Conformational Analysis. 120. Small Polyenes[1,2]

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Abstract: The conformations of a group of small polyenes containing two or three conjugated double bonds, with or without a methyl group, have been studied in some detail using a molecular mechanics method developed earlier for conjugated systems. The planarity, degree of distortion, and relative energies of the different conformations are of interest, both because of the effect on physical properties such as electronic spectra, and also because these are small model systems for large naturally occurring molecules such as the carotenoids.

Polyenes have long been intriguing to chemists, and a great body of literature exists concerning these compounds. Of special interest are the carotenoids,[3,4] a large group of naturally occurring polyenes, which illustrate regular periodicity in their substitution, following the isoprene rule. These compounds are generally quite reactive, and rather sensitive to air, to light, to acid, etc., and not very much in the way of accurate structural data concerning them is available. In recent papers we have advocated the use of calculational methods to study many different kinds of molecules. Because of the difficulties which attend experimental work with polyenes, these constitute a class of compounds which might be especially well suited to calculational studies.

Some time ago we described a calculational scheme which involved the marriage of a classical force field calculation with a quantum mechanical (self-consistent field) π system treatment for hydrocarbons,[5a] which was later extended to conjugated carbonyl compounds.[5b] Important features of this approach were that it is not limited to planar systems for determining geometries and energies, and it automatically included steric effects. As a prelude to studying more complex molecules, it seemed that a thorough study of some small polyenes was in order. In the present paper we will discuss calculations applied to butadiene, hexatriene, and some methylated derivatives. The most thorough study reported along these lines to date was that of Simmons,[6] which was restricted to planar (or assumed planar) polyenes, in which there existed no substantial steric effects, so that standard bond angles and lengths could be assumed as a starting point. When these restrictions are relaxed, the calculated geometries (and of course related attendant properties, such as ultraviolet spectra, etc.) may change slightly in most cases, and may change dramatically in selected cases. A few scattered examples have been previously studied and reported by ourselves,[5,7] and also by Karplus and Warshel.[8] These latter workers employed a somewhat similar SCF-force-field method.

Molecules with two or more conjugated double bonds may exist in *s*-cis or *s*-trans conformations. The energy difference between the conformers depends, among other things, on the location of the *s*-cis bond and on whether and where there are substituents on the carbon chain. In this study, we shall examine the changes that occur in butadiene, *cis*- and *trans*-hexatrienes, and their monomethyl derivatives.

The calculations were carried out by the methods described previously, using the 1973 force field.[7a,9] The molecules studied are shown in Table I. All stable conformational isomers were considered. The letters c or t following the name of a hexatriene molecule stands for cis or trans isomer or conformer. The first letter refers to the 2–3 bond, the second to the 3–4 bond, and the third the 4–5 bond. A capital letter indicates that the bond under consideration is a double bond (configurational isomer) and a small letter indicates a single bond (conformation). The calculated energies and structural features including bond lengths, bond angles, and dihedral angles of the carbon skeleton are also given in Table I. For convenience in discussion we shall divide the molecules in five groups: the butadienes; the hexatrienes; the 1-methylhexatrienes; the 2-methylhexatrienes; and the 3-methylhexatrienes. Attempts shall be made to compare and correlate the data among the groups. In the following discussion, unless otherwise specified, the structural features described are those of the carbon chain skeleton.

Butadienes

According to the calculations, when the *s-trans*-butadiene molecule changes to a *s*-cis conformation, the bond lengths remain the same but the C–C–C bond angles increase by nearly 4°. The energy increase ΔE was calculated to be 2.6 kcal/mol (1973 force field). Both conformations are planar, and the rotational barrier is 7.31 kcal/mol (from the trans conformation). These facts are consistent with experiment.[10,11]

If a methyl group is placed on a terminal carbon of butadiene, the 1,3-pentadiene molecule is obtained. For present purposes it will be convenient to consider this as 1-methylbutadiene. There are two geometric isomers possible, cis and trans, and for each there are two conformers, *s*-cis and *s*-trans. Looking first at the trans isomer which is the more stable, the two conformations are both planar. The *s*-trans conformation is lower in energy than the *s*-cis by 2.1 kcal/mol. With the cis isomer, again there are two conformations. The more stable *s*-trans is planar, while the *s*-cis conformation is twisted considerably about the 2–3 bond (46°). The energy difference between the two conformations (2.58 kcal/mol) is substantially the same as was found for the conformations of the trans isomer, however.

When a nonterminal hydrogen atom of butadiene is replaced by a methyl group to form isoprene, some changes occur in the vicinity of the methyl group. The methylated double bond lengthens (by 0.003 Å) and the methylated single bond lengthens (by 0.006 Å). The bond angle opposite the methyl group ($\angle 123$) decreases from 122.5 to 118.8° and the neighboring bond angle increases from 122.5 to 124.6°. Similar changes are calculated when *trans*-hexatriene is methylated, which are in agreement with experimental data.[12] While *s-trans*-isoprene is calculated to be planar, the *s-cis*-isoprene molecule is nonplanar. By twisting about the single bond it avoids much of the bending strain that would exist in the planar molecule. Thus the bond angles increase only about 2°, as compared with the 4° increase in going from *s-trans*-butadiene to *s-cis*-butadiene. All forms of steric energy decrease except the torsional energy which increases by 3.2 kcal/mol, resulting in a net increase of 2.2 kcal/mol in going from a methylated *s*-trans to a methylated *s*-cis conformation. The rotational barrier from the trans conformation was calculated to be 6.0 kcal/mol.

According to our calculations, the energy differences between the cis and the trans forms, and the rotational barriers, are rather similar in butadiene and in isoprene. The rotational barrier of isoprene is unknown experimentally, the energy change for trans → cis was quoted by Dodziuk[13] as 1.5 ± 0.3 kcal/mol, based on temperature dependence of band areas in vibrational spectra. Our calculated value appears to be slightly high. Dodziuk also calculated for butadiene and isoprene isomerization energies similar to those calculated here.

Next, 2,3-dimethylbutadiene was examined. The trans conformation is planar, and more stable than the cis by 0.78 kcal/mol. The cis conformation is not planar, but rather twisted 43°. It is noted that the twisted conformation, which has a reduced bond order for the 2–3 bond, has this bond stretched out 0.015 Å more than it is stretched in the planar trans isomer. The double bonds are correspondingly shortened (by 0.005 Å).

Hexatrienes

There are two geometric isomers of hexatriene which differ in configuration about the central double bond. Similar changes in energies and bond angles as with butadiene occurred when one of the single bonds in hexatriene tTt took on a *s*-cis conformation. $\Delta E_{\mathrm{tTt} \rightarrow \mathrm{cTt}} = 2.7$ kcal/mol, which is expected of an unmethylated single bond isomerization. When two *s*-cis bonds were introduced, the total energy increase was 5.6 kcal.

The lowest energy *cis*-hexatriene conformer is the tCt. The conversion of the (unmethylated) trans double bond to the cis form was found to cost 3.1 kcal/mol. When one *s*-trans bond of the latter is converted to the *s*-cis conformation, the molecule (cCt) was expected to become highly strained, as now there are two consecutive cis bonds. However, it again releases much of the strain by taking on a nonplanar geometry, and the increase in energy by the introduction of the cis single bond is an additional 2.7 kcal. The molecule twists around the cis single bond by 46°. The rest of the carbon skeleton remains coplanar to within10°. Incidentally, this single bond was found to be considerably longer than usual (1.477 Å vs. 1.468), consistent with the poor π overlap. Isomerization of the second *s*-cis bond (to cCc) costs another 2.2 kcal/mol. This is even less than the 2.7 kcal/mol for the simple unmethylated single bond conversion. A close examination of the calculated data showed that in cCc the torsional angles about the two single bonds are smaller than those about the *s*-cis bond in cCt. Therefore, while the torsional energy increase is 4 kcal/mol from tCt to cCt, it increases only 2 kcal during the conversion from cCt to cCc.

It should be pointed out that in the electron diffraction study of *cis*-hexatriene, Traetteberg[14] found the molecule to be twisted 10° about the central double bond. This is quite unexpected in view of the high barrier of rotation about a double bond. Our calculation predicts a planar geometry with slightly larger than usual CCC bond angles around the cis double bond. When a torsional angle of 10° was imposed, the energy was found to increase by 0.6 kcal. It seems more likely to us that this molecule is planar, but the amplitude of the torsional motion may be fairly large.

1-Methylhexatrienes

The isomers are known with the methyl group in both the cis and trans positions, and their heats of formation are known. Fitting this difference (Table I) allows assignment of the sp^3–sp^2–sp^2–sp^2 torsional parameter.

2-Methylhexatrienes

The changes in structure and steric energy on addition of a methyl group to the second carbon of hexatriene tTt are nearly identical with those which resulted from the corresponding methylation in butadiene. When 2-methylhexatriene tTt is converted to 2-methylhexatriene tTc, the converted *s*-cis bond is unmethylated and the energy increase is 2.9 kcal/mol. In the conversion to 2-methylhexatriene cTt, a methylated bond is involved, and the energy increase is less, namely, 2.3 kcal. In going from tTt to cTc, the energy increment for the introduction of the two cis bonds is less than the additive value; ΔE is 4.3 kcal.

In the case of planar 2-methyl-*cis*-hexatriene, the methyl group on carbon 2 and the hydrogen atom on carbon 5 are at a distance much smaller than the sum of their van der Waals radii, and the steric energy is expected to be very high. This is an example of what Pauling[15] called a "hindered cis bond". The molecule alleviates the hindrance by assuming a nonplanar geometry. The dihedral angles about the C_2–C_3, C_3–C_4, and C_4–C_5 bonds are 166, 19, and 176°, respectively. The amount of torsion about the C_3–C_4 bond is larger than one might have guessed. Compared to the energy difference between *cis*-hexatriene and *trans*-hexatriene, here in going from tTt to tCt the van der Waals energy increase is smaller, and the torsional energy has increased much more. The net energy increase is 5 kcal, which is 2 kcal higher than in the simple hexatrienes.

One of the most interesting findings of this study is that while the *s*-trans is usually much favored energetically over the *s*-cis conformation, the 2-methylhexatriene tCt is not the only stable conformer. It was found that if the methylated single bond also assumed a cis conformation, the strain caused by the methyl group was largely released. The increase in torsional energy brought about by the additional cis conformation and higher degree of nonplanarity was largely compensated by decreases in bending and van der Waals energies. The calculation predicts that the *s*-cis conformer is of only slightly higher energy. Electron diffraction data on 2-methyl-*cis*-hexatriene are ambiguous in assigning the conformation. It was found[16] that both a distorted trans form and a distorted cis form could fit the data, but that the latter with a torsional angle of 50–60° about the *s*-cis bond probably fit better. We predict a mixture of the two conformations. That the methylated cCt conformation was similar in energy to the hindered methylated tCt conformation was also found to be true experimentally in another compound, the 11-*cis*-retinal. The NMR and theoretical studies of this molecule[17] found both the 12-*s*-cis and the 12-*s*-trans conformers exist in appreciable amounts at room temperature. A subsequent X-ray crystal structure study found the *s*-cis, with a dihedral angle of 38° at the 12-*s* bond.[18] Our calculation gave similar results.

Another interesting example of a highly sterically hindered molecule which prefers to be in the *s*-cis conformation is found in 2,4-dimethyl-1,3-pentadiene (1,1,3-trimethylbutadiene). The UV spectrum[19] showed the $\pi \rightarrow \pi$ transition to have a very low extinction coefficient, indicating a highly nonplanar conjugated system. A recent NMR study[20] concluded that the molecule was in a distorted *s*-cis rather than a distorted *s*-trans conformation. The dihedral angle about the C_2–C_3 bond was estimated to be 50 ± 15°. Our calculations gave two minimum energy conformations, one with a dihedral angle of 162.7°, the other 52.2°, the latter being more stable by 0.32 kcal.

If, on the other hand, the unmethylated single bond in 2-methylhexatriene tCt is converted to a *s*-cis bond, the methyl group is still in a crowded environment, and energy increases by 2.3 kcal. The energy is found to increase only slightly from the conversion of 2-methylhexatriene tCc to the cCc confor-

Table I. Steric Energy and Geometry of Butadiene, Hexatriene, and Their Methylated Derivatives

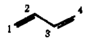
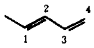
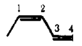
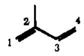
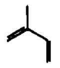
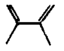
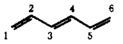
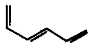
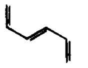
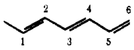
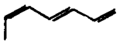
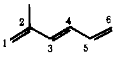
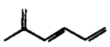
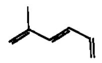
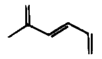
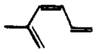
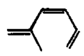
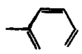
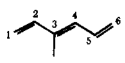
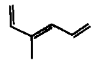
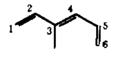
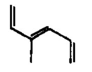
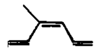
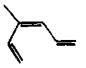
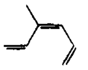
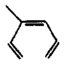
Molecule		ΔE_S,[a] kcal	R_{12}[b]	R_{23}[b]	R_{34}[b]	R_{45}[b]	R_{56}[b]	∠123[c]	∠234[c]	∠345[c]	∠456[c]	∠1234[c]	∠2345[c]	∠3456[c]
	t	0	1.346	1.471	1.346			122.5	122.5			180		
	c	2.62	1.346	1.471	1.346			126.4	126.4			0		
	Tt	0	1.348	1.471	1.346			122.7	122.5			180		
	Tc	2.71	1.348	1.471	1.346			126.7	126.6			0		
	Ct	0	1.349	1.471	1.347			127.2	122.3			180		
	Cc	2.58	1.345	1.480	1.342			126.2	123.4			46		
	t	0	1.349	1.477	1.346			118.8	124.6			180		
	c	2.26	1.346	1.480	1.344			120.7	124.5			37.4		
	t	0	1.350	1.486	1.350			120.5	120.5			180		
	c	0.78	1.345	1.511	1.345			120.3	120.3			43		
	tTt	0	1.347	1.468	1.355	1.468	1.347	122.5	122.7	122.7	122.4	180	180	180
	cTt	2.72	1.347	1.467	1.455	1.469	1.347	126.7	126.7	122.5	122.6	0	180	180
	cTc	5.59	1.347	1.468	1.355	1.468	1.347	127	126.6	126.6	127	0	180	0
	tCt	3.09	1.348	1.467	1.356	1.467	1.348	122.4	126.7	126.7	122.4	180	0	180
	cCt	6.12	1.343	1.477	1.352	1.468	1.347	123.3	126	125.2	122.5	45.7	8.1	177
	cCc	8.48	1.346	1.470	1.352	1.470	1.346	123.4	126.4	126.4	123.4	39.5	5.9	39.5
	1-Me TtTt	0	1.349	1.467	1.355	1.468	1.347	122.7	122.7	122.7	122.5	180	180	180
	1-Me CtTt	1.42	1.350	1.467	1.356	1.468	1.347	127.2	122.6	122.9	122.6	180	180	180
	2-Me tTt	0	1.351	1.474	1.355	1.468	1.347	118.8	125.0	122.7	122.6	180	180	180
	2-Me cTt	2.36	1.346	1.477	1.353	1.468	1.347	120.9	124.9	122.5	122.6	36.2	178.2	180
	2-Me tTc	2.87	1.351	1.475	1.355	1.468	1.347	118.8	125	126.8	127	180	180	0.7
	2-Me cTc	4.60	1.346	1.478	1.351	1.472	1.345	120.6	124.4	124.4	124.4	38.2	176.5	31.8
	2-Me tCt	5.19	1.350	1.477	1.355	1.467	1.347	118.2	128.1	126.3	122.6	166.4	19.2	175.7
	2-Me cCt	5.42	1.345	1.482	1.351	1.468	1.347	119.5	125.7	124.9	122.5	49.8	7.5	177.2
	2-Me tCc	7.38	1.349	1.478	1.351	1.475	1.343	118.3	127.3	126.2	122.2	167.3	16.1	43
	2-Me cCc	7.79	1.348	1.475	1.351	1.469	1.346	119.5	126	126.1	123.6	44.7	5.5	38.3
	3-Me tTt	0	1.347	1.478	1.361	1.469	1.348	126.9	117.8	126.0	122.5	173.4	179.0	178.3
	3-Me cTt	0.89	1.345	1.481	1.356	1.469	1.347	124.5	119.7	125.2	122.5	40.2	178.8	179.6
	3-Me tTc	2.32	1.347	1.478	1.356	1.479	1.343	125.1	118.1	126.5	123.5	174.8	179.6	47.1
	3-Me cTc	4.58	1.344	1.482	1.352	1.479	1.343	125.4	120.1	126.7	124.4	37.4	180	46.1
	3-Me tCt	2.05	1.348	1.474	1.361	1.469	1.348	124.9	122.2	129.1	122.4	180	0	180

Table I (*Continued*)

Molecule	ΔE_s,^{a} kcal	$R_{12}{}^b$	$R_{23}{}^b$	$R_{34}{}^b$	$R_{45}{}^b$	$R_{56}{}^b$	∠123^c	∠234^c	∠345^c	∠456^c	∠1234^c	∠2345^c	∠3456^c
 3-Me cCt	3.80	1.343	1.482	1.353	1.469	1.347	123.2	121.8	125.6	122.4	49.3	10.5	177.4
 3-Me tCc	4.41	1.347	1.476	1.355	1.478	1.343	124.5	120.1	126.6	123.2	172.7	12.4	44.9
 3-Me cCc	6.33	1.346	1.473	1.354	1.469	1.346	123.5	122.1	127.0	123.6	43	8	38.8

^{a}These are energies relative to the most stable conformation and isomer. ^{b}Distances are in angstroms. ^{c}Angles are in degrees.

mation, where again a hindered methyl group is traded for an *s*-cis conformation.

3-Methylhexatrienes

The 3-methylhexatriene molecule differs from the methylbutadiene and the 2-methylhexatriene in that the methyl group is no longer attached to an end double bond. It therefore sees two, instead of one, hydrogen atoms that are on the second nearest neighbor carbon atoms, namely, atoms 1 and 5. We shall refer to this kind of methyl group as "flanked". This arrangement has a high steric hindrance, for not only is the steric energy of 3-methylhexatriene tTt 1.6 kcal higher than that of 2-methylhexatriene tTt, but also the molecule has become nonplanar with the dihedral angle about the methylated *s*-trans bond equal to 173°. The changes upon methylation in bond lengths and angles in the neighborhood of the methyl group are also greater than in 2-methylhexatriene.

When the molecule is twisted along the methylated single bond (from 173°) to give cTt, it crosses an energy barrier to reach a second energy minimum at a dihedral angle of 40°. Other forms of steric energy decrease to balance most of the torsional energy increase. The net energy change (trans → cis) is 1.0 kcal compared to 2.2 and 2.3 kcal for the analogous changes in isoprene and in 2-methylhexatriene, respectively, where the methyl groups are not "flanked". This suggests that, other things being equal, a "flanked" methylated trans → cis single bond conversion is about 1.3 kcal lower in energy. In the other cis conformer, 3-methylhexatriene tTc, where the unmethylated single bond is the cis bond, the methyl group is in a position that makes this cis bond a "hindered *s*-cis" one. However, rotation about this bond is much easier than about a cis double bond. The stable conformation has a dihedral angle of 47° about the cis single bond compared to the 19° about the cis double bond in 2-methylhexatriene tCt. The energy increase from 3-methylhexatriene tTt to 3-methylhexatriene tTc is small, 2.3 kcal/mol (compared to 2.6 kcal in butadiene). The conversion of the 4–5 bond to a cis conformation releases much of the interaction between the methyl group and the hydrogen atom on carbon 5.

The energy difference between 3-methylhexatriene tTt and 3-methylhexatriene tCt is 2.1 kcal, which is 1.0 kcal lower than the difference between hexatriene tTt and hexatriene tCt. Although the cis bond is methylated, the molecule is planar.

In going from 3-methylhexatriene tCt to 3-methylhexatriene cCt, the energy increase is 1.7 kcal, which is in between the value of about 1.0 kcal for the conversion of a "flanked" methylated single bond and 2.3 for the conversion of an end-methylated single bond. This is not surprising because the methyl group on 3-methylhexatriene tCt is situated in a position between these two cases. When the unmethylated single bond is converted to a cis conformation, it costs 2.3 kcal, the same as a similar conversion in the 2-methylhexatriene molecule. The two energy increments were found to be essentially additive, thus $\Delta E_{\mathrm{tCt}\rightarrow\mathrm{cCc}} = 4.2$ kcal.

A survey of the calculated geometries of the molecules discussed above showed that the bond lengths and angles usually do not vary much upon conformational changes. The torsional angles take on a wide range of values, however, consistent with the small force constants for their deformation. It is noted that when there is no methyl group substitution and no consecutive cis double bond configurations, the molecule is planar. When a methyl group is on a trans single bond, experiencing no special steric hindrance from nearby bulky groups, the deviation from planarity is from 0 to 15° about the single bond. If it is situated on a cis single bond, then the deviation is in the neighborhood of 40°. When two or more consecutive cis double bonds are present, that part of the molecule takes on a helical shape with torsional angles near 40° about the *s*-cis bonds. The presence of a methyl group at an unhindered position merely increases the torsional angles by 3–4°, the basic features of the carbon skeleton are not altered. Note the similar geometrical features of hexatriene tCc and hexatriene cCc with their 2-methyl- and 3-methyl-substituted derivatives.

Comparison of the calculated geometries with available experimental data shows that, although the relative values agree well, in general the calculated carbon–carbon bond lengths are greater and the skeletal bond angles are smaller. Comparisons are not always straightforward for the following reasons. The experimental values were derived from electron diffraction data by fitting interatomic distances. Often assumptions were made about certain bond lengths and bond angles. Since the same distance between nonbonded atoms can be derived by simultaneously increasing the bond length and decreasing the bond angles or vice versa, our calculated geometries may fit the diffraction data about equally well.

Besides geometries of the molecules, the above analysis reveals that there are systematic energy changes accompanying geometrical and conformational changes. Some of the more important conclusions we have reached with regard to *s*-cis–*s*-trans interconversions are stated as follows. (1) When there exists a "flanked" methylated (or other unbranched alkylated) single bond in a molecule, the *s*-cis conformer population is appreciable. With an energy difference of 1.0 kcal, the equilibrium *s*-cis/*s*-trans population ratio would be about 0.2 at room temperature. (2) When there is a "hindered" cis bond, the single bond to which the methyl group is attached may take on either a cis or a trans conformation. The two conformers are of similar energy. (3) When there is steric hindrance due to the presence of several closely situated alkyl groups, a cis conformation may be energetically similar to or preferred over a trans conformation. (4) With the exceptions of the cases mentioned above, the *s*-cis conformer is usually much less stable than the *s*-trans one, and its contribution may be neglected.

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Experimental and Theoretical Studies on Magnetic Circular Dichroism and Circular Dichroism of Triptycene Derivatives

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Abstract: The MCD, CD, and UV spectra of substituted triptycenes were measured. Some overlapping absorption bands were separated in the MCD and CD spectra. Spectroscopic assignments were discussed on the basis of the signs of the MCD and CD spectra. Faraday *B* terms and rotational strengths were calculated using wave functions obtained from the "molecules in molecule" method and the results are in good agreement with experimental data. The absolute configurations of optically active triptycenes determined by the present CD spectral analysis are consistent with those obtained from X-ray crystallographic analysis using the Bijvoet method.

Triptycene, one of the most interesting cage compounds with conjugated systems around its cage, was first synthesized by Bartlett et al.[2] as early as 1942. It contains three benzene rings which are tightly connected at the ortho position by two sp^3-hybridized carbon atoms. If substituent groups are dissymmetrically introduced to the benzene rings of triptycene, the compound becomes optically active. The absolute configurations of optically active triptycenes have been determined using the Bijvoet method of X-ray crystallographic analysis,[3,4] and exciton theoretical analysis of the circular dichroism (CD) spectra.[5-9]

Triptycene derivatives show many absorption bands due to the $\pi \rightarrow \pi^*$ transitions of three benzene rings in the ultraviolet region. However, a detailed explanation of the spectra is not possible because of large overlaps of the absorption bands.

On the other hand, the magnetic circular dichroism (MCD) technique has made remarkable progress in elucidating magnetic moments of the ground and excited electronic states and in clarifying spectroscopic assignments of ions and molecules.[10-13] The molecules with an n-fold axis ($n > 2$) are expected to show Faraday A and C terms resulting from Zeeman splitting of the degenerate ground and excited state, whereas the lower symmetrical molecules exhibit only the Faraday B term due to mixing of the electronic states by the external magnetic fields. Recently, the effect of substituent groups on the signs of the Faraday B terms of substituted benzenes has become of great interest.[14-18] The signs of the MCD spectrum of monosubstituted benzene with electron-donating substituent groups are negative and positive for the first and second transitions, respectively, whereas the situation is reversed for benzene derivatives with electron-accepting groups.[18] From this point of view, it seems interesting to try to interpret the complex absorption spectra of triptycene derivatives using the signs of the MCD bands of constituent benzene derivatives. Although it is a matter of fact that the CD technique is a powerful tool in clarifying the assignments of the absorption bands of optically active triptycenes, the MCD technique should be noted to be useful in such a sense that it is applicable not only to optically active triptycenes, but also to optically inactive or racemic triptycenes. In this work, spectral assignments of the triptycene derivatives are examined not only by analyzing the CD spectrum of optically active triptycenes, but also by comparing the signs of the MCD spectra of triptycene derivatives with those of substituted benzenes. In addition, the Faraday B terms and rotational strengths of substituted triptycenes are calculated by the use of wave functions obtained from the "molecules in molecule" method.[19]

Experimental Section

Synthesis of the samples was described in previous papers.[20] Spectrograde methanol, ethanol, and dioxane were used as solvents. MCD and CD spectra were measured with a JASCO J-20A recording spectropolarimeter, and UV spectra were recorded on a Hitachi EPS-3T recording spectrophotometer. A 12.2-kG electromagnet was used for measurement of the MCD spectra.

Experimental rotational strengths (R) and Faraday B terms were obtained from

$$R = \frac{7.51 \times 10^{-5}}{\nu_{\max}} \int_{\text{band}} [\theta] \, d\nu \qquad (1)$$