# Electron Diffraction Studies of Free Radicals.[1] I. Indenyl

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**Abstract:** The decomposition products of diindenylcobalt, $Co(C_9H_7)_2$, have been studied by electron diffraction. An analysis of the experimental data showed the presence of indenyl free radical in the gaseous phase in a purity of at least 80%. This made possible a structural investigation of indenyl which produced the following results: $(C_1\text{–}H_1)_{av} = 1.072 \pm 0.02$ Å and $(C_1\text{–}C_2)_{av} = 1.415 \pm 0.01$ Å. The C–C bond-length average is found in good agreement with Hückel MO calculations. There is experimental evidence that the molecule possesses different C–C bonds, some of which seem to deviate more from the average than is predicted by HMO calculations. It is more likely that they fall in the range of 1.37–1.46 Å (±0.015) than in the theoretically predicted range of 1.398–1.431 Å. The bond angles of the best model, which cannot be claimed to be the only solution, are $\beta = 121°$ and $\alpha = 135°$ (Figure 1). Moreover, the described experiment represents the first example of an investigation of an unstable compound by electron diffraction. It proves that the method may be expected to be a powerful tool in the study of similar cases.

Electron diffraction (ED) has proved to be helpful in determining the structure of free-radical molecules. Complete structure determinations have been carried out for di-*t*-butyl nitroxide[2a] and triphenylmethyl.[2b]

Though radical species, these molecules possess features which prevent them from easy recombination and so stabilize the radical state. In principle, however, electron diffraction might be expected to supply satisfying information for radicals having a very short half-life. This paper presents, as a first example of the latter possibility, the investigation of the indenyl free radical.

The indenyl free radical was obtained by thermal decomposition of diindenylcobalt. The general scheme of the procedure, thermal decomposition of metal organic complexes, is a widely known source of free-radical molecules and is often applied in other fields.[3] It is astonishing that it has not yet been combined with the electron-diffraction technique, though, unfortunately, the author must admit that the present example is the fruit of sheer accident.

In 1965 ED pictures were taken of diindenylcobalt in order to determine the structure of this molecule. By the time the experimental radial distribution curve was obtained, it was clear that the molecule had decomposed during the experiment and the data were discarded.

At the same time an interest of the author in different electronic states of the cyclopentadienyl moiety, including studies of positively charged[4] and anionic cyclopentadienyl systems,[5,6] led to a search for a possible way to obtain more information on the cyclopentadienyl radical. Indenyl, in principle, is a substituted cyclopentadienyl free radical, so the discarded data were recovered and checked for the possibility of obtaining information on the indenyl radical. In the following the results of this investigation are presented.

## Experimental Section

The indenyl free radical has been produced by thermal decomposition of diindenylcobalt at 180° and 10 torr in the nozzle chamber of the Oslo diffraction apparatus. The reservoir in which the gas was heated was located 5 cm from the electron beam. The volatile compounds were thus able to flow immediately into the diffraction chamber where the electron diffraction patterns were recorded photographically. Two nozzle-to-plate distances were used, $d = 48.059$ and 19.351 cm, yielding two sets of plates. The optical densities obtained from these plates were added separately for each set and multiplied by the blackness and sector corrections. A polynomial of second order was subtracted from the 48-cm curve going through three points, at $s = 1.5$, 11.0, and 19.0, and a polynomial of third order was subtracted from the 19-cm curve going through $s = 7.0$, 13.0, 24.75, and 41.0. The resulting curves were multiplied by a modification function defined as $s/|f_C|\cdot|f_C|$ as described previously.[7] The intensities thus obtained are listed in Tables I and II, respectively. Their conversion into molecular intensities and the radial distribution curve (RD curve) followed the usual treatment.[8] The scattering factors used for calculating the theoretical intensities are those given by Cox and Bonham.[9] A sample of diindenylcobalt was kindly supplied by Professor E. O. Fischer and used without further purification. During this investigation a mass spectrum of decomposed $Co(C_9H_7)_2$ became useful. It was taken at 185° with an AEI-MS 9 mass spectrometer using a 70-V ionization potential.

## Results

A qualitative inspection of the experimental RD curve clearly indicates that significant decomposition of the parent molecule has taken place. That this is so can be seen by considering the difference between the theoretical RD curve for diindenylcobalt (Figure 2G) and the experimental RD curve (Figure 2A; note that the experimental curve is also represented by the dashed curves in the other figures). The decomposition is clearly established by the absence of the metal–carbon peak at about 2.1 Å in the experimental curve and by the differences in area that the experimental and theoretical RD curves possess when scaled with respect to the CC peak.

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(1) Contribution No. 1561 from the Chemical Laboratory of Indiana University. The author wishes to thank the National Science Foundation for their support of this work.

(2) (a) B. Anderson and P. Anderson, *Trans. Am. Cryst. Assoc.*, **2**, 193, (1966); (b) P. Anderson, *Acta Chem. Scand.*, **19**, 629 (1965).

(3) For example, P. J. Zandstra, *J. Chem. Phys.*, **40**, 612 (1964).

(4) H. P. Fritz and L. Schäfer, *J. Organometal. Chem.* (Amsterdam), **1**, 318 (1964).

(5) H. P. Fritz and L. Schäfer, *Chem. Ber.*, **97**, 1829 (1964).

(6) A. Sado, R. West, H. P. Fritz, and L. Schäfer, *Spectrochim. Acta*, **22**, 509 (1966).

(7) L. Schäfer and H. M. Seip, *Acta Chem. Scand.*, **21**, 737 (1967).

(8) A. Almenningen, O. Bastiansen, A. Haaland, and H. M. Seip, *Angew. Chem. Intern. Ed. Engl.*, **4**, 819 (1965).

(9) H. L. Cox and R. A. Bonham, *J. Chem. Phys.*, in press.

**Table I.** Experimental Intensities ($d$ = 19.351 cm) from $s$ = 7.00 to 41.75[a]

| | | | |
|---|---|---|---|
| 0.00 | −176.75 | −318.01 | −357.67 |
| −287.67 | −172.99 | −31.69 | 94.20 |
| 204.52 | 286.30 | 327.49 | 332.75 |
| 282.01 | 228.51 | 177.52 | 142.37 |
| 108.75 | 55.79 | 13.52 | −20.42 |
| −26.68 | −29.68 | −43.34 | −47.54 |
| 0.00 | 127.82 | 284.31 | 390.96 |
| 410.97 | 370.34 | 259.57 | 208.22 |
| 167.83 | 154.43 | 126.29 | 74.72 |
| 54.68 | 13.69 | −29.41 | −58.95 |
| −81.48 | −70.59 | −19.35 | 63.69 |
| 158.93 | 252.20 | 330.58 | 375.38 |
| 398.09 | 344.06 | 263.91 | 159.63 |
| 54.10 | −8.32 | −31.49 | −45.33 |
| −53.15 | −40.84 | −3.77 | 39.37 |
| 73.78 | 101.55 | 97.99 | 104.66 |
| 109.50 | 109.59 | 111.15 | 70.52 |
| 72.95 | 63.46 | 41.35 | 0.00 |
| −41.59 | −89.90 | −80.51 | −77.24 |
| −68.00 | −41.19 | −16.78 | 26.33 |
| 83.14 | 103.20 | 110.52 | 99.55 |
| 105.34 | 91.98 | 63.55 | 54.48 |
| 45.51 | 36.53 | 17.69 | 12.81 |
| 9.47 | 9.31 | 30.47 | 54.27 |
| 99.38 | 122.82 | 137.92 | 165.21 |
| 167.63 | 183.74 | 156.70 | 160.07 |
| 151.79 | 159.72 | 107.75 | 93.12 |
| 47.60 | 14.51 | −26.24 | −26.90 |
| −22.82 | 31.48 | 42.21 | 72.24 |
| 97.91 | 121.12 | 154.36 | 191.62 |
| 168.00 | 131.62 | 115.41 | 117.92 |
| 82.72 | 50.23 | 27.64 | 46.18 |
| 61.79 | 47.88 | 37.69 | 68.61 |
| 79.13 | 81.24 | 92.79 | 54.08 |
| 0.00 | −51.23 | −74.81 | −80.90 |

[a] $\Delta s = 0.25$. Table develops horizontally.

**Table II.** Experimental Intensities ($d$ = 48.059 cm) from $s$ = 1.25 to 19.75[a]

| | | | |
|---|---|---|---|
| | 9.078 | 0.000 | −0.737 |
| −2.773 | −8.130 | −9.214 | −3.363 |
| 6.633 | 16.219 | 20.926 | 19.682 |
| 13.519 | 8.965 | 10.406 | 20.411 |
| 37.623 | 58.006 | 75.343 | 83.152 |
| 78.956 | 67.940 | 54.630 | 39.527 |
| 25.383 | 10.251 | 0.354 | −3.301 |
| 0.874 | 9.799 | 18.120 | 24.716 |
| 28.958 | 30.396 | 30.440 | 27.085 |
| 21.336 | 14.074 | 10.040 | 6.771 |
| 0.000 | −7.660 | −16.055 | −23.050 |
| −27.636 | −30.194 | −32.850 | −35.295 |
| −30.979 | −19.587 | −5.697 | 1.424 |
| 0.095 | −6.091 | −17.299 | −23.748 |
| −27.251 | −31.296 | −35.890 | −39.243 |
| −40.374 | −39.997 | −41.028 | −43.095 |
| −45.683 | −46.360 | −43.087 | −33.023 |
| −25.599 | −17.042 | −9.231 | −3.400 |
| 0.000 | −1.552 | −8.010 | −12.693 |

[a] $\Delta s = 0.25$. Table develops horizontally.

The theoretical RD curve for indenyl alone, however, also cannot reproduce the experimental data. Very different models (Figures 2E and 2D) have in common the feature of producing too small an area in such a way that this effect cannot be compensated by differences in the experimental background.

In fact, the area of the experimental RD curve lies between that of an undissociated and that of a completely dissociated diindenylcobalt. It has, therefore, been assumed that the gaseous phase of the experiment consisted of a mixture of free indenyl and a small concentration of undissociated or partly dissociated diindenylcobalt. This assumption corresponds to the experience that in most reactions producing radicals by thermal decomposition the yield is not exactly 100%. Moreover, the mass spectrum of $Co(C_9H_7)_2$, taken under similar conditions as the ED data, shows a signal at an $m/e$ value corresponding to $Co(C_9H_7)_2$. The relative intensity of this signal is 26 compared to a value of 100 for signals at $m/e$ values corresponding to indenyl. Because of the different cross sections, these intensities do not give reliable information about the concentrations of the compounds involved. They show, however, that the volatile products of a pyrolysis of $Co(C_9H_7)_2$ at 180° contain a considerable amount of undissociated parent molecule. With this in mind one must assign the shoulder in the 2.1-Å area of the experimental RD curve to the metal–carbon contributions of undissociated $Co(C_9H_7)_2$. Its position corresponds very well to the 2.1-Å value of the metal–carbon bond found earlier in an X-ray investigation of diindenyliron[10] which should be expected in the same region. Its height (note that there is a big peak instead of a shoulder at 2.1 Å in the RD curve of 100% $Co(C_9H_7)_2$, Figure 2G) allows an estimation of the concentration of undissociated $Co(C_9H_7)_2$.

Such an estimation is possible using a least-squares procedure which refines a parameter $\alpha_{ij}$ for the metal–carbon bond in the expression for the modified intensities

$$I(s) = \text{constant} \sum_{i \neq j}\sum \alpha_{ij} g_{ij/kl}(s) \times \exp(-u_{ij}{}^2 s^2/2) \frac{\sin[(r_{ij} - ks^2)s]}{r_{ij}}$$

(for explanation of terminology see ref 7). This parameter is equal to 1.0 for each distance $r_{ij}$ belonging to a molecule which is present at a concentration of 100%. It is found to be less for any concentration less than 100%.

In the present case a concentration of about 10% has been found for the metal–carbon bond related to diindenylcobalt. There are several reasons for a considerable uncertainty in this value. Usually two parameters can be refined from one peak of the RD curve, a distance $r_{ij}$ and its vibrational amplitude $u_{ij}$. A third parameter may be dependent on one of the others. In this case $\alpha_{ij}$ is dependent on $u_{ij}$ and *vice versa*. When $u_{ij}$ for this peak is varied between 0.035 and 0.060 Å, $\alpha_{ij}$ was found to vary between 0.085 and 0.095 (8.5–9.5% metal complex). In addition the situation is complicated by the fact that, for indenyl, theoretical models can be found which contribute little (Figure 2E) or very much (Figure 2D) to the 2.1-Å shoulder. A description of these models will be given below. This, of course, has its effect on the value found for the metal–carbon concentration. Another possible uncertainty which must be considered is that the cobalt complex in question need not be the diindenylcobalt moiety. The metal–carbon shoulder at 2.1 Å in the experimental RD curve might very well be produced by a monoindenylcobalt radical. In the mass spectrum there is a peak with a relative intensity of 8.6 with a mass-to-charge ratio corresponding to such a half-sandwich. Of course, such a compound might

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(10) J. Trotter, *Acta Cryst.*, **11**, 355 (1958).

rather have been generated by electron impact than by thermal decomposition in the mass spectrometer. Its existence, however, shows that it is not possible to exclude it *a priori* from the ED investigation.

In spite of these ambiguities, one statement can be made as follows. During the experiment, at most about 10 ± 2% diindenylcobalt or, in case all metal–carbon bonds corresponded to a half-sandwich, at most 20% monoindenylcobalt was present.

This means at least about 80% of the gas mixture of the experiment consisted of the indenyl free radical. The data thus obtained are satisfactory for an investigation of this molecule. In fact, 10% of diindenylcobalt contributes little to the experimental data as is seen from Figure 2F which plots 10% of Figure 2G against the experimental RD curve. Therefore, the results described later have been found to be independent of whatever kind of model is chosen for diindenylcobalt: one having the ligands freely rotating, staggered, eclipsed, or *gauche*. The *gauche* model has been used in the following as this is the configuration of the iron homolog in the crystal,[10] although this shall not be taken to mean it is also the expected configuration of the gaseous state.

The refined metal–carbon distance is also dependent on how much is contributed to the 2.1-Å area by the model chosen for indenyl. It may vary between 2.05 and 2.09 Å and so is found in a reasonable region compared to the 2.1-Å crystal value for diindenyliron.[10] Again, by consideration of Figure 2F, it can be seen that this ambiguity does not affect the results described below for indenyl. A 20% concentration of monoindenylcobalt would not have any bigger an effect, as it contains only one ring. The weight of the metal–carbon peak for this compound is only half of that of diindenylcobalt. The C–C and C–H contributions are even less as there are no interligand distances.

It might be argued at this point that, if it were not for the mass spectrum, it was not necessary at all to take any diindenylcobalt contribution into consideration. One might say for instance that the 10% diindenylcobalt contribution (Figure 2F) looks like an envelope correction to the RD curve of indenyl alone (Figure 2D).

Such a correction, however, would be too pointed in the 1.4-, 2.1-, and 4.0-Å areas and would imply a background function that would not be legal. The uncertainty, introduced by this into the make-up of minor constituents, is admittedly an unfortunate aspect of this experiment. In future experiments it is hoped that this uncertainty can be removed in a way suggested below.

In the previous section, the observed decomposition of diindenylcobalt has been postulated to proceed as dissociation of diindenylcobalt into cobalt and free indenyl or into cobalt, monoindenylcobalt, and free indenyl without giving further evidence as to why no other split of the molecule has been assumed to exist. Two facts can be mentioned as a justification. As is well known in the case of ferrocene,[3] thermal decomposition at 800° leads to a radical split of the molecule yielding $C_5H_5$ and iron. This reaction should run the same in the case of diindenylcobalt. As diindenylcobalt is a much more unstable compound than ferrocene, dissociation is observed at much lower temperatures.

A second argument is based on the electron-diffraction data. The features of the experimental RD curve can all be assigned to the indenyl free radical. All peaks expected for indenyl are present (Figure 2D) in the proper amounts. At 1.1 Å the C–H bonds are found and the C–C bonds at 1.4 Å. Nonbonded distances across a valence angle find their peaks in the 2.1–2.5 Å region. Distances across the benzene ring are seen at 2.8 Å, and inter-ring distances are observed up to 4.7 Å. The latter peak corresponds to the distance between atoms 2 and 6 and 2 and 5 (Figure 1). Its presence confirms that the indenyl system has remained intact under measurement. The fact that it is the last peak found shows that there has been little if any dimerization. This does not hold for the mass spectrum which shows signals with relative intensity of 26.7 corresponding to diindene. This fact seems plausible if one compares the 2-m distance between the decomposition chamber and the detector in the mass spectrometer to the 5-cm distance between the heated reservoir and the electron beam in the ED diffraction unit.

It could be argued that, because of unfavorable experimental conditions, the parent substance had undergone an oxidative destruction, in spite of careful exclusion of oxygen during all parts of the experiment.

In a solution of diindenyliron such a reaction is known to yield indenone,[11] which, roughly, could produce an RD curve which is similar to that of indenyl. Though it is not known whether gaseous diindenylcobalt reacts in the same way, 20 different models of indenone were calculated. It was found that the additional C–O bond and the absence of one C–H bond introduce significant and principal variations into the RD curve, so the ED data would appear to exclude the presence of an appreciable amount of indenone during the experiment. The same holds for the mass spectrum which shows no signal at an $m/e$ value corresponding to indenone.

The refinement of a best model for the indenyl free radical was carried out by adding the results of various models of the radical to an RD curve with a 10% contribution from undissociated diindenylcobalt to give the best fitting theoretical RD curve. Two models for indenyl shall be described here. Some hundreds have been calculated. The first model which determines average quantities in the structure of indenyl was obtained in the following way. First the parameters of the six-membered ring were determined. The peak at 2.8 Å is only dependent on the average angle and average bond length in the six-membered ring. By assuming that the average valence angle was $\beta = 120°$ (Figure 1), the average C–C bond length for the six-membered ring is refined as 1.395 Å.

Having fixed this parameter, the determination of the average bond length in the five-membered ring is possible by refinement from the 1.4-Å peak. It is then found to be 1.432 Å. The average C–H bond for indenyl refined from the peak at 1.1 Å is found to be 1.072 Å.

The best reproduction of the shoulder at 2.1 Å which contains $C_1$–$H_2$ distances in this model was only possible by assuming that the C–H bond length in the

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(11) J. H. Osiecki, C. J. Hoffmann, and P. D. Hollis, *J. Organometal. Chem.* (Amsterdam), **3**, 107 (1965).

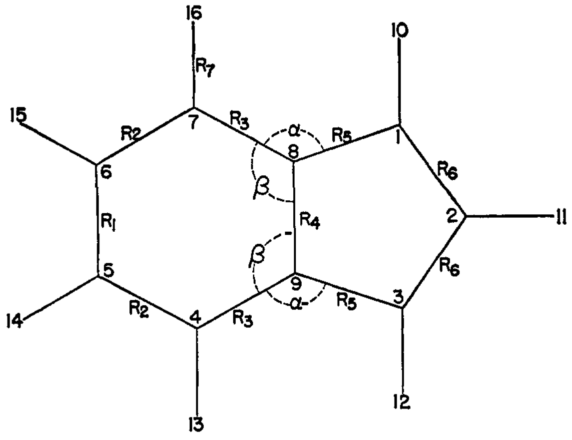

Figure 1. Indenyl. Numbering of the atoms and parameters.

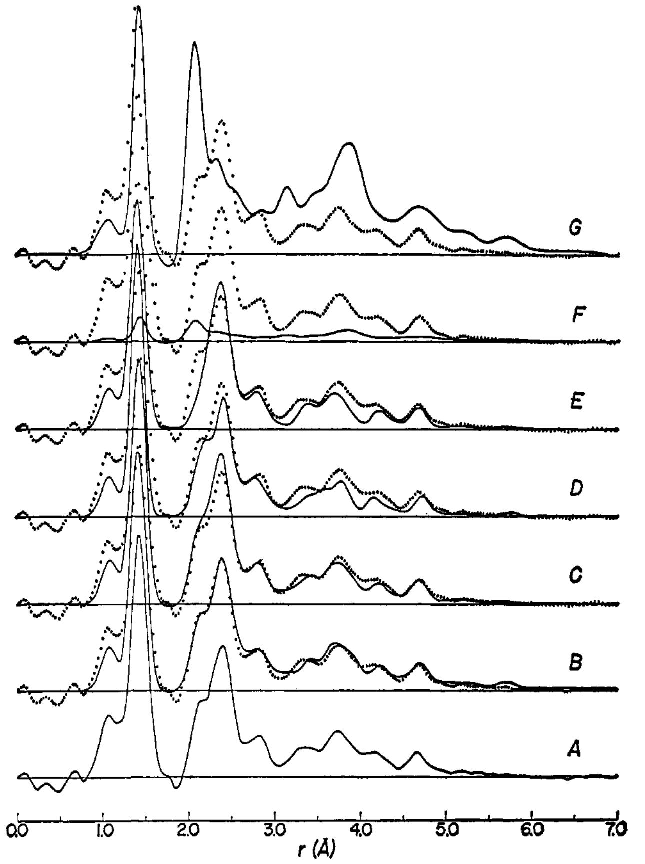

Figure 2. Experimental and theoretical radial distribution curves: (A) experimental (Fourier inverted experimental intensity from $s$ = 1.25 to 41.75 including theoretical values from model C between $s$ = 0.0 and 1.25; contributions of other models in this range did not cause important changes, so the same experimental curve is plotted as a dashed line on top of all theoretical curves); (B–E) theoretical curves for indenyl described in the text; (F–G) theoretical curve for 10 and 100% diindenylcobalt scaled to the experiment with respect to the C–C peak. All curves were Fourier inverted with an artificial damping factor $K$ = 0.0015 Å$^2$.

five-membered ring is different from that in the six-membered ring (1.053 and 1.105 Å, respectively; a further comment on this detail will be given with the description of the second model).

With these parameters and the assumption that the molecule possesses $C_{2v}$ symmetry, the peak at 4.669 Å allowed the determination of the angle $\alpha$. It was found to be 131.32°. This value has not been corrected for possible shrinkage effects. With these parameters the geometry of the molecule is determined. Figure 2E gives the resulting theoretical RD curve plotted on top of the experimental curve. The latter was obtained by inverting the experimental intensities including theoretical values from $s$ = 0.0 to 1.25.

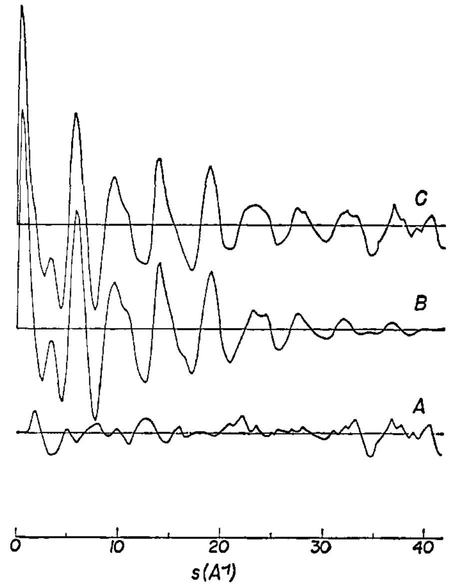

Figure 3. Experimental and theoretical intensities: (A) difference between experimental and theoretical curves (C − B); (B) theoretical intensities for model C, Figure 2; (C) experimental intensity curve.

By adding to Figure 2E the mentioned contribution of diindenylcobalt with a refined 1.438-Å average C–C bond, Figure 2C was obtained. It was found that the fit was best when 80% of the metal–carbon peak was assigned to a monoindenylcobalt radical. It must be emphasized that this figure cannot establish a proof for the existence of such a "half-sandwich." Inasmuch as this compound is unlikely to exist, the fact that it had to be taken into consideration is a disadvantage of the described model. This disadvantage could be removed in the best-fitting model which is described below.

The resulting theoretical RD curve shows good over-all agreement in shape compared with the experimental curve. There is a discrepancy in area in the 2.1–2.4-Å region which is typical for this model. The area difference in the 1.1-Å region was found for all models. It is probably due to hidden background errors which usually are found in the Fourier inverted intensities between $r$ = 0.0 and 1.2 Å. Changes in the background caused considerable variations in this area of the radial distribution curve. It was found, however, that background changes produced no effect on the RD curve in the region past 1.2 Å.

The theoretical intensities of the described model are given in Figure 3B, the experimental intensities in Figure 3C, and their difference curve in Figure 3A.

So far a model has been produced which shows average quantities. In reality the molecule should possess distinctly different C–C bonds and distinctly different valence angles. This holds irrespective of whether or not it is considered as a substituted cyclopentadienyl radical showing a static or dynamic

**Table III.** Average Parameters of Indenyl Compared to Corresponding Values in the Cyclopentadienyl Anion and Benzene[a]

| | Indenyl | | | Cyclopentadienyl anion | Benzene |
|---|---|---|---|---|---|
| | Six-membered ring | Five-membered ring | Total av | $C_5H_5$[16] | $C_6H_6$[15] |
| $C_1$–$C_2$ | 1.395 ± 0.005 | 1.432 ± 0.005 | 1.415 ± 0.004 | 1.429 ± 0.003 | 1.397 ± 0.003 |
| $u_{C-C}$ | 0.068 ± 0.005 | 0.054 ± 0.005 | 0.066 ± 0.005 | 0.047 ± 0.003 | 0.0455 |
| $C_1$–$H_1$ | | | 1.072 ± 0.020 | 1.116 ± 0.012 | 1.082 ± 0.003 |
| $u_{C-H}$ | | | 0.069 ± 0.020 | 0.084 ± 0.012 | 0.073 |

[a] Values are in Å; $u_{ij}$ is the vibrational amplitude of a distance $r_{ij}$. The deviations for the C–C bond parameters are based on the actual variations which were found when several different empirical envelopes were drawn to the purely experimental radial distribution curve in a range that covered or even exceeded the range of legal envelopes. The standard deviation of the average C–C bond if refined from the Re-Fourier inverted experimental C–C peak in all cases was of the order of magnitude of $10^{-4}$ to $10^{-3}$. All other quoted error limits are conventional error limits following the usual estimation; *e.g.*, T. Motzfeld, Thesis, Oslo, 1966.

Jahn-Teller effect,[12] or whether it simply is distorted as predicted by the Hückel MO calculations for indenyl.[13,14] That this must be so can be shown by the electron-diffraction data. By inspecting Table III, it is found that the vibrational amplitudes refined for the described model are much too big compared to the corresponding figures found for benzene[15] and the cyclopentadienyl anion[16] in ferrocene. The C–C bond amplitude found for benzene is 0.045 Å;[15] the same figure in the six-membered ring of the indenyl of this model is 0.068 Å. For the cyclopentadienyl anion the value is 0.047 Å, and here 0.054 Å.

At this point it must be emphasized that a vibrational amplitude of 0.068 Å is very probably not due to experimental errors. A good reproduction of spectroscopic values found for vibrational amplitudes can be achieved by electron diffraction and has also been done by the author himself in the case of $RuO_4$.[7] In another work based on data taken with the same machine at approximately the same time and by the same team,[17] it is claimed that root-mean-square amplitudes for C–C bonds are reproducible with an error not greater than 0.0002 Å. Quite apart from that number, the error, in any case, should not be as big as 0.02 Å as it would have to be in the present case.

One may discuss at this point how reasonable it is to compare the five- and six-membered rings of indenyl to the cyclopentadienyl anion and free benzene, respectively. Apart from the similar geometry of planar rings containing double bonds there are certainly differences to be expected between radicals and anions. Too, any sharing of the odd electron by the six-ring should loosen the whole system. However, it is not expected that a vibrational amplitude could be found as high or even higher than that for a C–C bond in saturated hydrocarbons where the value is 0.055 Å.[18]

It is common experience that unusually large vibrational amplitudes are found by ED studies in cases where closely spaced distances are replaced by one average value. It is thus possible to conclude from the electron-diffraction data that the bond lengths in indenyl must be different.

For the present investigation, this meant a new model had to be found constructed with different bond lengths and different valence angles. In addition the new model should explain the experimental data by use of one value for all C–H bonds as these are not expected to be different for the five- and six-membered rings in indenyl. As far as the model given above is concerned it must be emphasized that its picture of the average represents the best mathematical fit which could be obtained. A reason for this is the fact that a multiplicity of different bond lengths evokes a multiplicity of different nonbonded distances. This leads to an avalanche of unknown parameters. As their number exceeds the numbers of resolved peaks in the RD curve, they cannot be reasonably refined by least squares. In this case the number of unknown independent parameters for indenyl is equal to 9: six C–C bonds, one C–H bond, and two independent angles ($\alpha$ and $\beta$, Figure 1). The presence of diindenylcobalt introduces three more parameters: the concentration, the metal–carbon bond, and the average carbon distance in the complex. Thus there are 12 unknown parameters against eight peaks and one shoulder. This constellation prevents finding of an accurate solution.

The results described in the following, therefore, have been obtained by a visual method. To this purpose a computer program was written which, with bond lengths and angles as the only input parameters, calculated intensities, and from these a theoretical RD curve. After addition of a 10% diindenylcobalt contribution, the results were plotted on top of the experimental values. By this means hundreds of models could be calculated and inspected until the most satisfying was obtained (Figure 2B).

Since the experimental data were known from $s = 1.25$, in all models the same theoretical values were used between $s = 0.0$ and 1.25 (taken from the intensities corresponding to curve C, Figure 2). In view of the low experimental $s$ limit, this is a legal procedure and there is no need to make the experimental curve self-consistent with each model. A $\delta$ function error in the $s = 0.0$–1.25 area could produce a signal in the RD curve with a wavelength no shorter than ~5.0 Å. This could not possibly change individual features in the experimental RD curve.

The following parameters were used (Figure 1): $\alpha$, the angle between the five- and six-membered ring; $\beta$, one independent valence angle in the six-membered ring; $R_1$–$R_6$, six different, independent C–C bond lengths; and $R_7$, one C–H bond length for the entire molecule.

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During the investigation $\alpha$ was allowed to vary between 127 and 137°, in steps of 2°. $\beta$ varied between 115 and 125°, in steps of 1°. The variations were executed by a computer double DO-loop, so that all possible combinations were covered.

For the C–C bonds several sets of values were tested in combination with $\beta$ and $\alpha$ variations. As a starting set the values predicted by MO calculations were used. The HMO tables by Heilbronner and Straub[18] were used for the indenyl bond orders. From the bond orders, the bond lengths were calculated using formulas given by Longuet-Higgins and Salem[19] and Coulson and Golebiewski.[20] The results are listed in Table IV. Though both sets agree very well with the value of 1.415 Å found experimentally for the average C–C bond length, the latter set was used. The values in this set show greater deviations from the average which is required by the experimental data.

**Table IV.** C–C Distances for Indenyl (Test Values in Å)[a]

| | $H_0{}^a$ | $H_0{}^b$ | $H_1$ | $H_2$ | $H_3$ |
|---|---|---|---|---|---|
| $R_1$ | 1.401 | 1.398 | 1.384 | 1.370 | 1.356 |
| $R_2$ | 1.405 | 1.403 | 1.417 | 1.431 | 1.445 |
| $R_3$ | 1.409 | 1.408 | 1.394 | 1.380 | 1.366 |
| $R_4$ | 1.423 | 1.425 | 1.439 | 1.454 | 1.468 |
| $R_5$ | 1.428 | 1.431 | 1.445 | 1.460 | 1.474 |
| $R_6$ | 1.401 | 1.398 | 1.384 | 1.370 | 1.356 |
| Average | 1.411 | 1.410 | 1.410 | 1.411 | 1.411 |

[a] Set $H_0{}^a$ was obtained following ref 19, set $H_0{}^b$ following ref 20. The sets $H_1$, $H_2$, and $H_3$ were obtained from set $H_0{}^b$ by contracting its shorter and expanding its longer distances 1, 2, and 3%, respectively.

Another set was obtained by inverting the character of the Hückel solution and disregarding chemical reasoning, replacing the bigger distances by their small neighbors and *vice versa*.

Finally a series was started which inflated stepwise the longer distances by 1% of their value and, at the same time, contracted the small distances in the same way. This was done up to a 3% deviation of the starting values (figures in Table IV). With a deformation of 2 and 3%, an equally good fit between experimental and theoretical RD curves was found (Figure 2D). This proved to be the best fit of all investigated models. This result is shown with a 10% diindenylcobalt addition in Figure 2B. This was the only one of the tested models which allowed a good reproduction of the C–C peak when vibrational amplitudes $u$ = 0.045 Å were used. The experimental vibrational amplitudes found for the total average C–C bond (Table III) from experimental intensities containing no theoretical data between $s$ = 0.0 and 1.25 seem to be in favor of the distance set $H_2$ (Table IV). This may be deduced from the following. Theoretical intensities were calculated from the distance sets $H_0{}^b$, $H_1$, $H_2$, and $H_3$ (Table IV), with vibrational amplitudes of 0.045, 0.050, and 0.055 Å, respectively, yielding 12 different theoretical curves. From each curve one average C–C bond was refined and its vibrational amplitude listed in Table V. From this table it is seen that set $H_2$ (with vibrational amplitudes 0.050 and 0.055) is the only one from which an average C–C bond is refined with a vibrational amplitude lying in the range of the experimental value. Therefore set $H_2$ must be preferred from set $H_3$ though both gave an equally good fitting theoretical RD curve. It must be mentioned that the least-squares refinement in all cases was executed in the same way. All intensities were in the limit of $s$ = 1.25 and 41.75 since the experimental data are known in these limits. Too, in all functions, experimental and theoretical, the identical weighting scheme was applied giving less weight during refinement to data between $s$ = 1.25 and 5.0 and $s$ = 35.0 and 41.75.

**Table V.** Vibrational Amplitude of One Average C–C Bond Refined from Theoretical Intensities Calculated for Distance Sets $H_0{}^b$, $H_1$, $H_2$, and $H_3$ (Table IV) with Vibrational Amplitudes of 0.045, 0.050, and 0.055 Å

| | 0.045 | 0.050 | 0.055 |
|---|---|---|---|
| $H_0{}^b$ | 0.0468 | 0.0516 | 0.0565 |
| $H_1$ | 0.0516 | 0.0568 | 0.0594 |
| $H_2$ | 0.0616 | 0.065 | 0.0687 |
| $H_3$ | 0.0764 | 0.0786 | 0.0811 |

It is true that the given theoretical RD curve still shows some deviations from the experimental data, and the author admits to having seen much better agreement between experiment and theory in simpler cases. In Figure 2B some peaks still are slightly decentered, and some areas still do not quite overlap. In all other models tested in this investigation, however, peaks were grossly decentered and areas were in big disagreement with each other.

The angle values of the described best fitting model are $\alpha$ = 135° and $\beta$ = 121°. If all C–C parameters are changed at the same time by 1%, the fit becomes very poor. This, of course, does not mean that the error limit of the individual bond length is 1%. The individual figures are very uncertain and the model described above is no unique solution. Only the probable limits within which the individual C–C bonds should be found can be stated. This provides, however, some new information, since the experiment seems to indicate that the deviation from the average is greater than predicted by HMO calculations. The limits within which the C–C bonds should be found are more likely 1.37 and 1.46 Å (± 0.015) than 1.398 and 1.431 Å as in set $H_0{}^b$.[21]

Since this result is merely based on unusually high experimental vibrational amplitudes of the C–C bonds, it must be reminded that such a value, too, could be explained by a Jahn–Teller effect. In this case, at 180°, three quickly mutating systems have been predicted[22] for the cyclopentadienyl radical. The quick mutations could give rise to an observed vibrational amplitude which is much too big. The author would not like to have the result of this investigation understood as favoring the existence of a Jahn–Teller effect in the case of indenyl. However, he must admit that he cannot exclude such a possibility on the basis of his data.

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(19) H. C. Longuet-Higgins and L. Salem, *Proc. Roy. Soc.* (London), **A251**, 172 (1959).

(20) C. A. Coulson and A. Golebiewski, *Proc. Phys. Soc.* (London), **78**, 1310 (1961).

(21) It is not possible to exclude that this expansion of the C–C bond distance range is due to the observation of the molecule in some excited state following the decomposition.

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It is felt that the analysis has been carried as far as it can be reasonably expected. Any conclusion based on further subtleties would be unreliable since the purity of the investigated material was only 80%. Further refinements in the parameters might be compensated by changing the concentration or structure of the diindenylcobalt contribution. Up to this point, however, the parameters in their limits are little affected by the model chosen for the 10% diindenylcobalt model.

## Discussion

Two results were brought about by this investigation. First, information was obtained concerning the structure of the indenyl free radical. Though the more sophisticated second model described above does not represent a unique solution as far as the absolute values of its parameters are concerned, it establishes some likely structural features for indenyl. Thus, the data indicate that the molecule is constructed from a set of distinctly different C–C bonds. Their average is in good agreement with HMO calculations. In addition the experiment favors the assumption that some of the C–C bonds deviate more from the average than is predicted by HMO calculations.

Secondly, this study proves that the method of electron diffraction may be successfully applied to the investigation of highly unstable compounds. The procedure to be followed consists in the production of the desired molecules as close to the electron beam as is possible. As far as pyrolysis of the parent molecule is involved, a considerable improvement of the experimental technique used in the investigation at hand may be expected. Thus, uncertainties were introduced into the results of this work by the presence of undissociated starting material. This disadvantage might be removed by recording the ED patterns at different temperatures in order to find the optimal experimental conditions. As a valuable by-product, thermodynamic data might be obtained, as has already been done for another case recently studied in this laboratory.[23]

As a useful tool in such an investigation, a high-temperature nozzle has been designed, having a heated filament which makes it possible to obtain temperatures up to 1000°. With this, work has been started in an attempt to produce cyclobutadiene ($C_4H_4$), cyclopentadienyl ($C_5H_5$), cycloheptatrienyl ($C_7H_7$), and fluorenyl ($C_{13}H_9$), as well as a variety of other similar compounds.

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# Anodic Oxidation Pathways of Substituted Triphenylamines. II. Quantitative Studies of Benzidine Formation

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**Abstract:** A previous study concerned a general, qualitative picture of the anodic oxidation of triphenylamines in acetonitrile leading to substituted benzidines as products. The rates of the benzidine coupling reactions now have been measured. Marked substituent effects on these rates are shown to be qualitatively consistent with simple HMO reactivity parameters. A fairly complete picture of the anodic oxidation pathways of substituted triphenylamines is presented.

A previous study developed a general, qualitative picture of the behavior of substituted triphenylamines upon anodic oxidation in acetonitrile.[2] Two extremes in the oxidation pathways were noted. If the triphenylamine was completely *para* substituted, stable monocation radicals were obtained which could be completely characterized by the electrochemistry and electron paramagnetic resonance (epr) spectra. At the other extreme, with completely unsubstituted triphenylamine, the initial cation radical rapidly coupled to form the tetraphenylbenzidine which subsequently underwent further oxidation. The general scheme of this process is adequately described in part I. A few partially *para*-substituted triphenylamines were studied and *p*-benzidine formation was indicated but not unequivocally proven in all cases.

The present results have extended the initial studies to show that *p*-benzidine formation is the predominant coupling reaction. Furthermore, the marked substituent effects on the rates of benzidine formation

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(1) Author to whom correspondence should be addressed.

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