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## Circular dichroism of an optically active benzene chromophore-1-methylindan\*

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The gas phase circular dichroism and absorption spectra of a conformationally stable, optically active benzene chromophore,  $S \cdot (+)$ -1-methylindan, has been measured from 280 to 170 nm. The structure of the CD spectrum differs from that of the absorption in the  $B_{1u}$  region and this observation is interpreted as evidence for the presence of a  $\sigma - \pi^*$  or  $\pi - \sigma^* E_{1g}$  state in addition to the  $\pi - \pi^* B_{1u}$ state. Also, the CD spectrum near 190 nm requires the conclusion that an additional electronic state is located between the analogs of the  $B_{1u}$  and  $E_{1u}$  states. This state is assigned as  $E_{2g}$ , in agreement with consistent theoretical predictions. The observed CD spectra can be accounted for in a consistent manner on the basis of a scheme which uses the results of parametrized calculations of coupled-oscillator contributions and one-electron term calculation results due to Caldwell and Kauzmann for the molecule studied.

### I. INTRODUCTION

The excited states of benzene have been the subject of extensive studies and discussions.<sup>1</sup> The transitions to the lowest valence shell  $\pi - \pi^*$  excited states include the forbidden  $B_{2u}$  and  $B_{1u}$  transitions and the electric dipole allowed and therefore intense  $E_{1u}$  transition. Theoretical calculations have consistently predicted<sup>2</sup> in addition an  $E_{2e}$  excited state in the same spectral region, but experimental evidence for it is sparse. Bonneau and others<sup>3</sup> have investigated the absorption by molecules laser pumped into the excited  $B_{2u}$  state. An intense absorption was observed which has been assigned<sup>4</sup> as the  $B_{2u} \rightarrow E_{2g}$  transition which is inplane dipole allowed. Some evidence for an additional excited state has also been reported<sup>5</sup> near the  $B_{1u}$  state on the basis of an inelastic electron impact study. Interest in obtaining further and more definitive evidence for the  $E_{2r}$  state was one of the motivations for the present work.

In this connection there seemed to be an indication to study the circular dichroism spectrum of an optically active benzene chromophore. The CD spectrum has the advantage over the absorption spectrum inasmuch as it may be positive or negative for different electronic transitions. As a result, more structure often appears due to sign changes in regions where the absorption does not exhibit any distinctive features. The substance chosen for this investigation was 1-methylindan. This is a conformationally stable molecule which had been the subject of a theoretical study by Caldwell and Kauzmann.<sup>6</sup> These authors calculated the rotatory strengths for the  $B_{2u}$ ,  $B_{1u}$ , and  $E_{1u}$  benzenelike states using the one-electron formulation.<sup>7</sup> Their results are included in Table V.

Tinoco<sup>8</sup> has presented a formulation for the calculation of rotatory strengths including all terms which appear in first-order theory. In the oneelectron term a higher state is mixed into the excited state involved in the transition, generating a small magnetic or electric transition moment parallel to the allowed electric or magnetic transition moment of the symmetric chromophore. Another term, often referred to as the dipole-dipole term (or coupled oscillator model<sup>9</sup>), arises due to the interaction of two noncoplanar electric transition moments on two different chromophores in the same molecule. The other terms discussed by Tinoco<sup>8</sup> will not be considered here and are assumed to be small.

In the present work the gas phase CD and absorption spectra of 1-methylindan were measured in the spectral region 270–150 nm using an instrument specially developed for the vacuum ultraviolet and which has previously been described.<sup>10</sup> The dipole-dipole term contributions to the rotatory strengths of the  $B_{2u}$ ,  $B_{1u}$ , and  $E_{1u}$  states have been calculated on the basis of some assumptions and by using a limited number of adjustable parameters. The results of Caldwell and Kauzmann<sup>6</sup> for the one-electron term contributions were also used. In this manner the observed CD spectrum could be accounted for in a consistent manner. Also, strong evidence for the  $E_{2g}$  state and one additional state in the  $B_{1u}$  region was found.

### **II. EXPERIMENTAL DETAILS**

### A. Spectroscopic

The instrument used in this work has been previously described.<sup>10</sup> Several basic modifications have been made on the original design, however, to increase the performance capabilities. Schematic representations of the optical and electronic systems are given in Figs. 1 and 2. The commerical Hinteregger hydrogen lamp has been further



FIG. 1. Schematic representation of the optical system of the circular dichroism instrument (mono, monochromator; mod, modulator; sep. split, separating slit; L, lens; PMT, photomultiplier tube).

modified to force the hydrogen gas to flow through the capillary, and a thoriated tungsten point has been placed in the air-cooled cathode to stabilize the arc. With these changes and using a pressure of 10-12 mm Hg of hydrogen, the lamp can be operated at a current of 0.5 A with a voltage drop of 2 kV.

The collimating lens is made of lithium fluoride with a focal length of 12 cm. The polarizing prism is an air-spaced  $40^{\circ}$  Wollaston prism of magnesium fluoride with an angular separation of the emergent beams of 1.4°, twice that of the 40° Rochon prism used previously. The circular polarizing element is a stress plate modulator<sup>11</sup> of calcium fluoride, Model PEM-2, manufactured by Morvue Electronics, Tigard, Oregon.

The sample cell was made of glass, 20 cm long, with polished lithium fluoride windows cemented on with epoxy. An arm of the cell extended outside the vacuum chamber in such a manner that freezing mixture baths could be used to control the vapor pressure in the cell according to standard gas phase spectroscopic technique.

The two oppositely polarized beams are separated by a separating slit (Fig. 1). The remaining beam is focussed onto the slit-shaped cathode of the photomultiplier which is separated from the vacuum chamber by an LiF window. The photomultiplier housing is flushed with dry nitrogen for work below 200 nm. The photomultiplier tube is a Type F4085 1TT tube with a 0.4 in.  $\times 0.08$  in. photocathode and an MgF<sub>2</sub> entrance window.

The electronic processing of the signal from the photomultiplier tube differs from the previously described instrument<sup>10</sup> in that the dc output signal is kept constant at 1.0 V by controlling the voltage to the photomultiplier tube by a feedback circuit (AGC in Fig. 2). The output of the PAR (Princeton Applied Research) Model HR-8 lock-in amplifier, which is recorded on a strip chart recorder, is thus equivalent to the experimentally desired quantity, the V(ac)/V(dc) ratio. As before, <sup>10</sup> the peak voltage applied to the stress plate modulator is

linked to the wavelength drive of the monochromator. This is necessary since the voltage for quarter-wave retardation is roughly proportional to wavelength.

#### **B.** Synthesis

Optically active 1-methylindan was prepared according to the following reaction scheme<sup>12</sup>:



Resolution of the acid (1) was affected by forming the diastereomeric menthol ester, <sup>13</sup> one of which crystallizes readily. The recystallized ester had an  $[\alpha]_D$  of -79.6° (-76.3° reported<sup>13</sup>).

The resolved acid was cyclized with polyphosphoric  $acid^{14}$  to yield the optically active ketone IV. A Clemmensen reduction of  $IV^{15}$  yielded a mixture which was predominantly V but also contained a small amount of the corresponding indene. The two components were separated by preparative vapor phase chromatography on a 6-ft column of 20% tetracyanoethoxypropane on Gas Chrom P.<sup>16</sup>



FIG. 2. Block diagram of the electronics of the circular dichroism instrument (AGC, automatic gain control; PAR, PAR lock-in amplifier, A, preamplifier, OA-1, OA-3, operational amplifiers).



FIG. 3. The absorption and circular dichroism spectra of 1-methylindan in the gas phase are from 280 to 240 nm. The spectral splitwidth in absorption is 0.8 nm and in circular dichroism 1.6 nm. The noise level in the circular dichroism is indicated by vertical error bars.

The purified 1-methylindan has an  $[\alpha]_D = 14^\circ$  in benzene.<sup>17</sup>

Optically active 1-methylindan of a known configuration was prepared by Brewster and Buta.<sup>18</sup> (R)-(-)-1-methylindan has a reported  $[\alpha]_D = -7.2^{\circ}$ in isooctane ( $[\alpha]_D$  extrapolated from molar rotation data). The absolute configuration of the 1-methylindan in the present synthesis is thus (S). Vapor pressures were measured from room temperature to 0 °C with a mercury manometer and a cathetometer. The values obtained fitted well into a straight-line extrapolation (Clapeyron equation) from published boiling points at 760 and 10 mm Hg pressure.<sup>19</sup> The linear extrapolation was checked below 0 °C with transmission data.

#### **III. EXPERIMENTAL RESULTS**

### A. 260 nm Region

The absorption and circular dichroism spectra of S - (+) - 1-methylindan in the 260 nm region are given in Fig. 3. The circular dichroism spectrum was taken with 1.6 nm resolution while the absorption spectrum is 0.8 nm resolution. The first peak in the circular dichroism spectrum is probably resolution limited and should be more intense at 0.8 nm resolution corresponding to the intensity distribution in the absorption spectrum. Absorption spectra taken at 1.6 nm resolution show the first peak as less intense than the second, in agreement with the CD at that resolution. Table I summarizes the data for the various vibrational components of both spectra.

The second peak in the absorption spectrum of 1-methylindan is partially resolved into three components. The spacings of the two shoulders and the central peak from the first or 0-0 band as shown in Table I correspond quite well with the spacings found in *o*-xylene in the first excited state<sup>20</sup> and will be similarly assigned. The second vibrational peak is also partially resolved but the accuracy of the vibrational spacings is less.

The resolution of the circular dichroism spectrum is not sufficient to separate the three vibrational frequencies which form progressions in the absorption spectrum but the frequency at the cen-

TABLE I. Vibrational features of the first  $\pi \to \pi^*$  transition in 1-methylindan in absorption and circular dichroism. In absorption the first  $\Delta \tilde{\nu}$  column refers to spacing from the 0-0 band; the  $\Delta \tilde{\nu}'$  column refers to the spacing between the peaks of the main progression (260 nm region).

		Absorp	tion			Circular dichroism					
λ nm	Comments	$(\text{cm}^{-1})$	$\Delta \tilde{\nu}$ (cm <sup>-1</sup> )	$\Delta \tilde{\nu}'$ (cm <sup>-1</sup> )	$\epsilon \times 10^{-2}$	λ (nm)	Comments	ν (cm <sup>-1</sup> )	$\Delta \tilde{\nu}$ (cm <sup>-1</sup> )	Δε	$\Delta \epsilon / \epsilon  imes 10^4$
271.3		36 860	0		7.6	270.9		36 910		0.13	1.7
									890		
265.6	shoulder	37650	790								
264.5		37810	950	950	5.9	264.5		37810		0.16	2.6
262.8	shoulder	$38\ 050$	1190								
									920		
259.7	broad	38510	1650								
258.0	broad	38760	1900	950	3.6	258.2		38730		0.13	3.6
256.1	broad	39 050	2190								
									1270		
250.5	diffuse	39 920	3060	1160	1.8	250.0	diffuse	40000		0.05	2.7

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TABLE II. Vibrational features of the second  $\pi \rightarrow \pi^*$  transition in 1-methylindan in absorption and circular dichroism The  $\Delta \tilde{\nu}$  column refers to the spacing between the peaks (210 nm region).

	Aba	sorption		Circular dichroism						
λ (nm)	Comments	$\tilde{\nu}$ (cm <sup>-1</sup> )	$\Delta \tilde{\nu}$ (cm <sup>-1</sup> )	$\epsilon \times 10^{-3}$	λ (nm)	Comments	$\tilde{\nu}$ (cm <sup>-1</sup> )	$\Delta \tilde{\nu}$ (cm <sup>-1</sup> )	Δε	$\Delta\epsilon/\epsilon \times 10^4$
217.5	broad, diffuse	45 980		0.91	217.5		45 980		0.39	4.3
			1015					1280		
212.8	broad	46 990	993	2.6	211.6		47260		0.55	2.1
208.4	broad	47980	963	2.7				1620		
204.3	broad, diffuse	48 950		2.7	204.6		48 880		0.84	3.1

ter of each peak, including the 0-0, matches that of the absorption spectrum within the limits of resolution, and the relative intensities are similar except for the 0-0 band as discussed above.

The g values  $(=\Delta\epsilon/\epsilon)$  for each component of the predominant progression are given in the last column of Table I. Except for the 0-0 band, g remains approximately constant with an average value of  $3 \times 10^{-4}$ . This small an asymmetry factor is an indication of a transition which is magnetically forbidden in the symmetric unsubstituted indan.

### B. 210 nm Region

The absorption and circular dischroism in the 210 nm region for 1-methylindan are given in Fig. 4. As in the 260 nm region the absorption spectrum was taken with 0.8 nm resolution and the circular dichroism spectrum with 1.6 nm resolution, but the vibrational bands are so broad that neither the absorption nor circular dichroism spectrum is resolution limited. Table II lists the information on the absorption and circular dichroism peaks in this region. In the absorption spectrum only the first two diffuse bands at 212.8 and 208.4 nm are consistently observed with the second band being particularly broad.

Comparison of the two types of spectra shows little similarity between them. The circular dichroism spectrum has a maximum at 217.5 nm which is symmetrical and well separated from the rest of the system, while the absorption spectrum shows only a broad wing at that wavelength. The first peak in the absorption spectrum lies 1.2 nm to the red of the closest maximum in the circular dichroism spectrum. The broad band at 208.4 nm in the absorption has no analogous maximum in the circular dichroism and the next and largest peak in the circular dichroism falls in a very diffuse portion of the absorption spectrum. The spacings of the bands differ radically in the two types of spectra. The  $\Delta \nu$ 's between the three circular dichroism bands are 1280 and 1620 cm<sup>-1</sup>, respectively, whereas the absorption seems to show a progression in about 970 cm<sup>-1</sup> similar to the most intense progression in the 260 nm system.

Another anomaly in the circular dichroism spectrum is the intensity variation. The intensities of the circular dichroism peaks increase towards shorter wavelengths. The absorption spectrum, however, appears as a plateau of approximately



FIG. 4. The absorption and circular dichroism spectra of 1-methylindan in the gas phase are from 230 to 200 nm. The spectral slitwidth in absorption is 0.8 nm and in circular dichroism 1.6 nm. The noise level in the circular dichroism is indicated by vertical error bars.



FIG. 5. The absorption and circular dichroism spectra of 1-methylindan in the gas phase are from 250 to 190 nm. The spectral slitwidth is 0.16 nm absorption and 0.8 nm in the circular dichroism. The noise level in the circular dichroism is indicated by vertical error bars.

constant intensity between 212.5 and 200.0 nm but the tail of the large absorption at shorter wavelengths undoubtedly also contributes to the intensity in this region. Extrapolation of the contour of this strong absorption and subtraction from the 210 nm region yields a contour of decreasing intensity with decreasing wavelength.

### C. 195 nm Region

The absorption and circular dichroism spectra of 1-methylindan near 195 nm are given in Fig. 5. The absorption spectrum of this region is also included in Fig. 6 for comparison. The circular dichroism spectrum was taken with 0.8 nm resolution. The absorption spectrum was measured on a Mc-Pherson 225 equipped with a double beam attachment



FIG. 6. The absorption and circular dichroism spectra of 1-methylindan in the gas phase are from 200 to 150 nm and from 195 to 170 nm, respectively. The spectral slitwidth in absorption is 0.16 nm and in circular dicroism 1.6 nm. The noise level is indicated by vertical error bars.

and a 1200 lines/mm grating. The resolution in the absorption spectra is 0.16 nm or better. The data for this transition are summarized in Table III.

The absorption spectrum shows two small shoulders at about 196.7 and 193.6 nm on the background of the strong absorption centered at approximately 187.5 nm. The bands are broad and the wavelengths given for the maxima are highly approximate, particularly for the lower energy band which is less well defined. The circular dichroism spectrum, on the other hand, yields two sharp peaks of opposite sign which are quite definitely separated from the circular dichroism of the strong absorption. This apparently increased resolution relative to the absorption spectrum is possible because of the change in sign of  $\Delta \epsilon$ . The g values of the two peaks are comparable. The measured fre-

TABLE III. Features of the third transition in 1-methylindan in absorption and circular dichroism (195 nm region).

	Abs	sorption		Circular dichroism						
λ (nm)	Comments	$\tilde{\nu}$ (cm <sup>-1</sup> )	$\Delta \nu$ (cm <sup>-1</sup> )	$\epsilon \times 10^{-3}$	λ (nm)	Comments	ν (cm <sup>-1</sup> )	Δ̄ν (cm <sup>-1</sup> )	Δε	$\Delta\epsilon/\epsilon \times 10^4$
196.7	broad	50840	810	4.3	198.1		50 480	990	-1.2	-3.8
193.6	broad shoulder	51650		7.8	194.3		51 470		2.4	3.1

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TABLE IV. Features of the fourth transition in 1-methylindan in absorption and circular dichroism (187.5 nm region).

	Abs	sorption			Circular dichroism					
λ (nm)	Comments	₽ (cm <sup>-1</sup> )	$\Delta \tilde{\nu}$ (cm <sup>-1</sup> )	$\epsilon \times 10^{-4}$	λ (nm)	Comments	<i>v</i> (cm <sup>−1</sup> )	$\Delta \tilde{\nu}$ (cm <sup>-1</sup> )	Δε	$\Delta\epsilon/\epsilon  imes 10^4$
187.6		53 300		1.4	188.0		53190		5.4	3.8
183.6	shoulder, broad	54470	1160	1.1	184.2	shoulder, broad	54290	1098	4.5	3.9

quency difference between the two maxima of opposite sign is  $990 \text{ cm}^{-1}$ .

### D. 187.5 nm Region

The absorption and circular dichroism spectra are given in Fig. 6 with the corresponding data summarized in Table IV. The absorption spectrum was taken with 0.16 nm or better resolution as described in the previous paragraph while the circular dichroism spectrum has 1.6 nm resolution.

As the values in Table IV illustrate, the contours of both types of spectra are quite similar. The largest peak in absorption falls at 187.6 nm and in circular dichroism at 188.0 nm with a shoulder at about 184 nm in both spectra. The minimum in absorption also correlates well with a zero crossing in the circular dichroism. The symmetry factor is constant over the band.

### E. Higher-Energy Transitions

Figure 6 also gives the absorption spectrum to 150 nm and the circular dichroism spectrum to 170 nm. Experimental difficulties with base-line variation prevent extending the circular dichroism spectrum to shorter wavelengths at present.

### IV. THEORY

### A. Description of Calculations

As described in the Introduction, Tinoco's treatment of optical activity<sup>8</sup> of a molecule is a sum of terms arising from different origins. In the present work two of these terms only will be considered: The one-electron term which arises from mixing between excited states of a single chromophore and the dipole-dipole term which takes into account the interaction between the electric transition dipole moments on different chromophores in the same molecule.

The one-electron term for 1-methylindan has been treated by Caldwell and Kauzmann<sup>6</sup> as described in the Introduction. The perturbation potential used by these authors is due to the imperfect shielding of the nuclei of the methyl substituent as introduced by Kauzman, Walter, and Eyring, <sup>21</sup> originally for the calculation of the optical activity of the carbonyl chromophore. Caldwell and Kauzmann considered the mixing-in of a Rydberg  $3d_z^2$ orbital into the valence  $\pi$  system. This Rydberg transition contributes the transition magnetic dipole moment necessary to produce optical activity. In addition, a case can be made for considering the mixing-in of  $\sigma - \pi^*$  and  $\pi - \sigma^*$  transitions which also contain excited states of the required symmetry,  $E_{1g}$  in  $D_{6h}$ . Such excited states were not considered by Caldwell and Kauzmann, <sup>6</sup> and no such calculation has been carried out in the present work.

The contribution of dipole-dipole terms to the optical activity of 1-methylindan has been calculated here. The perturbing potential coupling the two interacting chromophores is represented as the first term in a multipole-multipole expansion of the charge distributions of the chromophores, i.e., the dipole-dipole interaction term. The molecule, 1-methylindan, is represented in Fig. 7 where the coordinate system is indicated. The carbon skeleton, except for the methyl substituent, is considered planar although the infrared and Raman spectra<sup>22</sup> suggest that the symmetry of the molecule indan is really  $C_x^s$ . The interacting chromophores are here *o*-xylene and the ethane chromophore involving carbon atoms  $C_7$  and  $C_9$  in Fig. 7.

The chromophore o-xylene has  $C_{2v}$  symmetry. The electric transition moments  $\mu_x$  and  $\mu_y$  are derived from transitions from the ground state to the excited states  $B_{2u}$  and  $B_{1u}$  of benzene, respectively. The magnitude of these transition dipole moments



FIG. 7. (S) - (+) - 1-methylindan with the corrdinate system used in the calculations.

for o-xylene were taken from Caldwell and Kauzmann's work. They are included in Table V. The energies of the transitions were taken from the spectrum of benzene. The transition dipole moments and energies for the components of the  $E_{1u}$ benzene state were also taken from the work of Caldwell and Kauzmann.<sup>6</sup> These authors calculated a splitting of 1300 cm<sup>-1</sup>. It was found in these calculations that the results were insensitive to the assumption of this splitting between the values 360 cm<sup>-1</sup> (reported by Katz and others<sup>23</sup> for *p*-xylene) and the above value of 1300 cm<sup>-1</sup>.

The first absorption system of ethane was investigated by Raymonda and Simpson<sup>24</sup> who calculated from their spectra an *f* number of 0.52. These authors assigned the spectrum to a  $\sigma - \sigma^*$ parallel transition. The same spectrum was also studied in some detail by Pearson and Innes<sup>25</sup> who assigned it to a perpendicular transition on the basis of rotational contour matching attempts for the first band. Lassettre and others<sup>26</sup> studied the spectrum by electron impact and assigned the system corresponding to the optical absorption as having a parallel transition moment. These authors also found a weak band preceding the system and assigned this as a perpendicular transition.

In the present calculations the *f* number of the ethane transition was allowed to vary in order to fit the results to the observed CD spectra. This variation affected the magnitude of the dipole-dipole rotational strength contribution relative to that of the one-electron term. A value of f = 0.3for this transition in 1-methylindan gave a small dipole-dipole contribution for the first two transitions relative to the one-electron contribution and a contribution of similar magnitude for the allowed transition components derived from the  $E_{1\mu}$  benzene state. The resulting rotational strengths agreed then quite well with experiment. The experimental and calculated rotational strengths for a parallel ethane transition are listed in Table V. The frequency of the ethane transition was taken

from the first maximum (136 nm) in the absorption spectrum of Raymonda and Simpson.<sup>24</sup> As described here, there exists a disagreement concerning the direction of the transition moment corresponding to the lowest absorption spectrum in ethane. Therefore, both possibilities, parallel and perpendicular moments, were considered in the dipole-dipole term calculations carried out here. With a parallel transition moment, the positive total  $E_{1u}$  rotational strength was obtained in agreement with experiment; with a perpendicular transition moment of the same magnitude, a negative total rotational strength was obtained of half the absolute value of that calculated for a parallel transition moment. The experimental results thus require the choice of the perturbing transition moment of the ethane moiety as parallel.

### **B.** Discussion of Theoretical Results

The dipole-dipole term contributions to the rotational strengths of the  $E_{1u}$  transition components were calculated assuming either a parallel or a perpendicular transition moment of the ethane moiety. The one-electron contributions were taken from the work of Caldwell and Kauzmann.<sup>6</sup> It was found that the parallel transition moment gives a total resultant positive rotational strength for this transition in agreement with experiment (see Table V). It is seen from the table that the dipoledipole term contribution predominates over the one-electron term. It should here be noted that the one-electron mechanism for the components of an originally degenerate transition  $E_{1u}$  gave<sup>6</sup> rotational strengths equal in magnitude and opposite in sign. However, for the dipole-dipole term, the rotational strengths of the two components do not necessarily sum to zero.

For the  $B_{2u}$  and  $B_{1u}$  transitions, the total rotational strengths are determined by the one-electron mechanism as seen from the results listed in Table V. For these transitions, the dipole-dipole contribution is secondary. For the  $E_{2x}$  transition

TABLE V.	Calculated and observ	ved rotational strengths of the excited states of $(S) - (+) - 1$ -methylindan corresponding
to the benzene	$B_{2u}$ , $B_{1u}$ , $E_{1u}$ states.	The $R_{dipole-dipole}$ are calculated assuming a parallel "ethane" transition; $f=0.3$ .

	Electric transition dipole moment <sup>a</sup>	Rotational strength $(D \cdot \mu_B)$							
Transition	(esu•cm)	One electron <sup>a</sup>	Dipole-dipole	Total	Experimental				
B <sub>2µ</sub>	5.1×10-19	$4.1 \times 10^{-41}$	2.4×10-41	6.5×10 <sup>-41</sup>	$1.6 \times 10^{-41}$				
$B_{1;i}^{2a}$	$5.7 imes 10^{-19}$	$9.9 \times 10^{-41}$	$-2.6 \times 10^{-41}$	7.3 $\times 10^{-41}$	9.5 $ imes$ 10 <sup>-41</sup>				
$E_{1uA}$		$-5.5 \times 10^{-39}$	$6.4 \times 10^{-39}$	$0.9  imes 10^{-39}$					
$E_{tuB}$		5.5 $\times 10^{-39}$	$-3.8 \times 10^{-39}$	$1.7  imes 10^{-39}$					
$E_{1u}$ (total)	$13.3 \times 10^{-18}$	0.0	2.6×10-39	2.6 $\times 10^{-39}$	5.7 $\times 10^{-40}$				

<sup>a</sup>D. J. Caldwell and H. Eyring, Ann. Rev. Phys. Chem. 15, 281 (1964).

components no specific calculation was carried out here, and no previous results are available. In view of the forbidden character of this transition, it may be expected that the one-electron treatment would apply. If the results were analogous to those obtained by Caldwell and Kauzmann<sup>6</sup> for the  $E_{1u}$  state, opposite signs may be expected in agreement with experimental observation.

It is concluded here that the observed CD spectrum could be fitted with a consistent scheme considering the one-electron and dipole-dipole term contributions. In this scheme the comparative contributions from the dipole-dipole vs the oneelectron term contributions are reasonable; i.e., the dipole-dipole mechanism makes the dominant contribution for electric dipole-allowed transitions whereas the one-electron term seems to be dominant for originally forbidden transitions.

### V. DISCUSSION

### A. The 290 nm Transition

As previously described and summarized in Table I, the vibrational structure of both the absorption and circular dichroism spectra are quite similar for this transition which corresponds to the  $B_{2u}$  transition in benzene. The apparent vibrational spacing is 950 cm<sup>-1</sup>. The 507 cm<sup>-1</sup>  $a_1$  vibration of o-xylene (606 cm<sup>-1</sup>,  $e_{2g}$  vibration in the ground state of benzene) does not seem to be important in the first absorption band of 1-methylindan; the frequency corresponding to 0-0+500 cm<sup>-1</sup> in 1methylindan lies at 268.0 nm which corresponds to a minimum in the absorption spectrum.

### B. The 210 nm Transition

A comparison between the vibrational structure and energy of the absorption spectrum of 1-methylindan and that of benzene requires the assignment of this transition as the analog of the  $B_{1u}$  transition in benzene. However, the circular dichroism structure is in no way analogous to that of the absorption. This result leads to the conclusion that different mechanisms are involved for the absorption and circular dichroism spectra. It is possible that the different mechanisms concern only the vibrational structure in the same electronic state or, alternately, an additional electronic state may manifest itself in the CD spectrum.

As described, the lowest-frequency peak in the CD spectrum is located at 45 980 cm<sup>-1</sup> (217.5 nm) and this corresponds to a weak and diffuse, barely discernible shoulder on the rise of the absorption, and is located 1015 cm<sup>-1</sup> to lower frequency from the first intense peak in the absorption at 46 990 cm<sup>-1</sup> (212.8 nm). It is not considered likely that the 45 980 cm<sup>-1</sup> CD peak represents the 0–0 band of the  $B_{1u}$  transition. It is noted in this connection

that the 0-0 band of the  $B_{2u}$  transition of every substituted benzene for which this transition is predicted to be symmetry allowed is one of the most intense features in the spectrum. For the  $B_{1u}$  transition the spectra are less well known. However, recently, some work has been reported<sup>23</sup> on the  $B_{1u}$  spectra of matrix-isolated toluene and two xylenes and in these cases also the 0-0 band was assigned to an intense feature in the  $B_{1u}$  absorption region. On the other hand, the absorption and CD spectra of toluene derivatives have been reported<sup>27</sup> in the  $B_{2u}$  region where the first strong absorption band was not assigned to the 0-0 transition because the most intense CD peak occurred 500 cm<sup>-1</sup> to lower frequency. This low-frequency CD band was assigned as the 0-0 transition in these cases.

Since it is not considered probable that the CD peak at 45 980 cm<sup>-1</sup> represents the 0-0 transition, the possibility of an excited electronic state in addition to the  $B_{1y}$  state in this region must be investigated. The circular dichroism spectrum can in fact be fitted by a superposition of a derivativetype curve (with the low-frequency positive lobe coinciding with the lowest-energy CD peak and the high-frequency negative lobe peaking near 215 nm) and two positive bands with peaks corresponding to the first and third absorption maxima. Also accounted for then would be the deep indentation in the CD spectrum following the first peak. The variation of the anisotropy factor *g* over the region also suggests that a negative CD peak may occur near 215 nm. This interpretation assumes then that a positive CD peak occurs at 217.5 nm and a negative peak near 215 nm, neither of which corresponds to an absorption feature. The experimental results therefore provide evidence for the occurrence of a magnetic-dipole-allowed and electricdipole-forbidden transition in the symmetric benzene chromophore in this spectral region. The simplest way to account for the occurrance of two oppositely signed bands in close proximity is on the basis of an originally degenerate state. For benzene, this would correspond to  $\sigma - \pi^*$  or a  $\pi - \sigma^* E_{1g}$ state. SCF molecular orbital calculations, <sup>28</sup> ex-tended Hückel calculations, <sup>29</sup> photoelectron<sup>30</sup> and photoionization spectra<sup>31</sup> show that there is at least one p orbital whose energy lies between that of the two filled  $\pi$  orbitals so that the postulation of a  $\sigma$ - $\pi^*$  state in this region is energetically reasonable. An extended Hückel calculation on naphthalene and anthracene<sup>32</sup> yields several electric-dipole-forbidden magnetic-dipole-allowed  $\sigma - \pi^*$  transitions in the energy range of the lower  $\pi - \pi^*$  transitions. An alternative assignment would be to a  $\pi$ -3so\* ( $e_{1g}$  $a_{1e}$ ) transition.

The interpretation of the CD spectrum in this re-

gion must be considered as uncertain since no interpretation based on the reproduction of the observed spectrum on the basis of superpositions of positive and negative systems is unique.

### C. The 195 nm Region

The circular dichroism spectrum near 195 nm exhibits a negative peak at 198.1 nm  $(50480 \text{ cm}^{-1})$ and a positive peak at 194.3 nm  $(51470 \text{ cm}^{-1})$  with a separation of  $990 \pm 100$  cm<sup>-1</sup>. The spectrum cannot be reproduced by assuming two negative peaks at 198 and 193 nm superimposed on the tail of the strong positive CD band peaking at 187.5 nm. The experimental result described requires the occurrence of at least one additional excited state between  $B_{1u}$  and  $E_{1u}$  benzene states.

Lassettre and others<sup>5</sup> found evidence for two electronic states in the 205 nm region in benzene from their electron impact studies. Also, an experiment by Bonneau and others, <sup>3</sup> which investigated the absorption by benzene molecules laser pumped to produce appreciable population in the  $B_{2\mu}$  state, has been interpreted by Birks<sup>4</sup> as representing the transition  $B_{2\mu} \rightarrow E_{2\epsilon}$ . This transition is electric dipole allowed with the transition moment in the molecular plane and the measurement located the  $E_{2r}$  state on the high-energy side of the  $E_{1u}$  absorption. Theoretical calculations have consistently predicted<sup>2</sup> an  $E_{2g}$  state near the  $E_{1u}$  excited state, as mentioned in the Introduction.

As previously discussed, a one-electron term calculation for 1-methylindan predicted two CD components of equal absolute magnitude of rotatory strengths and of opposite signs for the  $E_{1u}$  degenerate benzene state. The form of the circular dichroism spectrum observed here suggests, by analogy, that it is to be correlated with a degenerate electronic state under  $D_{6h}$  symmetry. The possibility that the two CD peaks are due to two different electronic states cannot be ruled out. Neither can we rule out a possible interpretation in terms of one electronic transition with a nonsymmetric vibration superimposed on it. The observation that the anisotropy factors (g values) are quite similar to the other  $\pi - \pi^*$  transitions lends support to the  $E_{2g}$  assignment. In addition, the absorption coefficients, as far as they can be determined, are of similar order of magnitude as those of the other formally forbidden  $\pi - \pi^*$  transitions.

Curve-fitting experiments indicate that the actual splitting of the two components is about 850 cm<sup>-1</sup> instead of the  $990 \text{ cm}^{-1}$  measured as the difference between the positive and negative peaks. The discrepancy is due to the fact that the contributions of opposite sign tend to cancel in the region of overlap and the resultant peaks appear to be farther

apart. This splitting is interpreted as due to the removal of the double degeneracy by the asymmetric substitution in the molecule studied. It is larger than the 350  $\text{cm}^{-1}$  splitting reported for the  $E_{1u}$  state of p-xylene by Katz and others<sup>23</sup> but it is considered to be of reasonable magnitude.

#### D. The 187.5 nm Spectral Region

The assignment of the transition at 187.5 nm (53 333 cm<sup>-1</sup>) as the analog of  $E_{1u}$  in benzene seems straightforward on the basis of the high absorption intensity corresponding to the allowed transition in the symmetric chromophore.<sup>1</sup> The absorption and CD spectra correlate as far as their contours are concerned. As has been discussed in a previous section, the CD spectrum observed in this work can be consistently accounted for by a theoretical scheme based on calculations of one-electron term and dipole-dipole term contributions to the rotational strengths of the different transitions. In this scheme a resultant positive rotational strength is calculated for the  $E_{1u}$  transition region in agreement with the experimental result.

Katz *et al.*  $^{23,33}$  reported a truncated vibrational progression in 930 cm<sup>-1</sup> in the  $E_{1u}$  transition of matrix-isolated benzene, toluene, and m-xylene. The spacing between the maximum and the short wavelength shoulder in absorption as well as CD is approximately 1100 cm<sup>-1</sup> in 1-methylindan. This discrepancy may however well be due to the inaccuracy of the peak measurements due to the large bandwidths. In fact an uncertainty of  $\pm 200$  cm<sup>-1</sup> must be assigned to the measured interval. It should be noted that the absorption spectrum of gas phase benzene reported by Wilkinson<sup>34</sup> exhibits an interval of 703 cm<sup>-1</sup>.

### E. 170 nm Spectral Region

The intense circular dichroism beginning at 180 nm has no analogous features in the absorption spectrum. The g value  $(g = -7.8 \times 10^{-4})$  at the peak of the circular dichroism (176 nm) is more than twice that of the lower energy states. As previously discussed, several electric-dipole-forbidden, magnetic-dipole-allowed  $\sigma - \pi^*$  or  $\pi - \sigma^*$  states could be expected to lie in this energy region.

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4555

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