No signals arising from the α-fructopyranose anomer (**2a**) were detected. Peak intensities yielded the following composition: 39 ± 4% **2b**, 20 ± 2% **2c**, 41 ± 4% **2d**, and less than 4% **2a**. We were not able to accumulate a spectrum quickly enough to observe a composition far removed from equilibrium. Specific assignments of the fructose resonances were made on the basis of the D-fructose chemical shifts (Table I). The fructose nonprotonated resonances of all the anomers fall in the same spectral region as the methine carbon at position 1 of the glucopyranose ring. The methine resonances were distinguished from the nonprotonated ones by means of partially relaxed Fourier transform spectra.[2] It is interesting that a separate glucopyranose C-1 resonance was observed for each anomer.[15] There was also evidence for chemical shift differences between the anomers at other glucopyranose positions. Thirty-one resonances were identified in the spectrum of aqueous D-turanose!

Carbon-13 Fourier transform nmr has a very promising future in detailed studies of anomeric processes in saccharide solutions.

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(15) Chemical shifts of 92.0, 94.5, and 96.0 ppm upfield from carbon disulfide.

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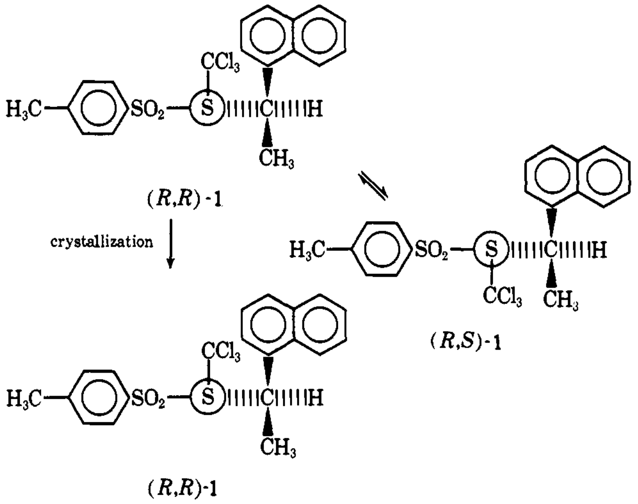
The Sulfenamide Chiral Axis. Nuclear Magnetic Resonance, Optical Rotatory Dispersion, and Circular Dichroism Spectra[1a,b]

Sir:

Nmr experiments have demonstrated that the sulfenamide grouping, $R_1SNR_2R_3$, is dissymmetric, and that the axial chirality of this moiety derives from restricted rotation about the N–S bond rather than slow inversion of the nitrogen pyramid.[2,3] Optical activity in compounds containing this chiral unit has not yet been reported. This communication describes the nmr, ORD, and CD spectra of a sulfenamide, the absolute configuration of which has been determined using single-crystal X-ray diffraction.[4] Correlation of the configuration in the solid state with that in solution was made using nmr spectroscopy.

Since the sulfenyl S–N bond is conformationally labile, with a free energy of activation for racemization of only 12–19 kcal/mol,[2,3] resolution of a racemic modification was not practical. However, asymmetry could be induced into the sulfenamide chiral axis from an asymmetric carbon atom in an equilibrium asymmetric induction[5] which occurs when both chiral units are present in the same molecule.

Accordingly, we chose for this study a compound which possesses an asymmetric carbon atom in addition to the sulfenamide unit, *N*-(1-α-naphthylethyl)-*N*-benzenesulfonyltrichloromethanesulfenamide (**1**). As two chiral units are present, diastereomerism is possible. Since **1** was prepared from the benzenesulfonamide of optically pure (*R*)-(+)-1-(1-naphthyl)ethylamine,[6] the configuration at the asymmetric carbon atom is determined and must be (*R*). The two diastereomers thus have the (*R*,*R*) and (*R*,*S*) absolute configurations,[7] *i.e.*, they are epimeric at the chiral axis. The configurations of the two isomers are represented in Newman–Fischer projection formulas (*R*,*R*)-**1** and (*R*,*S*)-**1**.



This diastereomerism is reflected in the room temperature nmr spectrum of **1** in methylene chloride, especially in the region of the C-methyl resonances, which appear as two unequal doublets centered at δ 1.72 (J = 7 Hz) and 2.06 (J = 7 Hz) corresponding to a ratio of diastereomers of 1.85:1.0 (Figure 1). A similar situation obtains in acetonitrile-d_3 solution; the two doublets resonate at δ 1.54 and 2.01, and the equilibrium constant is 2.0:1.0. Thus equilibrium asymmetric induction results in a ratio of torsional epimers which differs from unity.

The configuration of the major (upfield) isomer was shown to be (*R*,*R*) in the following manner. Crystallization of **1** is accompanied by second-order asymmetric transformation and the solid material is composed of a single diastereomer[8] which has been shown by single-crystal X-ray diffraction analysis to have the absolute (*R*,*R*) configuration.[4] Interconversion of the diastereomers is rapid on the nmr time scale, since the torsional barrier of the N–S bond has a magnitude of only *ca.* 18.0 kcal/mol ($\Delta\nu$ = 20.5 Hz, T_c = 78°). On

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(1) (a) XII. Stereochemistry at Trivalent Nitrogen. Part XI: M. Raban and F. B. Jones, Jr., *J. Amer. Chem. Soc.*, **93**, 2692 (1971). (b) Abstracted from the M.S. Thesis of S. K. Lauderback, Wayne State University, 1970.

(2) M. Raban and F. B. Jones, Jr., *J. Amer. Chem. Soc.*, **91**, 2180 (1969).

(3) M. Raban, G. W. J. Kenney, Jr., and F. B. Jones, Jr., *ibid.*, **91**, 6677 (1969).

(4) J. Kay, M. Glick, and M. Raban, *ibid.*, in press.

(5) M. Carmack and L. A. Neubert, *ibid.*, **89**, 7134 (1967).

(6) M. G. Drew, *Acta Crystallogr., Sect. B*, **25**, 1320 (1969); J. Jacobus, M. Raban, and K. Mislow, *J. Org. Chem.*, **33**, 1142 (1968).

(7) We have arbitrarily chosen the first designation as referring to the asymmetric carbon atom and the second to the sulfenyl chiral axis. In applying the Cahn–Ingold–Prelog convention for chiral axes to the sulfenamide bond it is necessary to use the ligancy complementation rule to generate an additional "phantom" ligand of zero atomic weight attached to sulfur on the side opposite to the trichloromethyl group. The order of priority of the ligands is CCl_3 > phantom > $C_6H_5SO_2$ > $C_{12}H_{11}$.

(8) M. Raban, G. W. J. Kenney, Jr., J. M. Moldowan, and F. B. Jones, Jr., *J. Amer. Chem. Soc.*, **90**, 2985 (1968).

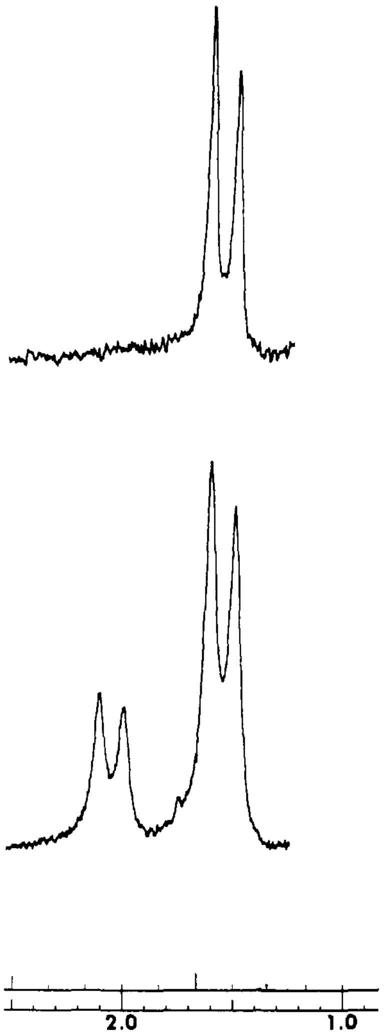

Figure 1. Nmr spectra of **1** in methylene chloride. The upper spectrum was measured at −50° after dissolution at *ca.* −70°. The lower spectrum was measured at −50° after dissolution at room temperature.

the basis of this free energy of activation for epimerization, we calculated that interconversion could be slowed on the isolation time scale at temperatures below about −50°. Accordingly, a sample of configurationally homogeneous, solid **1** was placed into solution at *ca.* −70°. When the nmr spectrum was measured at *ca.* −50° without prior warming of the sample, only one doublet was observed, that corresponding to the major (upfield) isomer (Figure 1). When the temperature was raised to −25° a small doublet centered at δ 2.1 appeared and grew in intensity as torsional epimerization occurred and the minor isomer was formed.

Since the absolute configuration of the solid isomer has been shown to be (*R*,*R*)-**1** using X-ray diffraction, we can now assign the (*R*,*R*) configuration to the major isomer (which corresponds to the upfield doublet) and the (*R*,*S*) configuration to the minor isomer (which gives rise to the low-field doublet). Thus, the conformation at the S–N chiral axis is the same in the solid as in the major isomer in solution. This situation does not always obtain; we have recently reported an example wherein the configurations at a labile configurational unit in the crystal and in the predominant isomer in solution are different.[9]

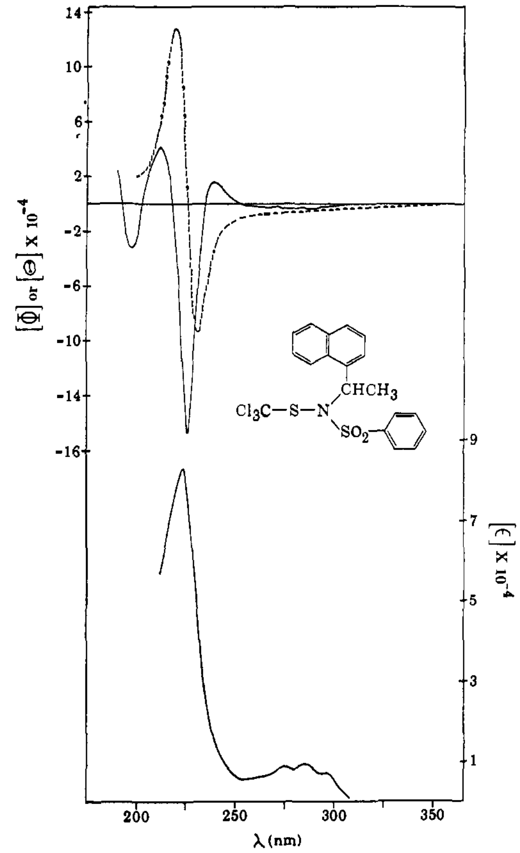

Figure 2. Optical rotatory dispersion, circular dichroism, and ultraviolet absorption spectra of **1** in acetonitrile: upper curves, CD (—), ORD (- - -); lower curve, uv.

The induction of asymmetry from the asymmetric carbon atom to the S–N chiral axis permits the measurement of the optical activity due to this chiral unit. Even though torsion about the S–N bond is rapid at room temperature, the presence of the (*R*)-naphthylethyl moiety ensures that the epimer with the (*R*) configuration at the S–N axis will be present in excess over the isomer with the (*S*) configuration.

The ORD, CD, and uv spectra of an equilibrium mixture of **1** in acetonitrile are shown in Figure 2. The ORD spectrum apparently features only a single high-amplitude negative Cotton effect centered at 226 nm [RD (*c* 0.02, CH_3CN): $[\phi]_{231}$ −94,000°; $[\phi]_{226}$ 0°; $[\phi]_{220}$ +127,000°], in addition to several weak inflections at longer wavelength. These weaker effects were noted as a shoulder at 240 nm and as a broad inflection in the 260–290-nm region, superimposed on the intense negative tail of the Cotton effect centered at 226 nm. The exceptionally large molecular amplitude of the major Cotton effect ($a = 2210°$) dominates the optical rotatory dispersion spectrum throughout the ultraviolet region and is responsible for the sign of rotation observed at the sodium D line, $[\alpha]^{28}\mathrm{D}$ −62° (*c* 0.20, acetonitrile); $[\alpha]^{28}\mathrm{D}$ −72° (*c* 0.40, absolute ethanol); $[\alpha]^{28}\mathrm{D}$ −82° (*c* 0.20, methylene chloride). Essentially identical spectra were measured in absolute ethanol [RD (*c* 0.02, CH_3CH_2OH): $[\phi]_{233}$ −89,900°; $[\phi]_{228}$ 0°; $[\phi]_{221}$ +144,000°].

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[9] E. Carlson, F. B. Jones, Jr., and M. Raban, *Chem. Commun.*, 1235 (1969); M. Raban and E. Carlson, *J. Amer. Chem. Soc.*, **93**, 685 (1971).

By contrast, the CD spectrum demonstrates that there are, in fact, a number of optically active transitions in the 195–255-nm region [CD (*c* 0.02, CH_3CN): $[\theta]_{198}$ −32,300°; $[\theta]_{212}$ +39,200°; $[\theta]_{226}$ −168,000°; $[\theta]_{239}$ +15,700°]. The large negative Cotton effect centered at 226 nm corresponds to the negative Cotton effect which dominates the rotatory dispersion curve. Although the positive Cotton effect at 239 nm does not give rise to extrema in the ORD, it is responsible for the reduction in intensity of the first extremum of the ORD curve. Moreover, the broad band in the 260–290-nm region appears clearly in the CD spectrum as a series of negative Cotton effects which appear to be associated with the fine structure in the uv spectrum.[10]

If the major low-wavelength Cotton effect observed in the ORD and CD spectra is determined by the configuration at the sulfenamide chiral axis rather than the configuration at the asymmetric carbon atom, the Cotton effects in the two diastereomers (*R*,*R*)-**1** and (*R*,*S*)-**1** will be different in sign.[11] If this is the case, and we believe it is likely, the molecular amplitude of the arenesulfonylsulfenamide chromophore must, in actuality, be substantially greater than that observed since there would be considerable cancellation. These rotations may be compared with those of other powerfully rotating chromophores which have been described as "inherently dissymmetric."[12]

Acknowledgment. We gratefully acknowledge support for this work in the form of grants from the National Science Foundation (GP 17092) and the Edmond de Rothschild Foundation. The Cary-60 spectropolarimeter used in this study was provided by an equipment grant from the National Science Foundation (GP-6936). We thank Mr. J. M. Moldowan for some preliminary experiments.

(10) Discussion of the chromophores and transitions involved is deferred to the detailed paper.

(11) If the diastereomers of (*R*,*R*)-**1** exhibit a Cotton effect at 226 nm, then either the epimer at the sulfenamide unit (*R*,*S*)-**1** or the epimer at the asymmetric carbon atom (*S*,*R*)-**1** must show a Cotton effect of inverted sign. We feel that it is at least as likely that a change in the configuration at the sulfenyl unit will reverse the sign since compounds containing only asymmetric carbon atoms as dissymmetric units do not usually exhibit Cotton effects of this magnitude.

(12) P. Crabbé, "Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry," Holden-Day, San Francisco, Calif., 1965, Chapter 8, and references therein.

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Effect of Pressure on the Kinetics of the Exchange of Oxygen-18 between Hexaaquochromium(III) Ion and Solvent Water. Evidence for an Associative Interchange Mechanism

Sir:

The volume of activation ΔV^* affords a useful criterion of reaction mechanism, since the spatial requirements of the various alternative models can be easily visualized. We have therefore measured the pressure dependence of the rate of reaction 1, since other evidence[1–3] has suggested that aqueous aquochromium(III) species may undergo substitution by an associative interchange mechanism (I_a).[4] Such mechanisms have hitherto been considered rare in octahedral complexes.[5]

$$Cr(H_2O)_6^{3+} + H_2{}^{18}O \longrightarrow Cr(H_2O)_5(H_2{}^{18}O)^{3+} + H_2O \qquad (1)$$

Aliquots (5.0 ml) of an aqueous solution of hexaaquochromium(III) perchlorate (1.00 *M*) in perchloric acid (1.00 *M*) were diluted to 50.0 ml with 1.5% $H_2{}^{18}O$ (Bio-Rad Laboratories) and thermostated at 45.00 ± 0.05° in a specially constructed Lucite syringe which was pressurized in a steel bomb with hydraulic oil from a hand pump, and from which samples could be withdrawn through a stainless-steel capillary tube fitted with a stainless-steel high-pressure valve.[6] At appropriate intervals, samples of the solution were withdrawn and chilled to 0°, and the hexaaquochromium(III) ion was precipitated as $Cr(H_2O)_6PO_4$.[7] The dried solid was decomposed at ~140° in a vacuum system and the liberated water was condensed onto guanidine hydrochloride for conversion to carbon dioxide.[8] The abundance of ${}^{12}C^{16}O^{18}O$ relative to ${}^{13}C^{16}O_2$ was measured using a Hitachi Perkin-Elmer RMU-6D mass spectrometer, taking the mean of ten scans; relative abundances measured in duplicate experiments agreed within 2%. The first-order rate coefficients *k* for the exchange of *all six* coordinated water molecules were determined at seven different pressures ranging from 1.0 bar to 2.48 kbars. Triplicate measurements at 1.0 bar showed the reproducibility of *k* to be better than ±3%, regardless of whether reaction 1 had been carried out in the pressure assembly or in a darkened Pyrex vessel, and the mean (4.47×10^{-5} sec^{-1}) agreed satisfactorily with the value obtained by Arrhenius extrapolation of the data of Hunt and Plane[7] (4.2×10^{-5} sec^{-1}).

Figure 1 shows that log *k* is accurately a linear function of the pressure *P* within the experimental uncertainty, with $|(\partial \Delta V^*/\partial P)_T|$ close to zero and certainly not greater than 2×10^{-4} cm^3 bar^{-1} mol^{-1}, up to 2.5 kbars at least. A least-squares analysis gave $k = (4.49 \pm 0.09) \times 10^{-5}$ sec^{-1} at zero pressure and $\Delta V^* = -9.3 \pm 0.3$ cm^3 mol^{-1}.

Clearly, the transition state of reaction 1 must occupy a markedly smaller volume than the reactants. Since electrostrictive effects will be absent in this reaction, we can conclude that activation by the incoming water molecule is important, *i.e.*, that this water molecule is in the first coordination sphere of the chromium(III) ion in the transition state. Hunt and Taube[9] found $\Delta V^* = +1.2$ cm^3 mol^{-1} for the reaction

$$Co(NH_3)_5{}^{18}OH_2^{3+} + H_2O \longrightarrow Co(NH_3)_5OH_2^{3+} + H_2{}^{18}O \qquad (2)$$

which almost certainly proceeds by a dissociative mechanism,[4] so the volume changes associated with the actual forming or breaking of an aquo-metal bond[10]

(1) R. J. Baltisberger and E. L. King, *J. Amer. Chem. Soc.*, **86**, 795 (1964).

(2) J. H. Espenson, *Inorg. Chem.*, **8**, 1554 (1969).

(3) L. R. Carey, W. E. Jones, and T. W. Swaddle, *ibid.*, in press.

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(7) J. P. Hunt and R. A. Plane, *J. Amer. Chem. Soc.*, **76**, 5960 (1954).

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(9) H. R. Hunt and H. Taube, *J. Amer. Chem. Soc.*, **80**, 2642 (1958).

(10) The volume decrease due to the partial formation of an aquo-metal bond in the transition state of an associative interchange process may be offset by a volume increase due to concomitant stretching of the bond to the ligand being replaced, so that the net contribution of bond