and 55% of **35b**. This mixture was subjected to preparative layer chromatography on silica gel (elution with 30% ethyl acetate in hexane). There was isolated 8 mg of unreacted **3** and 73 mg of a mixture of **34b** and **35b** which was not further separated: ^{1}H NMR ($CDCl_3$) δ 7.43 (overlapping d, J = 2.8 Hz, 1 H), 6.22 and 6.01 (m, 2 H, ratio 79:21), 4.23-3.58 (m, 7 H, including methoxyl singlets), 2.53-1.93 (m, 2 H), 1.56 (br s, 0.84 H), 1.52-1.17 (m, 1.58 H), 0.73 (m, 0.79 H), 0.62 (m, 0.79 H); m/e calcd 228.1150, obsd 228.1155. This material was directly subjected to thermal aromatization. A third band was determined to be **36b** (45 mg, 32%).

Aromatization of 34a and 35a. Dimethyl Benzonorbornadiene-2,3-dicarboxylate (36a). Into an NMR tube was placed 165 mg of a mixture of **34a** and **35a** and 0.4 mL of $CDCl_3$. The tube was immersed in a 50 °C bath and monitored periodically by ^{1}H NMR. After 21 h, the aromatization process was essentially complete, and the contents of the tube were subjected to preparative layer chromatography on silica gel. Elution with 30% ethyl acetate in hexane gave 120 mg (80%) of **36a** as a colorless viscous oil: IR (neat) 2950, 1708, 1615, 1426, 1253, and 740 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.25 and 6.98 (AA'BB', 4 H), 4.22 (t with further splitting, J = 1.5 Hz, 2 H), 3.77, (s, 6 H), 2.57 (dt, J = 7.8, 1.5 Hz, 1 H), 2.28 (dt, J = 7.8, 1.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$) 164.5, 150.9, 147.9, 124.9, 122.2, 67.8, 52.9, and 51.5 ppm; m/e calcd 258.0892, obsd 258.0897. Anal. Calcd for $C_{15}H_{14}O_2$: C, 69.76; H, 5.46. Found: C, 69.60; H, 5.52.

Aromatization of 34b and 35b. Methyl Benzonorbornadiene-2-carboxylate (36b). A solution of the **34b/35b** mixture (72 mg, 0.32 mmol) in benzene (4 mL) was heated at 50 °C for 24 h and filtered through silica gel (5 g) (elution with 20% ethyl acetate in hexane) to give 44 mg (69%) of **36b** as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 7.50 (d, J = 3.7 H, 2 H), 7.16 and 6.85 (m, 4 H), 4.15 (m, 1 H), 3.95 (m, 1 H), 3.67 (s, 3 H), 2.37 (m, 2 H); m/e calcd 200.0837, obsd 200.0843.

Benzyne Addition to 3. A solution of **3** (130 mg, 0.90 mmol) in dimethoxyethane (1 mL) was heated at reflux with stirring while 144 mg (1.05 mmol) of anthranilic acid dissolved in 5 mL of dimethoxyethane and 0.3 mL of isoamyl nitrite in 2 mL of dimethoxyethane were added simultaneously from separate addition funnels over a period of 10 min. The reaction mixture was heated at reflux for an additional 10 min and concentrated in vacuo. The residue was filtered through alumina (20 g) with hexane elution to give 165 mg of a white solid, ^{1}H NMR analysis of which showed it to consist of **37** (16%), **38** (69%), and dibenzonorbornadiene (15%). Preparative layer chromatography on basic alumina (elution with 15% dichloromethane in hexane) permitted the isolation of pure **38** as a white solid which decomposes with gas evolution above 80 °C: ^{1}H NMR ($CDCl_3$) δ 7.17 and 6.88 (m, 4 H), 6.36 (sextet, 2 H), 3.91 (m, 4 H), 2.03 (br s, 2 H), 1.07 (d with further splitting, J = 6.5 Hz, 2 H), 0.18 (d with further splitting, J = 6.5 Hz, 2 H); ^{13}C NMR ($CDCl_3$) 150.8, 134.8, 123.8, 121.6, 66.4, 51.8, 39.1, and 24.7 ppm; m/e calcd ($M^+ - C_2H_4$) 192.0939, obsd 192.0943.

Hydrocarbon **37** was not obtained in a form adequately free from **38** to allow complete ^{1}H NMR assignment to be made. ^{13}C ($CDCl_3$) assignments by subtraction of the signals for **38** and dibenzonorbornadiene are 155.7, 133.1, 123.5, 121.4, 67.0, 52.0, 38.2, and 25.8 ppm.

Dibenzonorborandiene by Aromatization of 37 and 38. A sample of the **37/38** mixture in $CDCl_3$ was heated at 45 °C for 16 h. Evaporation of the solvent gave dibenzonorbornadiene in quantitative yield as a white powder: mp 154.5-156 °C (lit.[60] mp 153.5 °C); ^{1}H NMR ($CDCl_3$) δ 7.35 and 6.80 (AA'BB, 8 H), 4.19 (t, J = 1.5 Hz, 2 H), 2.63 (t, J = 1.5 Hz, 2 H); ^{13}C NMR 150.5, 125.1, 121.7, 67.7, and 51.5 ppm; m/e calcd 192.0939, obsd 192.0943.

Acknowledgment. We are grateful to the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the National Cancer Institute (CA-12115) for financial support and to Professor H. Prinzbach for making available to us generous samples of **13**, **14**, and **30**.

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Chiral Perturbation of Olefins by Deuterium Substitution. The Optical Activity and Circular Dichroism Behavior of (1*S*)-[2-^{2}H]Norbornene and Deuterated Apobornenes

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Contribution from the Departments of Chemistry, The Ohio State University, Columbus, Ohio 43210, and King's College, London WC2R 2LS, England. *Received May 1, 1980*

Abstract: The deuterated, optically active hydrocarbons **11**, **13**, **16**, and **21** of known absolute configuration have been prepared and their absorption and circular dichroism spectra determined. These compounds represent the first examples of olefins which owe their chirality solely to isotopic substitution. The three apobornenes were prepared from *d*-10-camphorsulfonic acid (**7**) via (+)-ketopinic acid (**8**) and (1*S*)-1-bromo-α-fenchocamphorone (**9**). Replacement of the bridgehead bromine substituent by H or D was efficiently achieved by irradiation with tri-*n*-butyltin hydride or deuteride in refluxing benzene containing AIBN. (1*S*)-[2-^{2}H]norbornene (**21**) was made available by degradation of the (+)-carboxylic acid **17** to (+)-norbornen-2-one (**19**), followed by catalytic hydrogenation, Shapiro reaction on the tosylhydrazone, and a deuterium oxide quench. The contributions of the C-D bonds to the observed Cotton effects are analyzed, and comparisons between the effects of a deuterium atom and a methyl group on chiroptical activity are made.

Since the discovery of deuterium by Urey and co-workers in 1932,[2] many chiral compounds owing their optical activity to the presence of this isotope have been prepared.[3,4] Nonetheless, gaps in our knowledge of asymmetric perturbation by deuterium have managed to persist throughout this period. Recently, intense interest has materialized in clarifying certain of these questions. In particular, research activity in several laboratories during the last 5 years dealing with otherwise intrinsically symmetric carbonyl compounds has provided elegant experimental demonstration of the usual (though not invariant[10]) antioctant (dissignate) behavior of the isotope.[5-10] While conformationally flexible systems such

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(2) Urey, H. C.; Brickwedde, F.; Murphy, G. M. *Phys. Rev.* **1932**, *39*, 164. Washburn, E. W.; Urey, H. C. *Proc. Natl. Acad. Sci. U.S.A.* **1932**, *18*, 496.
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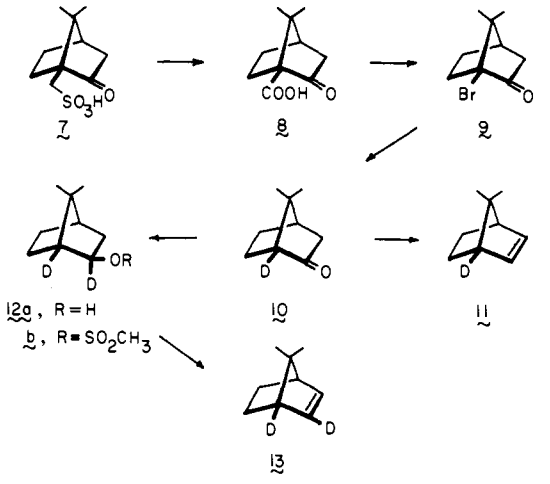
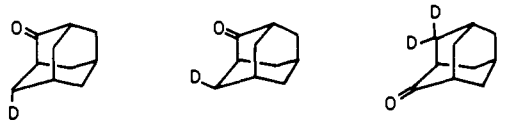
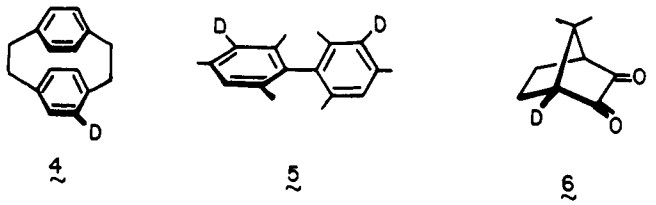
Scheme I



as (3*R*)-deuteriocyclopentanone[5a] and (3*S*)-deuteriocyclohexanone[5b] exhibit weak circular dichroism spectra, rigid molecules such as the deuterated adamantanones **1**,[6a,8] **2**,[8] and **3**[8] are characterized by variable, but generally stronger, circular dichroism (CD) Cotton effects for their magnetic dipole allowed $n \rightarrow \pi^*$ transitions.



In contrast, the effect of deuterium perturbation on the CD behavior of olefins has not been investigated. The rather complex aromatic molecule (−)-(*S*)-[4-^{2}H][2.2]paracyclophane (**4**) is



notable for the magnitude of its molecular ellipticity which is only 10^{-2} weaker than that of the corresponding methyl derivative.[11] This is as expected, since electric dipole forbidden transitions, like that giving the 260-nm benzene absorption, are relatively strongly enhanced by weak perturbations such as alkyl and, more particularly, isotopic substitution. (*S*)-[3,3′-^{2}H$_2$]Bimesityl **5** proved not to exhibit an observable rotation.[12]

It is well-known that Cotton effect data can be most exactly interpreted when rigid conformations are involved. For this reason, and because of the enhanced chiroptical effects associated with (1*R*)-[1-^{2}H]-α-fenchocamphoronequinone (**6**),[13] we chose to prepare four deuterated bicyclo[2.2.1]heptene derivatives of known absolute configuration and to carry out measurements of their CD spectra. The results of these studies form the subject of this paper.[14]

Table I. Optical Rotations of the Deuterated Apobornenes and **21** ($CHCl_3$ Solution)

α^a	**11** (*c* 0.74)	**13** (*c* 1.69)	**16** (*c* 0.79)	**21** (*c* 0.15)
589	−0.93	−0.82	0.0	−2.23
578	−0.78	−0.76	0.0	−0.84
546	−0.83	−0.84	0.0	0
436	−1.45	−1.26	0.0	−1.40
365	−2.38	−1.72	+0.84	−7.56

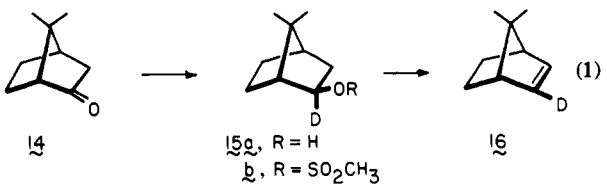
[a] Rotations are corrected for isotopic purity as determined by combustion or mass spectra analysis. In the case of **21**, a correction for enantiomeric purity has also been applied.

Synthesis. Preparation of the optically active apobornenes **11**, **13**, and **16** began with commercially available (+)-(1*S*)-**10**-camphorsulfonic acid (**7**) which, in view of its well-established derivation from *d*-camphor,[15] is recognized to have the absolute configuration indicated. Oxidation of the derived sulfonyl chloride according to the procedure of Bartlett and Knox[16] furnished (+)-ketopinic acid (**8**) (see Scheme I). Hunsdiecker degradation of **8** was readily accomplished in line with Scherer's directives,[17] and the resulting (1*S*)-1-bromo-α-fenchocamphorone (**9**) was shown by VPC analysis to contain none or minor amounts of the side product reported by Kokke and Varkevisser.[13a] The most expedient means found for clean, efficient replacement of the bromine atom in **9** by deuterium consisted of heating a benzene solution of the bromo ketone with a slight excess of tri-*n*-butyltin deuteride and a catalytic quantity of azobis(isobutyronitrile) with simultaneous irradiation from a 200-W medium-pressure Hanovia lamp.[18,19] After 26 h, ketone **10** of high isotopic purity was obtained in 90–95% yield upon suitable workup.[20] This procedure nicely obviated all of the difficulties previously experienced with the $LiAlD_4$–*N*-methylmorpholine reagent combination.[13a]

Conversion of **10** to its tosylhydrazone followed by Shapiro elimination with lithium diisopropylamide in tetrahydrofuran[21] gave a mixture of products in which (1*R*)-[1-^{2}H]apobornene (**11**) comprised the major component (70–80%). Preparative VPC purification of **11** afforded a colorless crystalline solid which was determined by combustion analysis to be 87.5% d_1 and which exhibited $[\alpha]_D$ −0.93° (corrected for isotopic purity) in chloroform solution (Table I).

To gain acess to the dideuterated derivative **13**, we reduced ketone **10** with $LiAlD_4$ and the resulting exo alcohol (**12a**) was converted to its mesylate following Crossland's procedure.[22] Attempts to effect elimination within **12b** with potassium *tert*-butoxide in dimethyl sulfoxide proved quite troublesome until the beneficial effect of added pyridine was noted. Under these conditions, smooth conversion to **13** (93% d_2) was realized. The optical rotations are collected in Table I.

Similar manipulations were used to transform (1*R*)-α-fenchocamphorone (**14**) via **15a** and **15b** into (1**R**)-[2-^{2}H]apobornene (**16**) of high quality (97% d_1) (see eq 1). Since these chemical



changes could have affected neither the enantiomeric excess nor the absolute configuration of the resultant olefin, the lack of optical

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(18) Della, E. W.; Patney, H. K. *Synthesis* **1976**, 251.
(19) A modification of this procedure recently developed by E. J. Corey and J. W. Suggs (*J. Org. Chem.* **1975**, *40*, 2554) resulted only in slow reaction and involved a messy workup.
(20) Leibner, J. E.; Jacobus, J. *J. Org. Chem.* **1979**, *44*, 449.
(21) Jefford, C. W.; Wallace, T. W.; Can, N.-T. H.; Rimbault, C. G. *J. Org. Chem.* **1979**, *44*, 689.
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Table II. ^{13}C Chemical Shift Data (ppm $CDCl_3$)

carbon	11	13	16
1	49.083, 50.199, 51.267 (J_{C-D} = 21.98 Hz)	49.010, 50.102, 51.194 (J_{C-D} = 21.97 Hz)	50.515
2	135.111	133.533, 134.820, 136.082 (J_{C-D} = 25.64 Hz)	133.582, 134.86, 136.131 (J_{C-D} = 25.64 Hz)
3	135.111	135.014	134.990
4	50.588	50.636	50.515
5	23.837	23.886[a]	23.958
6	23.837	23.958[a]	23.958
7	55.345	55.394	55.467
8	22.041[a]	22.065[a]	22.065[a]
9	21.749[a]	21.774[a]	21.749[a]

[a] The possibility exists that these values are interchanged.

rotation of **16** at the sodium line and other wavelenghts (Table I) is clearly an intrinsic property of this chiral substance. The inability of a deuterium atom at C-2 of the apobornene ring system to rotate plane-polarized light was actually foreshadowed by the optical behavior of **11** and **13**. The close correspondence (within experimental error) of the rotatory power of the latter two compounds pointed irrefutably to the fact that the deuterium atom bonded to the bridgehead carbon (C-1) is largely responsible for the measurable chiroptical interaction.

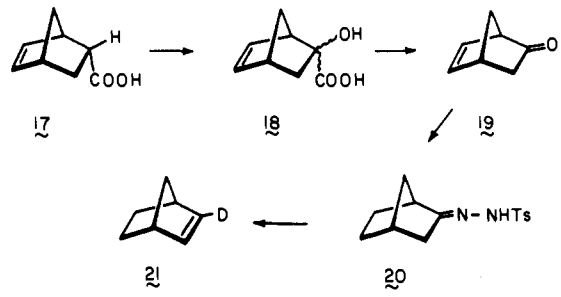
The broad band decoupled ^{13}C NMR spectra of the deuterated apobornenes are of some interest not only because they allow direct observation of C–D coupling in the form of 1:1:1 triplets but also because they provide some indication as well of the level of asymmetric perturbation caused by the deuterium substitution plan. The respective ethano bridge carbons (C-5 and C-6) prove to be particularly diagnostic. In **16**, for example, these carbons appear as a sharp singlet of area 2, denoting that they are not rendered measurably different by the presence of an isotopic perturber at C-2. For **11**, a single combined peak for C-5 and C-6 is still seen, but it is broader and is of diminished intensity relative to that in **16**. As concerns the dideuterated apobornene **13**, separate signals for C-5 and C-6 are clearly observable (Table II). Also, the more "asymmetric" the molecule due to isotopic substitution, the more shifted are the deuterium-bearing carbons relative to their protio counterparts.

The starting material for the prepartion of **21** was the (+)-*endo*-norbornenecarboxylic acid **17** of known absolute configuration[23] which had been previously resolved to 90.5% optical purity by recrystallization of its quinine salt.[24] After 10 recrystallizations, we obtained a sample of **17** having $[\alpha]^{23}_D$ +135.6° (94% optical purity based upon the reported maximum rotation). The level of recovery from racemic acid was 6%. Generation of the dianion of **17** with lithium diisopropylamide in tetrahydrofuran at 0 °C followed by oxygenation at −78 °C gave **18** (81%) which was directly reduced to the diol with lithium aluminum hydride (see Scheme II). Oxidative cleavage with buffered sodium metaperiodate gave ketone **19** having $[\alpha]^{23}_D$ +1033° (*c* 10.1, $CHCl_3$) after preparative VPC purification. The magnitude of this rotation is slightly below the value cited by Janusz, Gardiner, and Berson ($[\alpha]^{26}_D$ +1088° (*c* 1.7, $CHCl_3$)) for a sample of 88% enantiomeric purity[24] and is considered to indicate a minimal enantiomeric purity of 84% (**19** is thermally labile and suffers some decomposition at elevated temperatures). The elaboration of **21** from **19** was achieved by catalytic hydrogenation and application of those Shapiro reaction conditions described by Stemke and Bond,[25] culminating in a D_2O quench. Mass spectral analysis of **21** indicated the hydrocarbon to be 83% d_1.

Absorption and Circular Dichroism Spectra. The absorption and CD spectra of bicyclic alkenes **11**, **13**, **16**, and **21**, each owing its chirality to the presence of C–D bond or bonds at C-1 and/or C-2 in the achiral precursor, have been investigated over the 225–165-nm range. The spectra were obtained with the instruments previously described,[26] employing pentane solutions of the compounds. Gas-phase specta of **13** and **21** were recorded in addition at their ambient-temperature vapor pressure (10-mm path). The noise level of the CD spectra, initially ±5% at 220 nm, increased to ±15% at the CD and absorption maxima near 200 nm and reached ±50% at 180 nm where the CD spectra are truncated (Figure 1). No significant differences between the gas-phase and pentane solution spectra of **13** and **21** were observed, with the exception of vibrational structure shoulders in the gas-phase absorption spectrum of **21** at 48 600 and 49 900 cm^{-1}. The frequency interval between the two shoulders and their position on the red side of the main absorption band indicated that they arise from the olefin Rydberg $\pi \rightarrow 3s$ transition, which is overlaid by the principal $\pi \rightarrow \pi^*$ transition, as in the case of other chiral olefins.[26]

The olefin $\pi \rightarrow 3s$ Rydberg transition is not evident in the CD spectra of these bicyclo[2.2.1]heptenes which owe their chirality to deuterium substitution. The principal CD band in each case has a maximum close in frequency to that of the corresponding absorption, although there is evidence of a higher frequency CD band of opposite sign, forming a bisignate couplet, as previously observed with other chiral olefins[26] (Table III, Figure 1). The bisignate CD couplet is ascribed to the mixing of the electric dipole $\pi_x \rightarrow \pi_x^*$ transition with a magnetic dipole, electric quadrupole transition, either $\pi_y \rightarrow \pi_x^*$ or $\pi_x \rightarrow \pi_y^*$ in the description previously employed.[26] The negative specific rotations of **11** and **13** (Table I), compared with the corresponding positive lowest energy CD bands (Table III, Figure 1), show that the optical rotations

Scheme II



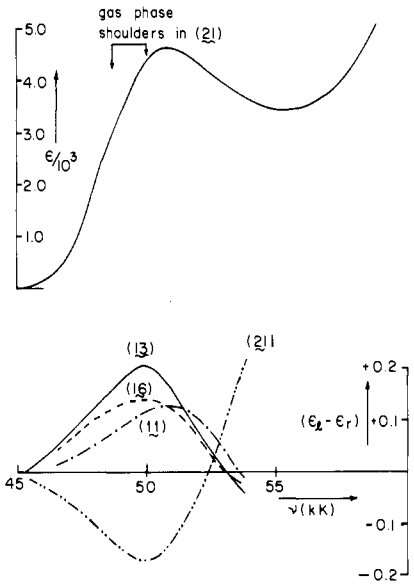


Figure 1. The absorption spectrum (upper curve) and CD spectra (lower curves) of (1*R*)-[2-^{2}H]norbornene (**21**) and the deuterated apobornenes **11**, **13**, and **16** in pentane solution at 20 °C.

(23) Berson, J. A.; Walia, J. S.; Remanick, A.; Suzuki, S.; Reynolds-Warnhoff, P.; Willner, D. *J. Am. Chem. Soc.* **1961**, *83*, 3986. Berson, J. A.; Bergman, R. G.; Clarke, G. M.; Wege, D. *Ibid.* **1969**, *91*, 5601.

(24) Janusz, J. M.; Gardiner, L. J.; Berson, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 8509.

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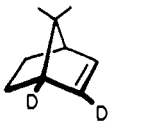
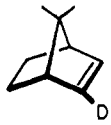
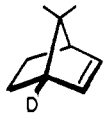
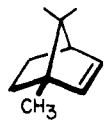
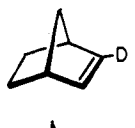
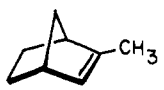
(26) Drake, A. F.; Mason, S. F. *Tetrahedron* **1977**, *33*, 937.

Table III. Circular Dichroism Spectra of Chiral Bicyclo[2.2.1]heptenes

compd		$10^3\bar{\nu}_{max}$, cm^{-1}	$\Delta\epsilon_{max}$, L M^{-1} cm^{-1}
	(13)	49.8 >54	+0.23 -ve
	(16)	49.8 >54	+0.14 -ve
	(11)	50.9 >54	+0.15 -ve
	(22)[a]	49.2 51.2 >54	-3.7 -2.6 +ve
	(21)	50.0 >54	-0.20 +ve
	(23)[b]	47.2	-7.3

[a] Data taken from ref 26. [b] The data for the antipodal isomer were taken from ref 14. [c] Sign of the higher frequency CD absorption.

of these enantiomers are dominated by the higher frequency member of the bisignate CD couplet or by another higher energy negative rotational strength. In the case of **16**, on the other hand, both the specific rotation at 365 nm and the CD at 201 nm are positive (Tables I and III), suggesting that the higher energy negative rotational strength in **16** either is smaller in magnitude than in **11** and **13** or is displaced to a higher frequency. Despite these differences, both the specific rotation at 365 nm and the $\Delta\epsilon_{max}$ near 200 nm of **13** are given in a crude approximation by the sum of the corresponding values for **11** and **16**, which individually embody each of the two isotopic perturbations incorporated into **13**.

The two isotopic perturbations in **13**, which confer chirality upon the otherwise achiral apobornene structure, are different in kind. A comparison of the CD spectra of **11** and **22** shows that the contributions of the C-D and C-CH_3 group in the 1-position of apobornene to the optical activity of the lowest energy olefin $\pi \rightarrow \pi^*$ transition are dissignate (Table III), following the general trend observed for other chromophoric systems, notably, the $n \rightarrow \pi^*$ transition of carbonyl enantiomers.[5-10] The corresponding comparison of the CD spectra of **21** and **23** indicates, however, that the contributions of the C-D and the C-CH_3 group in the 2-position of norbornene to the olefin $\pi \rightarrow \pi^*$ optical activity are consignate[3] (Table III), implying that the chiral perturbations introduced by C-1 and by C-2 substitution in the achiral parent structure are of different types.

Studies of the changes in the C-H bond properties due to the replacement of H by D indicate that the mean bond length and the mean square amplitude of vibrational motion at a given temperature are larger for the lighter isotope, as also is the electric dipole polarizability.[27-30] The chiral perturbation in **11** is of the same type as that in **6**, namely, the replacement of H by D at the bridgehead 1-position of an achiral bicyclo[2.2.1]heptane structure. A comparison of the CD spectra of **6** and of (1*R*)-camphorquinone[13] shows that the contributions of the C-D and the C-CH_3 to the $n \rightarrow \pi^*$ optical activity are dissignate, like **11** relative to **22** in the apobornene series. When the shorter C-D bond and its smaller polarizability relative to the C-H bond is taken into account, the sign of the $n \rightarrow \pi^*$ optical activity of **6** is accommodated, although the calculated rotational strength is 1 order of magnitude too small[13b] on the basis of the electron correlation or dynamic coupling model for optical activity.[31] A feature of the isotopic replacement giving **6** which was not considered[13b] and which would be difficult to take into account is the effectively larger size of the lighter isotope in the H/D pair due to the larger vibrational amplitude.[29] The lighter isotope effectively acts as a larger atom in repulsive interactions with its neighbors,[29] so that the bridgehead C-C-C bond angles are less compressed sterically in the 1-deuterio derivatives, **6** or **11**, relative to the achiral parent structures, while those angles are the more compressed in the corresponding 1-methyl derivatives, (1*R*)-camphorquinone or **22**, respectively. The dissignate effect of the C-D and the C-CH_3 group in the 1-position of the achiral apobornene structure emerges qualitatively as a consequence of the steric compression factor in H/D isotopic replacement, additional to the effects of the polarizability and bond length changes.

In the enantiomers **16** and **21**, the 2-deuterium atom is bonded directly to a carbon atom of the olefin chromophore, analogous to the case of the [2.2]paracyclophane **4**. The aromatic C-D and C-CH_3 groups in the [2.2]paracyclophane series have a consignate effect upon the $\pi \rightarrow \pi^*$ optical activity,[11] similar to the effect observed in the CD spectra of **21** and **23** (Table III). Although the amplitude of the vibrational motion of a C-H bond is larger than that of the corresponding C-D bond, the displacement of the carbon atom in the motion is smaller for the lighter isotope. In the diatomic and harmonic approximations, the displacement of the carbon atom in the stretching mode is larger by ~1.6 for the C-D than the C-H bond, on account of the larger mass of the deuterium atom. The mass of the methyl group is larger still, and the consignate effect of the C-D and the C-CH_3 groups upon the $\pi \rightarrow \pi^*$ optical activity of **21** and **23** is consistent with a chiral perturbation of the achiral parent structure due to the displacement of a carbon atom of the olefin chromophore in proportion to the mass of the bonded substituent atom or group. The optical activity of **4** is ascribed to a reorientation of the vibronic electric dipole $\pi \rightarrow \pi^*$ transition moment of the D-substituted benzene ring on account of the change of the atomic displacements in the ring-breathing vibrational mode due to the H/D replacement.[11] The vibrational displacements of the two carbon atoms in the olefin chromophore of achiral norbornene become inequivalent in a chiral 2-substituted derivative, producing a reorientation of the $\pi \rightarrow \pi^*$ transition moment direction in the same sense for **21** and **23**, a consignate $\pi \rightarrow \pi^*$ optical activity, given the expected chromophore carbon atom displacement proportional to the mass of the substituent.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 467 spectrophotometer. The ^1H NMR spectra were determined with Varian T-60, Varian A-60A, and Bruker HX-90 instruments, and apparent splittings are given in all cases. The ^{13}C NMR spectra were also obtained with the Bruker spectrometer. Mass spectra were measured on an AEI-MS9 spectrometer at an ionizing energy of 70 eV. The optical rotations were recorded on a Perkin-Elmer Model 241 polarimeter and concentrations, *c*, are expressed in g/100 mL. Preparative scale VPC separations were performed on Varian Aerograph Model A-90-P3 instruments equipped with thermal conductivity detectors. Microanalytical deuterium analyses were performed by Josef Nemeth, Urbana, Ill.

***d*-10-Camphorsulfonyl Chloride.** The procedure of Bartlett and Knox was followed.[15] In initial runs which made use of *d*-10-camphorsulfonic acid (**7**) directly as supplied by the Aldrich Chemical Co., yields of only 30-33% were obtained, perhaps because of residual moisture content.

(27) Bell, R. P. *Trans. Faraday Soc.* **1942**, *38*, 1209.
(28) Halevi, E. A. *Trans. Faraday Soc.* **1958**, *54*, 1441.
(29) Bartell, L. S. *J. Chem. Phys.* **1963**, *38*, 1827.
(30) Buckingham, A. D.; Urland, W. *Chem. Rev.* **1975**, *75* 113.
(31) Hhn, E. G.; Weigang, O. E. Jr. *Chem. Phys.* **1968**, *48*, 1127.
(32) "Consignate" and "dissignate" signify "same sign" and "opposite sign", respectively, without sector-rule implications.

When the commerical acid was first recrystallized from ethyl acetate and dried under high vacuum, the sulfonyl chloride was produced in essentially quantitative yield.

(+)-Ketopinic Acid (8). This material was prepared in 36% yield (after recrystallization) by the procedure of Bartlett and Knox:[16] mp 230–238 °C (sealed tube) (lit.[16] mp 226–228 °C); $[\alpha]^{23}_D$ +26.1° (*c* 0.7, CH_3OH) (lit.[16] $[\alpha]_D$ +25.8° (*c* 0.68, CH_3OH)).

(1*S*)-1-Bromo-α-fenchocamphorone (9) was obtained in 51% yield (after two recrystallizations from hexane) by using the procedure of Scherer et al.;[17] VPC analysis (SE-30) indicated none or very minor amounts of the side-product reported by Kokke[13a] to be present: mp 190–192.5 °C (sealed tube) (lit.[13a] mp 190–191 °C); $[\alpha]^{23}_D$ +74° (*c* 0.575, CH_3OH) (lit.[13a] +73.5° (*c* 0.61, CH_3OH)).

(1*R*)-[1-^{2}H]-α-Fenchocamphorone (10). The preparation of tri-*n*-butyltin deuteride was carried out in flame-dried glassware under a argon atmosphere. Lithium aluminum deuteride (1.0 g, 33.8 mmol) was suspended by magnetic stirring in 100 mL of dry ether which was cooled in an ice bath while 24 g (73.7 mmol) of tri-*n*-butyltin chloride was added dropwise. After the reaction mixture was stirred at room temperature for 18.5 h, it was cooled to 0 °C and Glauber's salt was added to destroy the excess deuteride. The solids were separated by filtration, and the filtrate was dried and evaporated. Distillation of the residue gave 11.6 g (54%) of tri-*n*-butyltin deuteride, bp 61–66.5 °C (0.10–0.12 torr), as a colorless liquid. A white precipitate formed slowly upon standing at room temperature.

To a solution of **9** (5.00 g, 23.1 mmol) in 8 mL of dried benzene under argon was added 8.82 g (30.2 mmol) of tri-*n*-butyltin deuteride and 30 mg of azobis(isobutyronitrile). The stirred reaction mixture was heated to reflux and irradiated from a distance of approximately 6 cm through Pyrex with a 200-W medium-pressure Hanovia lamp for 26 h. The resultant dark red solution was cooled, filtered, and evaporated. The residue was taken up in ether, and the mixture was stirred overnight with 5.6 g of potassium fluoride monohydrate in a few milliliters of water. The solution was filtered, the water layer was separated, and the organic layer was dried. Removal of solvent left a colorless semisolid, VPC analysis (6 ft × 0.25 in. 5% SE-30, 130 °C) of which showed only one compound to be present. Sublimation of this residue at 40 °C (30mm Hg) gave 2.93 g (91%) of **10**: mp 101.5–109 °C (sealed tube); *m/e* calculated 139.1107, found 139.111; $[\alpha]^{23}_D$ +66.4°, $[\alpha]^{23}_{578}$ +70.5° (*c* 0.75, C_2H_5OH); ^{1}H NMR ($CDCl_3$) δ 2.07–1.38 (series of m, 7 H), 105 (s, 6 H).

(1*R*)-[1-^{2}H]-Apobornene (11). Reaction of **10** (2.7 g, 19.42 mmol) with 4.15 g (22.31 mmol) of tosylhydrazine in 4.6 mL of absolute ethanol gave 4.49 g (83%) of the tosylhydrazone as a white crytalline solid: mp 161–164.5 °C (dec); *m/e* calculated 307.1465, found 307.1471; $[\alpha]^{23}_D$ −11.5°, $[\alpha]^{23}_{578}$ −11.9° (*c* 0.57, C_2H_5OH).

A tetrahydrofuran solution (50 mL) of diisopropylamine (6.05 g, 59.74 mmol) and 23.5 mL of 1.6 M butyllithium (in hexane) was stirred at 0 °C for 30 min. After the mixture was cooled to −78 °C, the tosylhydrazone (4.5 g, 14.66 mmol) dissolved in 35 mL of tetrahydrofuran was added during 35 min. The apobornene was isolated by preparative VPC (the 5% SE-30 column, 70–75 °C) as a colorless crystalline solid: mp 42–46 °C; 856 mg (47%); *m/e* calculated 123.1158, found 123.1162.

(1*R*)-[1,2-^{2}H]-*exo*-α-Fenchocamphorol (12a). Lithium aluminum deuteride (460 mg, 11 mmol) was suspended in 15 mL of dry ether under an argon atmosphere. To this stirred mixture was added dropwise a solution of **10** (2.88 g, 20.7 mmol) in 25 mL of the same solvent, and a gentle reflux was maintained overnight. Workup in the usual manner with water and 15% sodium hydroxide solution gave 2.79 g (95%) of **12a** as a clear, colorless solid: mp 132–140 °C (sealed tube) after sublimation at 40–50 °C (30 torr); IR ($CHCl_3$) 3610 and 3450 cm^{-1}; $[\alpha]^{23}_D$ δ −12.95°, $[\alpha]^{23}_{578}$ −13.51°, $[\alpha]^{23}_{365}$ −37.98° (*c* 0.97, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.75–1.57 (m, 7 H), 1.23 (s, 3 H), 1.02 (s, 1 H), 0.96 (s, 3H).

(1*R*)-[1,2-^{2}H]-*exo*-α-Fenchocamphorol Methanesulfonate (12b). To a cold (0 °C) solution of **12a** (2.503 g, 17.6 mmol) and triethylamine (2.67 g, 26.4 mmol) in dry dichloromethane (90 mL) was added dropwise during 10 min 2.22 g (19.4 mmol) of methanesulfonyl chloride. The reaction mixture was stirred at 0 °C for 1 h and at room temperature for 30 min before being poured into 200 g of an ice-water mixture. This mixture was shaken, and the organic layer was separated. The remaining aqueous emulsion was extracted with dichloromethane (2 × 50 mL), and the combined organic phases were washed successively with cold 12% hydrochloric acid (2 × 50 mL), saturated sodium bicarbonate solution, and brine prior to drying. Solvent evaporation gave **12b** as a pale yellow oil (3.97 g, 100%); $[\alpha]^{23}_D$ −23.44°, $[\alpha]^{23}_{365}$ −72.49° (*c* 0.86, $CHCl_3$). This material was used immediately without further purification.

(1*R*)-[1,2-^{2}H]-Aporbornene (13). Potassium *tert*-butoxide (1.19 g, 10.6, mmol) was dissolved in 10 mL of dry dimethyl sulfoxide under argon. Pyridine (0.42 g, 5.3 mmol) was added, followed by dropwise introduction during 30 min of a solution of **12b** (1.16 g, 5.3 mmol) in 8 mL of dimethyl sulfoxide. The mixture was stirred vigorously at room temperature for 22 h. Pentane (15 mL) was then added, and the mixture was poured onto crushed ice and shaken. After separation of the pentane layer, the aqueous phase was extracted three times with pentane. The combined organic solutions were washed with saturated sodium bicarbonate solution (2×) and water (3×) before drying. The solvent was carefully removed by distillation at atmospheric pressure to leave 3–4 mL of a yellow solution. This solution was passed through a short (1.5 × 6.0 cm) silica gel column (pentane elution), the solvent again carefully removed, and the concentrate subjected to preparative VPC purification (12 ft × 0.25 in. 15% SE-30, 72 °C). The major component was obtained as a colorless crystalline solid: mp 45.5–46.5 °C (sealed tube) (215 mg, 33% from **12a**); *m/e* calculated 124.1221, found 124.1225; ^{1}H NMR ($CDCl_3$) δ 5.95–5.8 (m, 1 H), 2.217 (m, 1 H), 1.9–1.6 (m, 2 H), 0.948 (s, 3 H), 0.886 (s, 3 H), 0.95–0.75 (m, 2 H).

(1*R*)-α-Fenchocamphorone (14). Following the predescribed procedure, the reaction of 5.00 g (23.1 mmol) of **9** with 8.05 g (27.7 mmol) of tri-*n*-butyltin hydride gave 2.59 g (81%) of **14**: mp 108–111 °C (sealed tube) after isolation by sublimation at 30–40 °C (30 torr); $[\alpha]^{23}_D$ +66.7° (*c* 0.6, C_2H_5OH) (lit.[13a] $[\alpha]_D$ +66.5°).

(1*R*)-[2-^{2}H]-*exo*-α-Fenchocamphorol (15a). Reduction of 2.72 g (19.7 mmol) of **14** with 420 mg (10 mmol) of lithium aluminum deuteride according to the method outlined above gave 2.07 g (74%) of **15a** as a colorless crystalline solid: mp 140–143 °C (sealed tube) after sublimation; $[\alpha]^{23}_D$ −13.1° (*c* 0.96, $CHCl_3$); *m/e* calculated 141.1263, found 141.1267; ^{1}H NMR ($CDCl_3$) δ 1.89–1.62 (m, 7 H), 1.25 (s, 3 H), 1.03 (s, 1 H), 0.97 (s, 3 H).

(1*R*)-[2-^{2}H]Aporbornene (16). From 1.7 g (12.1 mmol) of **15a**, 1.83 g (18.1 mmol) of triethylamine, and 1.52 g (13.3 mmol) of methanesulfonyl chloride, there was obtained 2.69 g (100%) of **15b** as an orange oil; $[\alpha]^{23}_D$ −22.93°, $[\alpha]^{23}_{578}$ −23.92°, $[\alpha]^{23}_{365}$ −71.14° (*c* 2.29, $CHCl_3$).

A solution of 1.16 g (5.3 mmol) of the unpurified mesylate in 8 mL of dimethyl sulfoxide was added to potassium *tert*-butoxide (1.19 g, 10.6 mmol) and pyridine (0.43 mL) in 10 mL of the same solvent. Following the procedure and workup described above, there was obtained a concentrated pentane solution which contained one major and one minor component (VPC analysis). The main component was isolated by preparative VPC (the 15% SE-30 column, 75–78 °Ce) to give **16** as a colorless crystalline solid (147 mg, 22.5% from **14**): *m/e* calculated 123.1158, found 123.1162; ^{1}H NMR ($CDCl_3$) δ 5.9 (m, 1 H), 2.21 (m, 2 H), 1.9–1.72 (m, 2 H), 0.948 (s, 3 H), 0.886 (s, 3 H), 0.9–0.80 (m, 2 H).

Resolution of *endo*-Norbornene-5-carboxylic Acid (17). The carboxylic acid (35.13 g, 0.254 mol) and quinine (87.08 g, 0.260 mol) were dissolved in 255 mL of boiling absolute methanol, and the solution was left to stand at room temperature overnight. The large crystals were filtered off, crushed with a mortar and pestle, washed with a small amount of ice-cold methanol in a large sintered-glass funnel, and left to air-dry overnight. A further 20.02 g (0.145 mol) of **17** was reacted as above, giving a total of 100.97 g of the quinine salt. The method of triangular recrystallization was used to achieve resolution with methanol as solvent.

The head fraction was recrystallized 10 times to give 6.5 g of salt which yielded 1.91 g of resolved **17**, $[\alpha]^{23}_D$ +135.6° (*c* 0.96, 95% C_2H_5OH), upon acidification with 2 N hydochloric acid and extraction with ether.

A second fraction was recrystallized 11 times to give after acidification 3.25 g of **17**; $[\alpha]^{23}_D$ +132.4–135.6° (*c* 0.86–0.84, 95% C_2H_5OH).

(+)-(1*R*)-Norbonen-2-one (19). A solution of dry diisopropylamine (2.25 mL, 15.9 mmol) in 10 mL of dry tetrahydrofuran under an argon atmosphere was cooled to 0 °C with stirring. *n*-Butyllithium (10 mL of 1.6 M in hexane, 16 mmol) was added dropwise, and the resultant mixture was stirred at 0 °C for 25 min. A solution of **17**, $[\alpha]^{23}_D$ +135.6° (1.00 g, 7.24 mmol), in 7 mL of dry tetrahydrofuran was introduced dropwise from a syringe, and the mixture was stirred at 0 °C for 3 h. The cloudy solution cooled to −78 °C and transferred via canula to an oxygenation vessel which contained 25 mL of O_2-purged ether at −78 °C. Upon completion of the transfer, the mixture was stirred at −78 °C for a few minutes and at room temperature for 5 min before being poured into a solution of sodium sulfite (2.74 g) in water (11 mL). This heterogeneous mixture was stirred until a peroxide test was negative. Most of the solvent was removed on a rotary evaporator, and the residue was cooled to 0 °C and acidified with concentrated hydrochloric acid. The solution was saturated with sodium chloride and extracted with ether (4×). The combined organic phases were washed once with water and brine before drying. Removal of solvent gave 908 mg (81%) of **18** as a yellowish oil. ^{1}H NMR ($CDCl_3$) δ 7.90–7.20 (m, 2 H), 6.65–5.95 (m, 2 H), 3.20–2.87 (m, 2 H), 2.63–1.25 (m, 4 H).

The α-hydroxy acid (908 mg, 5.89 mmol) in dry tetrahydrofuran (7 mL) was added dropwise via syringe to a stirred suspension of lithium

aluminum hydride (0.53 g, 13.94 mmol) in 10 mL of the same solvent. After completion of the addition, the mixture was heated overnight at reflux, cooled, treated with saturated sodium sulfate solution, and filtered. The inorganic solids were repeatedly leached with ether, and the combined filtrates were washed with brine, dried, and evaporated to give the diol as a semisolid (750 mg, 91%). ^{1}H NMR ($CDCl_3$) δ 6.49 and 6.16 (m, 2 H), 3.76 and 3.47 (m, 2 H), 2.89 and 2.75 (s, 2 H), 2.05-1.00 (m, 4 H).

Sodium metaperiodate (1.35 g, 6.3 mmol) was dissolved in 15 mL of water, and pH 7 buffer was added (~15 mL) to attain neutrality. Methanol (6 mL) was added followed by a solution of the diol (750 mg, 5.35 mmol) in 4 mL of methanol. The reaction mixture was stirred at room temperature for 5.25 h, filtered, and continuously extracted with pentane for 2 days. The pentane extract was dried and carefully distilled at atmospheric pressure to remove solvent. The norbornenone was obtained by bulb-to-bulb distillation at 110-120 °C (25 torr), the product being trapped at -78 °C. There was obtained 330 mg (75%) of **19**, $[\alpha]^{23}_D$ +1033° (*c* 1.01, $CHCl_3$), after purification of a small amount by VPC.

(1*S*)-2-Norbornanone Tosylhydrazone (20). A solution of **19** (298 mg, 2.76 mmol) in ether (10 mL) containing 15 mg of platinum oxide was hydrogenated at atmospheric pressure. When the uptake of hydrogen ceased, the catalyst was filtered off and the filtrate was concentrated to leave a semisolid mass, VPC analysis of which showed it to be homogeneous.

This material was dissolved in 2 mL of methanol and 617 mg (3.31 mmol) of tosylhydrazine was added. After gentle heating to dissolve the reagents, the solution was allowed to stand overnight, during which time crystals formed. Subsequent to cooling in the freezer, the crystals were filtered to give 300 mg (39% from **19**) of **20** as white crystals: mp 178-180 °C dec; ^{1}H NMR ($CDCl_3$) δ 7.8 and 7.3 (d, J = 8 Hz, 2 × 2 H), 2.85 (br s, 1 H), 2.5 (m, 1 H), 2.4 (s, 3 H), 2.1-1.3 (series of m, 8 H); *m/e* calculated 278.1089, found 278.1096.

(1*S*)-[2-^{2}H]Norbornene (21). A suspension of **20** (290 mg, 1.04 mmol) in 4 mL of anhydrous tetramethylethylenediamine was cooled to -45 °C, and *n*-butyllithium (4.16 mmol) in hexane was introduced by syringe. The -45 °C temperature was maintained for 1 h and subsequently was allowed to rise to room temperature. After 8 h, the reaction mixture was cooled to 0 °C, treated with 100% deuterium oxide, and taken up in a mixture of water (10 mL) and pentane (5 mL). The layers were separated, and the organic phase was washed with water (2 × 10 mL), saturated copper sulfate solution (2 × 10 mL), and brine (5 mL) prior to drying and careful distillative removal of the pentane. Preparative scale VPC isolation afforded 15 mg of **21**: *m/e* calculated 95.0845, found 95.0847.

Acknowledgment. Partial financial support for this research was provided by the national Science Foundation (Grant CHE 79-0033) to whom we are grateful.

Deuterium Isotope Effects on the Carbon-13 Chemical Shifts of Carbocations

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Abstract: The study of β-deuterium isotope effects on the carbon-13 chemical shifts of carbocations provides an unambiguous tool for probing the mechanism of charge delocalization in carbocations and a new criterion for differentiating carbocations with different charge-localization mechanisms. β-Deuterium isotope shifts on the cationic carbon centers are positive (downfield shift) for classical static carbonium ions, zero for classical delocalized ions, and negative (upfield shift) for nonclassical σ- or π-bridged nonclassical ions. For classical carbocations, the β effect is related to the demand for hyperconjugative stabilization by the alkyl group. For σ- or π-bridged nonclassical ions in general, the β effect arises from changes in the relative importance of the contributing resonance structures upon deuterium substitution. The observation of a remote γ or δ effect can provide further information as to the nature of the bridging.

Introduction

During the past decade, superacid solutions of carbocations have been prepared in increasing numbers and with increasing diversity. Differentiating between carbocations with classical or nonclassical structures has required considerable effort by numerous investigators using a variety of methods. Carbon-13 and proton NMR spectroscopy have proven to be valuable tools for the investigation of the structure of carbocations. By comparison with values for known compounds and related ions, ^{13}C chemical shfits and ^{13}C-H coupling constants provide information on carbon hybridization and charge density. For a pair of degenerate equilibrating classical carbenium ions, the observed chemical shifts and coupling constants are expected to be the averages of the static shifts and coupling constants of the two sites. For nonclassical ions, however, the cationic carbon centers are unusually shielded, with their chemical shifts differing substantially from the estimated values based on mixtures of equilibrating classical ions. The interpretations of the coupling constants and chemical shifts for these nonclassical ions suffer from the lack of suitable and reliable model compounds from which model values can be obtained.

Recently Saunders and his colleagues[1] have presented a new criterion for differentiating equilibrium processes from resonance phenomena. They have reported deuterium isotope induced splitting in the carbon-13 chemical shifts of some deuterium-substituted carbocations and proposed that the isotopic splitting should be considerably smaller for isotopic perturbation of resonance than for an equilibrium isotope effect. In the equilibrium case, the energy surface has two minima separated by a barrier and one observes a splitting as a result of the isotopic influence on the relative stability of the two minima. In the resonance case, there is only one minimum and one observes a splitting due to the change in a single structure perturbed over vibration upon isotopic substituion. The general applicability of this new criterion remains to be demonstrated. For the examples which have been reported, β-deuterium isotopic splittings for the equilibrium cases were compared with α-deuterium isotopic splittings for the res-

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