°. When the cation solution was warmed slowly to 25° before quenching, no methyl ether could be detected by chromatography; a mixture of products was formed containing some fluorine (by analysis).

A moderate stream of O₂ was prechilled by passage through a 6-ft stainless steel coil in Dry Ice-acetone and bubbled through a solution of the cation at −78°. After 2 min of O₂ bubbling, some BF₃ was passed into the solution and the mixture was then quenched in methanol as above. Only 30% of the methyl ether could be isolated, along with other unidentified materials. However, when prechilled BF₃ was passed in simultaneously with the O₂, the yield of methyl ether was 83% after 2 min, and 21% after 5 min. In a control, prechilled argon was substituted for O₂ in this last experiment. After 2 min, 86% of methyl ether could be obtained, and after 5 min only 37% was formed.

Authentic pentaphenylcyclopentadienyl methyl ether (III) was prepared by refluxing 0.2 g of pentaphenylcyclopentadienol in 50 ml of ether and 30 ml of benzene with 0.1 g of sodium hydride until H₂ evolution ceased; then 0.425 g of methyl iodide in 50 ml of ether was added, and the mixture was refluxed overnight. Aqueous work-up and chromatography afforded the methyl ether, mp 195–197°, in 92% yield along with some recovered alcohol. This material was identical with that described above.

A solution of pentaphenylcyclopentadienyl cation (IIa) prepared from 0.3 g of Ia in methylene chloride was treated at −60° with 0.12 g of pure cycloheptatriene, when the color of the solution changed from blue to purplish. Quenching at low temperature in methanol, followed by the usual work-up, afforded 0.286 g (98%) of pentaphenylcyclopentadiene (IV), mp 249–250°. On recrystallization this had mp 251–252° and was identical in all respects with an authentic sample.[9]

p-**Anisyltetraphenylcyclopentadienyl Cation (IIb).** A solution of 1.0 g of p-anisyltetraphenylcyclopentadienol (Ib) in methylene chloride was treated at −60° with BF₃, when a deep blue color appeared. Treatment with 0.37 g of cycloheptatriene and the usual work-up afforded 0.87 g of p-anisyltetraphenylcyclopentadiene (IVb), mp 183–187°, raised to 190–191° on successive recrystallizations.

$Anal.$ Calcd for $C_{36}H_{28}O$: C, 90.72; H, 5.92. Found: C, 90.49; H, 6.06.

In the ultraviolet the compound showed λλ$_{max}$ 252 mμ (ε 28,700) 270 (25,900 sh), and 347 (16,800). In the nmr a phenyl multiplet was found at 7.2 ppm, the single tertiary hydrogen at 5.0 ppm, and the methoxyl at 3.66 ppm.

p-**Chlorophenyltetraphenylcyclopentadienol (Ic).** A solution of 0.045 mole of p-chlorophenylmagnesium bromide and 10.1 g (0.03 mole) of tetracyclone was refluxed in ether for 4 hr. The usual work-up, followed by alumina chromatography, afforded 7.70 g (52%) of p-chlorophenyltetraphenylcyclopentadienol (Ic), mp 225–226°, raised to 228–229° on recrystallization.

$Anal.$ Calcd for $C_{35}H_{25}ClO$: C, 84.58; H, 5.07; Cl, 7.13. Found: C, 84.69; H, 5.16; Cl, 6.67.

In the ultraviolet the compound showed λλ$_{max}$ 245.5 mμ (ε 23,000), 253 (23,800), 277 (18,000), and 358 (6960).

p-**Chlorophenyltetraphenylcyclopentadienyl Cation (IIc).** A solution of 0.3 g of the above alcohol in 15 ml of methylene chloride was treated at −70° with BF₃. The resulting blue solution of the cation was treated with 0.084 g of cycloheptatriene and worked up in the usual way to afford p-chlorophenyltetraphenylcyclopentadiene (IVc), mp 174–175.5°, in 77% yield.

$Anal.$ Calcd for $C_{35}H_{25}Cl$: C, 87.39; H, 5.24. Found: C, 87.05; H, 5.27.

In the ultraviolet the compound had λλ$_{max}$ 250 mμ (ε 14,800),

268 (14,300), and 343 (8250). The nmr showed a phenyl multiplet at 6.85 ppm and the tertiary hydrogen as a singlet at 4.8 ppm.

Methyltetraphenylcyclopentadienyl Cation (IId). A solution of 0.5 g of 1-methyltetraphenylcyclopentadienol (Id) in methylene chloride was converted to the deep blue cation solution with BF_3 at $-70°$. After 5 min of standing at this temperature a purplish hue had developed. Then 0.23 g of cycloheptatriene was added, and after the usual work-up and chromatography 0.11 g (22%) of methyltetraphenylcyclopentadiene (IVd) was isolated, mp 177–179° (lit. mp 178.5–179.5°). In the ultraviolet the compound had $\lambda\lambda_{max}$ 243.5 (ϵ 18,000) and 336.5 mμ (ϵ 14,500). The nmr spectrum showed a broad phenyl multiplet at 7.22 ppm, the tertiary hydrogen at 5.04 ppm as a broad peak, and the methyl at 1.96 ppm as a doublet, $J = 2$ cps.

β-Naphthyltetraphenylcyclopentadienol (Ie). This compound was prepared in 75% yield by reaction of β-naphthylmagnesium bromide with tetracyclone. It was crystallized from benzene, mp 214–215°.

Anal. Calcd for $C_{39}H_{28}O$: C, 91.4; H, 5.5. Found: C, 91.1; H, 5.7.

Pentachlorocyclopentadienyl Cation (V). Hexachlorocyclopentadiene (1.0 g) was added to 8.0 g of SbF_5, and the mixture was shaken at room temperature for 2 min. This solution, containing pentachlorocyclopentadienyl cation (as revealed by the esr spectrum, see Discussion), could be stored at Dry Ice temperature.

Ten such mixtures were poured into well-stirred methanol at room temperature, and an excess of sodium bicarbonate was added. The methanol was then removed *in vacuo*, and the residue was taken up in methylene chloride, dried, and distilled. The major products were dimers of hexachlorocyclopentadiene, but 5% of the material was volatile *in vacuo*. The principal component of this volatile material was hexachlorocyclopentadiene, but about 20% was identified as 1,1-dimethoxytetrachlorocyclopentadiene (VI) by comparison of its vpc retention time, nmr, and mass spectrum with those of an authentic sample. A control experiment showed that the authentic ketal (VI) could be recovered in 70% yield if it was dissolved in the methanol and SbF_5 was then added as in the quenching experiment. When SbF_5 was quenched into methanol containing hexachlorocyclopentadiene, the volatile product was recovered hexachloro compound with no detectable trace of the ketal (VI).

Electron Spin Resonance Studies. Solutions of the carbonium ions were frozen at 77 °K and then examined in a Varian esr spectrometer. The results are presented in the Discussion section.

Magnetic Susceptibility Measurements. The nmr method described by Evans[13] was used. Solutions of the cyclopentadienols and of the corresponding cations were prepared in CH_2Cl_2, and each solution was placed in an nmr tube along with a capillary containing pure CH_2Cl_2. The separation in the nmr between the CH_2Cl_2 line of pure solvent and that of solution as measured at room temperature and at $-54.6°$ for the alcohols, and at $-54.6°$ for the cations (temperature measured with a copper–constantan thermocouple inside the nmr tube). The results are presented in Table I. This method was also applied to diphenylpicrylhydrazyl and gave results in good agreement with the known magnetic susceptibility of this radical.

Rates of Reaction of *exo-* and *endo*-5-Norbornene-2-boronic Acid with Mercuric Chloride

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Contribution from the Department of Chemistry, Washington State University, Pullman, Washington 99163. Received September 26, 1966

Abstract: The rates of reaction of mercuric chloride with *exo-* and *endo*-5-norbornene-2-boronic acid, both of which yield nortricyclylmercuric chloride, have been measured in the presence of excess chloride ion in aqueous acetone buffered with potassium acid phthalate and phthalic acid. Aliquots were analyzed for unreacted boronic acid by removal of the mercury(II) with stannous chloride oxidation of the boronic acid with hydrogen peroxide and gas chromatography of the resulting dehydronorborneol. The *exo/endo* rate ratio is 400 ($\pm$40) at 25°, 270 at 45°. The rate law is $-d[RB(OH)_2]/dt = k[RB(OH)_2][HgCl_3^-][RCO_2^-][RCO_2^-]/[Cl^-]$. The mechanism and its relation to other electrophilic displacements at saturated carbon are discussed.

Cyclopropane rings may be opened or closed by processes involving electrophilic displacement at one carbon atom, usually accompanied by nucleophilic displacement at the other. Electrophilic displacement with inversion occurs in the reaction of *exo*-5-norbornene-2-boronic acid (I) with mercuric chloride to yield nortricyclylmercuric chloride (III), and has been shown qualitatively to be much faster than the corresponding retention process with the *endo* isomer II.[2]

Although concerted electrophilic displacements ordinarily occur with retention, inversion has been observed recently in alkaline ring openings of cyclopropanols.[3,4] However, the transition states appear to

inversion   **I**   or   *retention*   **II**   **III**
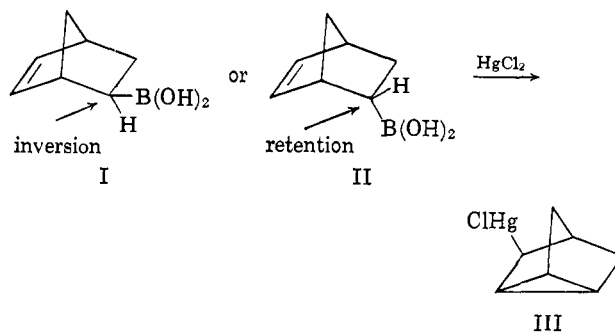
have a high degree of carbanion or S_E1 character. Ring opening by acid is clearly S_E2 but occurs with retention. An S_E2 reaction with preferred inversion evidently occurs in the bromination of quadricycloheptanedicarboxylic acid.[5]

(1) (a) We thank the National Science Foundation for financial support, Grant GP-2953. (b) Alfred P. Sloan Foundation Fellow.

(2) D. S. Matteson and J. O. Waldbillig, *J. Am. Chem. Soc.*, **86**, 3778 (1964).

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(4) A. Nickon, J. L. Lambert, R. O. Williams, and N. H. Werstiuk, *ibid.*, **88**, 3354 (1966).

(5) S. J. Cristol and R. T. LaLonde, *ibid.*, **80**, 4355 (1958).