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Temperature Dependence of Optical Rotation: α-Pinene, *β*-Pinene Pinane, Camphene, Camphor and Fenchone

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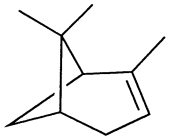
The temperature dependence of the specific rotations of α-pinene, *β*-pinene, pinane, camphene, camphor, and fenchone were measured in ethylcyclohexane solutions from 0 to 100 °C, and at several wavelengths. The rotations for α-pinene and camphene have only a very small temperature dependence. In contrast, the specific rotations of *β*-pinene and pinane decrease significantly with increasing temperature. This does not appear to be a result of a complex between pinane and the solvent, since changing to di-*n*-butyl ether leads to essentially the same temperature dependence. The specific rotations of camphor and fenchone are temperature sensitive, but in opposite directions. The observed temperature dependence of the specific rotations of these compounds has important consequences for variable temperature studies of chiral compounds having two or more conformers with similar energies.

Introduction

Studies of the effect of temperature on optical rotation of chiral molecules have the potential of giving information on the difference in free energy between conformers as well as an estimate of the specific rotations of the conformers.[1,2] The latter information is not available from any other type of experimental study.[1] However, before making more extensive use of this method, it seems appropriate to examine the temperature effect for chiral molecules that are relatively rigid and have just one conformation. Therefore we have examined α-pinene (**1**), *β*-pinene (**2**), pinane (**3**), camphene (**4**), fenchone (**5**), and camphor (**6**). Some of these compounds have been studied previously, but in less detail than in the present study.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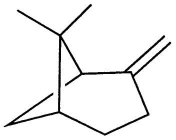
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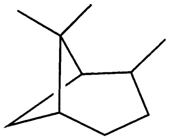
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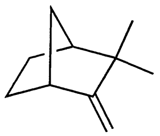
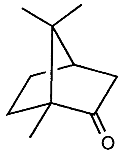
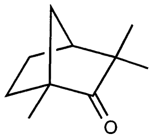

(-)-Camphene, **4**



(1R)-(+)-Camphor, **5**



(1R)-(-)-Fenchone, **6**

Solvent effects on specific rotations have received considerable study.[3,4] It has been proposed that the rotativity, θ, $(= \alpha/(n^2 + 2))$ is the more appropriate quantity.[3] We have measured the specific rotations of **1**, **2**, and **3** in the gas phase and in cyclohexane solution (Table 1). The refractive index of cyclohexane is about 1.4. If the rotativity were a constant independent of medium, the specific rotation in the gas phase should be about 3/4 of that in solution. It can be seen that this expectation is not realized.

TABLE 1: Comparison of Gas Phase and Solution Specific Rotations, 25 °C

	gas phase		cyclohexane solution	
compound	633 nm	355 nm	633 nm	355 nm
(1R,5R)-(+)-pinene (**1**)	48	192	46	165
(1S,5S)-(−)-pinene (**3**)	−12	71	−17	22
(1S)-(−)-cis-pinane (**2**)	5	−63	19	−88

An examination of the solvent effect on the specific rotation of pinane found that the rotativity was essentially constant over a wide range of solvents.[5] However, this is not the general case. Kumata, Furukawa, and Fueno[6] have measured the specific rotation of propylene oxide in a number of solvents, and we have reproduced their results. Here, the rotativity changes on going from one solvent to another and varies over a wide range (−1.1 to +7.2). A theoretical study of solvent effects on optical activity also concluded that the rotativity is not a useful quantity.[4] Thus, the following will be concerned with just the specific rotation.

Experimental Section

Materials. All of the compounds were commercial samples. α-Pinene, *β*-pinene, pinane, camphor, and fenchone had close to 100% ee. Camphene was sublimed and recrystallized from ethanol and had about 50% ee. The specific rotations given herein are the observed values, not corrected to 100% ee.

Temperature Dependence. The temperature dependence was determined in ethylcyclohexane solution at concentrations of 5−8 g/100 mL in a jacketed 1 dm cell with a volume of about 6 mL. The temperature was measured using a thermometer that had been calibrated against a set of reference thermometers, and it was placed just after the circulating thermostat fluid exited the cell. The optical rotation could be measured to 0.001° with a reproducibility of 0.001−0.002°. The thermal volume expansion of the solvent was measured by filling a 10 mL volumetric flask to the mark at 100 °C and cooling it to 0 °C. The amount of solvent required to bring it up to the mark was determined

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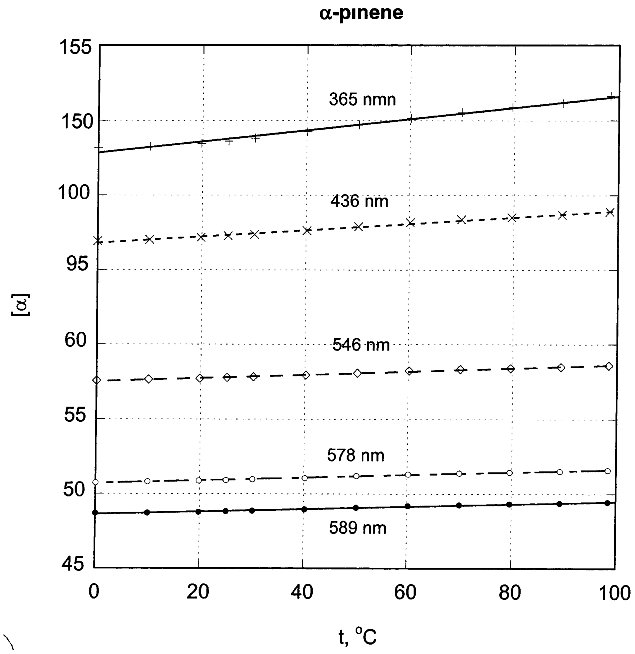

Figure 1. Effect of temperature on the specific rotation of α-pinene in ethylcyclohexane solution. The left-hand scale has uniform increases in rotation per major division, but the scale is broken at two places so that all of the lines could be conveniently displayed.

both volumetrically and gravimetrically, with the two methods being in good agreement. Ethylcyclohexane expands by 0.10% per °C.

Concentration Dependence. The concentration dependence of the specific rotation of α-pinene and of fenchone was determined at 25 °C in ethylcyclohexane solutions. The solutions covered a range of about 0.5−8 g/100 mL in five approximately uniform steps.

UV Spectra. The UV spectra of α- and *β*-pinene were obtained using a 1 M vacuum UV spectrometer operating in a double beam mode. No absorption was found below 40 000 cm^{-1}.

Results

(1*R*,5*R*)-(+)-α-Pinene (1). The temperature dependence of the specific rotation of **1** has been studied.[2b] We have reexamined it in order to have a wider range of temperatures, along with information on the effect of wavelength. Ethylcyclohexane was used as the solvent, and the observed rotations were corrected for the expansion of the solvent. The data are given in Table S1 (see Supporting Information)[7] and are summarized in Figure 1. It can be seen that the temperature has little effect on the specific rotation. The equations for the lines in Figure 1 are

589 nm: $[\alpha] = 48.64 + 0.00841t$ $R = 0.993$ $\text{slope}/[\alpha]_0 = 0.17 \times 10^{-3}$
578 nm: $[\alpha] = 50.72 + 0.00910t$ $R = 0.995$ $\text{slope}/[\alpha]_0 = 0.18 \times 10^{-3}$
546 nm: $[\alpha] = 57.53 + 0.01086t$ $R = 0.997$ $\text{slope}/[\alpha]_0 = 0.19 \times 10^{-3}$
436 nm: $[\alpha] = 96.80 + 0.02126t$ $R = 0.996$ $\text{slope}/[\alpha]_0 = 0.22 \times 10^{-3}$
365 nm: $[\alpha] = 147.84 + 0.03750t$ $R = 0.993$ $\text{slope}/[\alpha]_0 = 0.25 \times 10^{-3}$

The values of the slope divided by [α] at 0 °C are normalized values that allow compounds with different $[\alpha]_0$ to be compared. Here and in subsequent plots the temperature is given in °C.

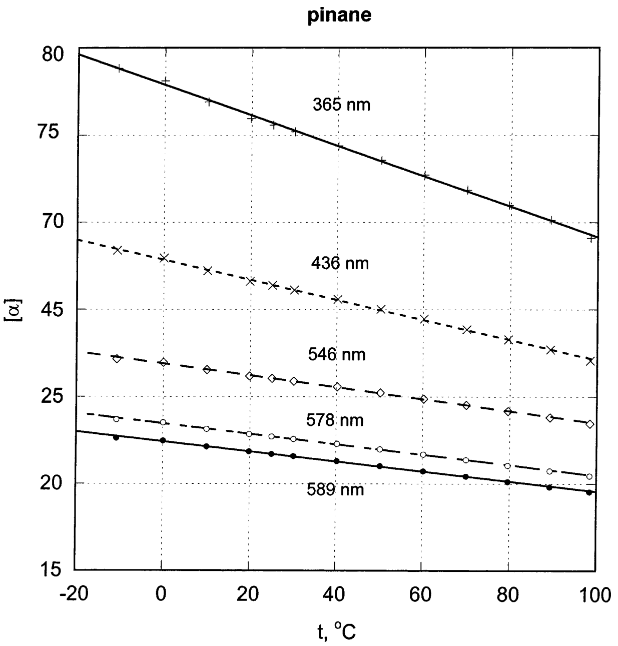

Figure 2. Effect of temperature on the specific rotation of pinane in ethylcyclohexane solution.

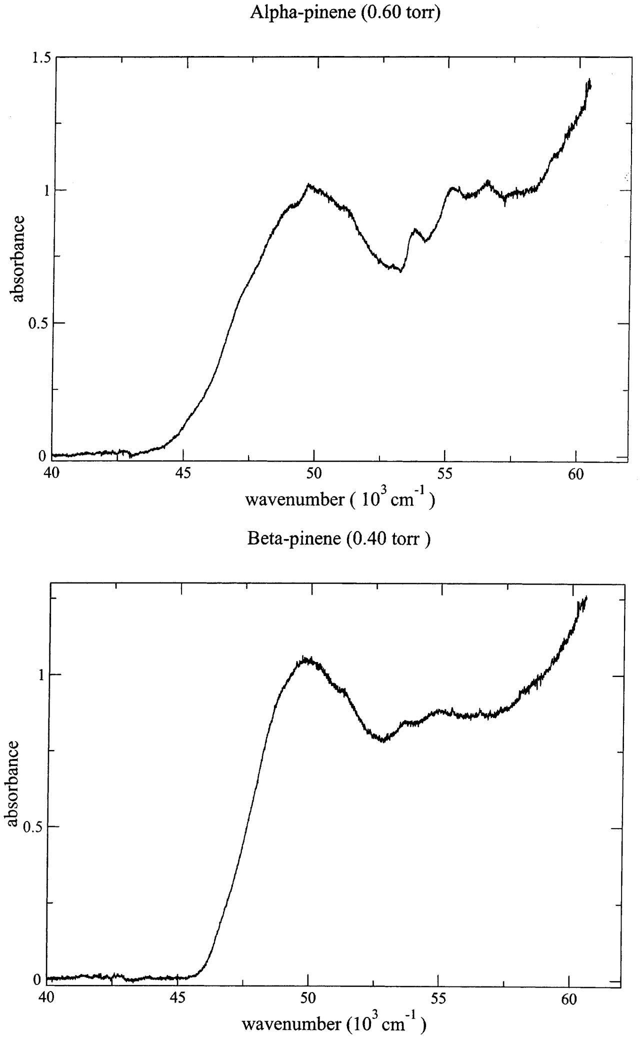

Figure 3. VUV spectra of α- and *β*-pinene.

Polavarapu has proposed that specific rotations determined in solution should be extrapolated to infinite dilution.[8] The specific rotation for **1** was measured at 589 nm and 25 °C from 0.5 to 7% in ethylcyclohexane, and it changed linearly from 47.8 at the lower concentration to 48.8 at the higher concentration. The latter corresponds to the concentration used in the

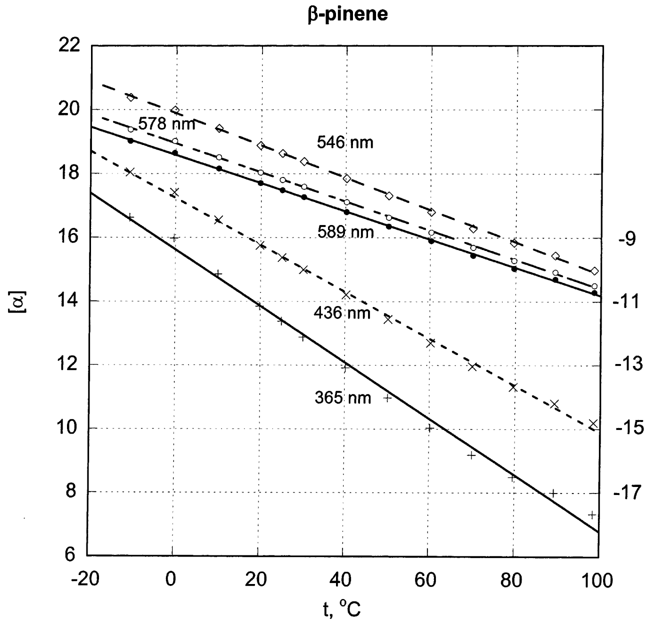

Figure 4. Effect of temperature on the specific rotation of β-pinene in ethylcyclohexane solution. The right-hand scale is for the 365 nm data.

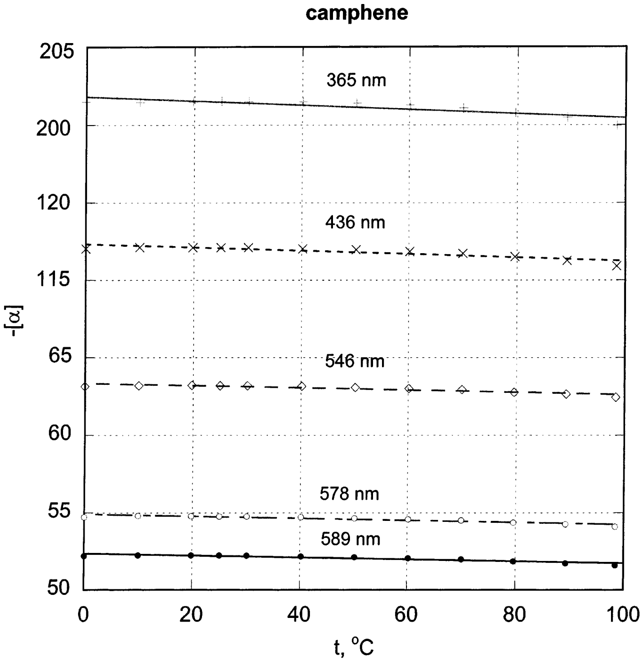

Figure 5. Effect of temperature on the specific rotation of camphene in ethylcyclohexane solution.

temperature dependence study. There is an effect of concentration, but it is small.

(1*R*)-cis-(+)-Pinane (3). We were interested in examining the effect of removing the double bond in α-pinene. Therefore (+)-**3** was examined in the same fashion as **1**, giving the data listed in Table S2 (see Supporting Information) and summarized in Figure 2. The specific rotation changes with temperature in a linear fashion, and the effect of temperature is much larger than for **1**. The equations for the lines in the Figure are:

589 nm:	$[\alpha] = 23.50 - 0.03083t$	$R = 0.999$	$\text{slope}/[\alpha]_0 = 1.3 \times 10^{-3}$
578 nm:	$[\alpha] = 24.58 - 0.03208t$	$R = 0.999$	$\text{slope}/[\alpha]_0 = 1.3 \times 10^{-3}$
546 nm:	$[\alpha] = 28.15 - 0.03615t$	$R = 0.999$	$\text{slope}/[\alpha]_0 = 1.3 \times 10^{-3}$
436 nm:	$[\alpha] = 50.07 - 0.06059t$	$R = 0.999$	$\text{slope}/[\alpha]_0 = 1.2 \times 10^{-3}$
365 nm:	$[\alpha] = 81.46 - 0.09125t$	$R = 0.999$	$\text{slope}/[\alpha]_0 = 1.1 \times 10^{-3}$

Could the effect of temperature on the specific rotation be due to complex formation between **2** and the solvent? The temperature dependence of the specific rotation in di-*n*-butyl ether was found to be essentially the same as that found with ethylcyclohexane. Thus, complex formation seems unlikely. In addition, the specific rotation was determined over the range of wavelengths in cyclohexane, di-*n*-butyl ether, and acetonitrile. Despite the change in polarity and refractive index, there was essentially no change in specific rotation with solvent (Figure S1, Supporting Information).

(1*R*,5*R*)-(+)-*β*-Pinene (2). We have noted that despite the similarity in structure between **1** and **2**, there is a remarkable difference in the change in specific rotation with wavelength.[1] It is found that **1** has a positive rotation at 589 nm, and it becomes increasingly more positive with decreasing wavelength. On the other hand, **2** has a positive rotation at 589 nm which at first changes slowly with decreasing wavelength. It changes sign at about 400 nm, and then becomes increasingly more negative as the wavelength is decreased. A change in the sign of the specific rotation is often related to a nearby electronic transition. However, the UV spectra of **1** and **2** are quite similar (Figure 3), and neither one absorbs light below 40 000 cm^{-1}.

The effect of temperature on the specific rotation of **2** was determined in ethylcyclohexane solution. The results are given in Table S3 (Supporting Information) and are summarized in Figure 4. The equations for the lines on the plot are:

589 nm:	$[\alpha] = 18.58 - 0.04405t$	$R = 0.999$	$\text{slope}/[\alpha]_0 = -2.4 \times 10^{-3}$
578 nm:	$[\alpha] = 18.94 - 0.04554t$	$R = 0.999$	$\text{slope}/[\alpha]_0 = -2.4 \times 10^{-3}$
546 nm:	$[\alpha] = 19.88 - 0.05046t$	$R = 0.999$	$\text{slope}/[\alpha]_0 = -2.5 \times 10^{-3}$
436 nm:	$[\alpha] = 17.23 - 0.07353t$	$R = 0.999$	$\text{slope}/[\alpha]_0 = -4.3 \times 10^{-3}$
365 nm:	$[\alpha] = -9.37 - 0.08844t$	$R = 0.997$	$\text{slope}/[\alpha]_0 = +9.4 \times 10^{-3}$

In contrast to α-pinene, the effect of temperature on the specific rotation of β-pinene is fairly large.

(−)-Camphene (4). The effect of temperature on the specific rotation of camphene has been examined and was found to be small.[2] We have reinvestigated camphene in ethylcyclohexane solution from 0 to 100 °C in order to have data for different wavelengths. The results are given in Table S4 (Supporting Information) and are shown in Figure 5. The temperature dependence is small at all wavelengths and the equations for the lines in the plot are:

589 nm:	$[\alpha] = -52.37 + 0.00637t$	$R = 0.929$	$\text{slope}/[\alpha]_0 = -0.12 \times 10^{-3}$
578 nm:	$[\alpha] = -54.90 + 0.00655t$	$R = 0.917$	$\text{slope}/[\alpha]_0 = -0.12 \times 10^{-3}$
546 nm:	$[\alpha] = -63.33 + 0.00712t$	$R = 0.904$	$\text{slope}/[\alpha]_0 = -0.11 \times 10^{-3}$
436 nm:	$[\alpha] = -117.31 + 0.0108t$	$R = 0.892$	$\text{slope}/[\alpha]_0 = -0.09 \times 10^{-3}$
365 nm:	$[\alpha] = -210.79 + 0.0135t$	$R = 0.867$	$\text{slope}/[\alpha]_0 = -0.06 \times 10^{-3}$

Here the *R* values are less satisfactory than for the other compounds because the change with temperature is quite small with respect to the magnitude of the specific rotation and there is a small curvature in the data. The results for camphene are similar to those for α-pinene.

(1*R*)-(+)-Camphor (5). The temperature dependence of the specific rotation of camphor has been studied from −15 to 65 °C at 546 nm.[2c] We wished to have data for a wider temperature range and for other wavelengths. The specific rotation was studied in ethylcyclohexane solution from 0 to 100 °C and using several wavelengths. The results are given in Table S5 (Supporting Information) and in Figure 6. The equations of the lines

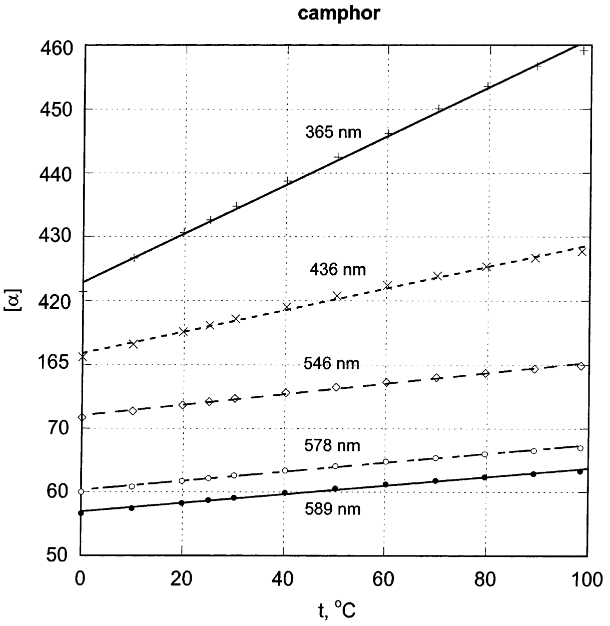

Figure 6. Effect of temperature on the specific rotation of camphor in ethylcyclohexane solution.

in the figure are:

589 nm: $[\alpha] = 56.92 + 0.0681t$ $R = 0.997$ $\text{slope}/[\alpha]_0 = 1.1 \times 10^{-3}$
578 nm: $[\alpha] = 60.30 + 0.0715t$ $R = 0.997$ $\text{slope}/[\alpha]_0 = 1.2 \times 10^{-3}$
546 nm: $[\alpha] = 72.07 + 0.0832t$ $R = 0.997$ $\text{slope}/[\alpha]_0 = 1.2 \times 10^{-3}$
436 nm: $[\alpha] = 166.8 + 0.169t$ $R = 0.997$ $\text{slope}/[\alpha]_0 = 1.0 \times 10^{-3}$
365 nm: $[\alpha] = 422.9 + 0.382t$ $R = 0.999$ $\text{slope}/[\alpha]_0 = 0.9 \times 10^{-3}$

The origin of the effect of temperature on the specific rotation of camphor and other chiral ketones has been the subject of several studies. Moscowitz et al. suggested that the effect arose from complex formation between the solvent and camphor,[9] but this seems unlikely.[2c] Gervais and Desalbres have proposed that the temperature dependence arises from a vibronic effect on the *n*-π* rotatory strength.[10] There appears to be general agreement in the literature that the carbonyl group vibrational modes are responsible for the temperature dependence.[11] However, as shown above, pinane shows an equally large temperature dependence. Thus, modes other than those associated with the carbonyl group must also be important.

(1*R*)-(−)-Fenchone (6). The temperature dependence of the specific rotation of **6** has been studied from −15 to 50 °C at 546 nm.[2] We wished to have a wider temperature range and to have data at different wavelengths. Fenchone was examined in the same fashion as the other compounds in this study giving the results summarized in Table S6 (Supporting Information), and in Figure 7. It is similar to camphor in the magnitude of the changes in specific rotation, but the normalized slopes of the lines in Figure 7 have the opposite sense to those for camphor. The equations of the lines in the Figure are:

589 nm: $[\alpha] = -46.76 + 0.0561t$ $R = 0.999$ $\text{slope}/[\alpha]_0 = -1.2 \times 10^{-3}$
578 nm: $[\alpha] = -49.11 + 0.0581t$ $R = 0.999$ $\text{slope}/[\alpha]_0 = -1.2 \times 10^{-3}$
546 nm: $[\alpha] = -57.17 + 0.0665t$ $R = 0.999$ $\text{slope}/[\alpha]_0 = -1.2 \times 10^{-3}$
436 nm: $[\alpha] = -113.8 + 0.1195t$ $R = 0.999$ $\text{slope}/[\alpha]_0 = -1.1 \times 10^{-3}$
365 nm: $[\alpha] = -231.8 + 0.1988t$ $R = 0.999$ $\text{slope}/[\alpha]_0 = -0.9 \times 10^{-3}$

The concentration dependence of the specific rotation was examined in ethylcyclohexane solution having concentrations from 0.6 to 8.2 g/100 mL. It changed linearly from −44.0° at the lowest concentration to −45.6° at the highest concentration. The concentration dependence is small.

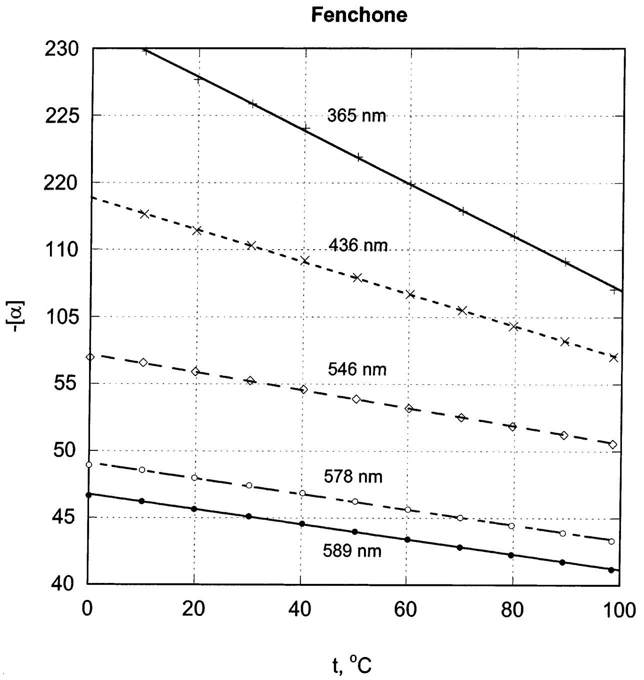

Figure 7. Effect of temperature on the specific rotation of fenchone in ethylcyclohexane solution.

Summary

The effect of temperature on the specific rotations of **1**−**6** was linear, but each compound led to a different slope. Since this appears to be a general phenomenon, the temperature dependence for molecules that are mixtures of conformers cannot in general give both the difference in energy between conformers and the specific rotation of the individual conformers. There is clearly an additional factor, the unknown effect of temperature on the specific rotation of the individual conformers. This did not appear to be a problem in our study of 3-chloro-1-butene because the ΔG obtained assuming no temperature effect for the individual conformers was 1.3 kcal/mol, close to the G2 calculated gas phase value of 1.1 kcal/mol. It has been found with related compounds that the conformational energy difference frequently increases somewhat on going from the gas phase to solutions.[12] However, in other cases we are studying, such as 2-chlorobutane, there must be a temperature dependence for the individual conformers.

For a case in which there are only two conformers, the observed specific rotation as a function of temperature, assuming no temperature dependence for the individual rotamers, would be

$$[\alpha]_{\text{obs}} = ([\alpha]_A + [\alpha]_B \exp(-\Delta G/RT))/(1 + \exp(-\Delta G/RT))$$

where $[\alpha]_A$ and $[\alpha]_B$ are the specific rotation of the two conformers and ΔG is the difference in energy. If the temperature effect on the rotations of A and B were approximately the same, $[\alpha]_A = (1 + cT)[\alpha]_A{}^0$ and $[\alpha]_B = (1 + cT)[\alpha]_B{}^0$ where $[\alpha]_A{}^0$ and $[\alpha]_B{}^0$ are the temperature independent values. Then,

$$[\alpha]_{\text{obs}} = (1 + cT)\,([\alpha]_A{}^0 + [\alpha]_B{}^0 \exp(-\Delta G/RT))/(1 + \exp(-\Delta G/RT))$$

In addition, the observed rotations must be corrected for the expansion of the solvent and $[\alpha]_{\text{obs}} = (1 + aT)\alpha'$ where α' is the uncorrected observed rotation. Thus

$$\frac{(1 + aT)\alpha'}{(1 + cT)} = ([\alpha]_A{}^0 + [\alpha]_B{}^0 \exp(-\Delta G/RT))/(1 + \exp(-\Delta G/RT))$$

For these molecules, the curvature of a plot of specific rotation vs temperature is an important quantity, and multiplying the observed values by a function linear in temperature will affect the curvature. Since c is not known, one approach is to take c as an adjustable variable and set it to make ΔG derived by fitting the above equation agree with independently obtained values of ΔG. We will subsequently present the results of applying this procedure to a set of 2-substituted butanes.

The temperature dependence for the present compounds is not a function of the solvent since it has quite different slopes for different compounds in ethylcyclohexane solutions, and therefore it must be due to the molecules themselves. With these molecules that have but one conformer, the only feature that is temperature dependent is the amplitude of the vibrational modes.

Although the compounds in this study are normally considered to be “rigid” because of their bicyclic structures, they do have many low-frequency vibrational modes. Some of these are methyl torsional modes, but there also are a number of skeletal modes below 400 cm^{-1} that will change vibrational amplitudes with increasing temperature. An examination of the effect of vibrational amplitude for these molecules that have many low-frequency vibrational modes presents a difficult computational problem.

In a continuation of this study, we are now examining a group of smaller compounds that have only one conformer. Here, a detailed analysis of the vibrational contribution to the temperature dependence of the specific rotation will be more practical.

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Supporting Information Available: Tables of temperature dependence of the specific rotation for compounds **1-6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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