mental evidence that **1**, **3**, and **4** are very easily reduced at both E_1 and E_2. By this experimental criterion it is certainly reasonable to consider that these annulene-diones are indeed quinones of an aromatic system.

Ronald Breslow,* Dennis Murayama, Robert Drury

*Department of Chemistry, Columbia University
New York, New York 10027*

Franz Sondheimer

*Chemistry Department, University College
London WC1H OAJ, England*
Received October 12, 1973

Infrared Circular Dichroism of Carbon–Hydrogen and Carbon–Deuterium Stretching Modes. Observations

Sir:

We report here the first measurements of optical activity arising from vibrations of molecules in the liquid state. Circular dichroism (CD) associated with the C*–H stretch (2920 cm⁻¹) is detected in the optically active liquids (S)-$(+)$- and (R)-$(-)$-2,2,2-trifluoro-1-phenylethanol, $CF_3CHOHC_6H_5$ (I). CD is also found at the C*–D stretch (2204 cm⁻¹) of (R)-$(-)$-neopentyl-*1-d* chloride, $(CH_3)_3CCHDCl$ (II). In our accompanying communication[1] the vibrational rotational strengths of these normal modes are calculated.

In contrast to optical activity arising from electronic transitions, which is readily measured in the visible and uv, Cotton effects of molecular vibrations had long eluded detection.[2] However, recent calculations[3–5] indicated the anticipated size of the vibrational effect and the kinds of structural information, such as absolute configuration or molecular conformation, which are latent in its measurement. Improved instruments have recently permitted the measurement of vibrational optical activity first in liquid crystals,[6] then in single crystals,[7] and now in fluids; our instrument has been previously described[8] except that a multiscan signal averager has been added. Observations of Raman circular intensity differentials[9] complement the present study.

In Figure 1 are shown the absorption and CD spectra

(1) T. R. Faulkner, A. Moscowitz, G. Holzwarth, E. C. Hsu, and H. S. Mosher, *J. Amer. Chem. Soc.*, **96**, 252 (1974).

(2) (a) T. M. Lowry, "Optical Rotary Power," Longmans Green and Co., London, 1935, Chapter 18; (b) H. R. Wyss and H. H. Günthard, *Helv. Chim. Acta*, **49**, 660 (1966).

(3) C. W. Deutsche and A. Moscowitz, *J. Chem. Phys.*, **49**, 3257 (1968); **53**, 2630 (1970).

(4) G. Holzwarth and I. Chabay, *J. Chem. Phys.*, **57**, 1632 (1972).

(5) J. A. Schellman, *J. Chem. Phys.*, **58**, 2882 (1973).

(6) (a) B. Schrader and E. H. Korte, *Angew. Chem.*, **84**, 218 (1972); (b) I. Chabay, *Chem. Phys. Lett.*, **17**, 283 (1972); (c) R. J. Dudley, S. F. Mason, and R. D. Peacock, *J. Chem. Soc., Chem. Commun.*, 1084 (1972); (d) G. Holzwarth, I. Chabay, and N. A. W. Holzwarth, *J. Chem. Phys.*, **58**, 4816 (1973).

(7) E. C. Hsu and G. Holzwarth, *J. Chem. Phys.*, in press.

(8) I. Chabay, E. C. Hsu, and G. Holzwarth, *Chem. Phys. Lett.*, **15**, 211 (1972).

(9) (a) B. Bosnich, M. Moskowitz, and G. A. Ozin, *J. Amer. Chem. Soc.*, **94**, 4750 (1972); (b) L. D. Barron, M. P. Bogaard, and A. D. Buckingham, *ibid.*, **95**, 605 (1973); *Nature (London)*, **241**, 113 (1973); (c) L. D. Barron and A. D. Buckingham, *J. Chem. Soc., Chem. Commun.*, 152 (1973); (d) M. Diem, J. L. Fry, and D. F. Burow, *J. Amer. Chem. Soc.*, **95**, 254 (1973).
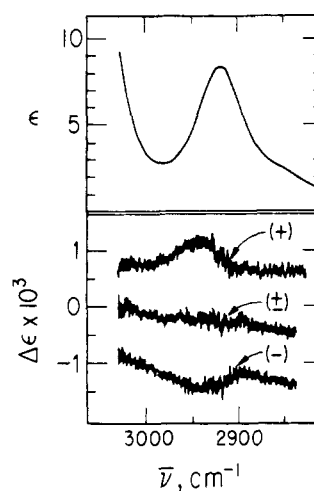

Figure 1. Infrared absorption (upper frame) and CD spectra (lower frame) of 2,2,2-trifluoro-1-phenylethanol, neat, with monochromator spectral bandpass 20 cm⁻¹ (full width at half-height). The CD spectra show the raw data exactly as recorded. A fivefold reduction in bandpass causes only 8% change in the absorption band half-width. The CD zero has been displaced between (+), (±), and (−) measurements; the actual curves are indistinguishable at 3030 cm⁻¹.

of (+)-, (−)-, and (±)-I between 3130 and 2800 cm⁻¹. The samples used compare favorably[10] to material prepared previously by us.[11] Moreover, it has been established that the (+)-enantiomer has the S configuration.[12] The absorption spectrum of I shows a peak at 2920 cm⁻¹, which must involve primarily a C*–H stretch at the α-carbon atom.[13] The increasing absorbance near 3030 cm⁻¹ arises from phenyl C–H stretching modes. Figure 1 shows that the C*–H band exhibits circular dichroism with $\Delta\epsilon/\epsilon = 6.5 \times 10^{-5}$. The rotational strength for this band is $+2 \times 10^{-44}$ esu² cm² for the (S)-$(+)$ enantiomer; the dipole strength is 1.4×10^{-39} esu² cm².

The CD maxima in Figure 1 occur about 20 cm⁻¹ higher in energy than the absorption maximum. Our calculations[1] show that this probably reflects a statistical weighting of the vibrational rotational strengths of various molecular conformations.

As shown in Figure 1, no CD is found, to present instrumental sensitivity, at the phenyl C–H stretching frequencies of I. This is not surprising, since these groups are well removed from the asymmetric center.

The second molecule in which we have detected vibrational optical activity, (R)-$(-)$-II, also possesses stretching modes involving a light atom attached to an asymmetric carbon (C*–H and C*–D). The CD and absorption spectra of (−)-II, synthesized as previously described,[14] reveal negative CD with $\Delta\epsilon/\epsilon = -2 \times 10^{-5}$ in the region of the C*–D stretch, 2204 cm⁻¹. The effect is small, so we are less certain of these data than

(10) Product of Burdick and Jackson Laboratories, Inc. Observed [α]D²⁷ +24.9 and −21.6° (c 2, CCl₄). A sample prepared by us and verified to be 99 + % enantiometrically pure (αD²⁶ −41.39° (neat); lit¹¹ αD²⁵ −41.18° (neat)) gave [α]D²⁰ −25.1° (c 3, CCl₄). The infrared absorption spectrum of the commercial sample between 4000 and 600 cm⁻¹ is identical with that of material prepared by Feigl and Mosher.¹¹

(11) D. M. Feigl and H. S. Mosher, *J. Org. Chem.*, **33**, 4242 (1968).

(12) H. M. Peters, D. M. Feigl, and H. S. Mosher, *J. Org. Chem.*, **33**, 4245 (1968).

(13) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen, London, 1958.

(14) B. Stephenson, G. Soladie, and H. S. Mosher, *J. Amer. Chem. Soc.*, **94**, 4814 (1972).

of those in Figure 1. The observed rotational strength is -2×10^{-45} esu^2 cm^2; the dipole strength is 1.0×10^{-39} esu^2 cm^2. The C*-H stretch, which is shown by the calculations[1] to enjoy a larger rotational strength, is difficult to study experimentally because of overlapping neopentyl C-H stretching modes.

The observed CD peaks shown in Figure 1 correspond to measured absorbance differences (base 10) of 2×10^{-5}. We checked for false peaks of this magnitude by three methods: (a) absorption base lines;[3] (b) racemic sample; (c) optically inactive molecules in an optically active solvent. No spurious CD was observed.

The present study has concentrated on C*-H and C*-D stretching modes of I and II because these are instrumentally favorable. We are now extending our experiments with these molecules to lower energies. A theoretical analysis of the structural sources of the observed vibrational CD is presented in our accompanying communication.[1]

G. Holzwarth,* Edward C. Hsu

*Departments of Biophysics and Chemistry, University of Chicago
Chicago, Illinois 60637*

Harry S. Mosher

*Department of Chemistry, Stanford University
Stanford, California 94305*

Thomas R. Faulkner, Albert Moscowitz

*Department of Chemistry, University of Minnesota
Minneapolis, Minnesota 55455*

Received September 18, 1973

Infrared Circular Dichroism of Carbon–Hydrogen and Carbon–Deuterium Stretching Modes. Calculations

Sir:

In our accompanying communication[1] we reported measurements of the circular dichroism (CD) associated with the C*-H stretch in (S)-$(+)$- and (R)-$(-)$-2,2,2-trifluoro-1-phenylethanol (I), and the C*-D stretch in (R)-$(-)$-neopentyl-*1-d*-chloride (II). Since these data represent the first observations of Cotton effects arising from molecular vibrations in the liquid state, it is of some current interest to inquire more fully into the molecular motions responsible for the optical activity. Accordingly, we have performed normal coordinate analyses for the molecules in question and calculated the vibrational rotational strengths for the pertinent Cotton effects.

The general equations employed for calculating the vibrational rotational strength R and the vibrational dipole strength D are essentially those given by Schellman[2] for the fixed atomic charge model but multiplied by a factor[3] of $(1/2\pi)$. The charges were initially chosen by a method described previously[4] so as to reproduce the bond dipole moments listed by Smith.[5] These charges were then scaled upward (factor of 1.6 for the C*-H moment in I, factor of 1.5 for the C*-D moment in II) so as to approximate the experimental D values obtained from the absorption spectra. These final charges were then used for computing the R values. Figure 1 shows the final charges (units of $e = 4.8 \times 10^{-10}$ esu) and the geometrical data employed.

The normal coordinate calculations were carried out in the manner described by Gwinn[6] and utilized a valence force field. In the case of I, the field consisted only of diagonal force constants chosen from standard references.[7-9] To keep the calculation of manageable size, the phenyl and CF$_3$ groups were treated as pseudoatoms of mass 28.0 and 24.0 amu, respectively. These values were chosen so as to put the C-C stretching modes near 900 cm^{-1}, the approximate frequency of a C-C stretch.[10] The final results for I are given in Table I for the staggered conformation

Table I. Rotational and Dipole Strengths for (S)-$(+)$-2,2,2-Trifluoro-1-phenylethanol

	$\bar{\nu}$ (cm^{-1})	R (esu cm)^2	D (esu cm)^2
Obsd	2910	2×10^{-44}	1.4×10^{-39}
Calcd	2936	2.5×10^{-45}	1.5×10^{-39}

shown in Figure 1, along with the experimental values. To test, in part, the effects of the pseudoatom approximation, a more elaborate calculation was performed in which the pseudoatom approximation for CF$_3$ was relaxed. This produced no qualitative changes in the optical activity associated with the C*-H stretching mode.

The calculations show that the R value for the 2900-cm^{-1} C*-H transition arises principally from the mixing of a small amount of the C-O-H angle bend (large magnetic dipole transition moment) with the C*-H stretching mode (large electric dipole transition moment). The mixing and the sign and magnitude of the resultant R value depend strongly on the position of the O-H bond relative to the C*-H bond. This interpretation is unaffected by modest changes in the diagonal force constants or by the introduction of off-diagonal force constants that connect motions in the C-O-H moiety to motions in the rest of the molecule. For example,

(3) Using a matrix formalism, we have also derived the equations pertinent to the fixed atomic charge model. Our final expressions for R and D are entirely equivalent to those published by Schellman except for a constant multiplicative factor of $(1/2\pi)$. Schellman (private communication) informs us that the missing factor of $(1/2\pi)$ is just the result of a typographical error, and that his calculations published in ref 2 actually include the $(1/2\pi)$.

(4) C. W. Deutsche and A. Moscowitz, *J. Chem. Phys.*, **49**, 3257 (1968); **53**, 2630 (1970).

(5) J. S. Smith, "Electric Dipole Moments," London, Butterworths, 1955.

(6) W. D. Gwinn, *J. Chem. Phys.*, **55**, 477 (1971).

(7) E. B. Wilson, J. C. Decius, and P. Cross, "Molecular Vibrations," McGraw-Hill, New York, N. Y., 1955.

(8) G. Herzberg, "Infrared and Raman Spectra," Van Nostrand-Rheinhold, New York, N. Y., 1955.

(9) A detailed listing of all the force constants used in the calculations described in this work for I and II and the resultant frequency assignments is available from the authors upon request.

(10) R. T. Conley, "Infrared Spectroscopy," Allyn and Bacon, Boston, Mass., 1966.

(1) G. Holzwarth, E. C. Hsu, H. S. Mosher, T. R. Faulkner, and A. Moscowitz, *J. Amer. Chem. Soc.*, **96**, 251 (1974).

(2) J. A. Schellman, *J. Chem. Phys.*, **58**, 2882 (1973).