

Registry No. **3a**, 55681-24-8; **3b**, 55681-23-7; **7**, 56742-34-8; **9**, 4734-51-4; **10**, 3333-35-5; **11**, 73378-22-0; **12**, 56742-35-9; (*E*)-**13**, 73378-23-1; (*Z*)-**13**, 73378-24-2; **14**, 73378-25-3; (*E*)-**17**, 73378-26-4; (*Z*)-**17**, 73384-21-1; **18**, 53555-45-6; **19**, 1120-65-6; **21**, 73378-28-6; **22**,

26223-16-5; **23**, 31909-46-3; **24**, 53555-44-5; ethylene dibromide, 106-93-4; dimethyl acetylenedicarboxylate, 762-42-5; acetaldehyde semicarbazone, 591-86-6; morpholine, 110-91-8; potassium cyanide, 151-50-8; selenium, 7782-49-2.

Chiroptical Properties of Sulfenamides¹

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The ORD (and in some cases CD) spectra are presented for 11 sulfenamides of the structure R'SN(SO₂Ar)CH(CH₃)R (R' = CCl₃, 4-chloro-2-methylphenyl, 2-nitrophenyl, 2,4-dinitrophenyl; R = phenyl, 1-naphthyl, benzyl; Ar = *p*-tolyl). A number of the spectra exhibit intense Cotton effects characteristic of inherently dissymmetric chromophores near 200 nm. The configuration at the asymmetric carbon atom seems to be related to the sign of the long-wavelength transition (near 350 nm) in the 2,4-dinitrobenzenesulfenamides. This is ascribed to an equilibrium asymmetric induction from the asymmetric center into the sulfenamide chiral axis whose configuration is reflected by the sign of this Cotton effect. It is suggested that examination of such derivatives may provide a useful method for determination of the absolute configuration of amines.

The chiroptical properties of compounds bearing sulfur-containing chromophores have been the subject of extensive experimental and theoretical work.² This work has been directed, for the most part, at functional groups with sulfur in the S^{II} and S^{IV} oxidation states. Among the S^{II} compounds, three classes are important, the sulfides, the disulfides, and the compounds with π bonding or π conjugation by divalent sulfur. The sulfenamides, however, represent a class of S^{II} compounds whose chirality is well established³⁻⁵ but whose chiroptical properties have received almost no attention.⁴

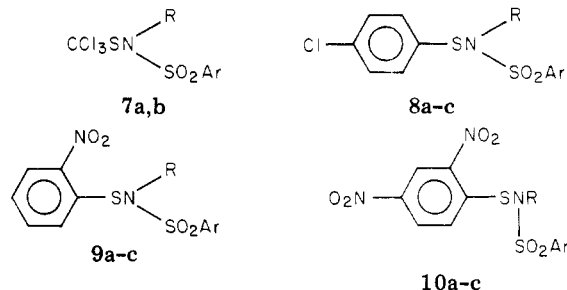
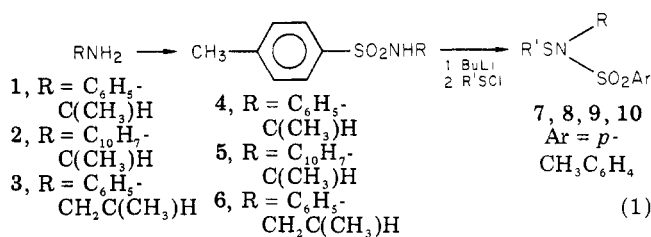
Extensive NMR studies have demonstrated that the sulfenamide moiety can function as an axially chiral configurational unit. Thus, it was supposed that the sulfenamide moiety, if involved in an optically active transition, might give rise to Cotton effects of large magnitude since the same structural feature can function both as a chiral unit and as a chromophore (or part of a chromophore). In this regard the sulfenamide group is like the disulfide chromophore which has been described as an "inherently dissymmetric chromophore" rather than like the sulfide chromophore which is a symmetric chromophore which can suffer dissymmetric perturbation.^{2a}

Ideally, examination of the chiroptical properties of the sulfenamide moiety would involve the optical activation of compounds containing the sulfenamide group as the sole chiral unit. However, the highest yet reported barrier for stereomutation at the sulfenamide chiral unit (21.4 kcal/mol)³ is insufficient for optical stability at room temperature, and this is not yet possible. Nevertheless, it is possible to induce chirality into the sulfenamide chiral

unit by equilibrium asymmetric induction.⁵ We have chosen this approach and have prepared several *N*-arenesulfonylsulfenamides whose ORD and/or CD spectra offer some information about the chiroptical properties of the sulfenamide group.

Results and Discussion

Three optically active amines of known absolute configuration, (+)-(*R*)- α -methylbenzylamine⁶ (**1**), (+)-(*R*)-1-(α -naphthyl)ethylamine⁷ (**2**), and (-)-(*R*)-1-methyl-2-phenylethylamine⁸ (**3**), were converted via their sulfonamides into the 11 *N*-(arenesulfonyl)sulfenamides **7**, **8**, **9**, and **10** as indicated in eq 1. The spectral features (ex-



a, R = C₆H₅C(CH₃)H; b, R = C₁₀H₇C(CH₃)H; c, R = C₆H₅CH₂C(CH₃)H

trema and crossover points) of their ORD spectra are summarized in Table I.

(1) (a) Stereochemistry in Trivalent Nitrogen Compounds. 36. For the previous paper in this series see ref 3. (b) This work was supported by the National Science Foundation.

(2) Reviews: (a) Tonolio, C. *Int. J. Sulfur Chem.* 1973, 8, 96. (b) Legrand, M.; Rougier, M. J. In "Stereochemistry—Fundamentals and Methods"; Kagan, H. B., Ed.; Georg Thieme Verlag: Stuttgart, 1977; Vol. 2, pp 33-183.

(3) Raban, M.; Yamamoto, G. *J. Am. Chem. Soc.*, 1979, 101, 5890; 1977, 99, 4160.

(4) Raban, M.; Lauderback, S. K. *J. Am. Chem. Soc.* 1971, 93, 2781.

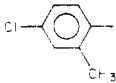
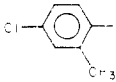
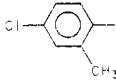



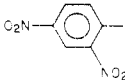
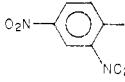
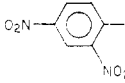
(5) Raban, M.; Carlson, E. M. *Isr. J. Chem.* 1976, 15, 106.

(6) Leithe, W. *Chem. Ber.* 1931, 64, 2827.

(7) Wolf, H.; Bunnenberg, E.; Djerassi, C. *Chem. Ber.* 1964, 97, 533.

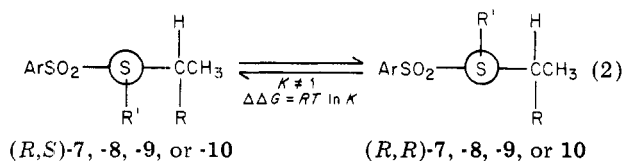
(8) Karrer, P.; Ehrhardt, E. *Helv. Chim. Acta* 1951, 34, 2202.

Table I. ORD Spectra of Sulfenamides 7-10 and 12 in Absolute Ethanol

compd	R'	R	ORD spectral features (molecular rotation in deg)
7a	CCl ₃	CH(CH ₃)C ₆ H ₅	[Φ] ₂₀₅ + 3400; ^a [Φ] ₂₁₃ + 18 700; [Φ] ₂₁₉ 0; [Φ] ₂₂₆ - 35 500; [Φ] ₂₄₀ 0; [Φ] ₂₅₃ + 11 900; [Φ] ₆₀₀ + 170 ^a
7b	CCl ₃	CH(CH ₃)C ₁₀ H ₇	[Φ] ₁₉₅ + 59 400; ^a [Φ] ₂₀₅ + 5990; [Φ] ₂₂₁ + 144 000; [Φ] ₂₂₈ 0; [Φ] ₂₃₂ - 89 900; [Φ] ₆₀₀ - 322 ^a
8a		CH(CH ₃)C ₆ H ₅	[Φ] ₂₁₃ + 37 700; [Φ] ₂₄₀ ~ 0; ^b [Φ] ₂₅₅ + 3940; [Φ] ₂₈₃ 0; [Φ] ₃₀₀ - 3020; [Φ] ₆₀₀ - 115 ^a
8b		CH(CH ₃)C ₁₀ H ₇	[Φ] ₂₀₂ 0; [Φ] ₂₁₄ + 192 000; [Φ] ₂₃₃ 0; [Φ] ₂₅₀ - 60 000; [Φ] ₆₀₀ - 1190 ^a
8c		CH(CH ₃)CH ₂ C ₆ H ₅	[Φ] ₂₁₃ 0; [Φ] ₂₂₃ - 6620; [Φ] ₂₆₀ - 87; [Φ] ₃₂₀ - 383; [Φ] ₆₀₀ - 89.7 ^a
9a		CH(CH ₃)C ₆ H ₅	[Φ] ₂₁₅ 0; [Φ] ₂₂₈ - 73 000; [Φ] ₂₄₀ 0; [Φ] ₂₄₉ + 47 700; [Φ] ₂₆₅ 0; [Φ] ₂₇₃ - 1840; [Φ] ₂₇₉ 0; [Φ] ₃₁₀ + 10 600; [Φ] ₃₆₃ 0; [Φ] ₃₉₀ - 5740; [Φ] ₆₀₀ - 549 ^a
9b		CH(CH ₃)C ₁₀ H ₇	[Φ] ₂₀₀ 0; [Φ] ₂₀₇ - 170 000; [Φ] ₂₁₆ 0; [Φ] ₂₂₄ + 414 000; [Φ] ₂₃₉ 0; [Φ] ₂₅₂ - 90 900; [Φ] ₂₉₂ 0; [Φ] ₃₁₈ + 12 200; [Φ] ₃₅₉ 0; [Φ] ₃₉₅ - 15 000; [Φ] ₆₀₀ - 2320 ^a
9c		CH(CH ₃)CH ₂ C ₆ H ₅	[Φ] ₂₁₀ - 637; ^a [Φ] ₂₄₃ - 1450; [Φ] ₂₉₀ 0; [Φ] ₃₀₅ + 67; [Φ] ₃₃₅ 0; [Φ] ₄₃₀ - 125; [Φ] ₆₀₀ - 73.8 ^a
10a		CH(CH ₃)C ₆ H ₅	[Φ] ₂₁₂ 0; [Φ] ₂₂₁ - 31 300; [Φ] ₂₃₀ 0; [Φ] ₂₃₅ + 8810; [Φ] ₂₄₃ + 1420; [Φ] ₂₈₀ + 10 900; [Φ] ₂₉₅ + 9190; [Φ] ₃₂₀ + 14 600; [Φ] ₃₅₇ 0; [Φ] ₃₈₀ - 8000; [Φ] ₆₀₀ - 545 ^a
10b		CH(CH ₃)C ₁₀ H ₇	[Φ] ₂₀₈ 0; [Φ] ₂₂₁ + 272 000; [Φ] ₂₂₉ 0; [Φ] ₂₃₂ - 31 400; [Φ] ₂₄₅ - 4190; [Φ] ₂₆₀ - 14 700; [Φ] ₂₇₇ 0; [Φ] ₃₀₇ + 28 800; [Φ] ₃₄₇ 0; [Φ] ₃₉₀ - 23 600; [Φ] ₆₀₀ - 2620 ^a
10c		CH(CH ₃)CH ₂ C ₆ H ₅	[Φ] ₂₆₀ - 585; ^a [Φ] ₂₇₄ - 5380; [Φ] ₂₉₆ 0; [Φ] ₃₁₀ + 2590; [Φ] ₃₅₃ 0; [Φ] ₃₉₀ - 1620; [Φ] ₆₀₀ - 142 ^a
12			[Φ] ₂₀₀ 0; [Φ] ₂₁₉ + 29 900; [Φ] ₂₂₇ 0; [Φ] ₂₃₀ - 11 400; [Φ] ₂₅₅ - 2820; [Φ] ₂₆₅ - 3770; [Φ] ₂₈₁ 0; [Φ] ₂₉₇ + 7640; [Φ] ₆₀₀ + 410

^a Labeled molecular rotations refer to rotations at ca. 600 nm or the short-wavelength end of the measured spectrum not to the extrema. ^b This point corresponds to a trough at which the rotation was too low to be measured (i.e., zero within experimental error).

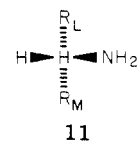
Each of these sulfenamides possesses a stereostable chiral unit of known absolute configuration (an asymmetric carbon atom) in addition to the stereolabile sulfenamide chiral axis. The equilibrium asymmetric induction⁵ involves the equilibrium in eq 2. While the equilibrium



R = phenyl, α -naphthyl, benzyl; Ar = *p*-tolyl

constant between two enantiomers which differ in configuration at a sulfenamide chiral axis must be unity, the presence of the asymmetric carbon atom destroys the degeneracy, and the two stereoisomers (diastereomers) in eq 2 must have different free energies of formation and be present in different amounts at equilibrium. This preference for one of the two possible configurations at the stereolabile chiral unit is the result of interaction with a stereostable chiral unit. Thus we regard the equilibrium constant between the two stereoisomers as a measure of the equilibrium asymmetric induction caused by the asymmetric carbon atom.

All three amines have the *R* configuration which corresponds to the arrangement of ligands 11 where R_L and R_M



represent large- and medium-sized ligands. Since the asymmetric synthesis is expected to be governed by steric factors, we expect all three asymmetric centers to induce a preference for the same configuration at carbon. The magnitude of the induction should be greatest when the difference in size between the large (R_L = phenyl, 1-naphthyl, or benzyl) and medium groups (R_M = CH₃) is greatest. The magnitude of the induction can be measured by NMR spectroscopy at temperatures where the stereomutation is rapid on the isolation time scale (assuming that equilibrium is reached) but is slow on the NMR time scale, allowing the ratio of stereoisomers to be determined by integration of corresponding signals from the two diastereomers. Under certain circumstances this induction should also be reflected in ORD/CD spectra. If the stereolabile chiral unit corresponds to a chromophore with a much greater rotatory power than that of the stereostable chiral unit and is not greatly perturbed by the stereostable

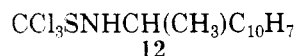
chiral unit, then the spectra of the two diastereomers will be quasi-enantiomeric. The ORD/CD spectra of the two diastereomers will then partially cancel one another, the resultant will be similar to the spectrum of the predominant diastereomer, although of diminished intensity, and the resultant intensity should reflect the magnitude of the induction. If this situation were to apply, it would be possible to determine the direction and magnitude of the asymmetric induction by examination of a characteristic absorption in the ORD or CD spectrum. Several readily obtainable sulfonyl halides were chosen to see if a derivative with a suitable ORD or CD spectrum would result from one of them.

The ORD spectrum of the initial compound examined, **7b**, suggested that trichloromethanesulfenamides might be suitable derivatives for this purpose. The ORD spectrum⁹ of **7b** featured only two extrema corresponding to a negative Cotton effect in the range of 210–600 nm, a trough at 232 nm, and a peak at 221 nm with a crossover point at 228 nm. The peak to trough difference was very large, 233 000°, suggestive of an inherently dissymmetric chromophore. The CD spectrum, however, indicated that there were actually several closely spaced Cotton effects in the short-wavelength region ($[\Phi]_{198} -32\,000^\circ$, $[\Phi]_{212} +39\,200^\circ$, $[\Phi]_{226} -168\,000^\circ$, $[\Phi]_{239} +15\,700^\circ$) and that the ORD spectrum was dominated by the negative Cotton effect at 226 nm which has a much greater amplitude than the others. Although there are several closely spaced transitions, it might still be possible to use this derivative if one of them were always more intense and dominated the ORD spectrum.

However, the examination of the ORD spectrum of **7a** (which has the corresponding configuration at the asymmetric carbon atom) indicated three extrema in this wavelength range: 253 nm (peak), 226 nm (trough), and 213 nm (peak). The peak to trough rotational difference ($[\Phi]_{213} - [\Phi]_{226} = 54\,200^\circ$) was also considerably smaller, but this likely reflects the considerably smaller induction by this asymmetric center.

Examination of the CD spectra of the two compounds indicates the reason for the dramatic difference in the appearance of the ORD spectra and the difference in the signs of their rotations at the sodium D line, although they have corresponding configurations at the asymmetric carbon atom. The CD spectra of both compounds feature positive Cotton effects at longer wavelengths followed by another negative effect at shorter wavelength. While this second effect is much more intense in **7b** and dominates the spectrum,⁹ the two effects are of comparable magnitude in **7a** (Figure 1).

In order to determine whether the *N*-sulfonyl group was necessary for the observation of optically active transitions of high rotatory strength, we also examined the spectrum of **12** which has the same structure as **7b**, but with a hy-



drogen replacing the toluenesulfonyl group on nitrogen. The ORD spectrum for this compound was also complex, featuring a positive long-wavelength Cotton effect centered near 280 nm and other overlapping Cotton effects at shorter wavelength (Figure 7). The most intense extremum, the peak at 219 nm ($[\Phi]_{219} +29\,900^\circ$), appears to be associated with a positive Cotton effect centered near 200

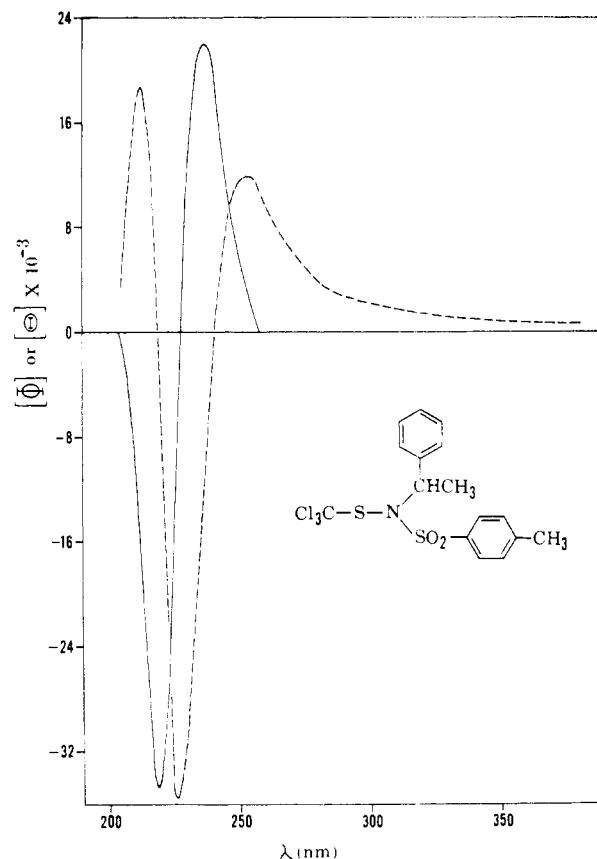


Figure 1. Optical rotatory dispersion and circular dichroism spectra of **7a** in absolute ethanol: CD (—), ORD (---).

nm which is fairly intense. Although the spectrum differs substantially from that of **7b**, it is clear that the presence of the arenesulfonyl group is not necessary for the observation of highly optically active transitions in these compounds.

Consideration of the transitions responsible for these bands can offer one possible explanation for the very different behavior of the phenyl and naphthyl compounds **7a** and **7b**. While it is not possible to make definitive assignments, we note the Cotton effects of **7a** occur in the expected region for aromatic ¹B and ¹L_a bands of the phenyl ring. Optically active transitions in this region are also observed in simple aralkylamines.¹⁰ We hypothesize that they derive from transitions which involve coupling between the aromatic and sulfenamide systems. If this is the case, they may not be reliable indicators of the configuration at the sulfenamide chiral axis when the groups at the asymmetric carbon atom are varied.

Since we desired a derivative which bears a chromophore that would be relatively unperturbed electronically by substituents at the asymmetric center but would reflect their effects in equilibrium asymmetric induction, we next examined the arenesulfenamides **8**, **9**, and **10**. All three sets of derivatives exhibit multiple Cotton effects in their ORD spectra. In general, there are Cotton effects of fairly high rotatory power in the short-wavelength region near 200 nm with effects of lower intensity at longer wavelength. In the chlorotolyl derivatives, **8**, the longer wavelength transitions occur below 300 nm (Figure 2) while in the nitrophenyl and dinitrophenyl derivatives **9** and **10**, they appear near 350 nm (Figures 3–6).

(9) The ORD and CD spectra of the closely related *N*-(benzenesulfonyl)trichloromethanesulfenamide is given in ref 4. The ORD and CD spectra of the corresponding *N*-(*p*-toluenesulfonyl) derivative **7b**, reported here, were the same within experimental error.

(10) (a) Smith, M. E.; Padilla, B. G.; Neergaard, J. R.; Chen, F. M. *J. Am. Chem. Soc.* **1978**, *100*, 6035. (b) Smith, H. E.; Burrows, E. P.; Chen, F. M. *J. Am. Chem. Soc.* **1978**, *100*, 371. (c) Gottarelli, G.; Samori, B. *J. Chem. Soc. B* **1971**, 2418.

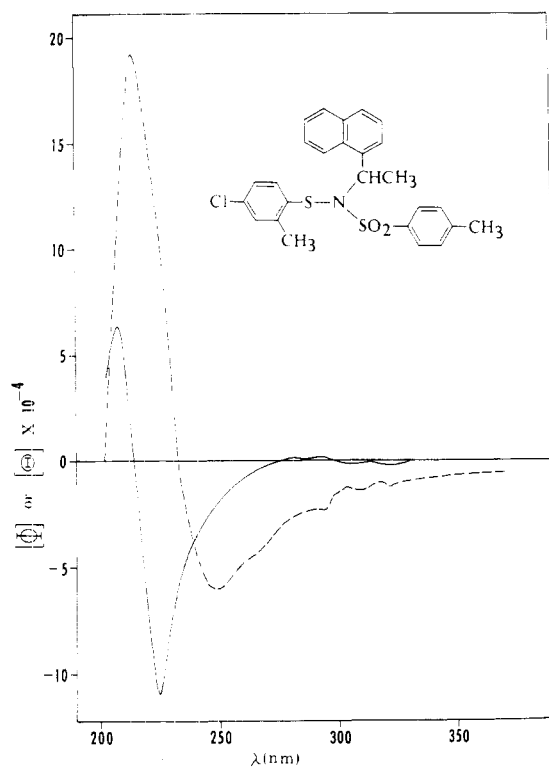


Figure 2. Optical rotatory dispersion and circular dichroism spectra of **8b** in absolute ethanol: CD (—), ORD (---).

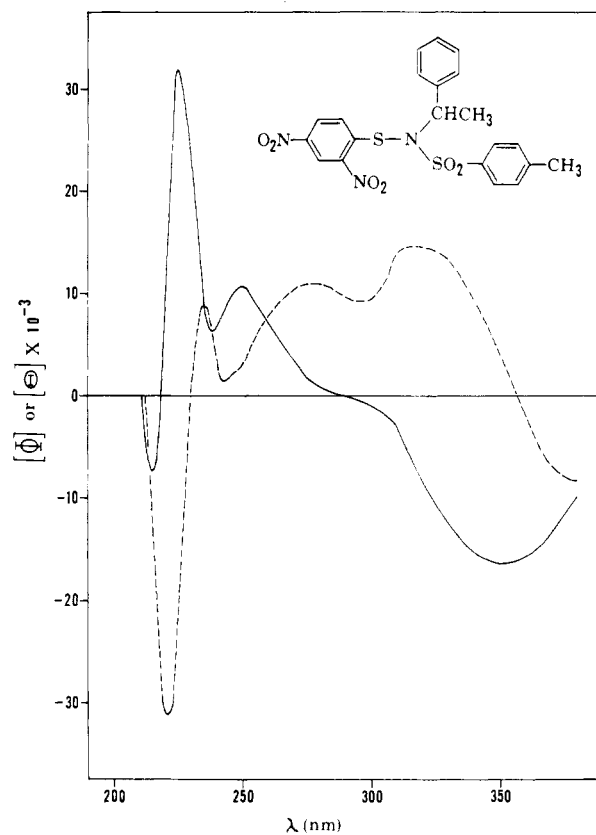


Figure 4. Optical rotatory dispersion and circular dichroism spectra of **10a** in absolute ethanol: CD (—), ORD (---).

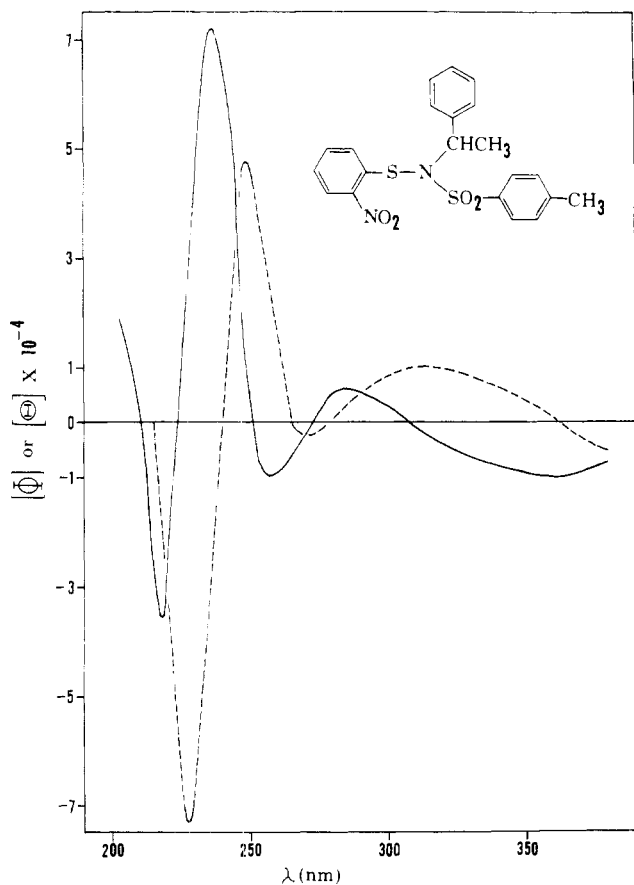


Figure 3. Optical rotatory dispersion and circular dichroism spectra of **9b** in absolute ethanol: CD (—), ORD (---).

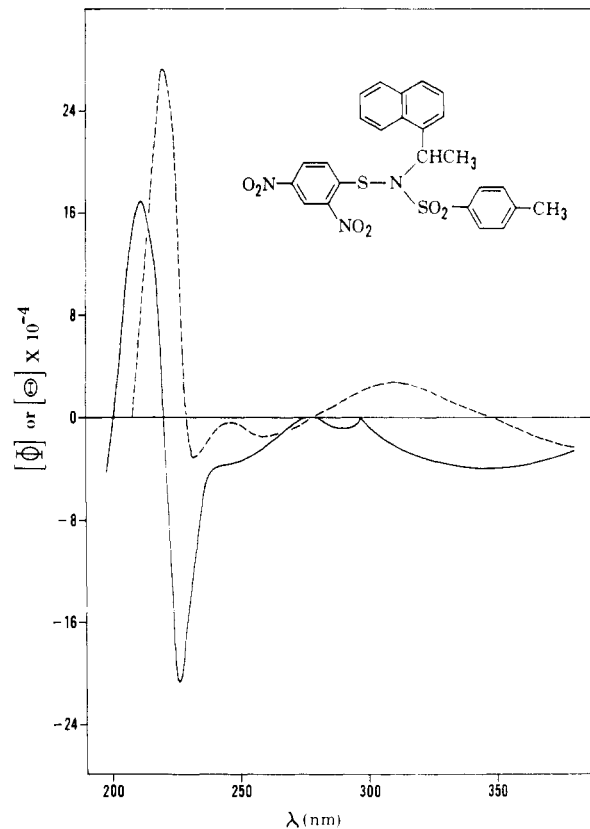


Figure 5. Optical rotatory dispersion and circular dichroism spectra of **10b** in absolute ethanol: CD (—), ORD (---).

The ORD spectra of the three 2-methyl-4-chlorobenzenesulfonyl derivatives **8a-c** all exhibit intense extrema near 200 nm. These are peaks for **8a** and **8b** but a trough for **8c**, although all three have corresponding

configurations at the asymmetric carbon atom. In addition, the CD spectrum of **8b** (Figure 2) indicates the presence of at least two oppositely signed Cotton effects in the short-wavelength region. The longer wavelength

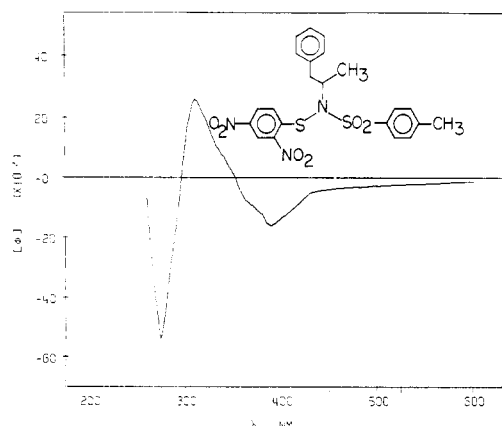


Figure 6. Optical rotatory dispersion spectrum of **10c** in absolute ethanol.

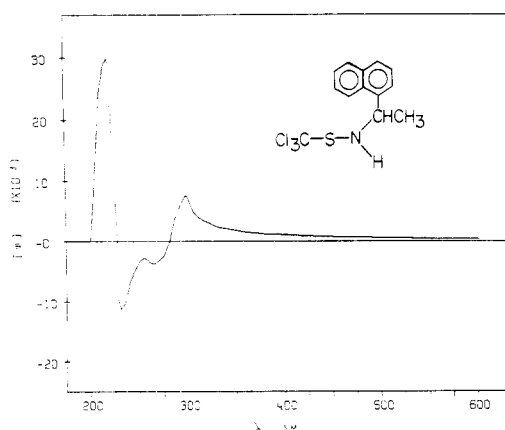


Figure 7. Optical rotatory dispersion spectrum of **12** in absolute ethanol.

Cotton effects, near 300 nm, appear as a well-defined peak and trough only in the ORD spectrum of **8a**; in those of **8b** and **8c** only small fluctuations were observed. This derivative was also judged to be unsuitable for our purposes.

The spectra (Figures 3–6) of the nitrobenzene derivatives also exhibit overlapping multiple Cotton effects in the low-wavelength region (200–250 nm). In addition, however, these compounds feature Cotton effects near 350 nm which appear to be associated with the nitrophenyl rings. These Cotton effects were better defined in all three of the dinitrobenzenesulfenyl derivatives. In the phenylpropyl derivative this was clearly visible in the dinitrobenzene derivative **10c** (Figure 6) but was not in the *o*-nitrobenzenesulfenyl derivative **9c**. Figures 4–6 indicate the ORD spectra for all of these compounds and the CD spectra for **10a** and **10b** as well. While the appearance of the spectra in the short-wavelength region does not seem to indicate any configurationally dependent regularities, all three derivatives exhibit reasonably prominent negative Cotton effects centered near 350 nm (crossover wavelengths: **10a**, 357 nm; **10b**, 347 nm; **10c**, 353 nm). The closeness of these crossover points suggests relatively little perturbation of the transitions by the aromatic substituents at the asymmetric carbon atom. This Cotton effect is well isolated from other effects, and there will not be problems from overlap with other transitions in the derivatives of most amines. Thus, it can serve as an easily recognizable diagnostic transition. Furthermore, because this is the longest wavelength transition, it is likely that the tail of this optically active Cotton effect will dominate the rotation at the sodium D line. This is the case in all three of these compounds. All three exhibit negative

Table II. Peak to Trough Difference in Rotation of the Long-Wavelength Transition and Diastereomeric Compositions in *N*-*p*-Toluenesulfonyl in **10**

compd	R	λ_0 , ^a nm	$[\Phi]_p$ - $[\Phi]_t$, ^b deg	K_{eq} ^c	diastereomeric excess, ^c %
10a	phenyl	357	22 600	2.4	41
10b	1-naphthyl	347	52 400	8.5	79
10c	benzyl	353	4 210	1.06	3

^a Crossover wavelength. ^b Difference in molecular rotations. ^c Calculated from the ratio of the C-methyl doublets in the NMR spectra.

Cotton effects, and all three have negative rotations at the sodium D line.

Since there is relatively little overlap with other transitions, the peak to trough difference in rotation can serve as a reasonable estimate of the intensity of the rotatory power of the transition. The peak to trough differences are quite different for the three compounds (Table II), but seem to be semiquantitatively related to the diastereomeric excess of the major diastereomer. The diastereomeric composition in each case can be determined from the room-temperature NMR spectra. Each of these compounds exhibits two doublets for the methyl groups attached to the asymmetric carbon atom. Integration of these signals affords a measure of the ratio of diastereomers from which the percent diastereomeric excess can be calculated ($DE(\%) = 100(K - 1)/(K + 1)$). These data are given in Table II. The most intense transition was observed for the naphthyl derivative **10b** for which the equilibrium asymmetric induction is much greater, while the phenylpropyl derivative **10c** which exhibits only a very small induction features a much less intense Cotton effect, in accord with our speculations about the possible effect of cancellation in spectra of the two derivatives.

The spectral behavior of the dinitrobenzenesulfenylamides **10** suggests a simple and convenient method for the determination of the absolute configuration of amines, although further examples are necessary in order to demonstrate the generality of this method. All that would be required is to convert the amine via its *p*-toluenesulfonamide into the *N*-(toluenesulfonyl)dinitrobenzenesulfenamide **10** and to measure its optical rotation at the sodium D line. If the rotation is negative, this corresponds to a negative Cotton effect in the 350-nm region which corresponds to the configuration **11**; if the D line rotation is positive, this indicates the enantiomeric configuration.

Experimental Section

Nuclear magnetic resonance spectra were measured by using a Varian A60-A spectrometer, and chemical shifts are reported in δ units relative to internal tetramethylsilane. Melting points were measured on a Thomas-Hoover apparatus and are uncorrected. Optical rotations at the sodium D line were measured on a Perkin-Elmer 141 polarimeter, and ORD/CD spectra were obtained on a Cary 60 recording spectropolarimeter with nitrogen purging. Sample concentrations were in the range of 0.1–1.0 mg/mL. The path length of the quartz cells was in the range of 0.1–100 mm. The cutoff value for the dynode voltage was 0.4 kV. Analyses were performed by Midwest Microlab, Inc.

Trichloromethanesulfenyl chloride and *o*-nitrobenzenesulfenyl chloride were obtained commercially and used without prior purification. *p*-Nitrobenzenesulfenyl chloride¹¹ and 2,4-dinitrobenzenesulfenyl chloride¹² were prepared according to the liter-

(11) Hubachey, M. H. "Organic Syntheses"; Wiley: New York, 1943; Collect. Vol. II, p 455.

Table III. Melting Points and Yields for 7, 8, 9, 10

compd ^a	formula	yield, %	mp, °C
7a	C ₁₆ H ₁₆ NO ₂ S ₂ Cl ₃	77	91.5-93
7b	C ₂₀ H ₁₈ NO ₂ S ₂ Cl ₃	89	131-132
8a	C ₂₂ H ₂₂ NO ₂ S ₂ Cl	60	119-120.5
8b	C ₂₆ H ₂₄ NO ₂ S ₂ Cl	70	166-167
8c	C ₂₃ H ₂₄ NO ₂ S ₂ Cl	90	109-110
9a	C ₂₁ H ₂₀ N ₂ O ₄ S ₂	81	142.5-143.5
9b	C ₂₅ H ₂₂ N ₂ O ₄ S ₂	69	167.5-168.5
9c	C ₂₂ H ₂₂ N ₂ O ₄ S ₂	80	127.5-129
10a	C ₂₁ H ₁₉ N ₃ O ₆ S ₂	63	134-136
10b	C ₂₅ H ₂₁ N ₃ O ₆ S ₂	80	205-206.5
10c	C ₂₂ H ₂₁ N ₃ O ₆ S ₂	56	152-154

^a Satisfactory combustion analytical data ($\pm 0.4\%$ in C, H, and N) were reported for these compounds.

ature. 4-Chloro-2-methylbenzenesulfonyl chloride was prepared by chlorination of 5-chloro-2-thiocresol using a literature procedure.¹³

p-Toluenesulfonamides 4, 5, and 6. The appropriate amine (10.0 g) was reacted with 1 equiv of *p*-toluenesulfonyl chloride in the presence of 1 equiv of triethylamine, and the product sulfonamide was recrystallized from methanol: 4, mp 97-99 °C,

(12) Kharasch, N.; Langford R. "Organic Syntheses"; Wiley: New York, 1973; Collect. Vol. V, p 474.

(13) Kurzer, F.; Powell, J. R. "Organic Syntheses"; Wiley: New York, 1963; Collect. Vol. IV, p 934.

$[\alpha]_D^{23} +7.2^\circ$ (c 0.4, EtOH); 5, mp 122.5-123.5 °C, $[\alpha]_D^{23} +7.5^\circ$ (c 0.4, EtOH); 6, mp 64-66 °C.

Sulfonylsulfonamides 7, 8, 9, and 10. A solution of 1-3 g of the appropriate sulfonamide in 150 mL of anhydrous ether was treated with 1 equiv of *n*-butyllithium, and an ethereal solution of 1 equiv of the sulfonyl chloride was added dropwise. The reaction mixture was filtered, washed with water, and dried, and the solvent was removed in vacuo. Methanol was added to induce crystallization and the product recrystallized from benzene, hexane, cyclohexane, 2-propanol, or a mixture of these solvents. Melting points, yields, and analytical data for these compounds are given in Table III.

(R)-(+)-N-[1-(1-Naphthyl)ethyl]trichloromethanesulfenamide (12). An ethereal solution of 3.25 g (0.0175 mol) of trichloromethanesulfonyl chloride was added dropwise to an ethereal solution of 3.0 g (0.0175 mol) of amine and 1.77 g (0.0175 mol) of triethylamine. After being stirred for 3 h, the reaction mixture was filtered, washed with water, and dried, and the solvent was removed in vacuo. The product was recrystallized from hexane/2-propanol (6:1): mp 64-65.5 °C; NMR (CCl₄) δ 1.66 (CH₃CH, d, $J = 6.5$ Hz), 4.28 (NH, br s, $W_{1/2} = 8$ Hz), 5.53 (CH₃CHNH, qd, $J_{AM} = 3.4$ Hz, $J_{AX3} = 6.5$ Hz), 7.2-8.2 (aromatic, complex multiplet).

Registry No. 1, 3886-69-9; 2, 3886-70-2; 3, 156-34-3; 4, 72984-27-1; 5, 72938-93-3; 6, 72938-94-4; 7a, 72938-95-5; 7b, 72938-96-6; 8a, 72938-97-7; 8b, 72938-98-8; 8c, 72938-99-9; 9a, 72939-00-5; 9b, 72939-01-6; 9c, 72939-02-7; 10a, 72939-03-8; 10b, 72953-41-4; 10c, 72953-42-5; 12, 72939-04-9; ClSCCl₃, 594-42-3; 4-chloro-2-methylbenzenesulfonyl chloride, 72939-05-0; 2-nitrobenzenesulfonyl chloride, 7669-54-7; 2,4-dinitrobenzenesulfonyl chloride, 528-76-7.

Stereospecific Transannular Cyclization of (*Z*)- and (*E*)-Thiacyclooct-4-enes: Synthesis and Carbon-13 Nuclear Magnetic Resonance Spectra of Substituted *cis*-1-Thionibicyclo[3.3.0]octane Salts. Conformational Analysis (Force Field) of (*E*)-Thiacyclooct-4-ene and Its 2- and 3-Methyl Derivatives

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Several substituted (*Z*)- and (*E*)-thiacyclooct-4-enes (1-11) have been synthesized and their acid-promoted transannular cyclizations studied. The reaction appears to be stereospecific: thus the *RR,SS* and *SR,RS* diastereomers of 2-methyl-(*E*)-thiacyclooct-4-ene give, respectively, the *exo*- and *endo*-2-methyl-*cis*-1-thionibicyclo[3.3.0]octane salts. Similarly, the halogen-promoted (Cl, Br) cyclization of (*Z*)- and (*E*)-thiacyclooct-4-ene gives the *endo*- and the *exo*-4-halogeno derivatives, respectively. Several bridgehead [3.3.0] sulfonium salts have been prepared in this way (12-24) and their ¹³C NMR spectra compared to those of structurally related systems. Some remarkable shielding effects are reported (a differential ϵ effect amounting to 4 ppm) which allow an insight into the conformational properties of this bicyclic system. Force field computations indicate the twist conformation of (*E*)-thiacyclooct-4-ene is more stable than the chair conformation by 5.06 kcal mol⁻¹. For confirmation of the configurational assignments based on ¹³C NMR shieldings, the energies of the *RR,SS* and *SR,RS* diastereomers of the 2- and 3-methyl derivatives have also been computed and related to the experimentally determined equilibrium constants.

A distinctive characteristic of medium-size rings (8-11-membered) is their ability to undergo facile transannular reactions, the best known examples being perhaps the hydride shifts accompanying solvolyses.¹ Mesoheterocyclic

compounds whose heteroatom possesses marked nucleophilic character display this behavior to the highest degree, strong physical and chemical interactions being established between the heteroatom and electrophilic centers across the ring. As far as S heterocycles are concerned,² trans-

(1) (a) Prelog, V.; Traynham, J. G. In "Molecular Rearrangements"; De Mayo, P., Ed.; Interscience: New York, 1964; Vol. 1, p 593. (b) Cope, A. C.; Martin, M. M.; McKervery, M. A. Q. Rev., Chem. Soc. 1966, 20, 119.

(2) There is evidence that transannular interactions involving sulfide sulfur may already take place in seven-membered rings.³