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Vibrational Circular Dichroism in (*R*)-Cyclohexanone-*3-d*, (*R*)-3-Methylcyclohexanone, and (1*S*)-2-Adamantanone-*4*-^{13}C

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Abstract: Vibrational rotational strengths are calculated for the CH-stretching modes in (*R*)-(+)-3-methylcyclohexanone (I), (*R*)-cyclohexanone-*3-d* (II), and (1*S*)-2-adamantanone-*4*-^{13}C (III) by using the fixed partial charge (fpc) model. The results indicate that the circular dichroism (CD) in the CH-stretching region is due to coupling among the CH_2 modes. Comparison of the patterns of the calculated and the observed rotational strengths for compound I suggests that the fpc model may be a reasonable one for interpretive purposes when coupled CH_2 stretches are involved. Replacing the methyl group in compound I with a deuterium had little effect on the calculated CD spectrum between 3000 and 2800 cm^{-1}. The calculated rotational strengths differ dramatically between alternative chair forms.

Introduction

Attempts to calculate vibrational circular dichroism (VCD) intensities in accord with the experimental data have, in general, met with only limited success.[2] In fact, rotational strengths calculated by using the fixed partial charge (fpc) model[3] are often 1–2 orders of magnitude less than the measured values.[2c,4] A recent paper by Keiderling and Stephens,[5] however, suggests that semiquantitative agreement between fpc model calculations and experiment can be achieved for coupled CH_2-stretching modes. Bisignate-shaped curves observed in the VCD spectrum of (*R*)-(+)-3-methylcyclohexanone[6] (I) are indicative of coupled CH_2 stretches, suggesting that this molecule may also be one for which the fpc model results agree qualitatively with experiment. This paper will show that this is indeed the case.

One facet of the problem in any fpc model calculation is to obtain accurate normal modes of vibration. This is a particularly difficult task for chiral molecules since there is usually no symmetry to help reduce the number of independent force constants. The molecule cyclohexanone, which has a plane of symmetry, is a logical starting point for a normal-coordinate analysis of the title compounds. Fuhrer et al.[7] determined a set of valence force constants for cyclohexanone by least squares adjusting the diagonal force constants to fit the observed frequencies of cyclohexanone, cyclohexanone-$\alpha,\alpha,\alpha',\alpha'$-$d_4$, cyclohexanone-$\beta,\beta,\beta',\beta',\gamma,\gamma'$-$d_6$, and cyclohexanone-$d_{10}$. We used the 44 valence force constants determined in ref 7 in obtaining all of the results that follow.

Table I. Calculated CH-Stretching Frequencies and Rotational Strengths (*R*) of (*R*)-Cyclohexanone-*3-d*$_1$

deuterium equatorial		deuterium axial		
ν, cm^{-1}	$10^{45}R$, $(esu\ cm)^2$	ν, cm^{-1}	$10^{45}R$, $(esu\ cm)^2$	descriptn[a]
2967	−4.62	2967	4.96	asym α-CH_2 ip
2964	−2.97	2964	3.29	asym α-CH_2 oop
2944	19.4	2944	−21.9	asym β-CH_2
2921	−17.4	2920	16.5	asym γ-CH_2
2910	−2.48	2912	−1.43	β-CH
2901	2.14	2901	0.156	sym α-CH_2 ip
2900	5.65	2900	0.544	sym α-CH_2 oop
2875	0.445	2875	−0.890	sym β-CH_2
2851	−0.124	2851	−1.28	sym γ-CH_2

[a] Abbreviations: ip = in phase; opp = out of phase.

(*R*)-Cyclohexanone-*3-d* (II)

We began by reproducing the results of Fuhrer et al.[7] on cyclohexanone and isotopically substituted cyclohexanone. Using our own computer program,[2c] we achieved agreement with the results of ref 7 to within 2 cm^{-1} for each of the 180 frequencies. Our next step was to repeat the normal-coordinate calculation

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[1] (a) The Proctor & Gamble Company. (b) University of Minnesota.

[2] (a) Faulkner, T. R.; Moscowitz, A.; Holzwarth, G.; Hsu, E. C.; Mosher, H. S. *J. Am. Chem. Soc.* **1974**, *96*, 252. (b) Keiderling, T. A.; Stephens, P. J. *Ibid.* **1977**, *99*, 8061. (c) Faulkner, T. R. Ph.D. Thesis, University of Minnesota, 1976.

[3] Schellman, J. A. *J. Chem. Phys.* **1973**, *58*, 2882; **1974**, *60*, 343.

[4] Marcott, C. Ph.D. Thesis, University of Minnesota, 1979.

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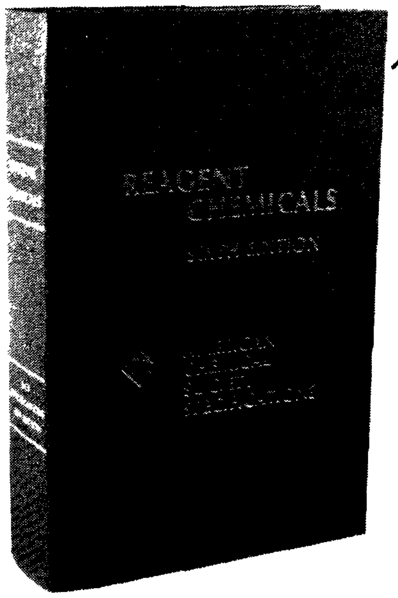

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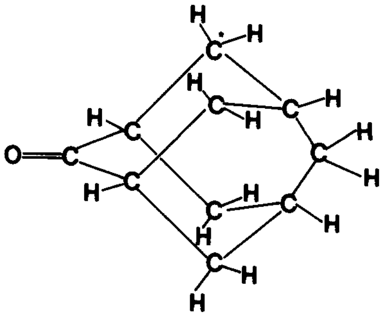

Figure 2. Structure of adamantanone. The carbon atom labeled with the asterisk is the location of the ^{13}C in (1*S*)-2-adamantanone-*4*-^{13}C.

solution. Although the chair form with the methyl group equatorial is the predominant form,[11] the molecule is conformationally mobile and some molecules are likely to be in the inverted chair form or some other conformation.

Table III. Calculated CH-Stretching Frequencies and Rotational Strengths (*R*) of (1*S*)-2-Adamantanone-*4*-^{13}C

ν, cm^{-1}	$10^{45}R$, (esu cm)^2	descriptn[a, b]
2949	−0.278	asym β,δ-CH_2
2948	−0.0205	asym β,δ-CH_2
2946	1.09	asym β,δ-CH_2
2945	0.0892	asym β,δ-CH_2
2937	−1.51	α-CH ip
2934	−2.37	asym β-$^{13}CH_2$
2934	2.87	α-CH oop
2887	0.0205	γ-CH ip
2885	−0.0161	γ-CH oop
2871	−0.160	sym β,δ-CH_2
2871	1.04	sym β,δ-CH_2
2870	−0.338	sym β,δ-CH_2
2870	−0.0242	sym β,δ-CH_2
2864	−0.401	sym β-CH_2

[a] The β and δ-CH_2 stretching modes are strongly mixed. [b] Abbreviations: ip = in phase; oop = out of phase.

Table IV. Calculated CH-Stretching Frequencies and Rotational Strengths (*R*) of (*S*)-Cyclohexanone-*3*-^{13}C

ν, cm^{-1}	$10^{45}R$, (esu cm)^2	descriptn[a]
2967	−2.75	asym α-CH_2 ip
2964	−1.32	asym α-CH_2 oop
2944	19.9	asym β-CH_2
2932	−22.7	asym β-$^{13}CH_2$
2919	5.83	asym γ-CH_2
2901	0.303	sym α-CH_2 ip
2900	0.509	sym α-CH_2 oop
2875	0.746	sym β-CH_2
2868	−0.259	sym β-$^{13}CH_2$
2851	−0.206	sym γ-CH_2

[a] Abbreviations: ip = in phase; oop = out of phase.

Conformational mobility is not a problem in the molecule adamantanone (see Figure 2). Its relationship to cyclohexanone, its C_{2v} symmetry, and its fixed conformation make the normal-coordinate problem less difficult than might appear at first glance. Although adamantanone itself is not optically active, (1*S*)-2-adamantanone-*4*-^{13}C (III) has been synthesized and its CD observed in the 295-nm electronic transition.[12] We have performed a normal-coordinate calculation on (1*S*)-2-adamantanone-*4*-^{13}C by using the force constants from the cyclohexanone calculation.[7] Since a literature force field was not available for adamantanone, the cyclohexanone field of ref 7 was chosen as a reasonable first guess. The force constants associated with the δ-CH_2 group were taken to be the same as for the β-CH_2 groups. No attempt was made to refine this force field. All CH bond lengths were taken to be 1.112 Å. The CC bond distances were assumed to be 1.54 Å except for the two involving the carbonyl carbon which were assigned a value of 1.484512 Å. All the bond angles were taken to be tetrahedral except for those about the carbonyl carbon. An OCC bond angle of 122.1146° was assumed.[13] The calculated frequencies and rotational strengths in the CH-stretching region are shown in Table III.[14] It is interesting to compare the results in Table III with calculations on cyclohexanone where one of the β-carbon atoms is taken to the ^{13}C (see Table IV).[15] The rotational strengths for the ^{13}C-substituted adamantanone tend to be about 1 order of magnitude less than those for the ^{13}C-substituted cyclohexanone. This appears to be due to the fact that none of the angles used in the cyclohexanone calculation were exactly tetrahedral.[7] We find that the magnitude of the circular dichroism calculated in the CH-stretching region of (1*S*)-2-adamantanone-*4*-^{13}C approaches that in Table IV for (*S*)-cyclohexanone-*3*-^{13}C if we allow the relevant bond angles to match those given in Figure 1 of ref 7. In this case the calculated VCD is again due to coupling in the CH_2 modes. Thus it appears that a measured VCD spectrum in the CH-stretching region of compound III could be useful for providing geometrical information on adamantanone in solution.

Acknowledgment. This work was supported in part by the National Science Foundation (Grant No. CHE 77-06752) and the National Institutes of Health (Grant No. HL 16833).

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(11) Djerassi, C. "Optical Rotatory Dispersion"; McGraw-Hill: New York, 1960.

(12) Sing, Y. L.; Numan, H.; Wynberg, H.; Djerassi, C. *J. Am. Chem. Soc.* **1979**, *101*, 5155.

(13) This geometry was constructed by first determining the coordinates for adamantane by using all tetrahedral angles. One of the CH_2 groups was then replaced with a C=O and the coordinates were adjusted so as to agree with the CC distance (1.50 Å) and CCO angle (122°) given in ref 7. These values had to be compromised somewhat in order that the coordinates be internally consistent and the C_{2v} symmetry maintained. We show seven significant figures so that it will be possible for the reader to reproduce our results.

(14) Torsional internal coordinates were not included in the calculation of Table III. A second calculation which included the torsional force constants demonstrated that the frequencies and rotational strengths in the CH-stretching region were not significantly affected by this omission.

(15) It is worth pointing out that cyclohexanone-*3*-^{13}C is optically active only in a conformational sense, i.e., there is no chiral center and the molecule can go from *S* to *R* by changing from one chair form to the other.