The Absorption and Circular Dichroism Spectra of Chiral Triquinacenes

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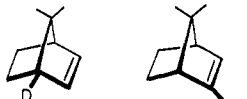
Abstract: The three deuterated, optically active 2,3-dihydrotriquinacenes **11a–c** of known absolute configuration have been prepared from (+)-(1*S*)-2,3-dihydrotriquinacen-2-one (**4**). The optically active monodeuterated triquinacene **12** was obtained from the same precursor and (−)-(1*S*)-2-methyltriquinacene (**15**) from (−)-triquinacene-2-carboxylic acid. The chirality in **11** and **12** is due solely to isotopic substitution. Although the three dihydrotriquinacenes have CD effects smaller than could be measured, presumably because of the distance between the deuterium atoms and the chromophore, the absorption and circular dichroism spectra of **12** and **15** proved very revealing. The contributions of the composite double bonds and peripheral substituents to the observed Cotton effects are analyzed in a manner which is consistent with the observed transitions.

The effect of deuterium as an isolated perturber on the electric dipole forbidden n → π* transitions of chiral deuterio ketones has recently been examined intensively and with considerable success.[1] Simultaneously, there have appeared a smaller number of reports dealing with experimental assessment of the extent to which chiral isotopic perturbation is seen in the weaker electric dipole allowed π → π* transitions of conformationally rigid olefins.[2-4] The placement of a C–D bond at various positions in relatively inflexible ketones generates chiroptical contributions which are dissignate (antioctant). The same effect has been observed in (1*S*)-(1-^{2}H)apobornene (**1**) but not in **2** where the octant con-

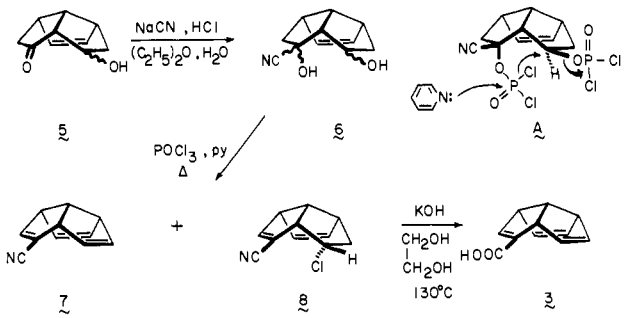


1 **2**

tribution is consignate.[4] Such net contributions of deuterium substituents to the rotary strength have been attributed to shorter C–D bond lengths, effectively smaller size, and reduced polarizability relative to their C–H counterparts.[4] Thus, a change in steric environment alone is presently considered capable of reversing the observed isotope-induced chiral perturbation.

Because new and different chiral molecular systems can be expected to constitute interesting test cases for advanced models of chirality function, we were led to examine the absorption and CD spectra of optically active (1*R*,4*S*,7*R*,10*S*)-(2-^{2}H)triquinacene,[5] the related methyl derivative, and several 2,3-dihydrotriquinacenes which owe their optical activity to deuterium substitution. Since the parent triquinacene hydrocarbon and the dihydro derivative possess C_{3v} and C_s symmetry, respectively, both ring systems are achiral. Consequently, these conformationally locked ring systems provide an ideal opportunity for observing the extrachromophoric dissymmetric perturbation caused by the D or CH_3 group.

Scheme I



5 **6** **A** **7** **8** **3**

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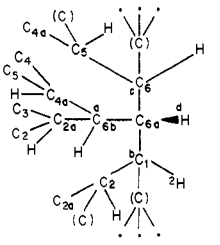
(5) Joy Merritt of Chemical Abstracts Service has informed us that the current CA index name for (+)-**12** is (2a*S*,4a*R*,6a*R*,6b*S*)-2a,4a,6a,6b-tetrahydro(1-^{2}H)cyclopenta[*cd*]pentalene, in accord with the IUPAC nomenclature recommendations issued in 1978. Importantly, a distinction must be made between isotopically substituted compounds and isotopically labeled compounds (rules H-1.23 and H-1.24). Since (+)-**12** is isotopically substituted, the naming must accord with rules H-2.11 and H-3.22. The specific assignment of *R* and *S* to the chiral centers follows Cahn, Ingold, and Prelog (*Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 385). For example, the tree diagram to the third level for the chiral center at position 6a is drawn as follows



At this level, it is determined that the pathway from C_{6a} to C_{6b} is preferred to either the pathway from C_{6a} to C_6 or the pathway from C_{6a} to C_1 because C_3, C_2, and H are preferred to three phantom atoms of atomic number zero. Further exploration on the remaining pathways from C_{6a} to C_6 and from C_{6a} to C_1 reveals that these pathways cannot be differentiated by subrule 1. Therefore, subrule 2, higher atomic mass number precedes lower, is applied to these two pathways. When the ^{2}H of the pathway C_{6a}–C_1 is compared to the H of pathway C_{6a}–C_6, the tie is broken with the C_{6a}–C_1 pathway having priority. Thus, the relative priorties of the substituents at C_{6a} are $C_{6b} > C_1 > C_6 > H$. This results in assignment of the chiral descriptor *R* to position 6a. Note that the explorations are carried to exhaustion under a subrule before proceeding to the next subrule.

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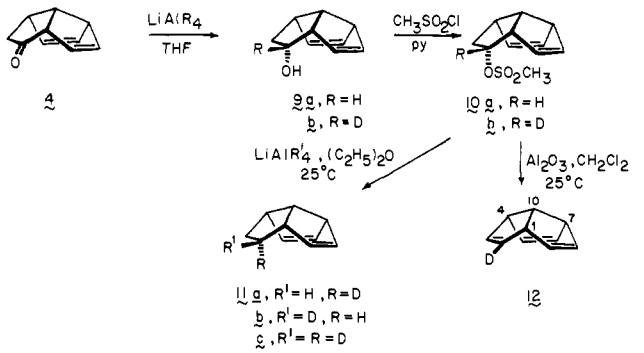
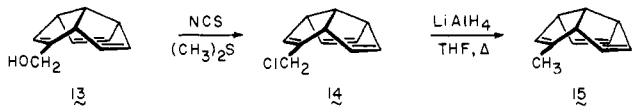
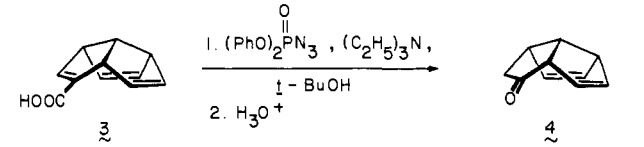
Scheme II



Scheme III



Synthesis. We previously reported an entry into optically active triquinacene derivatives through the resolution of triquinacene-2-carboxylic acid with (+)-(*R*)-α-methylbenzylamine.[6] The (−)-enantiomer so obtained (**3**) was converted by Curtius rearrangement to (+)-2,3-dihydrotriquinacen-2-one whose absolute configuration was established as 1*S* (e.g., **4**) on the basis of its chiroptical properties.[7] In the present study, a more expedient route to both **3** and **4** was devised (Scheme I).[8] Treatment of **5**[9] with hydrogen cyanide in a two-phase (ether–water) solvent system according to Ohkata[10] was most effective in delivering the desired cyanohydrin. The action of phosphorus oxychloride in pyridine on **6** provided a mixture of triene nitrile **7** and *endo*-chloronitrile **8** in a 40:60 ratio. The stereochemical assignment to **8** is based on spin-decoupling experiments and appropriate spectral comparison with other dihydrotriquinacenes of endo configuration. The observed stereochemistry was not anticipated in view of the concave nature of these cup-shaped molecules and may arise as the result of a unique intramolecular delivery mechanism as shown in A. Although conditions for the conversion of **8** to **7** were not found, the mixture of nitriles could be transformed into **3** by heating in wet ethylene glycol containig potassium hydroxide. Importantly, the steps outlined in Scheme I can be carried out on large scale if required.



Resolution of **3** as before provided a levorotatory sample of 93% ee as determined by conversion to (+)-**4**. Reduction of the ketone with $LiAlH_4$ or $LiAlD_4$ gave **9a** and **9b**, respectively, in high epimeric purity. Further reduction of the derived mesylates with the appropriate aluminate proceeded via efficient S_N2 substitution to provide all three deuterated hydrocarbons (**11a–c**, Scheme II). The monodeuterated triquinacene **12** was obtained by elimination of methanesulfonic acid from **10b** on activated alumina.[9,11]

(−)-2-Methyltriquinacene (**15**) was prepared by reduction of (−)-**3** with alane, conversion of the resulting alcohol (**13**) to chloride **14** with *N*-chlorosuccinimide and dimethyl sulfide,[12] and a second reduction with $LiAlH_4$ (Scheme III).

Table I. Experimental Polarimetric Data (93% ee in All Cases)

hydrocarbon	concn in $CHCl_3$, mg/mL	$[\alpha]^{22}_D$	$[\alpha]^{22}_{365}$
11a	1.0	−0.16 ± 0.05°	+0.07 ± 0.05°
11b	0.72	−0.24 ± 0.07°	−0.52 ± 0. 07
11c	0.80	−0.50 ± 0.06°	−1.09 ± 0.06°
12	0.87	+0.77 ± 0.06°	+4.29 ± 0.06°

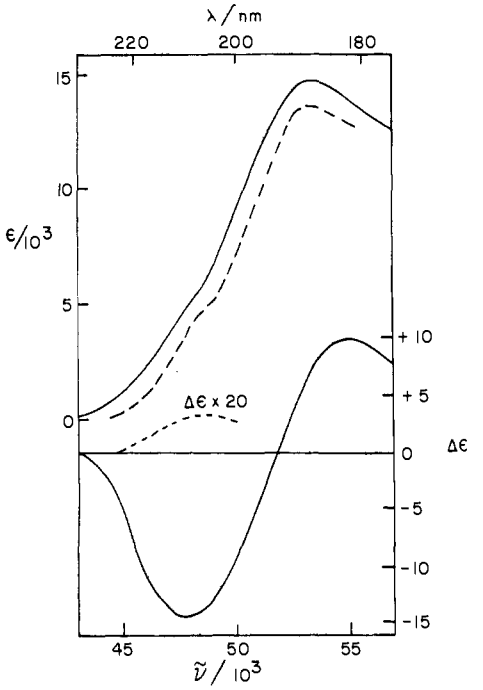


Figure 1. The absorption spectra (upper curves) and the circular dichroism (lower curves) of **15** in 3-methylpentane solution (full curve) and of **12** in pentane solution (broken curve).

The polarimetric data for **11** and **12** are compiled in Table I while the ^{13}C chemical shifts of the 2,3-dihydrotriquinacenes are listed in Table II. The unobserved signal in the case of **11c** is the result of C_2 substitution by two deuterium atoms which generate a quintet whose low peak heights are lost in the background noise. As concerns the monodeuterated derivatives **11a** and **11b**, the C_2 signal appears as a widely space triplet (J_{C-D} = 19.53 Hz) shifted to slightly higher field. Interestingly, a deuterium atom positioned endo generates a higher level of shielding ($\Delta\delta$ = 0.34 ppm) relative to the exo isomer ($\Delta\delta$ = 0.29 ppm). The vicinal contributions of these isotopic substituents in **11a** and **11b** to the shifts of C_1 and C_3 are small but decidedly shielding in line with existing precedent.[13] In **11c**, these effects are appropriately magnified.

Absorption and Circular Dichroism Spectra. The absorption and CD spectra of the triquinacenes **12** and **15** in paraffin solvents were obtained with the instruments previously described.[14] The spectra were measured at ambient temperature and, in the case of **15**, at liquid nitrogen temperature over the 225–175-nm range or, in the case of **12**, to the CD signal-to-noise 1:1 limit at 200 nm (Figure 1). The dissymmetry ratio ($g = \Delta\epsilon/\epsilon$) of **12** at the CD maximum (206.5 nm) has a value (3×10^{-5}) close to that of the instrumental limit ($g \approx 10^{-5}$), and the *g* ratios of the chiral

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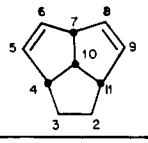
Table II. ^{13}C NMR Shifts of 2,3-Dihydrotriquinacene and Its Deuterated Analogues (20.1 MHz, $CDCl_3$ Solution)[a]



carbon		11a	11b	11c
1	50.539	50.490	50.490	50.393
2	34.469	35.100, 34.129, 34.129 (J_{C-D} = 19.53 Hz)	35.149, 34.138, 33.207 (J_{C-D} = 19.53 Hz)	
3	34.469	34.421	34.421	34.324
4	50.529	50.490	50.590	50.539
5	132.829	132.829	132.829	132.829
6	133.703	133.655	133.655	133.655
7	57.676	57.724	57.724	57.724
8	133.703	133.655	133.655	133.655
9	132.829	132.829	132.829	132.829
10	51.122	51.170	51.170	51.170

[a] Values in ppm relative to Me_4Si error limits = ±0.024 ppm.

deuterated dihydrotriquinacenes **11** unfortunately lie below this limit.

No significant differences were observed between the ambient- and the low-temperature spectra of **15**. A substantial blue shift of the absorption and CD due to the olefin Rydberg $\pi \rightarrow 3s$ transition on cooling has been reported for a range of chiral monoolefinic derivatives,[14] and it is concluded that the corresponding Rydberg transition or transitions do not make a prominent contribution to the isotropic and CD absorption of this triene.

The lower energy CD band of **15** lies in a frequency region where the isotropic absorption is small and the dissymmetry ratio is relatively large ($g_{max} = -3 \times 10^{-3}$), indicating that the corresponding electronic transition has a substantial magnetic dipole moment and a minor electric dipole moment. The indication is in accord with expectations of a simple independent-systems model for triquinacene, wherein it is assumed that there is no electron exchange between the three olefin chromophores, which interact only coulombically through the potential between the transitional charge distributions of the individual chromophores. This assumption is adopted here, although a very small overlap integral of 0.054 between the $2p_\pi$ orbitals of the nearest-neighbor carbon atoms in two different olefin groups of triquinacene has been estimated,[15] and the UV photoelectron spectrum suggests[16] a small splitting (0.35–0.4 eV) between the symmetric (a_1) and degenerate antisymmetric (e) combination of π orbitals in the C_{3v} system of the parent hydrocarbon.

The area of the isotropic absorption band of **15** corresponds to a dipole strength of 21 D^2 and, on the basis that the absorption arises from the $\pi \rightarrow \pi^*$ transitions of three olefin chromophores, each of the individual $\pi \rightarrow \pi^*$ transitions has an electric dipole moment of 2.65 D (Debye unit, 10^{-18} esu cm). The three electric transition moments, isoenergetic in the zero order, are coupled coulombically in a lower energy symmetric mode, with A_2 symmetry in the C_{3v} point group of the parent triquinacene molecule, and a higher energy degenerate mode with E symmetry (parts a and b of Figure 2, respectively). The energy interval between the two coupling modes is $3V_{12}$, where V_{12} refers to the potential between the individual transition moments of two olefin groups, μ_{o1} and μ_{o2}, given by[17]

$$V_{12} = \mu_{o1} \cdot \mathbf{G}_{21} \cdot \mu_{o2} \quad (1)$$

with

$$\mathbf{G}_{21} = [(R_{21})^2 - 3\mathbf{R}_{21}\mathbf{R}_{21}]R_{21}^{-5} \quad (2)$$

In eq 2, $\mathbf{R}_{21}$ refers to the position vector of the center of the first olefin chromophore in triquinacene from the center of the second olefin chromophore and R_{21} is the corresponding scalar distance. The structural data for the parent molecule[18] and the chromophore

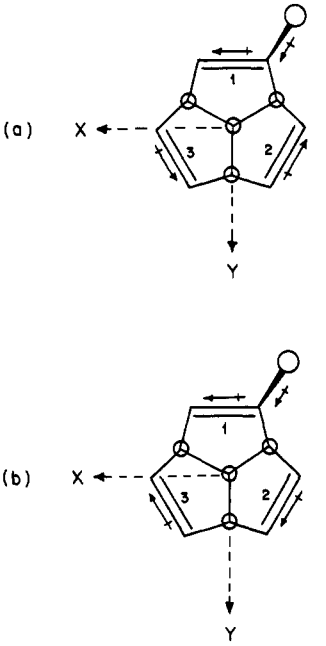


Figure 2. The independent-systems model for the $\pi \rightarrow \pi^*$ transition of **12** and the dipole induced in the substituent group by the transition charge distribution for (a) the A_2 coupling mode of the three olefin $\pi \rightarrow \pi^*$ excitation moments with $\Delta\bar{\alpha}(R)$ positive and (b) one component (eq 6) of the E coupling mode of the three olefin excitation moments with a positive polarizability anisotropy, $(\alpha_\parallel - \alpha_\perp)$, in the exocyclic C–R bond.

Table III. Observed and Calculated Rotational Strengths (cgs Unit, esu cm erg G^{-1}) of the Chiral Triquinacenes

compd	$\nu/10^3$ cm^{-1}	$R_{obsd}/10^{-40}$ cgs	$R_{calcd}/10^{-40}$ cgs
15	47.8	−36	−29 (A_2)
	54.9	+21	+16 (E)
12	48.4	+0.38	+0.34 (A_2)

transition moment of 2.65 D give V_{12} a value of −1480 cm^{-1}. The resultant molecular $\pi \rightarrow \pi^*$ transition to the A_2 and the E excited state thus have an expected separation of 4440 cm^{-1}, with the former transition, which is electric dipole forbidden in triquinacene itself, lying at the lower frequency. The observed interval between the absorption maximum of **12** and **15** at 187 nm and the weak shoulder, 205–210 nm, is some 5000–6000 cm^{-1}. The separation between the positive and the negative CD band of **15** is 7100 cm^{-1} (Table III). The larger interval in the latter is due, in part at least, to the frequency repulsion of the CD extrema, on account of the overlap of adjacent oppositely signed rotational strengths on the frequency ordinate.

The resultant molecular $\pi \rightarrow \pi^*$ transition to the A_2 excited state of **12**, while electric dipole forbidden, has a magnetic dipole moment with z polarization (Figure 2a). The magnetic dipole

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transition moment, $m_{\pi\pi^*}{}^z(A_2)$, is evaluated as 1.29 μ_BF (Bohr magneton unit, 9.27 × 10^{-21} erg g^{-1}) from the expression

$$m_{\pi\pi^*}{}^z(A_2) = -i\pi\bar{\nu}_{\pi\pi^*}(1/\sqrt{3})\sum_n(\mathbf{R}_n \times \mu_{on}) \quad (3)$$

where $\mathbf{R}_n$ is the position vector of the center of the nth olefin chromophore in triquinacene from the centroid of the eqilateral triangle formed by the three olefin groups in the XY plane common to those groups and μ_{on} is the local electric dipole $\pi \rightarrow \pi^*$ transition moment (2.65 D) of the nth chromophore.

In a 2-substituted triquinacene, the molecular $\pi \rightarrow \pi^*$ transition to the A_2 excited state acquires a first-order electric dipole moment which is induced in the substituent group (R) by the Coulomb potential of the $\pi \rightarrow \pi^*$ transitional charge distribution. A component of the electric dipole induced in the substituent group is collinear with the intrinsic magnetic dipole transition moment, $m_{\pi\pi^*}{}^z(A_2)$ (eq 3), giving a nonvanishing rotational strength

$$R_{\pi\pi^*}(A_2) = Im[\mu^z(R)m_{\pi\pi^*}{}^z(A_2)] \quad (4)$$

The z component of the electric dipole induced in the substituent is given by approximating the transitional charge distribution as a trimer of point dipoles (Figure 2a) in the form

$$\mu_{\pi\pi^*}{}^z(A_2) = -\Delta\bar{\alpha}(R)(1/\sqrt{3})\sum_n \mu_{on}G_{nz} \quad (5)$$

where the geometric tensor,[19] G_{nz}, analogous to eq 2, governs the potential between the z component of the dipole centered on the substituent (R) and the local electric dipole of the $\pi \rightarrow \pi^*$ transition in the nth olefin chromophore, with a polarization specified by the numbering n = 1, 2, or 3 (Figure 2a). The most important term in the sum of eq 5 refers to the olefin chromophore into which the group R is substituted, i.e., chromophore 1 where the local electric dipole $\pi \rightarrow \pi^*$ transition moment has x polarization (Figure 2a).

In eq (5), $\Delta\alpha(R)$ refers to the difference between the mean electric dipole polarizability of the substituent group (R), or substituent and bond (C–R), and the hydrogen atom or C–H group replaced, measured, strictly speaking, at the $\pi \rightarrow \pi^*$ transition frequency.[19] The mean polarizability of ethane ($\bar{\alpha}(C_2H_6)$ = 4.47 Å^3) measured[20] at 633 nm and of methane and its perdeuterio analogue ($\bar{\alpha}(CH_4)$ = 2.640 Å^3 and $\bar{\alpha}(CD_4)$ = 2.605 Å^3) measured[21] at 492 nm suggest for the visible wavelength region the $\Delta\bar{\alpha}(R)$ values of +1.83 and −0.01 Å^3 for the replacement of H by CH_3 and D, respectively, at the 2-position of triquinacene. These $\Delta\bar{\alpha}(R)$ values were employed without a correction to the higher frequency of the $\pi \rightarrow \pi^*$ transition of triquinacene for the conservative (minimum) estimates of the rotational strength, $R_{\pi\pi^*}(A_2)$, listed in Table III, which are based upon eq 3–5.

In the 225–175-nm region of the $\pi \rightarrow \pi^*$ absorption of triquinacene, the mean polarizabilities, $\bar{\alpha}(R)$, the increments, $\Delta\bar{\alpha}(R)$, are larger, but the correction to higher frequencies introduces uncertainties and limits the basis of the mechanism proposed, which is founded upon experimental structural, spectroscopic, and polarizability data. On this empirical basis, the estimates of the rotational strength, $R_{\pi\pi^*}(A_2)$, for **12** and **15** are found to have the correct sign and order of magnitude (Table III).

The isotropic $\pi \rightarrow \pi^*$ absorption intensity of triquinacene according to the independent-systems model arises principally from the doubly degenerate E coupling mode of the individual $\pi \rightarrow \pi^*$ excitations of the three olefin chromophores (Figure 2b). The individual components of the E excited state are represented by

$$\psi_1(E) = (1/\sqrt{6})[2\chi_1 - \chi_2 - \chi_3] \quad (6)$$

$$\psi_2(E) = (1/\sqrt{2})[\chi_2 - \chi_3] \quad (7)$$

where χ_n refers to the $(\pi^{-1}\pi^*)$ excited configuration of the nth olefin chromophore. The molecular $\pi \rightarrow \pi^*$ transition in triquinacene to each component of the E excited state is electric dipole allowed, to $\psi_1(E)$ with x polarization (Figure 2b), and to $\psi_2(E)$ with y polarization. In the parent molecule, the transition to the E excited state is devoid of a magnetic dipole moment, but the introduction of substituent group with an anisotropic polarizability tensor, as in the chiral derivative **12**, provides the $\pi \rightarrow \pi^*$ transition to the E state with a nonvanishing rotational strength.[19,22]

Specifically, for the transition to the component $\psi_1(E)$ (Figure 2b), the potential of each of the three chromophoric electric dipole excitation moments induces an electric dipole along the direction of the exocyclic C–CH_3 bond in **15** which is proportional to the bond polarizability anisotropy, $(\alpha_\parallel - \alpha_\perp)$. The anisotropy refers to the difference between the cylindrical symmetry, in the direction parallel ($\alpha_\parallel$) and perpendicular ($\alpha_\perp$) to the bond or principal axis direction. Values of the anisotropy, $(\alpha_\parallel - \alpha_\perp)$, are +0.72 Å^3 for the C–C bond[23] and +0.77 Å^3 for the ethane molecule.[20]

The major contribution to the electric dipole induced in the C–CH_3 bond of **15** in the transition to the E excited state derives from the potential of the local component excitation moment μ_{o1} of the particular olefin chromophore to which the methyl group is bonded (Figure 2b). The induced dipole, μ(C–CH_3), shares a common plane with the local chromophore transition dipole, μ_{o1}, but not with the corresponding component transition moments, μ_{o2} and μ_{o3}, of the other two olefin chromophores. The coupling of the induced dipole μ(C-CH_3) to the component transition moments μ_{o2} and μ_{o3} produces an overall helical charge displacement, right-handed for the configuration **15**, giving the transition to the E excited state the rotational strength

$$R_{\pi\pi^*}(E) = (\pi/\sqrt{6})\bar{\nu}_{\pi\pi^*}\sum_n[\mu_{on}\cdot\mathbf{R}_{nC} \times \mu(C\text{–}CH_3)] \quad (8)$$

The sum in eq 8 is restricted to the olefin chromophores n = 2 and 3 (Figure 2b), as the triple scalar product vanishes for the case n = 1. In eq 8 $\mathbf{R}_{nC}$ refers to the position vector of the center of the exocyclic C–CH_3 bond in **15** directed from the center of the nth olefin chromophore. The induced electric dipole μ(C–CH_3) effective in the generation of the rotational strength $R_{\pi\pi^*}(E)$ (eq 8) is evaluated as 0.62 D from the analogue of eq 5, employing the C–C bond polarizability anisotropy[23] of +0.72 Å^3 and the assumption that μ(C–CH_3) and the μ_{on} are point dipoles located at the center of the exocylic C–C bond and the center of the nth olefin chromophore, respectively. The structural data for the achiral parent molecule[18] and an exocyclic C-C bond length of 1.54 Å in **15**, together with the value of 2.65 D for each μ_{on} from the spectra recorded (Figure 1), give through eq 8 the value of $R_{\pi\pi^*}(E)$ listed, which is of the correct sign and order of magnitude (Table III). With the phases chosen, the second of the degenerate coupling modes (eq 7) makes a minor (<10%) additional positive contribution to $R_{\pi\pi^*}(E)$ in **15**, the two modes of eq 6 and 7 being no longer equivalent in the substituted molecule.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 467 spectrophotometer. The ^{1}H NMR spectra were determined with Varian EM-390, Bruker HX-90, and Bruker WP-200 instruments, and apparent splittings are given. The ^{13}C NMR spectra were obtained on a Bruker WP-80 spectrometer. An AEI-MS9 spectrometer operating at an ionization energy of 70 eV was used for the mass spectral measurements. Optical rotation data were determined on a Perkin-Elmer Model 241 polarimeter. Preparative scale VPC separations were performed with Varian Aerograph Model A90-P3 instruments equipped with thermal conductivity detectors. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

9-Hydroxy-2,3,8,9-tetrahydrotriquinacen-2-one (5). A modification of Deslongchamps' procedure[9] was utilized. Thiele's acid (200 g) was intimately mixed with sodium azide (140 g) in a 1-L flask and slowly added (*Caution* foaming) through Gooch tubing to 1.3 L of concentrated sulfuric acid contained in a 5-L Morton flask. Upon completion of the addition, the reaction mixture was stirred overnight, poured onto 6 L of

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crushed ice, and continuously extracted with dichloromethane for 5 days. The crude product (49.1 g) was filtered through a plug of Florisil to give 40 g (27%) of the diketone as a waxy white solid.

A solution of this diketone (10 g) in 400 mL of methanol contained in a quartz vessel was irradiated with a 450-W Hanovia lamp for 90 min. Five such runs were combined and evaporated in vacuo. No attempt was made to purify the keto aldehyde which was dissolved in 2.5 L of acetone and treated with 390 mL of 3 N hydrochloric acid. The reaction mixture was stirred for 2 h, neutralized with solid sodium bicarbonate, and placed under reduced pressure to remove the acetone. The aqueous phase was extracted with dichloromethane (2 × 250 mL), and the combined organic layers were washed with water, dried, and evaporated. The brownish oil was chromatographed on silica gel (150 g, elution with ether–hexane, 1:1) to furnish 39.3 g (78.6%) of **5** as a nearly colorless oil.

2-Cyano-2,9-dihydroxy-2,3,8,9-tetrahydrotriquinacene (6). A solution of **5** (28 g, 0.17 mol) dissolved in ether (200 mL) was stirred with 200 mL of water containing 50.2 g (1.04 mol) of sodium cyanide. With ice cooling, concentrated hydrochloric acid (56 ml) was added dropwise and stirring was maintained for 3 h. The layers were separated, and the aqueous phase was extracted with ether (2 × 100 mL). The combined ether layers were dried and evaporated to leave 32 g (98%) of crude cyanohydrin which was isolated as a white powder: mp 112–116 °C, from chloroform–ether; IR (KBr, cm^{-1}) 3445, 3350, 2228, 1155, 1055, 773; ^1H NMR ($CDCl_3$, δ) 5.67–5.27 (m, 2 H), 4.67–4.33 (br s, 2 H), 4.0–1.6 (series of m, 9 H); mass spectrum, *m/e* 191 (M^+).

2-Cyanotriquinacene (7) and 2-Cyano-*endo*-9-chloro-8,9-dihydrotriquinacene (8). The unpurified cyanohydrin prepared above dissolved in ice-cold pyridine (200 mL) was treated dropwise under argon with 80.4 g (48 mL, 0.524 mol) of phosphorus oxychloride. After 5 h at 0 °C, the mixture was heated at reflux for 1 h, cooled, and poured onto a mixture of 500 g of ice and 120 mL of concentrated hydrochloric acid. The products were extracted into dichloromethane (1 × 200 mL and 4 × 100 mL), dried, and freed of solvent. The resulting brown oil was passed down a column of silica gel (150 g, elution with ether–hexane, 1:1) to give 20 g (67% overall) of an oily solid consisting of approximately 40% of **7** and 60% of **8** (^1H NMR analysis). The components were easily separable by high-pressure liquid chromatography on silica gel (Waters Prep 500, elution with hexane–ethyl acetate, 95:5). However, the mixture can be used directly in the next step.

For **7**: colorless oil; molecular distillation, bp 37 °C (0.02 mm); IR (neat, cm^{-1}) 2212, 1598; ^1H NMR ($CDCl_3$, δ) 6.35 (s, 1 H), 5.68 (s, 2 H), 5.80–5.33 (m, 2 H), 3.80 (s, 4 H); mass spectrum, *m/e* calcd 155.0735, obsd 155.0738.

For **8**: colorless needles, mp 96–97 °C (from methanol); IR (KBr, cm^{-1}) 2215, 1605, 723; ^1H NMR ($CDCl_3$, δ) 6.76 (s, 1 H), 5.70 (m, 2 H), 4.39 (dt, $J_{8n,9}$ = 10.8, $J_{8x,9}$ = 6.3, $J_{1,9}$ = 6.3 Hz, 1 H), 4.00–3.76 (m, 1 H), 3.74–3.50 (m, 1 H), 3.43 (q, $J_{1,10} = J_{4,10} = J_{7,10}$ = 9 Hz, 1 H), 3.05 (m, 1 H), 2.42 (quintet, $J_{8n,8x}$ = 12.5, $J_{8x,9}$ = 6.3, $J_{7,8x}$ = 6.1 Hz, 1 H), 1.56 (m, 1 H); *m/e* calcd 191.0502, obsd 191.0506.

Anal. Calcd for $C_{11}H_{10}ClN$: C, 68.93; H, 5.26. Found: C, 68.79; H, 5.30.

Triquinacene-2-carboxylic Acid (3). An unpurified mixture of **7** and **8** (14.8 g, 0.085 mol equiv), ethylene glycol (150 mL), and water (10 mL) was heated gently under argon while potassium hydroxide pellets (14.2 g, 0.254 mol) were added. The mixture became homogeneous at about 70 °C. After being heated at 135–140 °C for 20 h, the mixture was cooled, diluted with water (400 mL), and extracted with ether (2 × 200 mL). The combined ether layers were washed with water (100 mL). Careful acidification of the cooled (0 °C) aqueous phases with 3 N hydrochloric acid was followed by extraction with dichloromethane (3 × 200 mL). The combined organic layers were washed with brine (150 mL), dried, and evaporated. Passage of the resulting brown oil through silica gel (dichloromethane elution) afforded 4.3 g (30%) of **3** as a white solid, mp 128–132 °C (lit.[7] mp 131–133 °C). The spectral properties of this material were identical with those previously reported.[7]

When pure samples of both **7** and **8** were separately caused to react in the above manner, similar yields of **3** were achieved.

Resolution of 3. The acid was resolved as its α-(+)-α-methylbenzylamine salt according to the procedure described previously.[7] Acidification of the head fraction after five recrystallizations gave white crystals: mp 112–113 °C;[24] $[\alpha]^{25}_D$ – 11.1°, $[\alpha]^{25}_{365}$ –329° (*c* 0.24, C_2H_5OH); 92% ee.

(+)-(1*S*)-2,3-Dihydrotriquinacen-2-one (4). Treatment of (–)-**3** (1.66 g, 9.54 mmol) as before[7] for 5.5 h gave 1.13 g (82%) of (+)-**4** after Florisil chromatography. A sample further purified by preparative VPC (5 ft × 0.25 in. 5% SE-30 on Chromosorb G, 110 °C) showed the following rotations: $[\alpha]^{25}_D$ +441°, $[\alpha]^{22}_{365}$ +2797° (*c* 1.05, C_2H_5OH); 93% ee.

(±)-2,3-Dihydrotriquinacen-2-one (4). A cold (0 °C) solution of **5** (20.0 g, 0.122 mmol) in 100 mL of dichloromethane and 24 mL of pyridine was treated portionwise with 46.5 g (0.244 mol) of *p*-toluenesulfonyl chloride and the mixture was stored in a refrigerator for 4 days, poured into ice water, and carefully acidified with 5% hydrochloric acid. The layers were separated, and the aqueous phase was extracted with dichloromethane (50 mL). The combined organic layers were washed with saturated sodium bicarbonate solution (100 mL) and brine (100 mL) before drying and solvent evaporation. Recyrstallization of the residue from acetone–hexane afforded 8.5 g (48%) of epimerically pure exo tosylate: mp 109.5–110.5 °C; IR (KBr, cm^{-1}) 3060, 2985, 2915, 1742, 1600, 1366, 1357, 1348, 1192, 1180; ^1H NMR ($CDCl_3$, δ) 7.8 (*J* = 8 Hz, 2 H), 7.3 (d, *J* = 8 Hz, 2 H), 5.7 (d, *J*. = 6 Hz, 1 H), 5.4 (d, *J* = 6 Hz, 1 H), 5.1–4.8 (m, 1 H), 3.8–3:1 (m, 3 H), 3.1–2.5 (m, 2 H), 2.4 (s, 3 H), 2.6–1.5 (series of m, 3 H); mass spectrum *m/e* calcd 318.0926, obsd 318.0934.

Anal. Calcd for $C_{17}H_{18}O_4S$: C, 64.12; H, 5.71. Found: C, 64.11; H, 5.76.

There was also obtained 4.5 g (11.7%) of endo tosylate: mp 140–144 °C; ^1H NMR ($CDCl_3$, δ) 7.7 (d, *J*. = 8 Hz, 2 H), 7.3 (d, *J* = 8 Hz, 2 H), 6.2–5.7 (m, 2 H), 4.8–4.4 (m, 1 H), 3.7–3.1 (m, 2 H), 3.1–2.6 (m, 3 H), 2.4 (s, 3 H), 2.6–1.5 (series of m, 3H); mass spectrum *m/e* calcd 318.0926, obsd 319.0934.

To a solution of the pure exo tosylate (11.5 g, 36.1 mmol) in dry dichloromethane was added 175 g of Woelm N-Super I alumina (previously activated at 420 °C and 0.05 torr overnight) with vigorous stirring under argon. After 20 h at room temperature, the mixture was filtered and the residue was leached extensively with dichloromethane and methanol. There was obtained 5.19 g (98%) of **4** as a colorless oil.

When the tosylate mixture was employed, the endo isomer was recovered unchanged.

(+)-(1*S*)-*endo*-2,3-Dihydrotriquinacen-2-ols (9a and 9b). Lithium aluminum hydride (522 mg, 13.7 mmol) was slurried in anhydrous tetrahydrofuran (20 mL) and 522 mg (3.6 mmol) of (+)-**4**, $[\alpha]^{22}_D$ +441°, dissolved in 3 mL of the same solvent was slowly introduced via syringe under argon. The reaction mixture was heated at reflux for 2.5 h, cooled, treated with saturated sodium sulfate solution, and diluted with ether. Following the addition of 5% hydrochloric acid, the ether layer was separated and washed with 5% hydrochloric acid (2 × 10 mL), saturated sodium bicarbonate solution (10 mL), and water (10 mL) prior to drying and evaporation. There was obtained 538 mg (100%) of **9a**[25] as a colorless oil, VPC analysis of which (FID detection, 9 ft × 0.12 in. 5% Carbowax 20M on Chromosorb P, 140 °C) demonstrated it to be 98% endo.

Comparable reduction of 1.57 g (10.8 mmol) of (+)-**4**, $[\alpha]^{22}_D$ +441°, with lithium aluminum deuteride afforded 1.7 g (100%) of **9b**.

For **9a**: IR (neat, cm^{-1}) 3360, 3045, 2970, 2875, 1607; ^1H NMR ($CDCl_3$, δ) 5.93–5.47 (m, 2 H), 5.67 (s, 2 H), 4.3–3.8 (br 7, 1 H), 3.9–3.5 (br s, 1 H), 3.5–2.5 (series of m, 4 H), 2.3–1.2 (series of m, 2 H); $[\alpha]^{22}_D$ +55°, $[\alpha]^{22}_{365}$ +157° (*c* 0.12, C_2H_5OH).

For **9b**: IR (neat, cm^{-1}) 3360, 2122; mass spectrum *m/e* calcd for $C_{10}H_{11}DO$ mass spectrum 149.0951, obsd 149.0957 (>95% d_1); $[\alpha]^{22}_D$ +56°, $[\alpha]^{22}_{365}$ +163° (*c* 0.49, C_2H_5OH).

(–)-(1*S*)-(2-*exo*-^{2}H)-2,3-Dihydrotriquinacene (11b). A stirred solution of **9a**, $[\alpha]^{22}_D$ +55° (538 mg, 3.6 mmol) in dichloromethane (10 mL) and pyridine (5 mL) was cooled to –15 °C and treated with methanesulfonyl chloride (419 μL, 5.39 mmol). Following storage of the flask in the refrigerator overnight, the reaction mixture was poured into water and extracted with dichloromethane (3 × 50 mL). The combined organic layers were washed several times with 5% hydrochloric acid, followed by saturated sodium bicarbonate solution and water. Drying and solvent evaporation gave 810 mg (99%) of **10a** as a light yellow oil. Its principal ^1H NMR signals ($CDCl_3$, δ) were seen at 5.93–5.40 (m, 2 H), 5.67 (s, 2 H), 5.29–4.80 (dt, *J* = 10 and 7 Hz), and 2.97 (s, 3 H).[26]

Lithium aluminum hydride (85.5 mg, 2.25 mmol) was slurried in dry ether (5 mL). A solution of **10a** (347 mg, 1.51 mmol) in 7 mL of ether was added via syringe, and the mixture was stirred at room temperature for 24 h before being quenched with 30 drops of saturated sodium sulfate solution. After 30 min, anhydrous sodium sulfate was added and stirring was continued for an additional 0.5 hr. The mixture was filtered through Celite, the filtrate was carefully concentrated, and the residue was distilled in a Kugelrohr apparatus (110 °C (20 mm)). There was obtained 135 mg (67%) of **11b** as a colorless oil. Further purification by prepa-

(24) Our earlier paper[7] cites 131–132 °C as the melting point of the optically pure acid. This is a misprint, the correct value being 112–113 °C.

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rative VPC (5 ft × 0.25 in. 5% SE-30 on Chromosorb G, 105 °C) furnished 81.6 mg of pure hydrocarbon. The ^{1}H NMR spectrum ($CDCl_3$) clearly shows the presence of only one exo proton at δ 1.88–1.81 and two endo protons at δ 1.53–1.31; integration indicated 98% D_1. Mass spectrum: m/e calcd for $C_{10}H_{11}D$, 133.1002, obsd 133.0998.

(−)-(1*S*)-(2-*endo*-^{2}H)-2,3-Dihydrotriquinacene (11a). Analogous treatment of **9b** (1.7 g, 11 mmol, $[\alpha]^{22}_D$ +55°) with methanesulfonyl chloride yielded 2.28 g (93%) of **10b**. Its ^{1}H NMR spectrum is essentially identical with that of **10a** except for the absence of the doublet of triplets at δ 5.29–4.80. Mass spectrum: m/e calcd for $C_{11}H_{13}DO_3S$ 227.0726, obsd 227.0732.

Lithium aluminum hydride reduction of **10b** (340 mg, 1.5 mmol) as previously described gave 145 mg (72%) of distilled **11a** (86 mg after further VPC purification). Its ^{1}H NMR spectrum (in $CDCl_3$) shows the presence of two exo protons at γ 1.93–1.67 and a single endo proton at 1.53–1.20; integration indicated 98% d_1. Mass spectrum, m/e calcd 133.1002, obsd 133.0997.

(+)-(1*S*)-(2,2-$^2H_2$)-2,3-Dihydrotriquinacene (11c). Reduction of **10b** (340 mg, 1.50 mmol) with lithium aluminum deuteride as before afforded 154 mg (77%) of 11c (94.5 mg after VPC purification). The single exo and endo saturated protons were seen (in $CDCl_3$) at δ 1.85–1.83 and 1.51–1.32, respectively (ca. 98% d_2). Mass spectrum m/e calcd for $C_{10}H_{10}D_2$ 134.1064, obsd 134.1060.

(+)-(1*R*,4*S*,7*R*,10*S*)-(2-^{2}H)-Triquinacene (12). A 200-mg (0.88-mmol) sample of **10b** in dichloromethane was treated with 4.4 g of alumina (Woelm N-Super I, activated as before) and stirred vigorously under argon for 2 days. Workup in the predescribed manner followed by Kugelrohr distillation at 100 °C (30 mm) furnished 60 mg (52%) of **12** as a colorless oil: IR (neat, cm^{-1}) 3045, 2955, 2875, 2260; ^{1}H NMR ($CDCl_3$, δ) 5.61 (s, 5 H), 3.72 (s, 4 H) with d incorporation = 97 ± 2%; mass spectrum m/e calcd for $C_{10}H_9D$ 131.0845, obsd 131.0840.

(1*S*)-2-(Hydroxymethyl)triquinacene (13). To an ice-cold stirred slurry of lithium aluminum hydride (492 mg, 12.9 mmol) in anhydrous ether (90 mL) was added aluminum chloride (574 mg, 4.3 mmol) in one portion, followed by (−)-**3** (1.00 g, 5.75 mmol, $[\alpha]^{22}_{365}$ −398°) in 30 mL of the same solvent. The reaction mixture was stirred overnight at room temperature, quenched with excess methanol, and washed with 5% hydrochloric acid (100 mL) and saturated sodium bicarbonate solution. The alkaline aqueous layer was back-extracted with ether, and the combined organic layers were dried and evaporated to leave 920 mg (100%) of a colorless oil. VPC analysis (10 ft × 0.12 in. 15% SE-30 on Chromosorb W, 150 °C) showed one component to be heavily dominant. For **13**: IR (neat, cm^{-1}) 3340, 3055, 2965, 2880; ^{1}H NMR ($CDCl_3$, δ) 5.8–5.3 (m, 5 H), 4.07 (s, 2 H), 3.8–3.6 (m, 4 H), 1.8 (br s, 1 H). This alcohol proved labile to gas chromatographic conditions.

(+)-(1*S*)-2-(Chloromethyl)triquinacene (14). To a cold (0 °C) solution of *N*-chlorosuccinimide (777 mg, 5.84 mmol) in dry dichloromethane (16 mL) was added 480 μL (6.53 mmol) of freshly distilled (from CaH_2) dimethyl sulfide. After the mixture was cooled to −20 °C, 850 mg (5.31 mmol) of **13** (84% ee) dissolved in 8 mL of dichloromethane was added. The reaction mixture was stirred at room temperature for 1 h and shaken with ice-cold brine (40 mL). The aqueous phase was extracted with dichloromethane (2 × 10 mL), and the combined organic layers were washed with cold brine (20 mL), dried, and evaporated. Chromatography of the yellow oil on Florisil (25 g) by using hexane–ether (3:1) as eluant afforded 657 mg (70%) of **14** which was pure by VPC analysis: IR (neat, cm^{-1}) 3060, 2965, 2885, 730, 683; ^{1}H NMR ($CDCl_3$, δ) 5.8–5.3 (m, 5 H), 4.11 (s, 2 H), 3.98–3.53 (m, 4 H); mass spectrum, m/e calcd for $C_{11}H_{11}Cl$ 178.0549, obsd 178.0542; $[\alpha]^{22}_D$ +55°, $[\alpha]^{22}_{365}$ +101.4° (c 0.91, $CHCl_3$).

(−)-(1*S*)-2-Methyltriquinacene (15). To a solution of **14** (600 mg, 3.37 mmol) in 15 mL of dry tetrahydrofuran was added 128 mg (3.37 mmol) of lithium aluminum hydride, and the mixture was heated at the reflux temperature for 2 h, cooled, diluted with ether, and quenched with saturated sodium sulfate solution. Following drying and filtration, the clear filtrate was carefully concentrated and the residual oil was purified by preparative VPC (6 ft × 0.25 in. 5% SE-30 on Chromosorb G, 120 °C). There was obtained 208 mg (43%) of **15**: IR (neat, cm^{-1}) 3010, 2920, 2850, 1600, 990, 943, 877, 726, 715; ^{1}H NMR ($CDCl_3$, δ) 5.69 (s, 2 H), 5.62 (s, 2 H), 5.36 (m, 1 H), 3.8–3.4 (m, 4 H), 1.7 (s, 3 H); mass spectrum, m/e calcd 144.0939, obsd 144.0940.

Anal. Calcd for $C_{11}H_{12}$: C, 91.61; H, 8.39. Found: C, 91.22; H, 8.59.

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Resonance Raman Spectra of Excited Triplet State *all-trans*-Retinal

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Abstract: The time-resolved resonance Raman (TR^3) spectra of the lowest-energy excited triplet state of *all-trans*-retinal are reported (Figure 2 and Table I). The triplet state was formed photolytically as a result of intersystem crossing from the lowest energy excited singlet state which was populated by 354.7 nm pulsed excitation. The TR^3 spectra of the excited triplet state were obtained with pulsed laser radiation tuned into resonance with the transient triplet–triplet absorption band of *all-trans*-retinal near 470 nm. Time delays between the two pulsed lasers ranged from 40 ns to 20 μs. The experimental conditions were chosen to ensure that the triplet state monitored by TR^3 spectroscopy derived from the all-trans isomer of retinal.

The major contribution made by the retinal chromophore to the activity of rhodopsin in visual processes is well-recognized and has been the subject of extensive study.[1-3] The photoisomerization of retinal itself, of course, underlies its function as the chromophoric group in rhodopsin. The mechanism by which photoisomerization occurs in retinal may be viewed in terms of two sequential steps: (1) photolytic population of an excited electronic state followed by some degree of photophysical decay and (2) molecular isomerization. The latter step, photolytically induced interconversion of retinal isomers, also has been examined in numerous studies.[4-7] In the specific case of retinal transformations in rhodopsin and bacteriorhodopsin, resonance Raman spectroscopy has been used to identify the conformations of ground-state intermediates.[8,9] It has remained difficult, however, to correlate

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