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Conformational Effects on Optical Rotation. 2-Substituted Butanes

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The specific rotations of 2-substituted butanes (X = F, Cl, CN, and HCC) were calculated at the B3LYP/aug-cc-pVDZ level as a function of the C−C−C−C torsion angle. The results for the four compounds are remarkably similar, despite large differences in the electronic transition energies. The temperature dependence of the specific rotations for 2-methylbutyronitrile and for 2-chlorobutane was studied to give experimental information about the effect of the torsion angle on the specific rotation. The results were in good accord with B3LYP/aug-cc-pVDZ calculations. The specific rotations derived from the study of 2-chlorobutane are similar to those previously obtained for 3-chloro-1-butene, indicating that the double bond does not have a large effect on the optical rotations, but it did lead to a large difference between calculated and observed specific rotations.

1. Introduction

In a previous study, we examined rotation about the central C−C bond of 3-substituted-1-butenes and calculated a remarkably large effect on the specific rotation.[1] The data for 3-chloro-1-butene suggested that the specific rotation should change with temperature, reflecting the change in populations of the three conformers. An experimental study confirmed this expectation. In analyzing the results, the two higher energy conformers that had about the same conformational energy were taken as a group with an average specific rotation, [α′]. The data, which had significant curvature, allowed the calculation of the specific rotation of the low energy conformer, $[\alpha]_A$, as well as [α′] and the difference in free energy between the low and higher energy conformers.

The ΔG thus obtained agreed with the expected energy difference, and the derived specific rotations were in constant ratio with the calculated values for several wavelengths between 589 and 365 nm. Thus, the temperature dependence study confirmed the large effect of conformation on specific rotation, along with finding that the calculated rotations were larger than the observed values by a factor greater than 2.

Is the large effect of conformation on specific rotation due to the presence of the double bond, and does the latter contribute in some way to the difference between the observed and calculated specific rotations? To examine these questions, we have now studied the saturated analogues, the 2-substituted butanes, where X = F (**1**), Cl (**2**), CN (**3**), and HCC (**4**). These substituents are convenient in that they do not add to the number of conformers. In addition, they would be expected to lead to considerable differences in electronic transition levels. These levels are involved in the ab initio calculations of optical rotation.[2]

2. Conformational Energies

The potential energies of the three stable conformers and of the transition states for conformational interconversion have been calculated at several theoretical levels including G2, G3, CBS, and CCSD(T)/6-311++G(2d,p).[3] They were also estimated from the intensities of characteristic vibrational bands for individual conformers.[3] The relative free energies are summarized in Figure 1 and Table 1. There are some small changes on going from the gas phase (calculations) to the liquid phase. This has been found in other cases including butane itself.[4]

As expected,[5] the conformers with a *trans*-butane arrangement (Figure 2) have the lowest free energy, and when the carbon chain adopts a *gauche*-butane conformation, the energy is somewhat higher. The four substituents give similar relative free energy curves. The main difference is found in the transition states when the substituent is eclipsed with the remote methyl group, and here the size of the substituent appears to be the determining factor.

The potential energy curves were obtained by geometry optimization at 20° intervals of the C−C−C−C torsional angle at the MP2/6-311+G* level. The torsional angles for the minima and maxima are in good agreement with those found in the G3 calculations. The MP2/6-311+G* geometries were used for the following calculations of specific rotation.

3. Calculated Specific Rotations

The specific rotations of the (*R*) forms were calculated using B3LYP with the basis sets 6-311++G**, aug-cc-pVDZ, daug-cc-pVDZ, and aug-cc-pVTZ. The results are summarized in Table 2. With most compounds, 6-311++G** and aug-cc-pVDZ give essentially the same calculated specific rotations,[6] but there are cases where there is a substantial difference.[7] This is found in the present cases. Further increases in basis set flexibility to daug-cc-pVDZ and aug-cc-pVTZ led to relatively small changes in specific rotation, and therefore the specific

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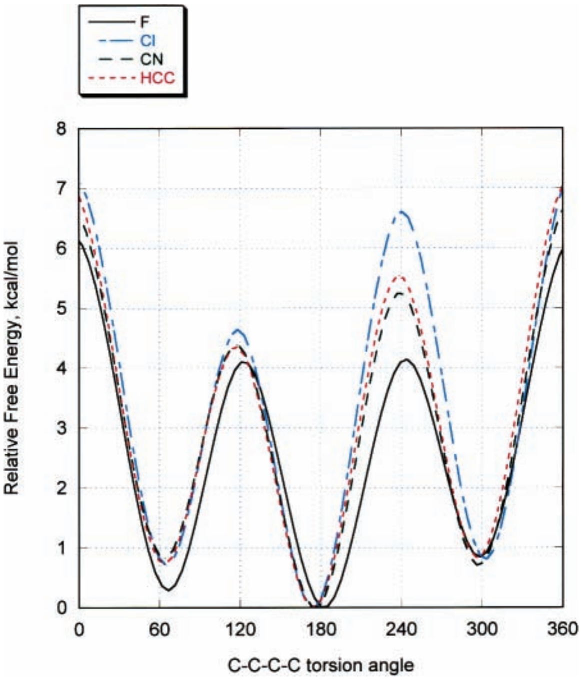

Figure 1. Relative free energies of 2-substituted butanes calculated at the G3 level.

TABLE 1: Calculated and IR Derived Relative Free Energies, kcal/mol

	calculated[a]		IR derived[b]	
X	g+	g−	g+	g−
F (**1**)	0.53 ± 0.05	0.83 ± 0.05		
Cl (**2**)	0.70 ± 0.05	0.80 ± 0.05	0.46 ± 0.10	0.73 ± 0.10[c]
CN (**3**)	0.85 ± 0.05	0.75 ± 0.05	0.81 ± 0.10	1.08 ± 0.10
CCH (**4**)	0.77 ± 0.05	0.83 ± 0.05	0.72 ± 0.10	1.01 ± 0.10

[a] The indicated uncertainties represent the range of energies obtained using the higher level theoretical methods. [b] Reference 3a. [c] Reference 3b gave $\Delta H = 0.48$ and 0.70 kcal/mol, respectively.

rotations as a function of C−C−C−C torsional angle were calculated at 20° intervals using aug-cc-pVDZ. The result is shown in Figure 3.

There is a remarkable similarity between the curves for the four compounds, suggesting that the C−C−C−C torsional angle is the major factor determining the magnitude of the specific rotation. The substituents have a quite small effect other than creating the chiral center.

The observed specific rotation is the weighted average of the values for the three conformers. Using the relative free energies and the calculated specific rotations for the conformers, the predicted values for the conformational mixtures at 25 °C were calculated, and are compared with the observed specific rotations in Table 3. The values are fairly close for 2-chlorobutane (10% deviation), but with 2-methylbutyronitrile, the calculated specific rotation is 25% larger than the observed rotation. The same deviation was found with 3-methyl-1-pentyne.

4. Electronic Excitation

The similarities of the specific rotation/torsional angle plots (Figure 3) despite the expected differences in electronic transitions led us to determine the vacuum UV spectra of **1**−**4** (Figure 4). As expected, there are considerable differences in transition energies, with X = Cl or HCC giving relatively low energy transitions and X = F or CN giving relatively high transition energies. The characters of the lower energy transitions are different with that of the ethynyl derivative, being $\pi-\pi^*$, whereas with X = Cl or F they are probably Rydberg transitions. These differences are not reflected in the calculated specific rotations. A detailed examination of the electronic transitions of these compounds will be presented subsequently.

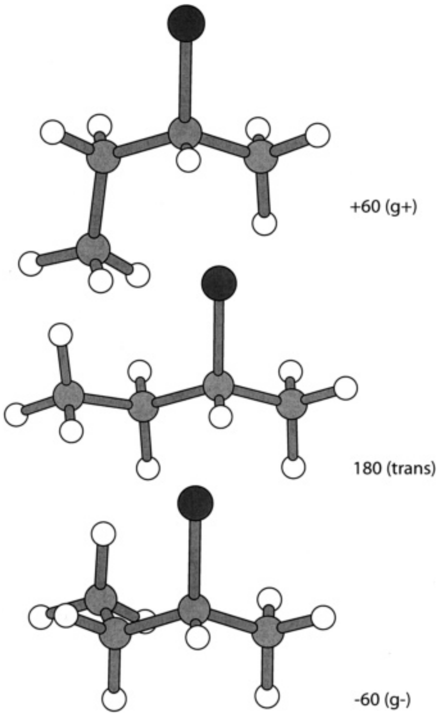

Figure 2. 2-Substituted butane conformers.

5. Temperature Dependence of the Specific Rotation

A study of the temperature dependence of the specific rotation has the potential for giving information about the specific rotations of the several conformations. If the conformers have significantly different rotations and free energies, the observed rotation will change with temperature in accord with the change in populations of the conformers. This method has been used a number of times.[1,8] However, it assumes that the conformational equilibrium is the only significant factor that affects the observed specific rotation.

We have examined a number of relatively rigid molecules and have found that they give a variety of responses to a change in temperature.[9] Therefore, it is possible that the simple approach previously used may not be satisfactory in some cases in obtaining estimates of the specific rotations of the individual conformers. The temperature dependence of individual conformers results from one or more relatively low frequency vibrational modes that give large nonlinear changes in specific rotation when vibrationally excited. We are studying this problem in some detail, but for the present time we will need to resort to some approximation when such cases arise.

5.a. 2-Chlorobutane (2). (*R*)-(−)-**2** was prepared from (*S*)-(+)-2-butanol ($\alpha_D = 10.13$, $l = 1$, neat, $[\alpha]_D^{25} = 12.60°$, $d = 0.804$ g/mL, 93.3% enantiomeric excess (ee)[10]) by its reaction with chlorodiphenylphosphine[11] and had $\alpha_D^{25} = -27.5°$ ($l = 1$, neat). With $d = 0.873$ g/mL, $[\alpha]_D^{25} = -31.5°$. It was found to have 93.2% ee by gas chromatography using a chiral column, and therefore the optically pure compound has $[\alpha]_D^{25} = -33.8°$. This is in good agreement with a previous study.[9] The specific rotations at other wavelengths are given in the Supporting Information.

TABLE 2: Calculated Specific Rotations at 589 nm, B3LYP Using MP2/6-311+G* Geometries

X	t	6-311++G**	aug-cc-pVDZ	daug-cc-pVDZ	aug-cc-pVTZ
F (**1**)	64.3	28.8	54.1	52.5	50.3
	180.1	−69.6	−57.0	−55.7	−54.9
	303.9	41.7	12.8	10.7	12.7
Cl (**2**)	62.2	23.5	32.6	32.9	30.7
	175.0	−95.5	−80.9	−80.7	−77.6
	304.9	58.8	35.3	34.7	38.5
CN (**3**)	62.0	26.8	33.8	34.0	32.8
	177.9	−150.4	−88.0	−87.2	−85.1
	296.9	47.1	32.4	34.4	31.4
HCC (**4**)	61.8	30.3	26.0	29.1	25.3
	176.5	−120.3	−104.9	−103.5	−101.3
	296.9	36.3	32.2	26.6	27.1

TABLE 3: Calculated and Observed Specific Rotations at 589 nm for Conformational Mixtures at 25 °C

		observed	
X	calculated[a]	neat	solution[b]
F (**1**)	−17.2	na	
Cl (**2**)	−37.1	−33.8	−33.8
CN (**3**)	−45.1	36.3[c]	34.1[c]
HCC (**4**)	−57.8	−46.5[d]	

[a] (*R*) enantiomers, aug-cc-pVTZ. [b] Ethylcyclohexane solutions. [c] (*S*) enantiomers were used in the experimental studies. [d] Marcacci, F.; Giacomelli, G.; Menicagli, R. *Gazz. Chim. Ital.* **1980**, *110*, 195.

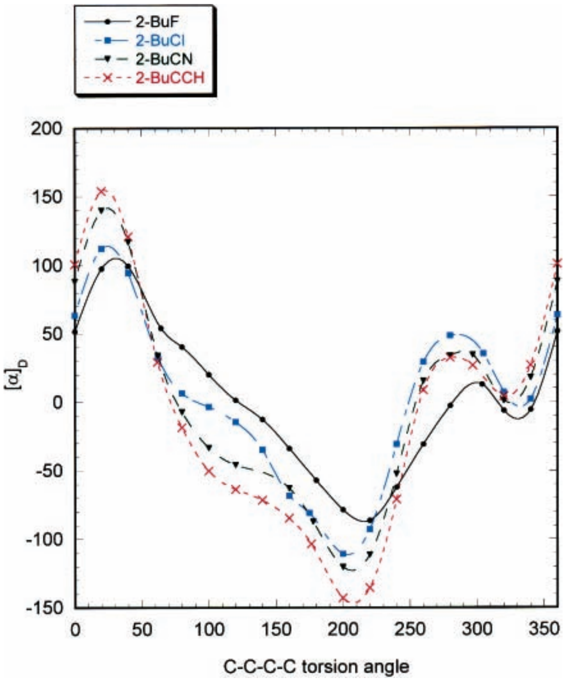

Figure 3. Calculated effect of C−C−C−C torsional angle on specific rotation.

The temperature dependence was determined in ethylcyclohexane solution over the temperature range 0−100 °C, giving the data summarized in Table 4. The solution phase conformational energies have been obtained in two independent experimental studies, where Zhu et al. found $\Delta H = 0.48$ and 0.70 kcal/mol[3b] and we found $\Delta G = 0.46$ and 0.73 kcal/mol for the g+ and g− conformers,[3a] respectively. The entropy terms are expected to be small, so $\Delta H \approx \Delta G$. The data in Table 4 show a marked temperature dependence that clearly indicates the conformers to have quite different specific rotations. With the small free energy differences, the temperature dependence curve should show marked curvature. However, the curve, after correction for solvent expansion, was nearly linear (Figure 5). This is probably the result of an intrinsic temperature dependence of one or more of the conformers. Such a temperature dependence can reduce the curvature of the specific rotation/torsional angle plot.

The calculated free energies of the two higher energy conformers were about the same, so they were taken as a group. The free energy difference was taken as the maximum value that is consistent with the experimental study, 700 cal/mol. As a first approximation to the temperature effect on the individual conformers, the experimental data excluding the volume expansion terms was taken, effectively assuming that the volume correction terms and the temperature effect on the individual conformers, which would have the same form (i.e., $1 + c(T - 25)$), would approximately cancel. The data were fit to

$$[\alpha]_{\text{obs}} = \frac{[\alpha]_A + 2[\alpha']e^{-\Delta G/RT}}{1 + 2e^{-\Delta G/RT}} \qquad (1)$$

by a least-squares procedure. Here, $[\alpha]_A$ is the specific rotation of the lower energy trans conformer, $[\alpha']$ is the average specific rotation of the gauche conformers, and ΔG is the free energy difference; $[\alpha]_A$ and $[\alpha']$ were taken as the unknowns.

The analysis of the 589 nm data gave a root-mean-square (rms) error of 0.07° and specific rotations of −77.4° for the low energy conformer and 37.4° for the average of the higher energy conformers. They may be compared with the calculated values of −77.6° and 34.6°. The 436 nm data gave an rms error of 0.25° with specific rotations of −154.5° for the low energy conformer and 73.8° for the average of the higher energy conformers. The calculated values are −156.8° and 65.9°. The good agreement is undoubtedly partially fortuitous, but again clearly indicates that the large calculated conformational effect is correct. Also, unlike the unsaturated analogue, the calculated and observed specific rotations are in good agreement.

It is interesting to note that the specific rotations for 3-chloro-1-butene derived from the temperature dependence study are essentially the same as for 2-chlorobutane; i.e., $[\alpha]_A = -74°$ and $[\alpha'] = +35°$ at 589 nm. Thus, the double bond in this compound does not lead to a large increase in specific rotations as compared to the saturated analogue, but it does lead to exaggerated calculated values of specific rotations. The calculated specific rotations for the low energy conformers of the two chlorides are related (Figure 6), and the smooth curve continues to 205 nm where 2-chlorobutane has $[\alpha] = -668$ and 3-chloro-1-butene has $[\alpha] = -5120$.

5.b. 2-Cyanobutane (2-Methylbutyronitrile) (3). (*S*)-(+)-**3** was prepared from (*S*)-(+)-2-methylbutyric acid via the amide and dehydration with phosphorus pentoxide.[12] It had $\alpha_D^{25} = 28.5°$ ($l = 1$, neat), and with $d = 0.786$, $[\alpha]_D^{25} = 36.3°$.

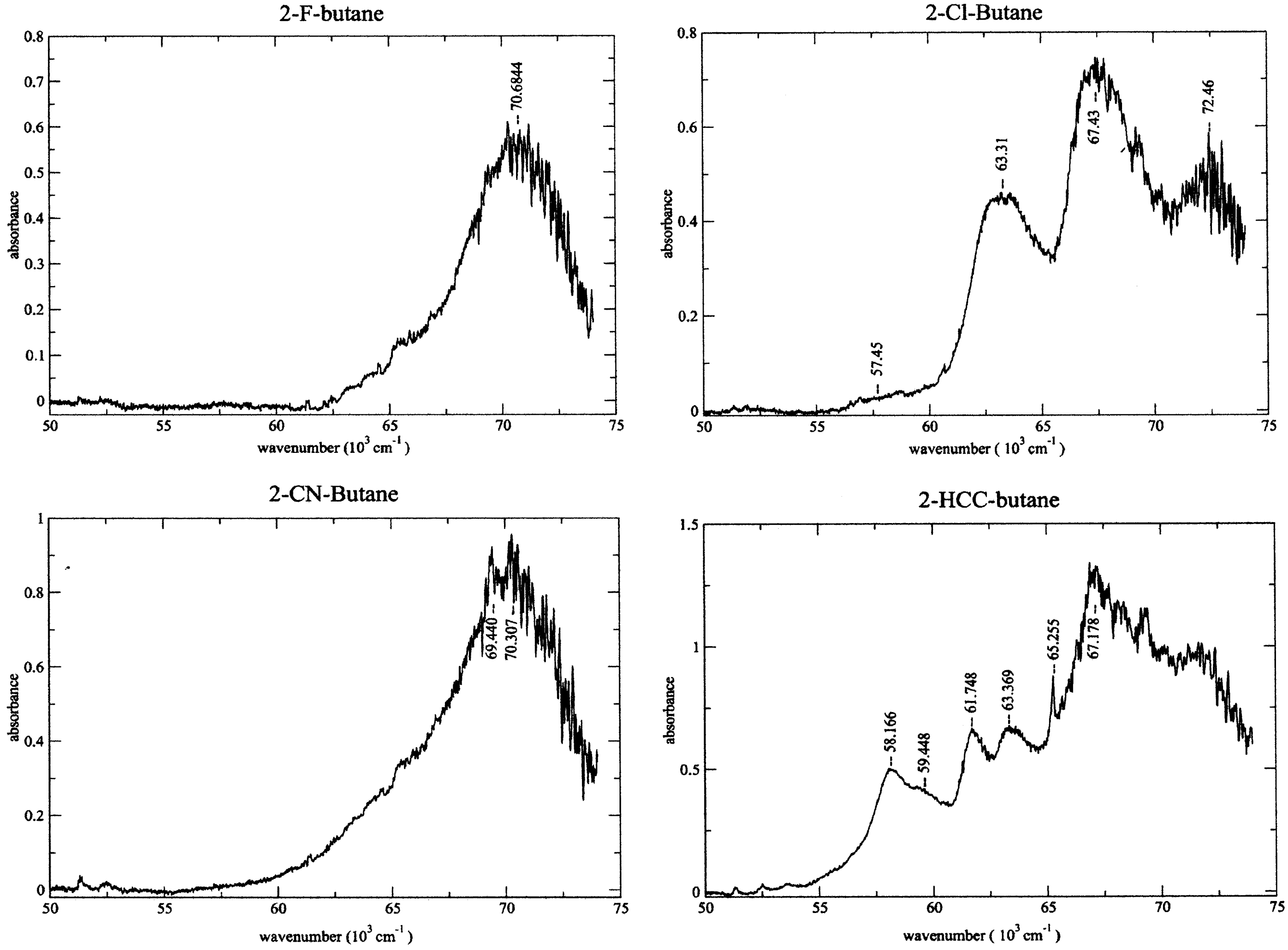

Figure 4. Vacuum UV spectra of 2-substituted butanes.

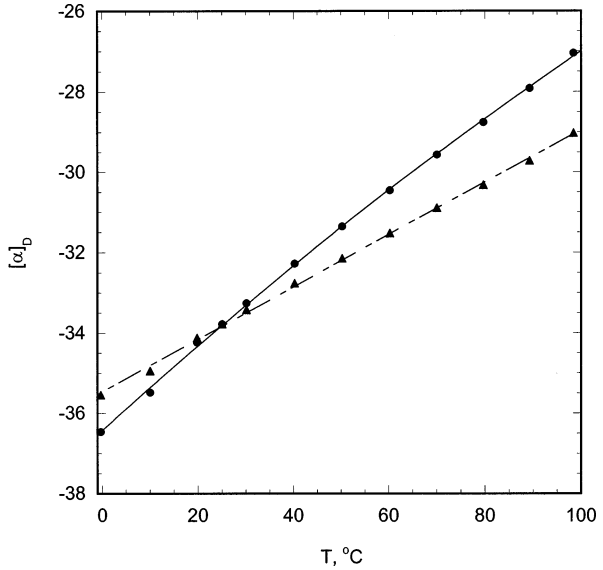

Figure 5. Temperature dependence of specific rotation of 2-chlorobutane (**2**). The solid circles are for the uncorrected data and are fit with a second-order polynomial, and the triangles are for the data corrected for volume expansion of the solvent and are fit with a linear function.

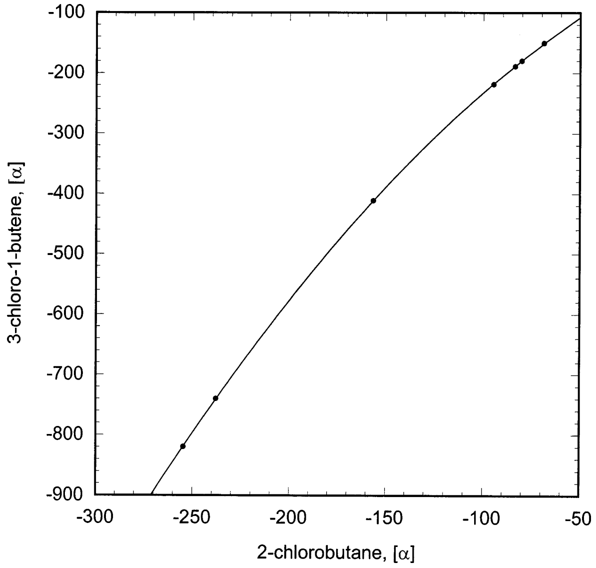

Figure 6. Correlation between the B3LYP/aug-cc-pVDZ calculated specific rotations for 2-chlorobutane and 3-chloro-1-butene. The wavelengths are, from left to right, 355, 365, 436, 546, 578, 589, and 633 nm.

It was found to have 99+% ee using a chiral gas chromatographic column. The specific rotations at other wavelengths are given in the Supporting Information.

The temperature dependence was determined in ethylcyclohexane solution over the temperature range 0−100 °C, giving the data summarized in Table 5. The observed rotations have been corrected for the expansion of the solvent with increasing temperature. As found with **2**, the resulting plots were essentially linear (Figure 7), whereas the experimentally observed conformational energy differences would predict a plot with significant curvature.

TABLE 4: Temperature Dependence of the Specific Rotation of 2-Chlorobutane (2)

	specific rotation, not corrected[a]					specific rotation, corrected[a]				
T, °C	589 nm	578 nm	546 nm	436 nm	365 nm	589 nm	578 nm	546 nm	436 nm	365 nm
−0.3	−36.46	−38.02	−43.19	−73.23	−112.61	−35.54	−37.06	−42.09	−71.38	−109.76
10.0	−35.48	−36.98	−41.98	−70.980	−109.06	−34.94	−36.42	−41.35	−69.91	−107.43
19.8	−34.230	−35.79	−40.63	−68.71	−105.54	−34.12	−35.61	−40.42	−68.36	−104.99
25.0	−33.77	−35.25	−40.02	−67.70	−103.98	−33.77	−35.25	−40.02	−67.70	−103.98
30.1	−33.25	−34.71	−39.41	−66.72	−102.47	−33.42	−34.89	−39.61	−67.06	−103.00
40.2	−32.27	−33.70	−38.27	−64.74	−99.45	−32.76	−34.21	−38.85	−65.73	−100.96
50.2	−31.35	−32.70	−37.13	−62.89	−96.60	−32.14	−33.52	−38.07	−64.48	−99.04
60.2	−30.45	−31.76	−36.07	−61.11	−93.95	−31.52	−32.88	−37.34	−63.26	−97.26
70.0	−29.56	−30.85	−35.03	−59.36	−91.28	−30.89	−32.24	−36.60	−62.03	−95.39
79.6	−28.75	−30.00	−34.06	−57.70	−88.80	−30.32	−31.63	−35.92	−60.85	−93.64
89.2	−27.91	−29.12	−33.07	−56.06	−86.32	−29.71	−30.99	−35.19	−59.66	−91.87
98.4	−27.04	−28.22	−32.06	−54.37	−83.78	−29.02	−30.29	−34.41	−58.36	−89.93

[a] The correction for the volume expansion of ethylcyclohexane referred to the volume at 25 °C is given by $1 + 0.0010(T - 25)$.

TABLE 5: Temperature Dependence of the Specific Rotation of 2-Methylbutyronitrile (3)

	specific rotation, not corrected[a]					specific rotation, corrected[a]				
T, °C	589 nm	578 nm	546 nm	436 nm	365 nm	589 nm	578 nm	546 nm	436 nm	365 nm
−0.3	36.36	37.93	43.00	72.19	109.95	35.44	36.97	41.91	70.36	107.17
4.9	35.90	37.43	42.45	71.24	108.46	35.18	36.68	41.60	69.81	106.28
10	35.44	36.95	41.90	70.32	107.04	34.90	36.40	41.27	69.27	105.44
14.9	34.99	36.49	41.37	69.43	105.69	34.64	36.12	40.95	68.73	104.62
19.8	34.53	36.00	40.82	68.52	104.29	34.35	35.81	40.61	68.17	103.75
25	34.09	35.54	40.29	67.62	102.96	34.09	35.54	40.29	67.62	102.96
30.1	33.61	35.04	39.74	66.71	101.55	33.78	35.22	39.94	67.05	102.07
35.1	33.15	34.56	39.18	65.79	100.17	33.48	34.91	39.58	66.45	101.18
40.2	32.66	34.06	38.62	64.87	98.80	33.16	34.58	39.21	65.85	100.30
45.2	32.24	33.61	38.11	64.02	97.49	32.89	34.29	38.88	65.31	99.46
50.2	31.77	33.14	37.58	63.14	96.16	32.57	33.97	38.53	64.73	98.59
60.2	30.93	32.26	36.58	61.48	93.68	32.02	33.39	37.87	63.64	96.98
70	30.15	31.44	35.65	59.92	91.34	31.51	32.85	37.25	62.62	95.45
74.8	29.75	31.01	35.17	59.13	90.13	31.23	32.56	36.92	62.07	94.62
79.6	29.34	30.59	34.70	58.33	88.98	30.94	32.26	36.59	61.51	93.84
84.5	28.97	30.20	34.24	57.59	87.83	30.69	32.00	36.28	61.02	93.06
89.2	28.58	29.81	33.81	56.84	86.74	30.42	31.72	35.98	60.49	92.31
94	28.23	29.43	33.37	56.12	85.69	30.18	31.46	35.67	60.00	91.60
98.4	27.78	28.98	32.86	55.28	84.43	29.82	31.10	35.28	59.34	90.63

[a] Correction for the volume expansion of ethylcyclohexane referred to the volume at 25 °C.

The approach in this case is the same as that used for **2**, taking the observed specific rotations without the solvent expansion correction. Values of ΔG have been obtained for these compounds, and the average ΔG found in solution (950 cal/mol) for the higher energy conformers was taken as a constant. The equation was solved via a least-squares method for the specific rotation of the low energy conformer and the average rotation of the higher energy conformers. There were significant differences with respect to the calculated values, but the fit could be improved by multiplying the left-hand side of eq 1 by a term that would slightly amplify the effect of temperature on the individual conformers, i.e., $(1 + c'(T - 25))$.[9] Using $c' = -0.0003$, at 589 nm, the rms error was 0.05°, $[\alpha]_A$ was 63.7°, and α' was −34.3°. The calculated values are 85.1° and −32.0°. At 436 nm, the rms error was 0.21°, $[\alpha]_A$ was 126.9°, and α' was −67.6°, whereas the calculated values were 167.1° and −61.7°. The agreement is not as good as that found with **2**, but they still confirm the large effect of conformation on the specific rotation. It might be noted that the data for the conformational mixture indicates that the calculated specific rotations are about 25% larger than the experimental values (Table 3).

5.c. 2-Fluorobutane (1). (*S*)-(+)-2-Butanol with 93.3% ee was treated with the HF−pyridine complex[13] to give **1**. In the initial distillation of the reaction mixture through a 6 in. Vigreux column, the fraction bp 22−40 °C was collected. It was redistilled through a micro spinning-band column with approximately six theoretical plates, collecting the material with bp 22 °C. It had only a very small observed rotation, indicating

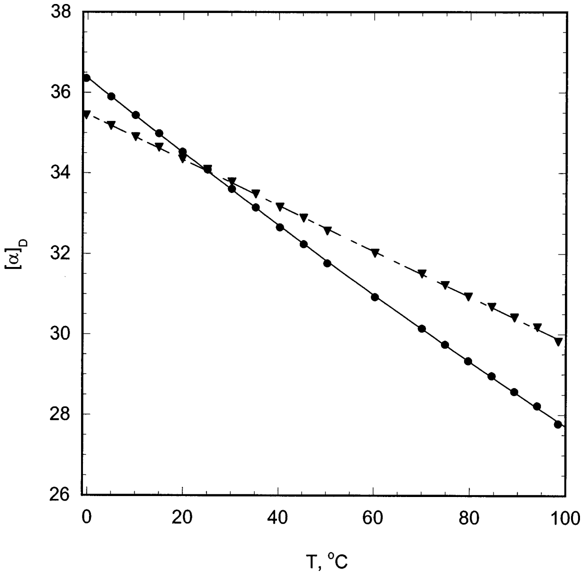

Figure 7. Temperature dependence of specific rotation of 2-methylbutyronitrile (**3**). The solid circles are for the uncorrected data and are fit with a second-order polynomial, and the triangles are for the data corrected for volume expansion of the solvent and are fit with a linear function.

that it is largely racemized. Another reaction using DAST as the fluorinating agent[14] gave a similar result. This compound has not as yet been obtained in a chiral form. The largely racemic material was used for the vacuum UV spectrum measurement.

6. Summary

(1) The large calculated effect of conformation on the specific rotation of 2-chlorobutane (**2**) been confirmed by a study of the temperature dependence of the specific rotation. In this way, it is similar to 3-chloro-1-butene. The specific rotations of the low energy conformers and of the average for the higher energy conformers are similar for the two compounds. The main difference is that the calculated specific rotations for 2-chlorobutane are close to the experimental values, whereas those for 3-chloro-1-butene are much larger than the experimental values.

(2) The temperature dependence of the specific rotation for 2-methylbutyronitrile (**3**) also confirms the large predicted change in rotation with rotation about the C−C−C−C bond, although the results are not in as good agreement with the calculated values as those found with **2**.

(3) The calculated conformational effects on specific rotations are essentially the same for the four 2-substituted butanes, despite the large difference in the electronic spectra.

7. Experimental Section

(*S*)-(+)-2-Butanol was converted to the chloride as previously described.[11] It was found that if the reaction mixture was allowed to stand overnight before isolating the chloride, the yield was increased. (*S*)-(+)-2-Methylbutyric acid was converted to the acid chloride by its reaction with thionyl chloride, and it was converted to the amide by slow addition to aqueous ammonium hydroxide with stirring and ice−salt bath cooling. The amide was treated with phosphorus pentoxide and the mixture was heated to 200 °C.[12] The pure 2-methylbutyronitrile distilled from the mixture, bp 124−125 °C.

7.a. Determination of Percent Enantiomeric Excess (% ee). The analysis was carried out using a 30 m × 0.25 mm Chiraldex B-Dm column with 4 psi hydrogen as the carrier gas and a sample split of ∼100:1. The oven holding the column was cooled using dry ice because of the high volatility of the compounds, and the analysis was run at 12 °C.

7.b. Calculations. The specific rotations were calculated using Gaussian03.[15]

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Supporting Information Available: Tables of calculated rotations at different wavelengths and with different basis sets. Tables of the observed specific rotations of **2** and **3** in the liquid phase and in ethylcyclohexane solution. This material is available free of charge via the Internet at http://pubs.acs.org.

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