processes which are unique to the pyrazolylborates.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council (Canada) for financial support through Operating and Strategic Grants.

Supplementary Material Available: IR, NMR, and analytical data for **2a**, **3**, and **4** (1 page). Ordering information is given on any current masthead page.

Vibrational Circular Dichroism in the Carbon-Hydrogen and Carbon-Deuterium Stretching Modes of (S,S)-[2,3-$^2H_2$]Oxirane

Teresa B. Freedman,* M. Germana Paterlini, Nam-Soo Lee, and Laurence A. Nafie*

Department of Chemistry, Syracuse University
Syracuse, New York 13244-1200

John M. Schwab and Tapan Ray

Department of Medicinal Chemistry and Pharmacognosy
School of Pharmacy and Pharmacal Sciences
Purdue University, West Lafayette, Indiana 47907

Received February 17, 1987

We report vibrational circular dichroism[1] (VCD) spectra of (S,S)-[2,3-$^2H_2$]oxirane (**1**) in the carbon-hydrogen and carbon-deuterium stretching regions. Three- and four-membered chiral ring molecules have been the focus of several previous VCD studies[2-7] owing to their conformational rigidity, low molecular weight, and the relative simplicity of their vibrational spectra. The chiral oxirane featured in this study is the smallest and simplest molecule for which VCD has been observed to date. The observed VCD spectra are correspondingly simple, consisting of a bisignate couplet in each spectral region corresponding to the in-phase and out-of-phase hydrogen, or deuterium, stretching modes. The general features of the couplets are readily interpreted in terms of the coupled oscillator[8] and ring current[9] intensity mechanisms as well as theoretical vibronic coupling calculations.[10] The significance of the reported VCD spectra is that they provide the experimental basis for comparison to the results of the most sophisticated theoretical calculations which can be performed for a molecule as large as oxirane.

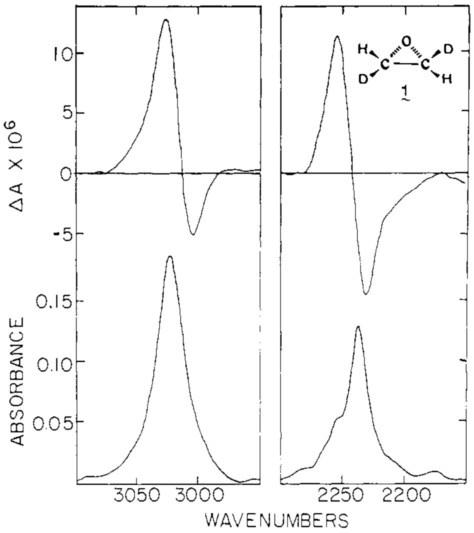


Figure 1. VCD (upper curves) and absorption (lower curves) spectra for (S,S)-[2,3-$^2H_2$]oxirane in CCl_4 in the CH- and CD-stretching regions, obtained at 8-cm^{-1} resolution with 10-s time constant and 100-μm sample path length.

(R,R)- and (S,S)-[2,3-$^2H_2$]oxirane were prepared as described previously,[11] except that 3-(triphenylsilyl)-2,3-epoxypropanol was oxidized to the corresponding aldehyde by using MnO_2[12] rather than Ag_2CO_3/Celite, and a modified version[13] of the Sharpless epoxidation[14] was employed. In the final reaction, 1.00 mmol of (triphenylsilyl)oxirane was treated with Et_4NF in Me_2SO, and the oxirane thus generated was trapped in 1.0 mL of CCl_4 at −18 °C. Enantiomeric excesses were greater than 90%.[15] ^1H NMR analysis of synthetic oxirane revealed the presence of a small amount of benzene (also detected by IR), presumably arising through attack of fluoride on silicon, with expulsion of the phenyl anion.[18]

The VCD spectra shown in Figure 1 represent an average of four scans for each enantiomer obtained on a dispersive VCD instrument.[20] Spectra recorded for samples from two earlier, less pure synthetic batches were similar to those in Figure 1. In order to eliminate base line artifacts, the VCD spectra in Figure 1 were obtained by subtraction of the raw VCD spectra of the (R,R)-enantiomer from that of the (S,S)-enantiomer and dividing by two.

Absorption features in the CH-stretching region due to benzene and an unidentified achiral impurity[21] in each synthetic batch were

---

[1] For recent reviews, see: (a) Freedman, T. B.; Nafie, L. A. In *Topics in Stereochemistry*; Eliel, E. L., Wilen, S., Eds.; Wiley: New York, 1987; Vol. 17, pp 113-206. (b) Stephens, P. J.; Lowe, M. A. *Annu. Rev. Phys. Chem.* **1985**, *36*, 213-241. (c) Nafie, L. A. In *Advances in Infrared and Raman Spectroscopy*; Clark, R. J. M., Hester, R. E., Eds.; Wiley-Heyden: Chichester, 1984; Vol. 11, pp 49-93.

[2] Heintz, V. J.; Keiderling, T. A. *J. Am. Chem. Soc.* **1981**, *103*, 2395-2403.

[3] Polavarapu, P. L.; Michalska, D. F. *J. Am. Chem. Soc.* **1983**, *105*, 6190-6191. Polavarapu, P. A.; Michalska, D. F. *Mol. Phys.* **1984**, *52*, 1225-1235; **1985**, *55*, 723. Polavarapu, P. L.; Hess, B. A., Jr.; Schaad, L. F. *J. Chem. Phys.* **1985**, *82*, 1705-1710.

[4] Annamalai, A.; Keiderling, T. A.; Chickos, J. S. *J. Am. Chem. Soc.* **1984**, *106*, 6254-6262; **1985**, *107*, 2285-2291. Chickos, J. S.; Annamalai, A.; Keiderling, T. A. *J. Am. Chem. Soc.* **1986**, *108*, 4398-4402.

[5] Shaw, R. A.; Ibrahim, N.; Nafie, L. A.; Rauk, A.; Wieser, H. In *1985 Conference on Fourier and Computerized Infrared Spectroscopy*; Grasselli et al., Eds.; SPIE: Bellingham, WA, 1985; pp 433-434.

[6] Lowe, M. A.; Stephens, P. J.; Segal, G. A. *Chem. Phys. Lett.* **1986**, *123*, 108-116. Lowe, M. A.; Segal, G. A.; Stephens, P. J. *J. Am. Chem. Soc.* **1986**, *108*, 248-256.

[7] Polavarapu, P. L.; Hess, B. A., Jr.; Schaad, L. J.; Henderson, D. O.; Fontana, L. P.; Smith, H. E.; Nafie, L. A.; Freedman, T. B.; Zuk, W. M. *J. Chem. Phys.* **1987**, *86*, 1140-1146.

[8] Holzwarth, G.; Chabay, I. *J. Chem. Phys.* **1972**, *57*, 1632-1635. Sugeta, H.; Marcott, C.; Faulkner, T. R.; Overend, J.; Moscowitz, A. *Chem. Phys. Lett.* **1976**, *40*, 397-398.

[9] (a) Nafie, L. A.; Freedman, T. B. *J. Phys. Chem.* **1986**, *90*, 763-767. (b) Freedman, T. B.; Balukjian, G. A.; Nafie, L. A. *J. Am. Chem. Soc.* **1985**, *107*, 6213-6222. (c) Young, D. A.; Freedman, T. B.; Lipp, E. D.; Nafie, L. A. *Ibid.* **1986**, *108*, 7255-7263.

[10] Freedman, T. B.; Nafie, L. A. *J. Chem. Phys.*, in press.

[11] Schwab, J. M.; Ho, C.-K. *J. Chem. Soc., Chem. Commun.* **1986**, 872-873.

[12] Ray, T.; Schwab, J. M., manuscript in preparation.

[13] Wang, Z.-m.; Zhou, W.-s.; Lin, G.-q. *Tetrahedron Lett.* **1985**, *26*, 6221-6224.

[14] Katsuki, T.; Sharpless, K. B. *J. Am. Chem. Soc.* **1980**, *102*, 5974-5976.

[15] Samples of [$^2H_2$]oxirane synthesized in this manner were reacted with phenyllithium, and the resulting 2-phenylethanol samples were converted to esters of (−)-camphanic acid.[16] ^2H NMR analysis[17] showed that the enantiomeric excesses of the (R,R)- and (S,S)-enantiomers were ca. 92% and 94%, respectively.

[16] Gerlach, H.; Zagalak, B. *J. Chem. Soc., Chem. Commun.* **1973**, 274-275.

[17] Schwab, J. M.; Klassen, J. B. *J. Am. Chem. Soc.* **1984**, *106*, 7217-7227.

[18] The observation of benzene as a byproduct is consistent with the mechanism originally proposed by Chan et al.[19] for the desilylation reaction.

[19] Chan, T. H.; Lau, P. W. K.; Li, M. P. *Tetrahedron Lett.* **1976**, 2667-2670.

[20] Diem, M.; Gotkin, P. J.; Kupfer, J. M.; Nafie, L. A. *J. Am. Chem. Soc.* **1978**, *100*, 5644-5650. Diem, M.; Photos, E.; Khouri, H.; Nafie, L. A. *J. Am. Chem. Soc.* **1979**, *101*, 6829-6837. Lal, B. B.; Diem, M.; Polavarapu, P. L.; Oboodi, M.; Freedman, T. B.; Nafie, L. A. *J. Am. Chem. Soc.* **1982**, *104*, 3336-3342.

0002-7863/87/1509-4727$01.50/0

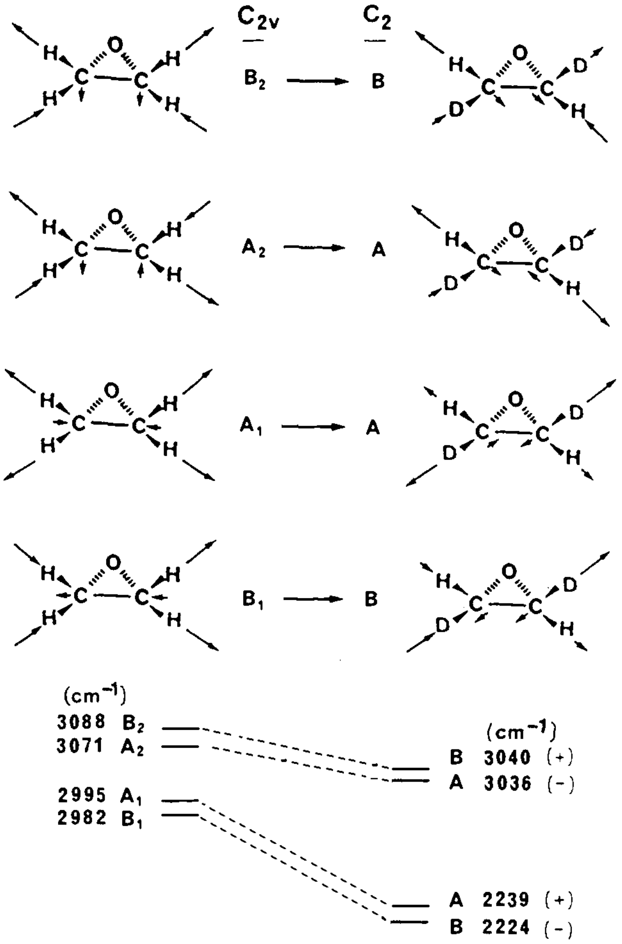


Figure 2. Correlation of calculated hydrogen stretching modes of oxirane (C_{2v} symmetry) and (S,S)-[2,3-$^2H_2$]oxirane (C_2 symmetry). Long arrows indicate directions of predominant atomic displacements. The minor displacements (small arrows) have been exaggerated for clarity.

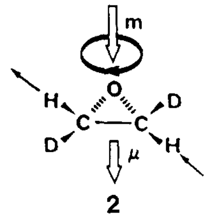
removed by spectral subtraction, since the impurity and benzene were present at unequal concentration for the two enantiomers. No interfering bands were observed in the CD-stretching region. For the spectra shown in Figure 1, the maximum absorbance in the CH stretching region due to impurity bands was less than 20% of the sample absorbance.

The VCD spectra consist of a CH-stretching couplet (3026 (+), 3004 cm^{-1} (−)), corresponding to the intense absorption band at 3022 cm^{-1} and a weak, unresolved band, and a CD-stretching couplet (2254 (+), 2228 cm^{-1} (−)) associated with the weak 2254-cm^{-1} and intense 2237-cm^{-1} absorption bands. The CH-stretching couplet is distinctly biased to positive intensity, whereas a smaller, but significant negative VCD bias is present in the CD-stretching region. Similar VCD biases were observed for all three synthetic batches.

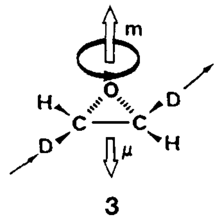
Normal coordinate analyses for both the tetraprotiooxirane and **1** were carried out with the ab initio force field of Lowe et al.[22] Calculated frequencies, mode symmetries, and schematic mode descriptions are shown in Figure 2. The mode correlation in Figure 2 shows that, although the relative magnitudes of the atomic displacements in the four modes change upon deuteriation, the relative phasings of the displacements do not change. The four modes maintain the symmetry order B, A, A, B from high to low frequency for both isotopomers.

From purely geometric considerations for the CH and CD oscillators in **1**, the A modes are predicted to be weak and the B modes intense. On the basis of the coupled oscillator model for the two chirally oriented CH or CD oscillators,[8] the four modes of **1** depicted in Figure 2 should give rise to a conservative (+,−) couplet, with the positive lobe at higher frequency, in each spectral region. The overall absorption and VCD patterns agree with these predictions.

The bias in the two couplets can arise from the ring current mechanism for VCD.[9] On the basis of the empirical rule 1 for an oscillator external to a ring but adjacent to a heteroatom in the ring,[1a,9b] contraction of a CH (or CD) bond injects electronic charge into the ring preferentially toward the oxygen, whereas elongation of the bond preferentially withdraws electronic charge from the oxygen. Positive ring current at constant electron density is initiated around the oxirane ring as shown in **2** and **3** for the B-symmetry stretches. The electric dipole transition moments μ and ring current magnetic dipole transition moment m for the B modes thus result in positive VCD bias in the CH-stretching region and negative VCD bias in the CD-stretching region, since the A modes are not enhanced. The smaller bias observed for the CD-stretching bands may be due partly to overlapping positive VCD intensity at ~2220 due to an A mode in Fermi resonance with the A fundamental.



2



3

Recent VCD intensity calculations in our laboratory using a vibronic coupling formulation with floating basis functions[10] have also predicted VCD couplets for these modes with the observed sense and bias. Investigation of the other chiral deuteriated isotopomers of oxirane and extension to the mid-infrared region are in progress.

Acknowledgment. This work was supported by grants from the National Institutes of Health (GM-23567 to L.A.N. and GM-36285 to J.M.S.) and the National Science Foundation (CHE 86-02854 to L.A.N. and T.B.F.).

Electrochromic Effects of Charge Separation in Bacterial Photosynthesis: Theoretical Models

Louise Karle Hanson and Jack Fajer*

Department of Applied Science
Brookhaven National Laboratory
Upton, New York 11973

Mark A. Thompson and Michael C. Zerner

Quantum Theory Project, University of Florida
Gainesville, Florida 32611

Received September 29, 1986

The primary charge separation in photosynthetic bacteria generates a dimeric bacteriochlorophyll (BChl) cation and a bacteriopheophytin (BPheo) anion[1-5] which lie within close proximity of each other (~10 Å).[6,7] The two radicals also lie

---

[21] The impurities are present as artifacts of the preparative procedure and thus can be eliminated in future batches of **1**.

[22] Lowe, M. A.; Alper, J. S.; Kawiecki, R.; Stephens, P. J. *J. Phys. Chem.* **1986**, *90*, 41-50.

[1] *Antennas and Reaction Centers of Photosynthetic Bacteria*: Michel-Beyerle, M. E., Ed.: Springer-Verlag: Berlin, 1985.

[2] Fajer, J.; Brune, D. C.; Davis, M. S.; Forman, A.; Spaulding, L. D. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 4956.

[3] Breton, J.; Martin, J.-L.; Migus, A.; Antonetti, A.; Orszag, A. *Proc. Natl. Acad. Sci. U.S.A.* **1986**, *83*, 5121. Martin, J.-L.; Breton, J.; Hoff, A. J.; Migus, A.; Antonetti, A. *Ibid.* **1986**, *83*, 957.

[4] Kirmaier, C.; Holten, D.; Parson, W. W. *Biochim. Biophys. Acta* **1983**, *725*, 190. Kirmaier, C.; Holten, D.; Parson, W. W. *Ibid.* **1985**, *810*, 33. Kirmaier, C.; Holten, D.; Parson, W. W. *Ibid.* **1985**, *810*, 49. Maroti, P.; Kirmaier, C.; Wraight, C.; Holten, D.; Pearlstein, R. M. *Ibid.* **1985**, *810*, 132. Kirmaier, C.; Holten, D.; Parson, W. W. *FEBS Lett.* **1985**, *185*, 76.

[5] Wasielewski, M. R.; Tiede, D. M. *FEBS Lett.* **1986**, *204*, 368.

0002-7863/87/1509-4728$01.50/0