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Optical Rotatory Dispersion of 2,3-Hexadiene and 2,3-Pentadiene

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The specific rotation of (*P*)-2,3-hexadiene (**1**) was measured as a function of wavelength for the gas phase, the neat liquid, and solutions. There was a surprisingly large difference between the gas phase and condensed phase values. The specific rotation was calculated using B3LYP and CCSD, and the difference in energy between the three low energy conformers was estimated at the G3 level. The Boltzmann-averaged CCSD-calculated rotations using the gauge independent velocity gauge representation, as well as the B3LYP values, are in agreement with the gas-phase experimental values. In order to avoid possible problems associated with the conformers of **1**, 2,3-pentadiene (**2**) also was examined. Here again, there was a large difference between the gas-phase and condensed-phase specific rotations, with the CCSD velocity gauge (and B3LYP) results being close to the gas-phase experimental values. The possibility that 2,3-pentadiene could be distorted on going from the gas to liquid phase, thereby accounting for the effect of phase on the specific rotation, was examined via a Monte Carlo statistical mechanics simulation. No effect on the geometry was found. Specific rotations of **1** found in solutions were similar to those for the liquid phase, indicating that the phase difference was not due to association.

Introduction

We have examined the effect of conformation on the optical rotation of chiral 3-substituted-1-butenes[1] and 2-substituted butanes.[2] Calculations of the specific rotations as a function of the C−C−C−C torsion angles predicted a remarkably large effect with large swings in rotation including a sign change (Figure 1). It was, however, found that the shapes of the curves were quite similar despite the considerable differences between the substituents (Cl, F, CN, and CCH). The optical rotation is related to quantities associated with the electronically excited states. The differences in the first group of electronic transition energies among the substituted compounds were explored via the measurement of their vacuum UV spectra, and they were quite large, suggesting that the lower energy excited states are not the more important ones in determining the specific rotation.[2]

The computational results could be tested experimentally. In each case, there is one low energy conformer and two others that have similar and somewhat higher energies. The three conformers have quite different calculated specific rotations. As a result, the observed specific rotation should be temperature dependent, and it should be possible to obtain information about the rotations of the individual conformers from an analysis of the temperature dependence. These experiments were carried out for 3-chloro-1-butene, 2-chlorobutane, and 2-methylbutyronitrile (2-cyanobutane), and in each case the predicted effect of torsion angle on the specific rotation was confirmed.

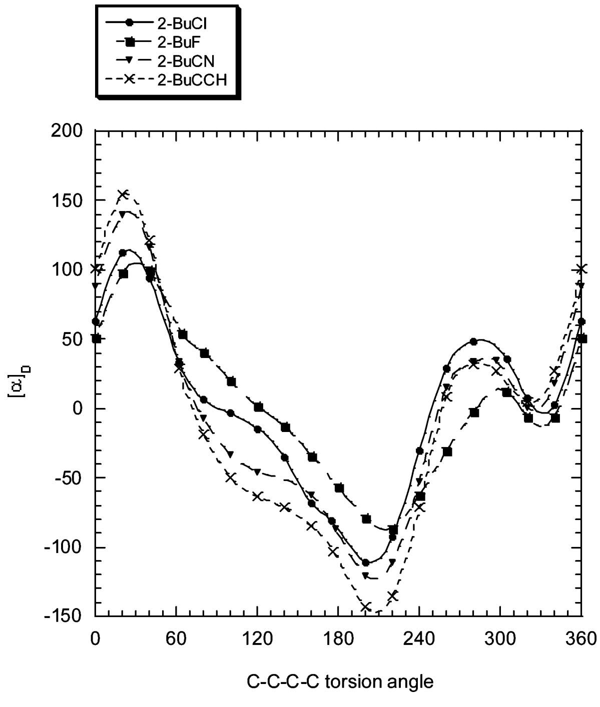

Figure 1. Effect of the C−C−C−C torsion angle on the calculated specific rotation of some 2-substituted butanes.

The results made it appear that the "shape" of the molecules, as described by the C−C−C−C torsion angle, is the major factor in determining the specific rotation and that the main effect of the substituent is the creation of a chiral center. We wished to examine this effect in a different system where the

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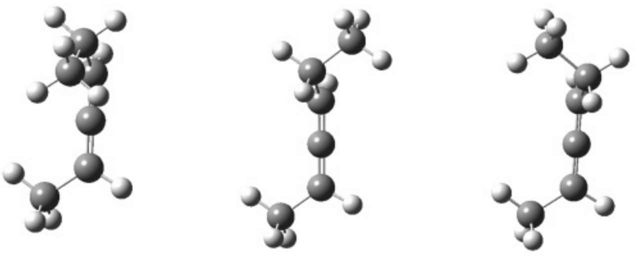

cis (0°) gauche$^+$(120°) gauche$^-$(240°)

Figure 2. The three conformers of 2,3-hexadiene.

TABLE 1: Specific Rotation of 2,3-Hexadiene (1)

α-pinene	%ee[a]	*n* steps	$[\alpha]_D$	%ee	$[\alpha]_D$
(1*S*)-(−)	99	1	−16.31[b]	19.0	−85.8
(1*S*)-(−)	87	3	−27.47	31.1	−88.3
(1*S*)-(−)	87[c]	1	−22.97	27.0	−85.1
(1*R*)-(+)	99	1	+24.67	28.4	+86.9

[a] %ee of the α-pinene reagent used in the preparation of diisopinocampheylborane. [b] Neat diene, $l = 1$, $d = 0.7227$. The *P* conformer has a positive sign of rotation. [c] 87% ee α-pinene was first converted to ∼99% ee IPC_2BH.

TABLE 2: Relative Free Energies (kcal/mol) of 2,3-Hexadiene Conformers

conformer	torsion angle	G3: Δ*G*rel	CBS-APNO: Δ*G*rel
Cis	0.2	0.000	0.000
gauche$^+$	119.5	0.269	0.209
gauche$^-$	−119.9	0.272	0.272

chirality was not due to a substituent. Therefore, we have now studied a chiral allene, 2,3-hexadiene (**1**), where there is no chiral center. It is, however, similar to the compounds mentioned above in that there are three conformers associated with rotation about the $CH-CH_2$ bond.

The specific rotation was measured as a function of wavelength and phase (gas, liquid, and solution), and the relative energies of the conformers were calculated, allowing a comparison of the observed and calculated specific rotations. A remarkably large effect on the specific rotation of going from the liquid to the gas phase was observed. In order to see if the effect might be due to a change in conformer populations with phase, 2,3-pentadiene (**2**) that has only one conformer was also examined. Similar results were obtained.

Results and Discussion

1. 2,3-Hexadiene (1). The diene is readily prepared by the addition of dibromocarbene to 2-pentene followed by treatment of the dibromocyclopropane with methyllithium.[3] It was subjected to a kinetic resolution in the same fashion that has been reported for other allenes, i.e., via a reaction with chiral diisopinocampheylborane.[4] Table 1 reports the results of several kinetic resolutions and the %ee determined using a chiral GC column. The specific rotation for the pure *P*-enantiomer is $[\alpha]_D = 86.5 \pm 1.8$. This is similar to that for 2,3-pentadiene (**2**), $[\alpha]_D = 81.0 \pm 0.2$.[5]

The allene, **1**, is expected to have three conformers, with the methyl group (cis, C−C−C−C angle ∼0°), or one of the CH_2 hydrogens eclipsed with the carbon−carbon double bond (gauche$^+$ and gauche$^-$).[6] They are shown in Figure 2. Their relative energies were calculated at several theoretical levels including G3 and CBS-APNO, and these data are recorded in Table 2.

TABLE 3: Calculated Specific Rotations (deg dm^{-1} (g/mL)$^{-1}$) for the (*P*)-2,3-Hexadiene Conformers, $[\alpha]_D$

	cis	gauche$^+$	gauche$^-$	Boltzmann averaged[a]
		B3LYP/aug-cc-pVDZ		
velocity	205.2	415.9	−179.8	156.8
length-GIAO	220.6	440.1	−169.0	173.4
length	207.9	424.3	−184.8	158.9
		B3LYP/aug-cc-pVTZ		
velocity	226.7	448.5	−180.7	175.1
length-GIAO	224.6	436.5	−169.8	173.9
length	224.6	447.7	−177.9	174.8
		CCSD/aug-cc-pVDZ		
velocity[b]	208.5	376.7	−120.6	163.8
length[b]	115.0	329.6	−200.3	87.1

[a] Using the G3 relative free energies, the mol fractions of the conformers are 0°, 0.441; 120°, 0.280; 240°, 0.279. [b] Velocity-gauge refers to the modified dipole-velocity gauge of Pedersen et al.,[9] and length gauge is the commonly used method.[8] Dipole-length gauge values calculated without using GIAO's used the center of mass as the coordinate origin.

TABLE 4: Boltzmann-Averaged Specific Rotation (deg dm^{-1} (g/mL)$^{-1}$) of (*P*)-2,3-Hexadiene (1) as a Function of Wavelength, Aug-cc-pVDZ[a]

	B3LYP[b]			CCSD		observed	
nm	velocity	GIAO	length	velocity	length	liquid	gas
633	134.7	149.1	136.7	140.6	75.0		122 ± 4.4
589	156.8	173.4	158.9	163.8	87.1	86.5 ± 1.8	
578	163.1	180.4	165.3	180.2	96.4	90.2 ± 1.9	
546	183.8	203.3	186.3	203.6	108.7	102.0 ± 2.1	
436	293.3	325.4	297.4	313.2	162.8	166.7 ± 3.2	
365	409.7	458.4	415.7	492.5	249.0	243.3 ± 5.0	
355	427.5	479.5	433.8	489.3	241.9		511 ± 7.2

[a] B3LYP/6-311+G* structures were used for 633, 589, 436, and 355 nm calculations while CCSD/6-311+G* structures were used for 578, 546, and 365 nm. [b] The B3LYP/aug-cc-pVTZ calculations changed the GIAO values by only a small amount but increased the velocity and length gauge calculations so that both were in very good agreement with the GIAO values.

In order to see if the conformation may have an important effect on the optical activity, the specific rotations, $[\alpha]_D$, of the conformers were initially calculated at the B3LYP/aug-cc-pVDZ and aug-cc-pVTZ levels, giving results that are summarized in Table 3. These calculations can be carried out in three ways: using the velocity gauge representation that is origin independent or using the length gauge representation with or without gauge-including atomic orbitals (GIAO). The two basis sets give almost the same calculated rotations and the gauge representation has little effect. The results indicate that there is a large effect of conformation on the rotation. When the calculated rotations are combined with the conformer populations derived from the G3-calculated relative free energies, the estimated rotation is about 173°, which is about twice the observed rotation of the neat liquid.

The calculations also were carried out using the coupled cluster singles and doubles (CCSD) model[7] that is generally considered to be superior to the DFT-based methods.[8] This appeared to be the case with 2,3-pentadiene (**2**) where B3LYP gave $[\alpha]_D = 125$, and CCSD gave 84 that is close to the observed liquid-phase value $[\alpha]_D = 81$.[5] The results from these calculations are included in Table 3, and here there is a large difference between the values obtained using the two gauge representations. The length gauge result is close to the liquid-phase experimental value, whereas the modified velocity gauge[9] gave larger calculated rotations.

TABLE 5: Specific Rotation (deg dm^{-1} $(g/mL)^{-1}$) of (*P*)-2,3-pentadiene (2) as a Function of Wavelength, Aug-cc-pVDZ[a]

	B3LYP[b]			CCSD[b]		observed	
nm	velocity	GIAO	length	velocity	length	liquid	gas
633	108.0	108.4	106.6	116.5	65.4		127.8 ± 1.9
589	124.8	125.1	123.0	135.4	75.6	81.0 ± 0.2	
578	129.5	129.9	127.7	140.8	78.5	84.3 ± 0.2	
546	144.9	145.3	142.7	158.5	87.9	94.9 ± 0.2	
436	219.4	220.1	215.0	253.1	135.4	151.2 ± 0.4	
365	270.6	271.7	262.0	360.0	178.5	209.2 ± 0.5	
355	271.3	272.4	261.6	378.5	183.7		409.8 ± 1.3

[a] The B3LYP/aug-cc-pVDZ structure was used. Non-GIAO-based dipole-length gauge rotations were computed with the center of mass as the origin. [b] aug-cc-pVTZ calculations led to a small increase in the calculated values. For 589 nm, the B3LYP values are 133.9, 130.0, and 131.7; for CCSD the velocity and length values are 149.6 and 77, respectively. [c] The maximum liquid-phase rotation at 589 nm was given by ref 5 as 81.0 ± 0.2, and the observed rotations were corrected to 100% ee using this value.

TABLE 6: Effect of Solvent on the Specific Rotation of 1, [α]

nm	C_6H_{12}	Bu_2O	MeCN	acetone	benzene	methanol	CCl_4
589	76.8	85.3	88.8	85.5	80.0	95.7	68.1
578	80.0	89.1	92.8	88.8	83.6	100.3	71.2
546	90.3	100.8	105.2	100.5	94.4	113.4	80.5
436	146.4	165.2	171.7	164.3	145.5	186.8	130.1
365	211.6	242.3	252.2	241.0	210.3	276.6	185.

The velocity gauge is origin independent, whereas this is not the case using the length gauge. This strong dependence on the arbitrary choice of origin indicates that the length-gauge results are not useful for comparison to experiment.

We have measured the specific rotation of the neat liquid as a function of wavelength, and the values are compared with the Boltzmann-averaged calculated values in Table 4. All of the DFT values and the CCSD velocity-gauge values are much larger than either the CCSD length gauge or the liquid-phase experimental values. However, when the specific rotation was measured in the gas phase by means of cavity ring-down polarimetry,[10] there was a remarkable increase. The gas-phase values are in fairly good agreement with both the DFT and CCSD velocity-gauge-calculated rotations (Table 4). The difference between liquid- and gas-phase values could be a result of a change in conformer populations in going from the liquid to the gas phase. In order to see if this might be the case, we have also examined 2,3-pentadiene (**2**) that has only one conformer.

A sample of (**2**) was prepared as previously described,[11] and the rotation was determined at several wavelengths as both the neat liquid and in the gas phase. The specific rotation was calculated using both B3LYP/aug-cc-pVDZ and CCSD/aug-cc-pVDZ, giving the results summarized in Table 5. The results are similar to those obtained with **1**.

2. Effect of Medium on the Specific Rotation. There are frequently some differences in specific rotation for a given compound on going from the liquid phase to the solution phase.[12] The effects of solvent and wavelength were explored using dilute solutions (5−8%) of **1** in several solvents including cyclohexane, di-n-butyl ether, acetone, and acetonitrile (Table 6). These solvents were of special interest because they give solvent effects that are usually well correlated with the Onsager dielectric constant function, $(\epsilon - 1/2\epsilon + 1)$.[13] Solvents, such as methanol, that form hydrogen bonds with solutes and others, such as benzene and carbon tetrachloride, that have no dipole moment and hence a low dielectric constant but still can interact with solutes via their quadrupole moments, are generally not suitable for a reaction field type calculation. Figure 3 shows the correlation between the observed specific rotation at 589 nm and the Onsager function. The line is defined by MeCN, Me_2CO, n-Bu_2O, and cyclohexane.

Methanol and carbon tetrachloride give large deviations with respect to the other solvents, as is frequently observed.[14] The values for the other solvents are not much different than that for the neat liquid. In the case of solutions in benzene, the observed rotation was measured at a number of concentrations and was found to be linearly related to the concentration. Therefore, the difference between the gas phase and the neat liquid cannot be due to association between the (*P*)-2,3-hexadiene molecules.

What is the origin of the large change in specific rotation for the allenes on going from the gas phase to the liquid phase or solution? Since both allenes give the same behavior, it cannot be due to a change in conformer populations for **1**. An examination of the change in energy on twisting the terminal bonds of **2** (changing the dihedral angle between the two Me−CH bonds away from the normal 90°) (Figure 4) showed that this is a relatively soft mode. Could "pressure" from a solvent change the average dihedral angle, and is the specific rotation affected by the dihedral angle?

The calculated effect of the torsion angle on the specific rotation is shown in Figure 5. The maximum rotation is found at 80°, and the rotation decreases rapidly with an increase in the angle. If "solvent pressure" would lead to an increase in the angle, the experimental observations could be reconciled.

In order to explore the possibility of a medium effect on the torsion angle, Monte Carlo (MC) statistical mechanics simulations were carried out for 2,3-pentadiene in the gas and pure liquid phases. This was done using classical potential energy functions in the OPLS-AA format.[15] Standard procedures were followed, as described elsewhere,[16] including use of the NPT ensemble for the liquid at 25 °C and 1 atm with Metropolis sampling for all degrees of freedom, a periodic cube containing 267 monomers (Figure 6) with the same chirality, 12-Å intermolecular cutoffs based on the C3−C3 distance, and a standard correction for Lennard−Jones interactions neglected beyond the cutoff. OPLS-AA potential function parameters were optimized to reproduce the B3LYP/6-311++G** torsional energetics for a single molecule in Figure 4 and experimental data for gas-phase structures and liquid-phase densities and heats of vaporization for allenes.[17]

From the MC simulations, the computed density and heat of vaporization of liquid 2,3-pentadiene are 0.666 ± 0.002 g/cm^3

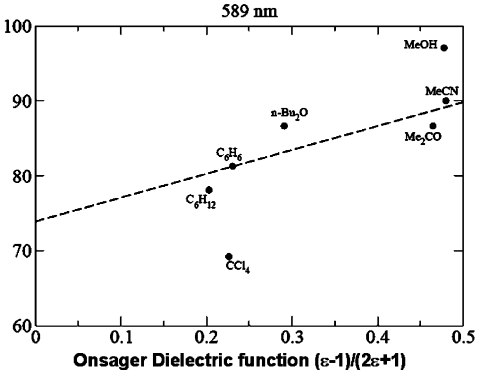

Figure 3. Relationship between the observed specific rotation and the dielectric constant function.

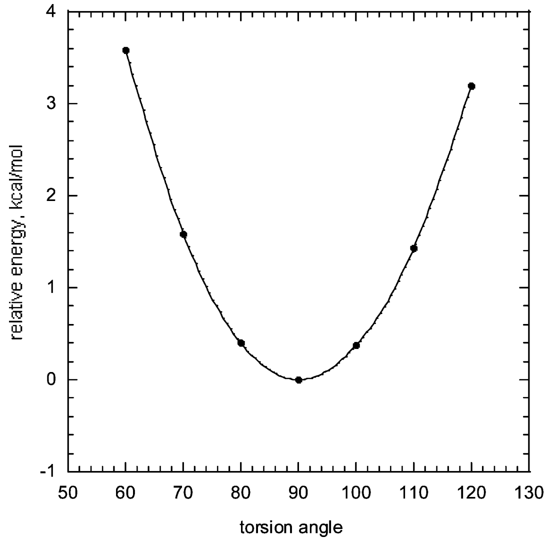

Figure 4. Effect of the Me−C(C)C−Me torsion angle on the B3LYP/6-311++G**-calculated energy of 2,3-pentadiene.

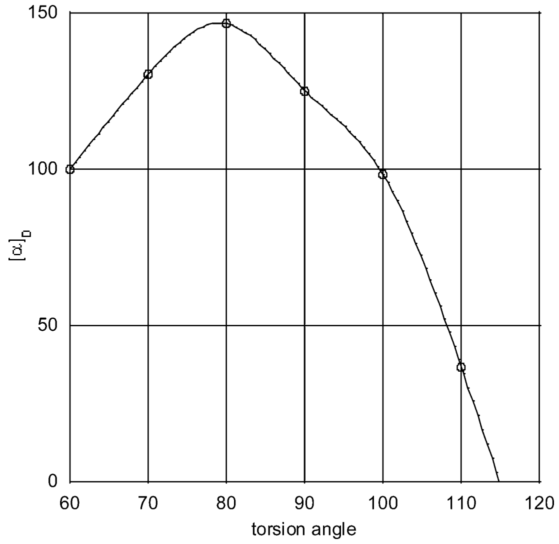

Figure 5. Effect of the torsion angle on the calculated specific rotation of 2.

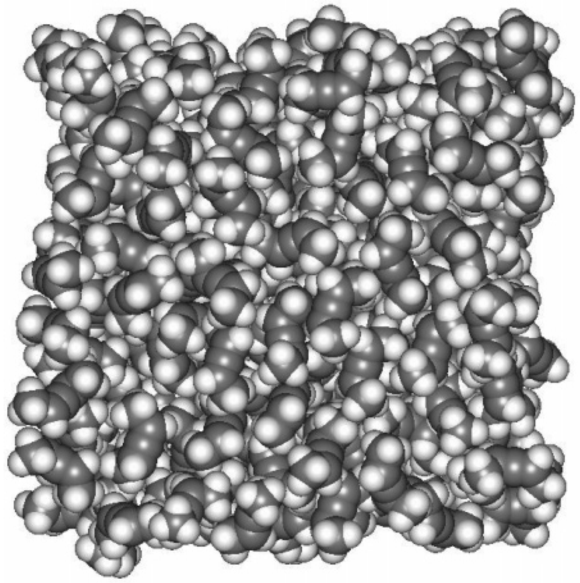

Figure 6. CPK illustration of a configuration from the MC simulation of liquid 2,3-pentadiene (**2**). An amount of 267 monomers was modeled in a cubic periodic cell at 25 °C and 1 atm.

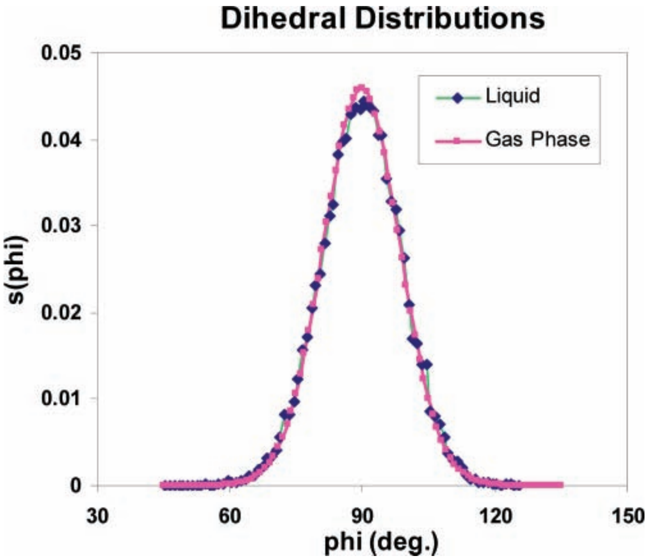

Figure 7. Computed dihedral angle distributions for the C1−C2−C4−C5 angle in 2,3-pentadiene in the gas and liquid phases at 25 °C and 1 atm.

and 6.40 ± 0.08 kcal/mol at 25 °C and 1 atm (Figure 6). Experimental values of 0.690 and 0.702 g/cm^3 are available for the density,[18] and the heat of vaporization can be estimated as ca. 6.9 kcal/mol based on experimental data for 3-methylbuta-1,2-diene (6.67 kcal/mol)[19] and data for isomeric butenes and pentenes. This level of accord between OPLS-AA results and experiment is typical.[15,16] The key findings in the current context are illustrated in Figure 7, which compares the computed C1C2C4C5 dihedral angle distributions for 2,3-pentadiene in the gas and pure liquid phases. Though dihedral angle values spanning a 60° range centered on 90° are sampled in both cases, the dihedral angle distributions for the gas and liquid phases are essentially identical. Thus, the MC simulations do not support a medium dependence for the geometry of 2,3-pentadiene at normal densities. This result is consistent with extensive studies of lower n-alkanes, which also show no condensed-phase effect on conformer populations for transfer from the gas phase to the pure liquids at 25 °C and 1 atm.[16]

3. Electronic Transitions of 2,3-Hexadiene (1). The calculation of specific rotations involves a summation of products of electronic and magnetic transition dipoles for each of the excited states divided by an energy denominator.[7] If the energies of the excited states changed significantly on going from one conformer to another, it could result in a change in specific rotation.

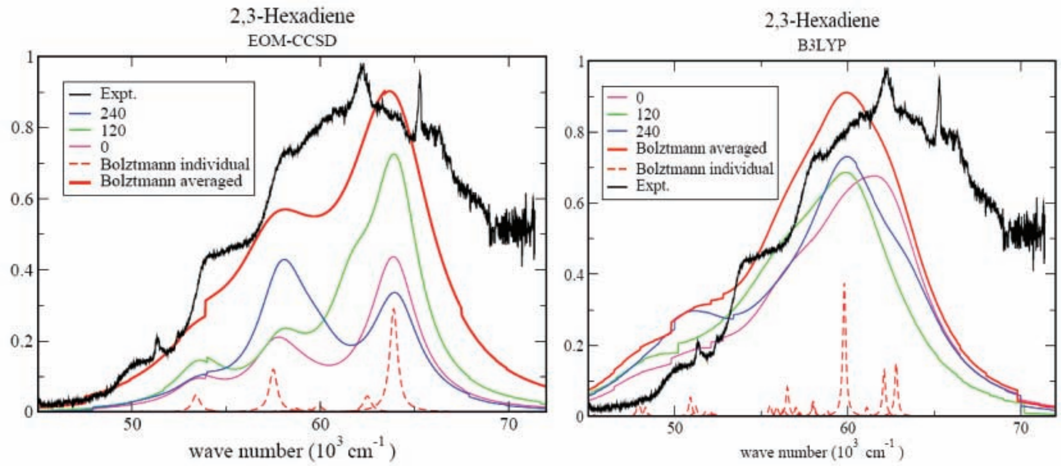

Figure 8. Comparison of observed and calculated electronic spectra. The dashed lines indicate the positions of the individual transitions.

TABLE 7: EOM-CCSD/6-311++G Excitation Energies of 1 with the CCSD/6-311+G* Structures**[a]

	0°-conformer		120°-conformer		240°-conformer		
no.	EV	*f*	eV	*f*	eV	*f*	expt, eV
1	6.01	0.001	6.00	0.001	6.00	0.000	
2	6.29	0.001	6.30	0.004	6.32	0.004	
3	6.62	0.044	6.63	0.074	6.62	0.030	6.4
4	6.72	0.004	6.73	0.005	6.72	0.008	
5	7.14	0.089	7.17	0.085	7.18	0.205	6.9
6	7.17	0.007	7.21	0.003	7.22	0.003	
7	7.23	0.004	7.25	0.005	7.24	0.008	
8	7.27	0.013	7.26	0.002	7.27	0.016	
9	7.36	0.011	7.37	0.002	7.30	0.012	
10	7.43	0.003	7.40	0.002	7.43	0.061	
11	7.75	0.005	7.66	0.150	7.79	0.003	
12	7.92	0.271	7.94	0.416	7.94	0.193	7.7

[a] The B3LYP/aug-cc-pVDZ transition energies may be found in the Supporting Information. Since the molecule is chiral, all the transitions are A_1.

TABLE 8: The SOS and LR $[\alpha]_D$ for 1 at the B3LYP/aug-cc-pVDZ Level

	0°-conformer		120°-conformer		240°-conformer	
	velocity	length	velocity	length	velocity	length
SOS	206.9	210.4	415.0	425.4	-176.4	-183.0
LR	205.2	207.9	415.9	424.3	−179.8	−184.8

It seemed unlikely that the three conformers of **1** would have markedly different electronic transitions, but to be certain, the transition energies were calculated. The observed VUV spectrum is shown in Figure 8. The electronic transitions were calculated using TDDFT (B3LYP/aug-cc-pVDZ) that is related to the B3LYP specific rotation calculations and using the equations-of-motion EOM-CCSD method[20] that is related to the CCSD specific rotation calculations. The calculated transitions at the EOM-CCSD/6-311++G**//CCSD/6-311+G* level are given in Table 7, and the spectra predicted by convoluting the transitions with Lorentzian curves are included in Figure 8. The B3LYP/aug-cc-pVDZ gives about two times as many excited states as EOM-CCSD for the energies lower than 7.95 eV (Table S3). For the Boltzmann-averaged curve in Figure 9, the oscillator strength at B3LYP level was reduced by 1/1.89 compared to EOM-CCSD ones.

It may be noted that the transition energies do not change much on going from one conformer to another. However, there are significant changes in the calculated oscillator strengths. The EOM-CCSD transition energies reproduce the observed spectrum fairly well. The TDDFT energies have somewhat lower values but still give a reasonable approximation to the observed spectrum.

TABLE 9: Effect of the Cumulene Size on the Calculated Specific Rotation

	number of cumulene carbons			
	3	5	7	9
$[\alpha]_D$	125.1	238.2	231.4	233.4
$[\alpha]_D$(static)	122.5	193.8	174.8	154.1
first ES(Ev)	5.6	3.72	2.8	2.2
N	11	13	15	17
$[\alpha]_D$	169.5	434.6	340.0	282.1
$[\alpha]_D$(static)	142.3	132.6	129.5	37.8
first ES(Ev)	1.8	1.6	1.4	1.2

4. Sum-over-States Study of 1. The specific rotation by itself provides little information on the relationship between structure and optical activity. We have calculated the specific rotation with linear response methods at the TDDFT and CCSD levels of theory, but these calculations do not give information on the role of particular excited states in determining the specific rotation. We have found a sum-over-states approach to be useful in giving this type of information.[21] A TDDFT calculation of excited states will provide the excitation energies (ΔE_{0n}) and rotational strength (R_{0n}), so contributions to the length gauge specific rotation on a state by state basis can be analyzed through the following equation:

$$\alpha = \frac{k}{M} \sum_{i=1}^{n} \frac{\omega^2}{\Delta E_{0n}^{\ 2} - \omega^2} R_{0n} \tag{1}$$

in which R is the rotary strength (10^{-40} erg-esu-cm/Gauss) for a transition to a given excited state, ω is the light energy (using the same units as ΔE_{0n}), M is the molar mass in g/mol, and k is equal to 9143.028.

The results of such a calculation (excluding six core molecular orbitals which have energies lower that −10.0 au) are shown in Figure 9. The specific optical rotations calculated from TDDFT linear response method are given as the horizontal lines in Figure 9.

An interesting aspect of the results in Figure 9 is that the first 20 states do not even give a qualitative agreement with the linear response. Although some agreement appears to have been achieved after about 100 states, this is not born out by inclusion of further states. About 1800 states are needed to get convergence.

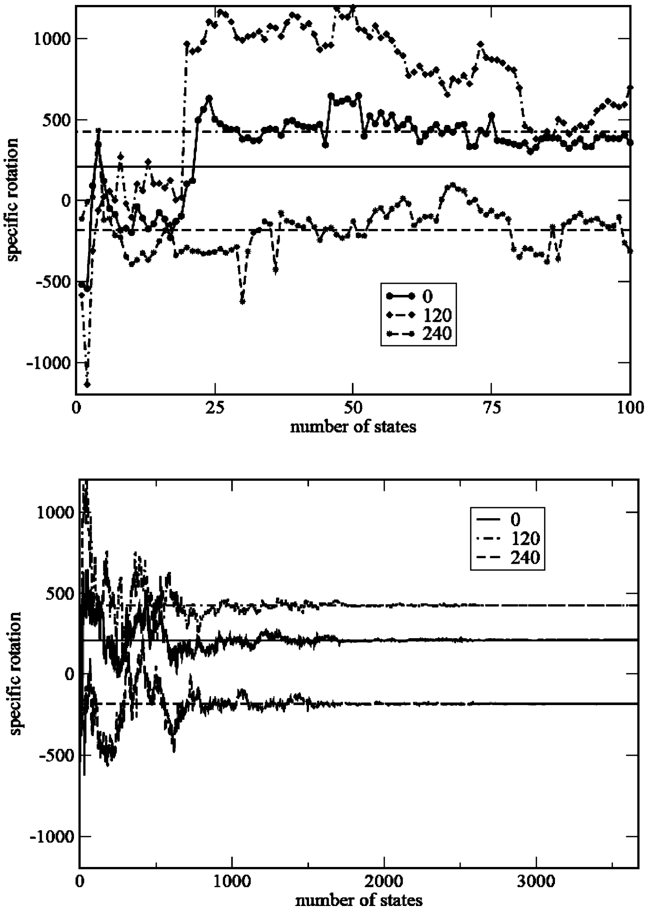

Figure 9. Sum-over-states results for 2,3-hexadiene (1).

The inclusion of this large number of states is, of course, physically unrealistic. However, in a perturbation treatment, the functions used need not have physical significance and are just used to try to get the best representation of the quantity of interest. The need for a large number of terms to reach convergence indicates that the excited states do not have a good match to the quantity of interest.

With this number of states, the SOS method leads to $[\alpha]_D$ that agree with those calculated by the corresponding linear response (LR) method (Table 8).

The double bonds are involved with a number of the excited states, and therefore we wondered if additional double bonds would significantly affect the specific rotation. B3LYP/aug-cc-pVDZ-calculated $[\alpha]_D$ values for several dimethyl-substituted cumulenes are listed in Table 9. It is interesting that it increases on going from $n = 3$ to $n = 5$, but then the calculated specific rotation changes in an irregular fashion. This occurs because, as the chain length increases, the lowest-lying electronic transitions shift to longer and longer wavelengths into the visible region. Then as a transition approaches the wavelength of the incident light (the sodium D-line in Table 9), the specific rotation exhibits a first-order pole (cf. eq 1). This interpretation is supported by the static-limit rotations (also reported in the Table 9) for which such poles naturally do not exist; the values of $[\alpha]_0$ decrease smoothly with an increase in chain length beyond the C5 cumulene.

5. Vibrational Contributions to Specific Rotation of 2,3-Pentadiene (2). Several recent studies have highlighted the potential importance of vibrational effects on specific rotation. In 2003, Wiberg and co-workers examined mode-by-mode vibrational contributions to the specific rotation of one conformer of 3-chloro-1-butene and found that the total correction (omitting the large-amplitude torsional motion of the carbon backbone) was small compared to the total rotation.[1] On the other hand, Ruud and Zanasi[22] and later Kongsted et al.[23,24] demonstrated that qualitative discrepancies between CC-level specific rotations and the gas-phase experimental results of Wilson et al. for (*S*)-methyloxirane at short wavelengths[25] could be overcome by inclusion of zero-point vibrational and temperature corrections, in addition to higher levels of electron correlation. In addition, Mort and Autschbach[26] examined a set of 22 conformationally rigid molecules at the B3LYP level of theory and found that zero-point vibrational corrections can account for as much as 20% of the total rotation. More recently, Crawford, Tam, and Abrams demonstrated that harmonic vibrational corrections serve to worsen the agreement between theory and gas-phase experiment for the problematic methylthiirane species.[27]

TABLE 10: Harmonic Vibrational Corrections to $[\alpha]_D$ (deg/[dm (g/mL)]) of (*P*)-2,3-Pentadiene (2)

freq, cm^{-1}	B3LYP	CCSD	vibrational mode
134.6	−19.4	−6.7	methyl bend
149.3	29.0	23.6	methyl twist
165.0	21.3	20.1	methyl twist
217.3	32.2	21.2	methyl rock + chain bend
294.3	−29.3	−19.4	chain bend
523.2	−112.7	−75.8	chain bend
555.5	91.5	58.4	chain bend
706.6	−2.2	−1.5	
821.9	−4.3	−2.3	
894.9	−6.5	−4.5	
959.0	3.5	2.8	
1041.3	1.4	1.4	
1042.8	4.0	3.2	
1081.0	−18.3	−11.4	methyl rock
1090.2	19.7	13.1	methyl CC stretch
1164.9	−2.9	−2.0	
1304.6	3.4	2.4	
1379.3	3.3	2.5	
1382.3	1.9	1.8	
1430.5	−1.2	−0.4	
1452.8	1.7	1.4	
1453.6	1.5	1.4	
1463.5	0.5	0.4	
1494.5	0.1	0.5	
2057.6	3.9	11.9	antisymmetric C=C=C stretch
3019.0	0.2	0.0	
3020.0	0.0	0.3	
3071.8	−2.2	−2.3	
3071.9	2.1	1.5	
3109.9	−1.0	−0.8	
3111.8	−2.6	−1.8	
3126.9	0.1	0.8	
total correction	16.4	37.8	
$\langle[\alpha]_D\rangle$	142.3	171.9	

We have evaluated the contributions of temperature-dependent molecular vibrations to the specific rotation of (*P*)-2,3-pentadiene following the approach described by Wiberg et al. modified by an additional step-size factor to allow for testing the convergence and stability of the numerical second derivatives of the rotation with respect to the normal modes. In agreement with Mort and Autschbach[26] and with Crawford et al.,[27] we find that the vibrational corrections are very sensitive to several factors: (1) the choice of step size, (2) the numerical precision to which the equilibrium structure is optimized, and (3) for DFT methods, the density of the numerical integration grid.

Table 10 summarizes the B3LYP/aug-cc-pVDZ and CCSD/aug-cc-pVDZ mode-by-mode harmonic vibrational corrections at 300K for the 589 nm specific rotation of (*P*)-2,3-pentadiene based on the B3LYP/aug-cc-pVDZ-optimized structure. The B3LYP calculations were carried out using a pruned grid of 99 radial shells and 509 angular points per shell, and the structure was optimized to an rms force of 10^{-6} Hartrees/Bohr. The grid density is not an issue for the CC-level vibrational corrections, though tight rms convergence of the CC amplitude and perturbed wave function equations is necessary to at least 10^{-8} for numerically stable results. The step-size was varied systematically from 1.0 to 0.1; the results in Table 10 are based on a value of 0.5, which was found to provide converged numerical second derivatives. (It is worth noting that the CC-level derivatives appear to be more stable than their B3LYP counterparts over a wider range of step-sizes, a point that appears to be related to the numerical integration grid density for the latter.) The modified dipole-velocity gauge formalism was used for the CCSD calculations and the GIAO-based dipole-length formalism was used for the B3LYP calculations, both of which are origin independent.

For every vibrational mode, B3LYP and CCSD corrections are of the same sign, though the size of the correction is often considerably different, with B3LYP producing a larger correction in almost every case. (Indeed, the only significant exception is for the C═C═C antisymmetric stretch at 2057.6 cm^{-1}.) However, because the total correction involves substantial cancelation of opposite-sign terms, the final B3LYP correction is more than a factor of 2 smaller than that of CCSD. The final vibrationally averaged specific rotations are higher than the equilibrium values, with B3LYP ending up closer to the gas-phase experimental value than CCSD. Basis-set effects appear to be relatively small in this case and do not account for the discrepancy between CCSD and experiment. However, it is, of course, possible that a higher-level correlation treatment is necessary to obtain a converged result.

Conclusion

Summary. (*P*)-2,3-Hexadiene (**1**) has been prepared in chiral form, and the specific rotation of both **1** and (*P*)-2,3-pentadiene (**2**) have been studied in both the gas and liquid phase. There was a remarkable effect of phase, where the specific rotation is about twice as large in the gas phase as in the liquid phase. The difference is not due to conformational effects or association in the condensed phase.

The compounds also were studied theoretically, making use of linear response theory with B3LYP/aug-cc-pVDZ and CCSD/aug-cc-pVDZ. The DFT-calculated rotations were almost the same using velocity or length gauge without GIAO's, or using the length gauge with GIAO's. The calculated rotations were in fair agreement with the gas-phase experimental values. However, the CCSD/aug-cc-pVDZ results were quite sensitive to the gauge representation, with the (modified) velocity gauge being in agreement with both DFT and the gas-phase measurements, and the length gauge giving much smaller calculated specific rotations. The vibrational correction to the specific rotation was calculated and was found to be relatively small as compared to the observed rotation.

Although the specific rotation is found to depend strongly on the value of the Me−C(C)C−Me torsion angle, MC simulations of an ensemble of **2** do not yield an appreciable change in the angle's value. Nevertheless, it is possible that a complete MC simulation of the specific rotation in the liquid could yield a closer comparison with experiment, perhaps due to changes in other structural features in the condensed phase. However, the computational expense of such an analysis is immense and thus outside the scope of the current work.

Calculations. The B3LYP calculations were carried out using Gaussian-Development Version E[28] and the CCSD calculations made use of PSI3.[29] The Monte Carlo simulation was carried out using BOSS.[30]

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Supporting Information Available: Tables of calculated structures and TDDFT-calculated transition energies. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) The resultant OPLS-AA atomic charges and Lennard−Jones parameters for 2,3-pentadiene are for C2 (−0.10 e, 3.30 Å, 0.086 kcal/mol), C3 (−0.10, 3.30, 0.086) and HC2 (0.15, 2.42, 0.030). The methyl groups are represented as usual (ref. 15): C (−0.18, 3.50, 0.066) and HC (0.06, 2.50, 0.030). If C1 of an allene is CH_2 or $C(CH_3)_2$, the only difference is that the charge for C1 would be −0.25 or 0.05 e. The torsional energetics includes four terms (C1−C2−C4−C5; C1−C2−C4−H; H−C2−C4−C5; H−C2−C4−H), all with $V_2 = -8.0$ kcal/mol. The sp-hybridized carbon of allenes was given the two-letter code C:. For bond stretching, r_{eq}(C:-CM) = 1.305 Å and k_r = 700 kcal/mol-Å^2, and for C:-CM-CT, C:-CM-HC, and CM-C:-CM angle bending, θ_{eq} = 122.0, 121.0, and 180.0°, and k_θ = 80.0, 40.0, and 160.0 kcal/mol-rad^2, respectively. Otherwise, OPLS-AA parameters for alkenes and alkanes are used.

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