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Optical Activity of 1-Butene, Butane, and Related Hydrocarbons

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All molecules except those conformations that have a plane of symmetry, a center of inversion, or an improper axis of rotation are chiral. The magnitudes of the optical rotation of the chiral rotamers of 1-butene, butane, propene, propane, and ethane have been examined. Changes in optical rotation with torsional angle are quite large. The calculated specific rotations for 1-butene are about as large as those for the substituted 1-butenes previously studied, and changes in the basis set used in the calculations have relatively small effects on the rotations. With butane, the calculated specific rotations are somewhat smaller than found with 1-butene, and here, going from 6-311++G** to aug-cc-pVDZ has a major effect on the relationship between the C−C−C−C torsional angle and the calculated rotation. With propene, a change in basis set led to a change in the calculated rotation with torsional angle, and with propane, the magnitude of the specific rotation is markedly reduced, and the sign is changed on going from 6-311++G** to aug-cc-pVDZ or aug-cc-pVTZ. The same is found with ethane. The sign change for ethane is found to originate with the p-type diffuse orbitals in the aug-cc-pVDZ basis set.

Introduction

We have examined the optical rotation of 3-chloro-1-butene both experimentally and computationally.[1] The changes in optical rotation with respect to changes in the C−C−C═C torsional angle are remarkable, with large positive rotations around 0° and large negative rotations around 180°. In addition, some vibrational modes lead to large changes in optical rotation, although the changes for positive and negative displacements averaged to essentially zero in each case. To gain further information related to the origin of the change in optical rotation with torsional angle, we have now examined a group of simple molecules such as 1-butene, butane, and similar hydrocarbons.

A thermal ensemble of molecules that possess a mirror plane, a center of inversion, or an improper axis of rotation (in any accessible conformation) cannot be optically active. Nevertheless, an individual member of this ensemble, distorted to remove these symmetry constraints, is predicted to exhibit a chiroptical response of surprisingly strong magnitude.[2]

Results and Discussion

1-Butene. 1-Butene is, of course, an achiral molecular system. However, this is true for a given molecule only when it has a plane of symmetry, and in the case of 1-butene, only when the C−C−C═C torsional angle is either 0° or 180°, the latter of which is a transition state. Only a relatively small number of molecules will have a plane of symmetry, and with any other torsional angle, a given molecule will have C_1 symmetry and will be chiral. It is only the fact that its mirror image will always be present that makes the ensemble of molecules appear to be achiral in measurements of optical activity.

The torsional potential energy function, calculated at the B3LYP/6-311+G* level, is shown in Figure 1 and is in good agreement with higher level calculations.[3] The two lower energy minima correspond to a hydrogen being eclipsed with the double bond, whereas the higher energy conformer has the methyl group eclipsed with the double bond. The specific rotation of 1-butene was calculated at 20° intervals from 20° to 160° at the B3LYP/6-311++G** level[4] by use of the B3LYP/6-311+G* geometries. The data for 589 nm are shown in Figure 2. The calculated specific rotation becomes quite large at 60° and 150°, with values approaching 300°. The calculated rotations as a function of excitation wavelength are available in the Supporting Information.

Although the above theoretical level was found appropriate for substituted 1-butenes, the results presented below suggested that additional calculations should be carried out with aug-cc-pVDZ. The calculated specific rotations are shown in Figure 2. There is a change, especially at 100°, but the values of the specific rotation are similar.

The range of specific rotations calculated for 1-butene (+250° at a 60° C−C−C═H torsional angle to −250° at a 300° torsional angle) is half as large as that for 3-chloro-1-butene (−520° at a 180° C−C−C−C torsional angle and +420° at a 320° torsional angle) and as large as that for 3-fluoro-1-butene (−290° at a 200° torsional angle and +60° at a 60° torsional angle). Although the halogen substituents have an effect on the specific rotation, the effect is far from dramatic.

Butane. Is the large specific rotation a result of having a double bond in the molecule? This question might be examined by studying butane. Here, it is achiral only when the C−C−C−C torsional angle is 0° or 180°, and the former is a transition state. The torsional potential energy curve is shown in Figure 3, and it is in satisfactory agreement with higher level calculations.[3,5] The specific rotation was calculated by use of B3LYP/6-311++G** at 20° intervals from 20° to 160°, with the

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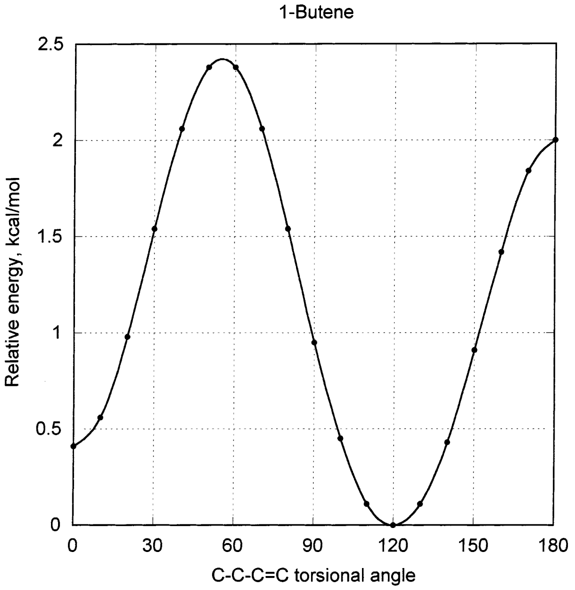

Figure 1. Torsional potential energy function for 1-butene (B3LYP/6-311+G*).

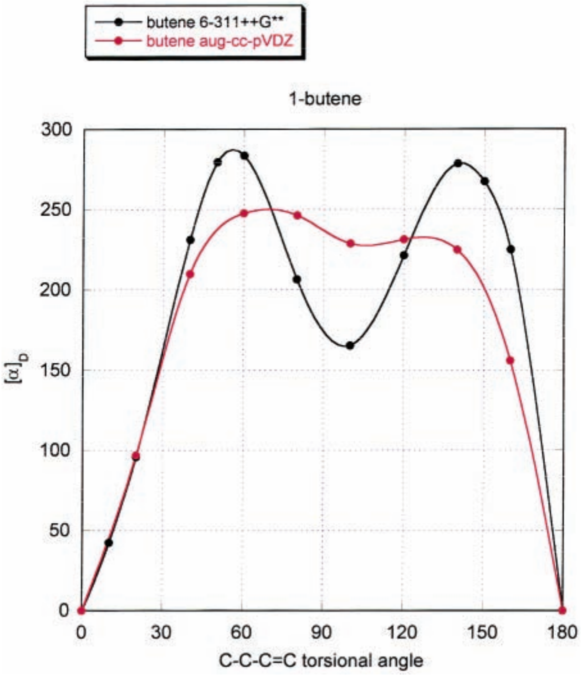

Figure 2. Calculated specific rotation of 1-butene as a function of the C−C−C═C torsional angle. Smooth curves are drawn between the calculated points as a convenience for the reader.

B3LYP/6-311+G* geometries, giving the data for 589 nm that are shown in Figure 4. The specific rotation takes a large value at 90°, which is 65% of that found with 1-butene.

Although 6-311++G** has been found to be a fairly satisfactory basis set for 1-butene derivatives, this might not be the case with butane, which has much higher electronic transition energies. The specific rotations were calculated as a function of the C−C−C−C torsional angle by use of aug-cc-pVDZ and aug-cc-pVTZ. The calculated rotations are included in Figure 4 and are somewhat smaller than those found with 6-311++G** along with a change in the shape of the curve.

The most interesting observation is that a large specific rotation (100° with aug-cc-pVDZ) is found at a 90° torsional angle where the two terminal C−C bonds are orthogonal and

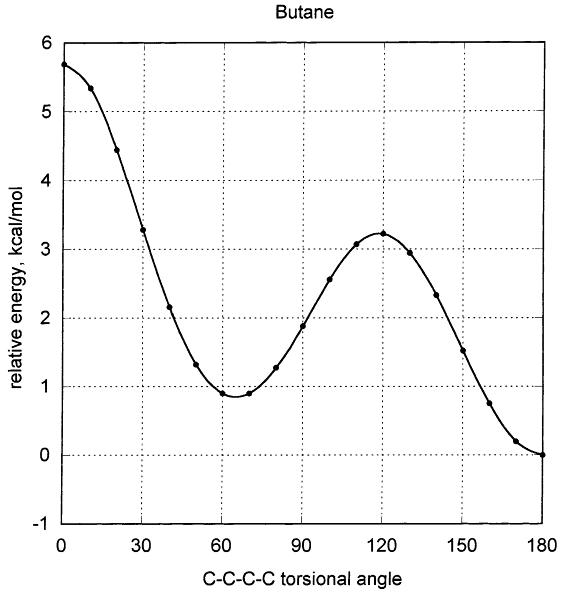

Figure 3. Torsional potential energy function for butane (B3LYP/6-311+G*).

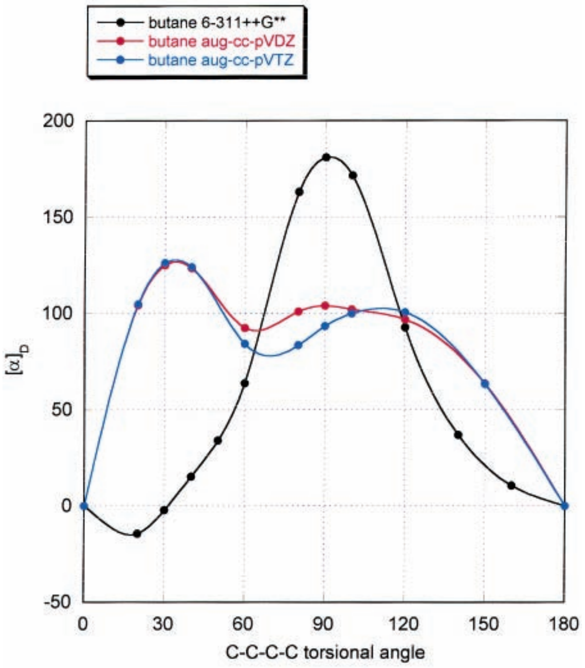

Figure 4. Calculated specific rotation of butane as a function of the C−C−C−C torsional angle.

have a minimum interaction. Models that predict the rotation to be a function of the polarizabilities of bonds and the cosine of the angle between the bonds[6] would lead to a small rotation.

Propene. Is the C−C−C−C torsional angle the main determinant of the optical rotation in these cases? To answer this question, we have examined the specific rotation of propene as a function of the rotation of the methyl group. The rotational potential energy curve was calculated at the B3LYP/6-311+G* level,[7] and the specific rotation was calculated at several wavelengths by use of B3LYP/6-311++G**. These data may be found in the Supporting Information. The specific rotation at 589 nm as a function of the methyl torsional angle is shown in Figure 5.

In view of the changes in specific rotation with torsional angle found with butane, additional calculations were carried out for propene with the aug-cc-pVDZ and aug-cc-pVTZ basis sets,

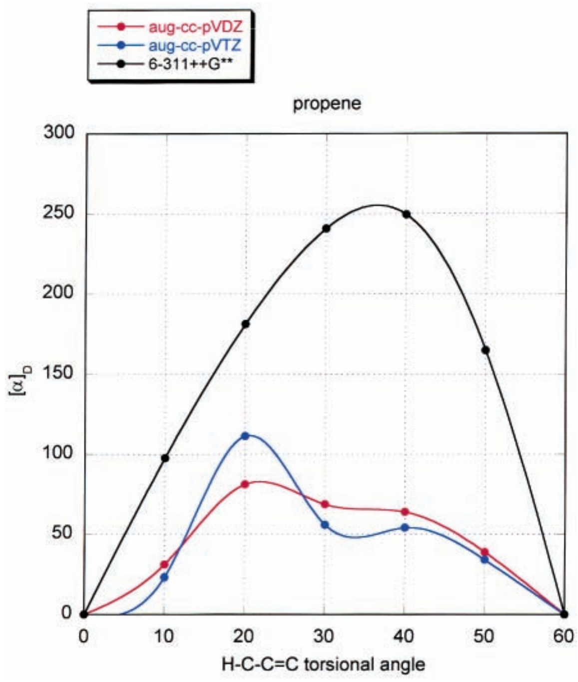

Figure 5. Calculated specific rotation of propene as a function of the H−C−C═C torsional angle.

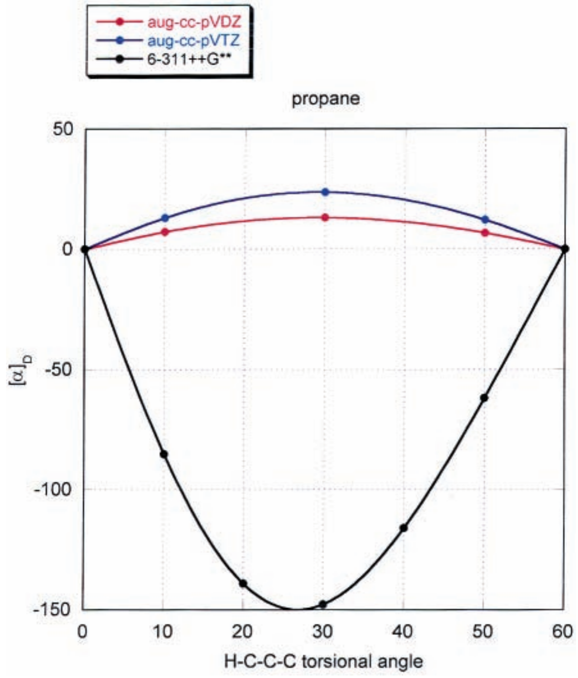

Figure 6. Calculated specific rotation of propane as a function of the H−C−C−C torsional angle.

giving the results shown in Figure 5. The best that one can say about the comparison is that the sign of the specific rotation does not change!

Propane. To again examine the question of the role of the carbon−carbon double bond on the optical rotation, we have studied propane. The rotational potential energy curve was calculated at the B3LYP/6-311+G* level[8] and the specific rotation was calculated at each of several wavelengths by use of B3LYP/6-311++G**. The specific rotation at 589 nm as a function of the methyl torsional angle is shown in Figure 6.

The effect of basis set on the relationship between the specific rotation and the torsional angle was examined by using two aug-cc basis sets, and the results are shown in Figure 6. The specific rotation changes sign on going from the 6-311++G** basis set to aug-cc-pVDZ, and the sign remains positive on increasing the flexibility of the correlation-consistent basis sets. Basis set effects will be further studied below.

TABLE 1: Effect of Basis Set on the B3LYP Calculated Specific Rotation at 589 nm for Ethane with a 30° Torsional Angle

basis set	bf [a]	$E(H)$	$[\alpha]_D$, deg
6-31G*	42	−79.828 11	−341.2
6-31G*, efd[b]	42	−79.828 11	+15.3
6-311++G*	86	−79.854 38	−495.1
6-311(2+,2+)G**	100	−79.854 40	−505.1
6-311(3+,3+)G**	114	−79.854 41	−509.1
6-311++G(2d,2f)	114	−79.858 81	-226.3
6-311++G(2d,2f), efd[b]	114	−79.858 81	+42.6
6-311++G(3df,p)	120	−79.857 22	−25.4
6-311++G(3df,3pd)	186	−79.860 58	−19.5
cc-pVDZ	58	−79.826 63	−208.4
cc-pVTZ	144	−79.862 16	−215.3
Sadlej pbs	102	−79.837 78	+81.1
aug-cc-pVDZ	100	−79.833 76	+41.2
aug-cc-pVDZ, efd[b]	100	−79.833 76	+59.3
daug-cc-pVDZ	142	−79.834 22	+56.6
aug-cc-pVTZ	230	−79.862 57	+53.6
daug-cc-pVTZ	316	−79.862 62	+59.4
aug-cc-pVQZ	436	−79.868 61	+57.8
UGBS1P	766	−79.869 49	+59.1

[a] Number of basis functions. [b] Electric field-dependent functions.

Ethane. Will as simple a molecule as ethane have a significant optical rotation when rotated away from one of its symmetrical forms? A geometry optimization was carried out with the H−C−C−H torsional angles set at 30°, halfway between staggered and eclipsed. The specific rotation at 589 nm was calculated to be 486° with B3LYP/6-311++G**. This remarkably large calculated rotation led us to examine the effect of basis set on the calculated rotation (Table 1).

The aug-cc-pVDZ basis set gives a less satisfactory total energy than 6-311++G** even though the former uses a larger number of basis functions. However, it also gives a calculated specific rotation with a much smaller magnitude and with the opposite sign. It was possible that the 6-311++G** did not lead to a satisfactory representation of the electronically excited states. Therefore, 6-311(2+,2+)G** was used since it is known to give a marked improvement in the prediction of excited states.[9] However, it had little effect on the calculated specific rotation. Increasing the flexibility of the Pople-type basis set to 6-311++G(3df,3pd) led to a marked reduction of the magnitude of the calculated rotation, but it still has the opposite sign from the results of the Dunning correlation-consistent basis sets. Increasing the flexibility of the latter, going to pVTZ and pVQZ, led to small increases in the calculated rotation and suggests that the correct calculated specific rotation is about +60°. However, if the extra diffuse functions (indicated by aug and daug) are not included in these basis sets, the calculated specific rotations have the incorrect sign. Finally, the very large uncontracted UGBS1P basis set[10] was used, giving $[\alpha]_D = +59.1°$.

All of the calculations were carried out with GIAOs in order to make the magnetic terms gauge-independent. It is also possible to build in some functional dependence on the applied electric field. Following the method of Darling and Schlegel,[11] the center for each Gaussian is chosen to depend on the electric field according to

$$A_i(\epsilon) = A_i - \lambda_i \epsilon$$

TABLE 2: Effect of Mixed Basis Sets on the B3LYP Calculated Specific Rotation at 589 nm for Ethane with a 30° Torsional Angle

C basis set	H basis set	$[\alpha]_D$
cc-pVDZ	aug-cc-pVDZ	+88.0
aug-cc-pVDZ	cc-pVDZ	+99.7
cc-pVDZ	6-311++(2d,2p)	−119.3
cc-pVTZ	aug-cc-pVTZ	+60.3
aug-cc-pVTZ	cc-pVTZ	+100.4
aug-cc-pVQZ	cc-pVQZ	+83.9
cc-pVDZ	aug-cc-pVDZ less last s function	+73.6
cc-pVDZ	aug-cc-pVDZ less last p function	−202.2
cc-pVDZ	6-311++(2d,2p) with last p on H changed to that from aug-cc-pVDZ	+67.7
cc-pVDZ	6-311++(2d,2p) plus diffuse p on H from aug-cc-pVDZ	+71.9
6-311++G(2d,2p)	6-311++G(2d,2p) with last p changed to that from aug-cc-pVDZ	+39.4
6-311++G(2d,2p)	6-311++G(2d,2p) plus diffuse p on H from aug-cc-pVDZ	+42.6

where the isotropic field-dependent parameter λ is chosen to maximize the atomic polarizabilities for a series of reference molecules. The electric field dependence of a (contracted) basis function, χ_μ, is then

$$\left.\frac{\partial \chi_\mu}{\partial \epsilon}\right|_{\epsilon=0} = -\lambda_i \frac{\partial \chi_\mu}{\partial A_i}$$

where A_i is the center for χ_μ.

Optical rotations computed with these electric field-dependent functions for the 6-31G*, 6-311++G(2d,2p), and aug-cc-pVDZ basis sets are shown in Table 1. Their use markedly improves the specific rotations obtained with these basis sets. For 6-31G*, the use of electric field-dependent functions changes the calculated rotation from −341.2° to +15.3°. For 6-311++G(2d,2p) the rotation changes from −226.3° to +42.6°, and for aug-cc-pVDZ it changes from +41.2° to +59.3°, which is essentially the basis set limit.

The origin of the marked basis-set dependence of the calculated specific rotations can be seen in Table 2, where different basis sets have been used for the carbons and the hydrogens. When cc-pVDZ is used at carbon and 6-311(2d,2p) is used at hydrogen, the incorrect sign of rotation is found, but when aug-cc-pVDZ is used at hydrogen, the correct sign of rotation is obtained.

When cc-pVDZ is used at carbon and aug-cc-pVDZ is used at hydrogen, and the most diffuse s function of the latter is deleted, the correct sign of rotation is still found, but when the most diffuse p function is deleted, the sign of rotation is incorrect. Similarly, when cc-pVDZ is used at carbon and 6-311++(2d,2p) plus the most diffuse p function for aug-cc-pVDZ is used at hydrogen, the correct sign of rotation is found. Also, when 6-311++(2d,2p) is used at both carbon and hydrogen but the most diffuse p function is changed to that in aug-cc-pVDZ, the correct sign of rotation is obtained.

These results make it clear that very diffuse p functions at hydrogen are important for the correct calculation of the optical rotation. This explains the poor results obtained using 6-311-(2+,2+)G** basis set since it only includes very diffuse s functions at hydrogens. It also may be related to the changes in charge density on going from 6-311++G** to aug-cc-pVDZ (Figure 7). The contours for the charge depletion on going from the former to the latter (magenta contours at $\rho = 0.0001$) have a helical sense. If the ethane torsional angle is changed to −30°, leading a reversal of the sign of the calculated specific rotation, the helical sense is reversed.

Helicity has frequently been correlated with optical activity.[12] Although it is only speculation at this time, it seems possible that the helical sense noted in Figure 7 is an important factor in obtaining the correct calculated sign of rotation. It also explains why diffuse s functions are not effective. Their spherical symmetry would not lead to the helicity that results from the directional p functions.

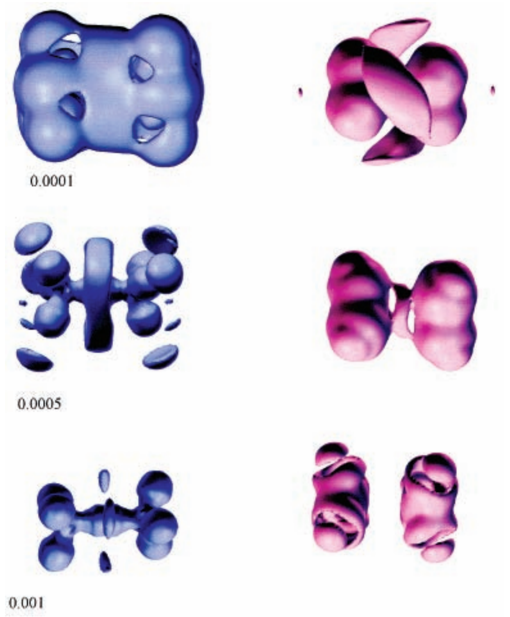

Figure 7. Electron density difference maps for +30 rotated ethane from the 6-311++G** and aug-cc-pVDZ basis sets. The left-hand (blue) contours show regions in which the electron density is increased on going from the former to the latter, and the right-hand (magenta) contours show regions where it is decreased. The net shift in electron density is 0.17 electron.

Effect of Vibrational Modes of 1-Butene on the Optical Rotation. In our examination of 3-chloro-1-butene[1] we found that a few of the vibrational modes led to very large predicted changes in optical rotation, which averaged to near zero when positive and negative displacement were combined. In an effort to gain information on which types of vibrations lead to large effects on the optical rotation, we have examined the vibrational modes of 1-butene. The root-mean-square amplitude for normal mode displacement at temperature T, Δx (in angstroms), is given by[13]

$$\Delta x = \pm(16.8576/\nu)[\coth(0.719384\nu/T)]^{1/2}$$

where ν is the calculated vibrational frequency (in reciprocal centimeters). The hyperbolic cotangent embodies contributions from higher-lying vibrational levels and, in the case of room temperature ensembles ($T = 300$ K), rapidly approaches unity for vibrational frequencies in excess of ~1100 cm^{-1}.

The optimized coordinates for the 120° (gauche) conformer were modified by the product of Δx and the Cartesian displace-

TABLE 3: Effect of Some Vibrational Modes on the B3LYP/6-311++G Calculated Specific Rotations of *gauche*-1-Butene**[a]

			$E_{\rm rel}$ (kcal/ mol)[b]		$[\alpha]_{\rm D}$[c]			
mode	ν (cm^{-1})	Δx	positive	negative	positive	negative	average[d]	% dev[e]
gs							221.3	
20	1030	0.12879	0.98	1.00	606.6	−169.8	218.4	−1.3
21	1019	0.12955	1.33	1.41	−26.8	490.1	231.7	4.7
26	653	0.16738	0.77	0.75	398.2	41.5	219.9	−0.7

[a] The full table may be found in the Supporting Information. [b] Changes in energy for positive and negative distortions from the ground state (gs) geometry. [c] Calculated specific rotations for positive and negative distortions from the gs geometry. [d] Average of the values for positive and negative distortions. [e] Percent deviation of the average rotation from that of the gs geometry.

ment coordinates for a given mode. The optical rotation was calculated with both $+\Delta x$ and $-\Delta x$ for each of the normal modes by use of B3LYP/6-311++G**. The modes that lead to large changes in specific rotation are given in Table 3, and the full table is available in the Supporting Information.

The nature of the modes that give very large changes in calculated rotation (20, 21, and 26) was examined by calculating the values of the internal coordinates for each of the above vibrationally deformed modes and subtracting them from the original (optimized) set of internal coordinates. The common characteristic of the three modes was torsional motion of the olefinic hydrogens. Therefore, the following torsional internal coordinates were examined where $\tau 1$ and $\tau 2$ refer to the C−C═C−H torsional angles for the terminal methylene hydrogens and $\tau 3$ refers to the C−C−C−H torsional angle for the central olefinic hydrogen.

$$\mathrm{Sa} = 2^{-1/2}(\tau 1 + \tau 2) \qquad \text{terminal methylene twist}$$

$$\mathrm{Sb} = 2^{-1/2}(\tau 1 - \tau 2) \qquad \text{terminal methylene wag}$$

$$\mathrm{Sc} = \tau 3 \qquad \text{central CH wag}$$

The value of Δx for the 1-butene vibrational modes in question is about 0.13. With this value, the angular distortions corresponding to Sa and Sb are 5.3°, and for Sc it is 7.5°. The specific rotations calculated by use of 6-311++G** at 589 nm for 1-butene distorted by these values are 536° for Sa, 473° for Sb, and 284° for Sc. They may be compared with the specific rotation of the undistorted molecule, 221°. The corresponding specific rotations calculated by use of aug-cc-pVDZ are 542° for Sa, 469° for Sb, and 277° for Sc as compared to 231° for the undistorted molecule. One effect of the methylene group distortions is to affect the interaction of the p−π orbital at the terminal carbon with the adjacent atoms, and this may be an important factor in giving the large changes in optical rotation.

Having the changes in specific rotation that result from vibrational distortion, the effect of these distortions on the calculated rotation could be examined as previously described.[1] The effect of a given mode is given by

$$\Delta\alpha = (\alpha^{+} + \alpha^{-} - 2\alpha_0)/2$$

where $\Delta\alpha$ is the correction to the rotation for a given vibrational mode, α_0 is the calculated rotation for the undistorted geometry, and α^{+} and α^{-} are the rotations of the vibrationally distorted molecule. The values of $\Delta\alpha$ are given in the last column of the tables in the Supporting Information, and the net effect is given by the sum of these values. In the case of 1-butene with τ = 120°, it is −4.8°.

Excited States. The isotropic optical rotation of a molecule, ϕ, is given by

$$\phi = \frac{16\pi^3 N \nu^2}{c^2}\gamma_{\rm s}\beta$$

TABLE 4: Calculated Electronic Transitions of Ethane, 6-311++G** [a]

	TDDFT			EOM-CCSD		
state	0°	30°	60°	0°	30°	60°
E″, Eg	8.27	8.26	8.32	9.19	9.17	9.25
	8.27	8.30	8.32	9.19	9.25	9.25
E′, Eu	8.94	8.93	9.01	9.98	9.82	10.02
	8.94	9.00	9.01	9.98	9.98	10.02
A′, Ag	9.06	9.09	9.06	9.79	10.03	9.79
A″, Au	9.30	9.34	9.33	10.30	10.31	10.44
E′, Eu	9.25	9.24	9.30	10.35	10.34	10.37
	9.25	9.26	9.30	10.35	10.37	10.37
A″, Au	9.33	9.37	9.39	10.53	10.45	10.51
A″, Au	9.67	9.71	9.70	10.79	10.57	10.71

[a] The symmetries are given for the transitions of the 0° and 60° rotamers; the 30° rotamer transitions are all A_1.

where β is $^1/_3$ the trace of the electric dipole−magnetic dipole polarizability tensor ($\beta_{\alpha\beta}$):

$$\beta_{\alpha\beta} = \frac{c}{3\pi h}\,\mathrm{Im}\left[\sum_{k=0}\frac{\langle 0|(\mu^{\rm e}_{\rm el})_{\alpha}|k\rangle\langle k|(\mu^{\rm e}_{\rm mag})_{\beta}|0\rangle}{\nu_{k0}^{2} - \nu^{2}}\right]$$

The summation is over the products of the electric and magnetic transition dipoles from the ground state to each of the electronically excited states.

It can be seen that the electronically excited states are important components of the optical rotation. Therefore, we have examined the effect of conformation on the excited states using two of the common single reference models: time-dependent density functional theory (TDDFT) and equations of motion-coupled cluster (EOM-CCSD). TDDFT corresponds to the level of theory used in the optical rotation calculations. We have previously made comparisons of these methods for the calculation of the excited-state energies of ethene, isobutene, formaldehyde, and acetone.[14]

The calculated transition energies for ethane with τ(HCCH) = 0° (eclipsed), τ = 30°, and τ = 60° (staggered) are given in Table 4. Here, the states are given for the eclipsed and staggered forms; the 30° states are all A_1. The E′ and Eg states are forbidden, and the first allowed Eu electronic transition for the staggered form is calculated to be at 9.09 eV (TDDFT) and 10.0 eV (EOM-CCSD). The observed band is found at 9.4 eV,[15] midway between the TDDFT and EOM-CCSD values. The 6-311++G** basis set was used for these calculations, and aug-cc-pVDZ gives essentially the same transition energies (rms difference = 0.1 eV).

It is important to note that there is little change in the predicted electronic transitions on going from the eclipsed to the staggered form, and the 30° form has quite similar transition energies.

All of the excited states of ethane result from Rydberg transitions.[16] The Rydberg states of a given type converge on

TABLE 5: Calculated Vertical Ionization Potentials, 6-311++G, EV**

compound	torsion	UHF	UB3LYP	UCCSD	expt
ethane	0	12.21	12.22	12.62	
	30	12.18	12.19	12.60	
	60	12.29	12.26	12.67[a]	12.09
propane	0	11.57	11.42	11.97	
	30	11.58	11.44	12.00	
	60	11.67	11.53	12.09	11.39
propene	0	8.38	9.78	9.74	9.92
	30	8.37	9.78	9.78	
	60	8.34	9.75	9.71	
ethene		8.90	10.54	10.35	10.51

[a] IPs are from UCCSD calculations with different basis sets: 6-311(2+,2+)G**, 12.66 eV; aug-cc-pVDZ, 12.66 eV; aug-cc-pVTZ, 12.76 eV.

the ionization potential. To better evaluate the calculated transition energies, the vertical ionization potential was calculated at the UHF, UB3LYP, and UCCSD levels (corresponding to CIS, TDDFT, and EOM-CCSD electronic excitation calculations), giving the results shown in Table 5. The considerable error in the CCSD calculated ionization potential was surprising, and therefore we examined the possibility that the 6-311++G** basis set was inadequate. However, larger basis sets did not lead to a significant change in calculated ionization potential.

The calculated electronic transition energies for propane are given in Table 6. Here, the calculated transition energies for the first allowed band of the ground-state structure with a 60° torsional angle are 8.23 eV for TDDFT and 9.02 eV for EOM-CCSD. The observed transition energy is 8.9 eV.[17] Here, the EOM-CCSD transition energy is quite close to the observed value. The transition energies again are relatively insensitive to conformational change.

The calculated electronic transition energies for propene are given in Table 7. The $\pi-\pi^*$ band is calculated to be 6.73 eV for TDDFT and 7.50 eV for EOM-CCSD. The observed band is at 7.2 eV.[18] The lower energy (Rydberg) transition is calculated to be 6.14 eV for TDDFT and 6.86 eV for EOM-CCSD. It is observed to be 6.6 eV. The EOM-CCSD transition energies give better agreement with experiments. Again, the transition energies are relatively insensitive to conformational change. These calculations were carried out with 6-311++G**, and aug-cc-pVDZ again gave essentially the same transition energies (rms difference = 0.12 eV).

Both of these methods for estimating transition energies agree that the conformation does not have a large effect, and therefore the excited-state energies are not the factors that determine the effect of conformation on the optical rotation. In principle, the manifestations of chiroptical response in these nominally achiral species stem from the reduction in overall symmetry for the rotamers, a situation that enables electric dipole and magnetic dipole transitions to occur simultaneously for specific electronically excited states.

Conclusions

These simple “achiral” molecules have large calculated optical rotations when distorted. Although the basis set effect on the optical rotation is relatively small with 1-butene, it becomes larger with butane, propane, propene, and especially with ethane. Butane has a large optical rotation when the two terminal C$-$CH$_3$ bonds are orthogonal.

In an examination of the enhancement of the optical rotation for vibrationally distorted 1-butenes. it was found that a few vibrational modes give remarkably large changes in rotation. They, in large measure, involve the torsional modes of the olefinic hydrogens. When these distortions were examined separately, it was found that the terminal $=$CH$_2$ group has a remarkably large effect on the optical rotation, whereas the central olefinic C$-$H bond has a relatively small effect.

TABLE 6: Calculated Electronically Excited States of Propane, 6-311++G [a]**

	TDDFT			EOM-CCSD		
	0°	30°	60°	0°	30°	60°
A″	7.79 (0.00)	7.83 (0.00)	7.91 (0.00)	8.72 (0.00)	8.76 (0.00)	8.86 (0.00)
A′	8.20 (0.04)	8.24 (0.04)	8.23 (0.01)	8.99 (0.05)	9.03 (0.04)	9.03 (0.04)
A′	8.24 (0.00)	8.27 (0.01)	8.23 (0.04)	9.10 (0.00)	9.13 (0.00)	9.10 (0.00)
A″	8.46 (0.00)	8.50 (0.00)	8.60 (0.00)	9.49 (0.01)	9.53 (0.00)	9.63 (0.16)
A″	8.51 (0.05)	8.55 (0.06)	8.64 (0.08)	9.55 (0.10)	9.67 (0.08)	9.64 (0.00)
A′	8.63 (0.03)	8.67 (0.04)	8.76 (0.05)	9.62 (0.06)	9.74 (0.02)	9.73 (0.19)
A′	8.85 (0.02)	8.88 (0.01)	8.84 (0.01)	9.71 (0.06)	9.80 (0.07)	9.74 (0.01)
A′	8.87 (0.02)	8.91 (0.04)	8.90 (0.10)	9.75 (0.05)	9.83 (0.01)	9.84 (0.01)
A′	8.91 (0.10)	8.94 (0.08)	8.92 (0.03)	9.80 (0.02)	9.88 (0.00)	9.87 (0.00)
A″	8.92 (0.01)	8.96 (0.02)	8.97 (0.00)	9.84 (0.04)	9.96 (0.02)	9.93 (0.03)

[a] The symmetries are given for the transitions of the 0° and 60° rotamers; with 30° all transitions are A$_1$. The oscillator strengths are given in parentheses.

TABLE 7: Calculated Electronic Transitions of Propene, 6-311++G [a]**

	TDDFT			EOM-CCSD		
	0°	30°	60°	0°	30°	60°
A″	6.17 (0.01)	6.16 (0.01)	6.14 (0.02)	6.89 (0.03)	6.89 (0.03)	6.86 (0.03)
A″	6.73 (0.00)	6.71 (0.00)	6.17 (0.01)	7.51 (0.00)	7.49 (0.00)	7.47 (0.00)
A′	7.06 (0.28)	6.90 (0.24)	6.73 (0.23)	7.81 (0.28)	7.64 (0.16)	7.50(0.25)
A″	6.81 (0.02)	6.79 (0.03)	6.77 (0.01)	7.67 (0.01)	7.68 (0.10)	7.65 (0.01)
A′	7.44 (0.05)	7.45 (0.04)	7.57 (0.00)	8.26 (0.04)	8.27 (0.03)	8.33 (0.05)
A″	7.60(0.00)	7.60(0.01)	7.58 (0.06)	8.49 (0.00)	8.49 (0.00)	8.45 (0.00)
A″	7.91 (0.00)	7.91 (0.01)	7.73 (0.00)	8.79 (0.00)	8.69 (0.00)	8.59 (0.00)
A″	8.11 (0.00)	7.99 (0.00)	7.88 (0.00)	8.85 (0.00)	8.82 (0.01)	8.68 (0.00)
A″	8.43 (0.04)	8.46 (0.04)	8.34 (0.03)	9.18 (0.06)	9.21 (0.06)	9.15 (0.05)
A′	8.59 (0.01)	8.56 (0.02)	8.52 (0.02)	9.42 (0.01)	9.39 (0.02)	9.34 (0.00)

[a] The symmetries are given for the 0° and 60° rotamers; the transitions for the 30° rotamer are all A$_1$. The oscillator strengths are given in parentheses.

The conformation of the molecules has a relatively small effect on the calculated electronic transition energies, and therefore this is not the major factor that determines the large effects of conformation on optical activity. On the other hand, the lifting of symmetry constraints imposed on the simultaneous occurrence of electric dipole and magnetic dipole transitions (to a given electronically excited state) presumably is responsible for the manifestation of chiroptical response in these prototypical achiral species.

The large effect of basis sets on the calculated specific rotations has been found to be associated with very diffuse p-type functions on hydrogens. In the case of ethane, electron density difference plots between 6-311++G** and aug-cc-pVDZ basis sets showed remarkable helicity in the depletion region, which is converted to its mirror image when the H−C−C−H torsional angle is changed from +30° to −30°.

Calculations. The geometry optimizations and the optical rotation calculations were carried out with Gaussian-99.[19] The geometries for rotated methyl groups were effectively for CH2D groups where the D−C−C−X torsional angles were fixed and all other geometrical parameters were optimized. This was done to eliminate the problem associated with permuting indistinguishable atoms (i.e., in the rotation of a methyl group). The very small effect of deuterium on optical rotation due to the anharmonicity of methyl C−H vibrations[20] was ignored. The frequency-dependent optical rotations calculations made use of GIAOs (gauge-including atomic orbitals) to ensure origin-independent results and were obtained in terms of electric and magnetic derivatives of the ground-state electronic wave function.[21]

EOM-CCSD calculations were carried out with ACES-II.[22]

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Supporting Information Available: Tables of calculated specific rotations as a function of wavelength and torsional angle and of the effect of vibrational modes on the specific rotations. This information is available free of charge via the Internet at http://pubs.acs.org.

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