

# MAGNETIC CIRCULAR DICHROISM STUDIES—XLVI<sup>1</sup>

## STRUCTURE AND THE MAGNETIC CIRCULAR DICHROISM OF TRANS-2-DECALONES AND BICYCLO[2.2.2]OCTAN-2-ONES<sup>†</sup>

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**Abstract**—The magnetic CD spectra of a number of Me substituted *trans*-2-decalones and bicyclo[2.2.2]octan-2-ones were measured. The results showed a large, and sometimes dominant, contribution to the MCD intensity which could be correlated with the presence of  $\alpha$ -substituents lying outside of the plane of the carbonyl chromophore.

The magnetic circular dichroism (MCD) spectra of saturated ketones have been the subject of considerable interest.<sup>2-5</sup> Earlier work correlated the structures of a large number of saturated ketones with the  $B$ -values obtained from the MCD spectra for their  $n \rightarrow \pi^*$  transitions.<sup>2</sup> In arriving at these correlations one utilized the fact that the MCD spectrum for the electric dipole forbidden  $n \rightarrow \pi^*$  transition of a saturated ketone is zero except in the presence of vibrational or structural perturbations that are nontotally symmetric as regards the local  $C_{2v}$  symmetry of the carbonyl chromophore. In order to clarify the correlations and further test the procedures involved, it was desirable to obtain a series of closely related compounds in which vibrational variations and conformational ambiguities would be minimized. In *trans*-2-decalone (1), the *trans* ring juncture prevents either of the two 6-membered rings from flipping from one chair conformation to the other; calculations and electron diffraction studies<sup>6,7</sup> indicate that the major species is in the chair-chair conformation.<sup>§</sup> Bicyclo[2.2.2]octan-2-one (12) is a conformationally unambiguous compound since the two-carbon bridge across the 6-membered ring locks it into a boat conformation. Therefore, we have synthesized a series of methyl substituted *trans*-2-decalones and bicyclo[2.2.2]octan-2-ones, measured their MCD spectra, and subjected the data to the correlative analysis presented earlier.<sup>1</sup>

### RESULTS AND DISCUSSION

The MCD and UV data for the ketones studied are summarized in Table 1. The  $B$ -values for the methyl substituted *trans*-2-decalones and bicyclo[2.2.2]octan-2-ones may be compared to the  $B$ -values for the parent compounds of the two respective series in the manner previously described,<sup>1</sup> and which is illustrated in Fig. 1. The perturbing atoms, i.e. those which are not part of the CO chromophore, are projected onto quadrant diagrams. The total structural perturbation is thereby decomposed into its various components, each of which transforms as a different nontotally symmetric representation of the  $C_{2v}$  point group. Each such component, if nonzero, has associated with it a signed partial  $B$ -value, and the pertinent signs here are:

$$B(A_2) > 0, \quad B(B_1) > 0, \quad B(B_2) < 0.$$

The totally symmetric component  $B(A_1)$  is neglected since only an *overall* nontotally symmetric perturbation

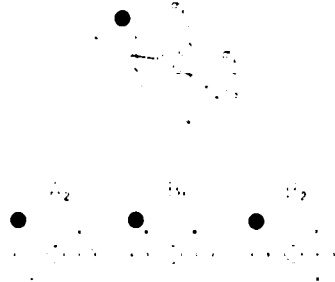


Fig. 1. Symmetry operations and projection diagrams for saturated ketones. A perturber (solid circle) constitutes an atom which, for a given irreducible representation, does not fall on a nodal plane and is not cancelled by a contribution of equal and opposite magnitude from another atom. (The sign of the net effect of all perturbing atoms for a given irreducible representation is determined from the inequalities given in the text since the phases given in the projection diagrams are arbitrary.)

<sup>\*</sup>Taken in part from the Ph.D. Thesis of Kent Morrill, to be submitted to Stanford University.

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<sup>§</sup>Force field calculations for the 1- and 3-axial Me substituted *trans*-2-decalones indicated an energy difference between the chair and boat conformations, for the ring containing the CO, of ca 6 kcal/mole.<sup>6,7</sup> As a referee has pointed out, recent *ab initio* calculations<sup>8</sup> indicate a corresponding energy difference of 2.92 and 0.69 kcal/mole for the 1- and 3-axial methyl compounds, respectively. Thus the chair-chair conformer is assumed to be the more populated one in each case (> 99% for (15), and > 75% for (16)).

Table 1. MCD and absorption data\* for *trans*-2-decalones and bicyclo[2.2.2]octan-2-ones

Compound	Absorption <sup>b</sup> $\lambda_{max}(\epsilon)$	$D(n \rightarrow \pi^*)$ $\times 10^2$	MCD <sup>c</sup> $\lambda_{max}( \theta _m \cdot 10^3)$	$B(n \rightarrow \pi^*)$ $\times 10^6$	Pred (obs) <sup>d</sup>
1 <i>trans</i> -2-Decalone	288(16)	2.3	277(-7)	28.9	
2 1(eq)-Methyl- <i>trans</i> -2-decalone <sup>e</sup>	295(16)	2.5	307(4) 275(-2)	5.3	- (-)
3 3(eq)-Methyl- <i>trans</i> -2-decalone	294(20)	2.8	289(-9)	34.7	+ (+)
4 1(eq),3(eq)-Dimethyl- <i>trans</i> -2-decalone	292(23)	3.1	282(-6)	27.2	- (=)
5 1(ax)-Methyl- <i>trans</i> -2-decalone	297(22)	3.4	313(6) 272(-4)	0.5	- (-)
6 3(ax)-Methyl- <i>trans</i> -2-decalone	297(21)	3.2	300(18) s260(-2)	-46.5	+ (-)
7 1,1-Dimethyl- <i>trans</i> -2-decalone	296(20)	3.0	300(11) s255(-3)	28.0	- (-)
8 1,1,3(eq)-Trimethyl- <i>trans</i> -2-decalone	295(28)	4.1	307(9) 268(-5)	-12.0	- (-)
9 8,8,10-Trimethyl- <i>trans</i> -2-decalone <sup>e</sup>	287(16)	2.4	288(-11)	37.8	+ (+)
10 5(eq),10-Dimethyl- <i>trans</i> -2-decalone <sup>e</sup>	285(18)	2.8	283(-6)	22.3	? (-)
11 5,5,9(ax)-Trimethyl- <i>trans</i> -2-decalone <sup>e</sup>	290(17)	2.6	290(-6)	30.2	? (-)
12 Bicyclo[2.2.2]octan-2-one	297(25)	3.6	285(-18)	72.6	
13 1-Methyl-bicyclo[2.2.2]octan-2-one	292(21)	3.5	283(-15)	73.4	(=)
14 3-Methyl-bicyclo[2.2.2]octan-2-one	298(23)	3.4	290(-16)	65.5	+ (-)
15 3,3-Dimethyl-bicyclo[2.2.2]octan-2-one	293(14)	2.5	300(4) 260(-2)	-9.9	? (-)
16 4-Methyl-bicyclo[2.2.2]octan-2-one	296(23)	3.5	283(-12)	46.8	? (-)
17 5(endo)-Methyl-bicyclo[2.2.2]octan-2-one	295(24)	4.2	306(6) 260(-24)	70.4	+ (-)
18 6(endo)-Methyl-bicyclo[2.2.2]octan-2-one	295(24)	3.7	297(-21)	86.0	+ (+)

\*Spectrograde cyclohexane.

<sup>b</sup>Wavelength in nm; molar extinction coefficient in 1000 cm<sup>2</sup> mol<sup>-1</sup>.<sup>c</sup>Dipole strength in (debye)<sup>2</sup>.<sup>d</sup>Magnetic molar ellipticity in deg cm<sup>2</sup> dmol<sup>-1</sup> G<sup>-1</sup>; s = shoulder.<sup>e</sup>*B*-value in units of (debye)<sup>2</sup> bohr magneton/cm<sup>-1</sup>.<sup>f</sup>Predicted (observed) change [ $\Delta B(n \rightarrow \pi^*)$ ] in  $B(n \rightarrow \pi^*)$  relative to the parent compound for the series.<sup>g</sup>See ref. 13.<sup>h</sup>G. Ohloff, F. Naf, R. Decorzant, W. Thommen and E. Sundt, *Helv. Chim. Acta* **56**, 1414 (1973).<sup>i</sup>E. Piers and M. B. Geraghty, *Can. J. Chem.* **51**, 2166 (1973).

can induce MCD intensity. Further, these partial *B*-values are additive:<sup>7</sup>

$$B(n \rightarrow \pi^*) = B(A_1) + B(B_1) + B(B_2) \quad (\text{structural perturbation}).$$

Thus one is able to estimate the sign of the difference in  $B(n \rightarrow \pi^*)$ -values,  $\Delta B(n \rightarrow \pi^*)$ , between a compound and a reference parent compound by noting the differences in the contributions of their partial *B*-values from the projection diagrams.

The projection diagrams for several of the ketones studied are illustrated in Figs. 2 and 3; predicted and observed signs for  $\Delta B(n \rightarrow \pi^*)$  are given there also. The results for the entire series of compounds are listed in Table 1.

In the case of the *trans*-2-decalones, the bulk of the predicted and observed signs of  $\Delta B(n \rightarrow \pi^*)$  are in agreement. However, there is one especially notable exception. The compound 3(ax)-methyl-*trans*-2-decalone

(6), exhibits a change in *B*-value of appreciable magnitude *vis-à-vis* (1), and of sign opposite to that predicted. Similarly, four of the bicyclo[2.2.2]octan-2-ones show changes in the *B*-values which clearly disagree with the predicted results. In addition, the differences between the *B*-values for 3,3-dimethyl-bicyclo[2.2.2]octan-2-one (15) and those of the other bicyclo[2.2.2]octan-2-ones are far larger than would be predicted if they arose simply from the same type of static structural perturbations assumed to be the cause of the variations in *B*-values among the other bicyclo[2.2.2]octan-2-ones.

The discrepancies just noted have forced us to reexamine the basis of our analysis, and we recognize now the potential importance of an effect associated with the *totally symmetric* structural perturbations previously neglected. As noted above, a totally symmetric structural perturbation cannot *per se* provide any MCD intensity. However, a totally symmetric structural perturbation can exert a marked synergistic, or antienergetic, effect on the MCD intensity associated with nontotally symmetric

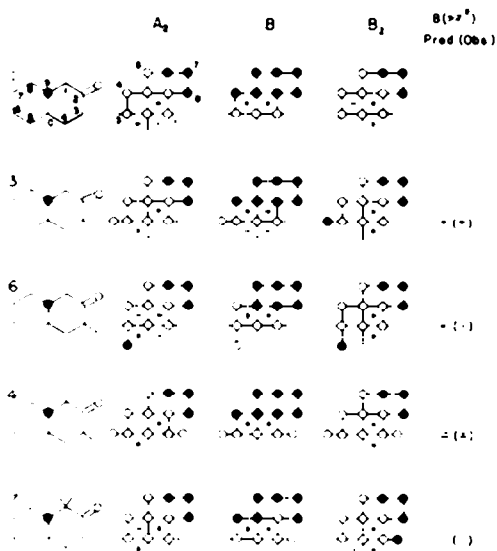


Fig. 2. Projection diagrams for the *trans*-2-decalones. The reference compound for  $\Delta B(n \rightarrow \pi^*)$  is 1

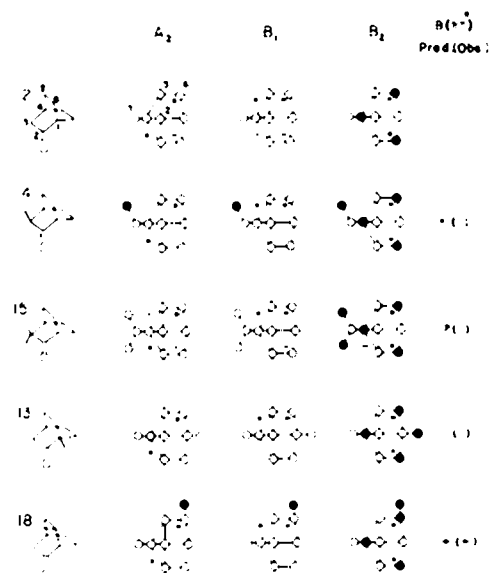


Fig. 3. Projection diagrams for the bicyclo[2.2.2]octan-2-ones. The reference compound for  $\Delta B(n \rightarrow \pi^*)$  is 12. Note that an unusual degree of cancellation exists in the  $B_2$  partial  $B$ -value diagrams, leading in certain cases to ambiguity in the predictions.

vibrational perturbations. The mechanism for the synergistic effect operates by altering the efficacy of the vibronic coupling through which a forbidden transition borrows MCD intensity.

The details of these cooperative vibrational-structural effects are elaborated in separate publications.<sup>9</sup> We note here only that such effects are dependent upon the relative stereochemistry of the perturbing atoms *vis-à-vis* the CO group, and that the stereochemistry of out-of-plane  $\alpha$ -substituents is particularly conducive to them. This is already manifest in some of the raw MCD data.

For example, among the decalones, the MCD curves for 6 and 7 (Fig. 4) exhibit very prominent positive MCD components that are absent in 1, 3 and 4 where there are no out-of-plane  $\alpha$ -alkyl substituents. Of course, the *static*

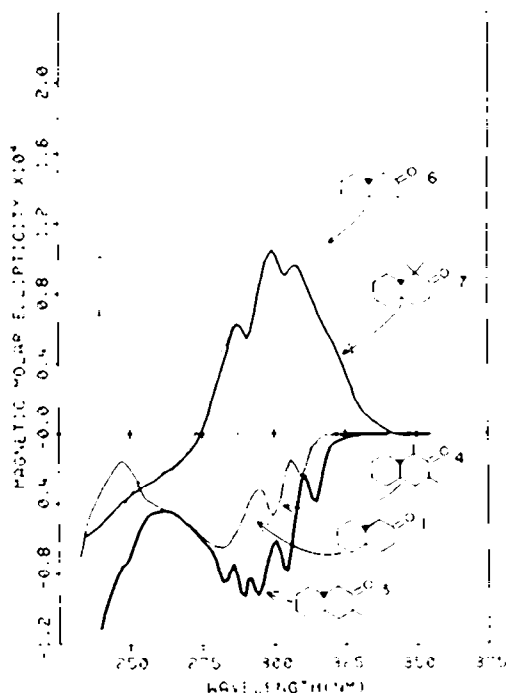


Fig. 4. Representative MCD spectra of methyl-substituted *trans*-2-decalones and the parent compound. The vertical bar indicates the experimental noise level.

structural perturbations are always operative, and these may contribute to the MCD intensity in a direction opposite to that of the  $\alpha$ -alkyl effect noted. In such instances, manifestation of the out-of-plane  $\alpha$ -alkyl effect in the raw data may tend to be obscured. For example, the positive component in the MCD curves is less prominent in 15 (Fig. 5) than in 6 or 7, and is overridden in 14 by

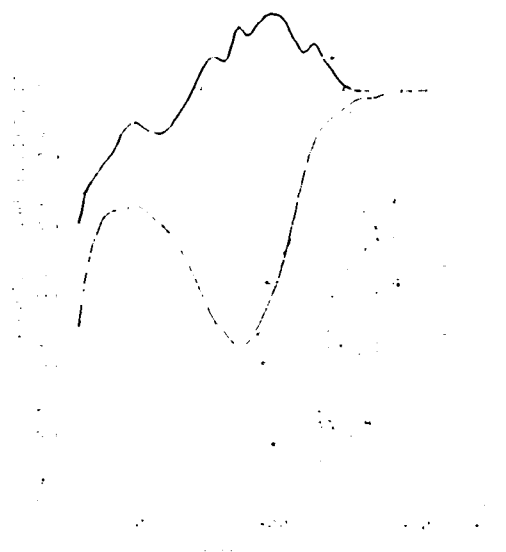


Fig. 5. Representative MCD spectra of methyl-substituted bicyclo[2.2.2]octan-2-ones and the parent compound. The vertical bar indicates the experimental noise level.

strong  $B(A_2)$  and  $B(B_1)$ , and diminished  $B(B_2)$  static contributions (see projection diagrams). Thus although the raw data are at times instructive, a more informative structural interpretation is provided by analysis of the  $B$ -values. Such analyses<sup>4</sup> must take into account both static structural and vibrational-structural effects.

### EXPERIMENTAL

The magnetic circular dichroism and experimental procedure have been described elsewhere.<sup>1,2</sup> The sources of the compounds which were not synthesized in these laboratories are listed in Table I. The NMR spectra were measured on a Varian T-60 NMR spectrometer using  $\text{CCl}_4$  as the solvent.

Because the MCD is weak for saturated ketones, it was necessary to monitor all of the compounds—synthesized or donated—for the presence of impurities, some of which dominated the MCD spectra at very small concentrations (e.g. as little as 0.1% of an  $\alpha,\beta$ -unsaturated ketone). This was done by examining the GLC traces and UV spectra of the samples as well as the MCD spectra themselves. When necessary, the compounds were purified as much as possible using GLC and high pressure liquid chromatography (HPLC). Even with these precautions, however, sufficient impurities remained to prevent the negative bands in the high frequency regions of many of the MCD spectra from returning to the baseline (Figs. 4 and 5). In these cases, the curves were extrapolated to the baseline so that they could be integrated and the  $B$ -values determined.

*(3ax)-Methyl-(6) and (3eq)-methyl-trans-2-decalone (3)* *Trans*- $\Delta^2$ -octalin was prepared from quinone and 1,3-butadiene according to the method of Mion *et al.*<sup>10</sup> with slight alterations in the conditions of the Diels-Alder reaction<sup>10</sup> and in the separation of the *cis* and *trans* isomers.<sup>11</sup> NMR  $\delta$  5.6 (unresolved narrow vinylic multiplet). The octalin was reacted in chloroform with *meta*-chloroperbenzoic acid in the usual manner to form the epoxide. The reaction was followed using NMR by the disappearance of the vinylic protons of the octalin and the appearance of a new peak at 3.0 ppm. The epoxide was treated under nitrogen with MeLi in refluxing hexane to form the alcohol. Oxidation of the alcohol using chromic acid in acetic acid<sup>12</sup> gave the desired *(3ax)*-methyl-*trans*-2-decalone (6): NMR  $\delta$  1.18 (d,  $J = 6.5$  Hz); reported<sup>11</sup> 1.2 (d,  $J = 6.5$  Hz). The equatorial isomer 3 was produced by epimerization of the axial isomer 6 in methanolic KOH as described by Mion *et al.*<sup>10</sup> NMR  $\delta$  0.97 (d,  $J = 6.0$  Hz); reported<sup>11</sup> 1.0 (d,  $J = 6.5$  Hz).

*(1ax)-Methyl-trans-2-decalone (5)*. Compound 2<sup>12</sup> was epimerized to a 50:50 mixture of the axial and equatorial isomers via the pyrrolidine enamine intermediate (not isolated) by refluxing with pyrrolidine in xylene over 3 Å molecular sieves for one day. The two isomers were separated using HPLC: NMR  $\delta$  1.03 (d,  $J = 6.5$  Hz); reported<sup>13</sup> 1.03 (d,  $J = 6.5$  Hz).

*(1eq),3(eq)-Dimethyl-trans-2-decalone (4)*. Methyl isopropenyl ketone and the pyrrolidine enamine of cyclohexanone were reacted in the manner described by Stork *et al.*<sup>14</sup> to produce 3-methyl- $\Delta^1$ -2-octalone (*M*<sup>+</sup> *m/e* 164) which was reductively alkylated using MeI and K in liquid ammonia<sup>15</sup> to give 4 as the major product: *M*<sup>+</sup> *m/e* 180; NMR  $\delta$  0.92 (two overlapping Me doublets,  $J = 6$  Hz). (Found: C, 80.14; H, 11.06. Calc. for  $\text{C}_{12}\text{H}_{20}\text{O}$ : C, 79.94; H, 11.18%).

*1,1-Dimethyl-(7) and 1,1,3(eq)-trimethyl-trans-2-decalone (8)*. 1-Methyl- $\Delta^1$ -2-octalone was synthesized and reductively alkylated using K and MeI in liquid ammonia and THF as described by Stork *et al.*<sup>14</sup> The resultant oily liquid obtained on bulb-to-bulb distillation contained two components which were separable using HPLC. One component proved to be 7: *M*<sup>+</sup> *m/e* 180; NMR  $\delta$  1.00 (s); reported<sup>16</sup> 0.99 (s). The second component had a mass spectral molecular ion of *m/e* 194, indicating the presence of an additional Me group. A large NMR singlet ( $\delta$  0.99) and an overlapping doublet ( $\delta$  0.97) indicated the presence of a gem-dimethyl and an equatorial Me group. Of the two possibilities, 1,1,3(eq)-trimethyl-*trans*-2-decalone and 3,3,1(eq)-trimethyl-*trans*-2-decalone, the former is the only one which could result from the reductive methylation of 1-methyl- $\Delta^1$ -2-octalone. Evidently, a base catalyzed methylation producing

the additional 3-Me substituent took place during the work-up of the reaction mixture. (Found: C, 80.21; H, 11.08. Calc. for  $\text{C}_{13}\text{H}_{22}\text{O}$ : C, 80.35; H, 11.41%).

*Bicyclo[2.2.2]octan-2-one (12)*.<sup>17</sup> Bicyclo[2.2.2]oct-2-en-5-ol was prepared as described by Goering *et al.*<sup>18</sup> followed by catalytic reduction and Jones oxidation: NMR  $\delta$  1.72 (s, 8H), 2.20 (s, 2H).

*3-Methyl-bicyclo[2.2.2]octan-2-one (14)* was prepared according to the method described by Tichý *et al.*<sup>19</sup> *M*<sup>+</sup> *m/e* 138; NMR  $\delta$  1.10 (d,  $J = 6$  Hz).

*3,3-Dimethyl-bicyclo[2.2.2]octan-2-one (15)*<sup>18</sup> was synthesized from 14 via a base catalyzed methylation using MeI and trityl lithium: *M*<sup>+</sup> *m/e* 152; NMR  $\delta$  1.07 (s).

*5-endo-(17) and 6-endo-Methyl-bicyclo[2.2.2]octan-2-one (18)*. These compounds were prepared by the method of Tichý *et al.*<sup>19</sup> Both compounds had mass spectral molecular ion peaks at *m/e* 138. The distinctive peaks in their NMR spectra were: *5-endo*-Me isomer,  $\delta$  0.99 (d,  $J = 6$  Hz); *6-endo*-Me isomer,  $\delta$  0.93 (d,  $J = 6$  Hz).

*1-Methyl-(13) and 4-methyl-bicyclo[2.2.2]octan-2-one (16)*. The lithium reduction of toluene in liquid ammonia<sup>20</sup> gave 1-methyl-1,4-cyclohexadiene. The unconjugated diene was equilibrated by refluxing overnight with *t*-BuOH and *t*-BuOK<sup>21</sup> to give a colorless liquid which on distillation had an odor resembling that of 1,3-cyclohexadiene. This liquid was placed in a flask and successive small amounts of maleic anhydride added. An NMR spectrum of the crude adduct displayed a sharp singlet at 1.54 ppm. The material from the Diels-Alder reaction was hydrogenated in THF using 10% Pd/C until H<sub>2</sub> uptake ceased. The NMR spectrum of the hydrogenation product contained a sharp singlet at 1.12 ppm and a very small doublet centered at 0.98 ppm. The hydrogenation product was placed with 1/2 equiv  $\text{KHCO}_3$  in water and left on a steam bath for several hr. The residue, after removal of the water, was bis-decarboxylated using lead tetraacetate in pyridine.<sup>22</sup> NMR  $\delta$  1.1 (s), 6.1 (m). Hydroboration yielded an alcohol which was oxidized by sodium dichromate in a mixture of  $\text{H}_2\text{SO}_4$ , water and ether. After several hours, the soln was extracted with ether to give a ketone mixture. The components of the mixture were separated by GLC (diethylene-glycol-adipate cross-linked on Chromosorb W) into two fractions. The first fraction proved to be 13: *M*<sup>+</sup> *m/e* 138; NMR  $\delta$  0.83 (s, 3H), 1.63 (s, 8H), 2.17 (s, 2H); reported<sup>23</sup> 0.82 (s, 3H), 1.62 (s, 8H), 2.17 (s, 2H). The second fraction was 16:<sup>24</sup> *M*<sup>+</sup> *m/e* 138, NMR  $\delta$  0.93 (s, 3H), 1.99 (s, 2H), 2.13 (m, 1H).

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