A Correlation between the Absolute Configurations of Acyclic Aliphatic and Benzylic Secondary Alcohols and the Optical Rotations of Their 2,4-Dinitrobenzenesulfenyl Derivatives

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The 2,4-dinitrobenzenesulfenate esters **2a-v** of 11 acyclic aliphatic and 11 benzylic chiral secondary alcohols of known configuration were synthesized, and their sodium D line optical rotations and CD spectra were determined. The sign of the sodium D line rotations of the derivatives was consistently correlated with the absolute configuration of the carbinol carbon in the original alcohols. The CD spectra exhibited optically active transitions in the 320-400-nm region that corresponded in sign to the sodium D line optical rotations and were strong enough to dominate the sign of rotation at the sodium D line. Thus the optical rotations and CD spectra of these sulfenate ester derivatives are diagnostic for the absolute configurations of chiral secondary acyclic aliphatic and benzylic alcohols.

Introduction

Sulfenate esters, a well-known class of compounds,[1] derived from the reaction of alcohols with 2,4-dinitrobenzenesulfenyl chloride have been used to characterize alcohols.[2] Although much experimental and theoretical work has been done on the chiroptical properties of sulfur-containing compounds,[3] little is known about the chiroptical properties of compounds containing the sulfenate ester functional group[4] and the potential use of this functional group for the characterization of optically active alcohols. The 2,4-dinitrobenzenesulfenate esters of optically active alcohols are of particular interest because the sodium D line optical rotations of their sulfenamide analogues have been successfully used to determine the absolute configurations of chiral amines and amino acids.[3-7] The sulfenate ester derivatives of alcohols can be synthesized in a simple one-step procedure, using readily available starting materials. Therefore, if the CD spectra or the sodium D line optical rotations of these derivatives can be used for the determination of absolute configurations, such a method would be very attractive.

Sulfenate esters are analogous to sulfenamides, which exhibit chirality when appropriately substituted because of restricted rotation around the S-N bond.[5] Asymmetric induction in the conformation around this bond in sulfenamides derived from chiral amines produces ORD/CD Cotton effects characteristic of the presence of an inherently dissymmetric chromophore, the sulfenamide group.[3] In the case of 2,4-dinitrobenzenesulfenyl derivatives, a Cotton effect observed near 350 nm and attributed to the 2,4-dinitrophenyl chromophore has proven useful for determination of the absolute configurations in chiral primary amines[6] and amino acids.[7]

Both theoretical calculations[8] and crystallographic data[9] indicate that the optimal geometry for sulfenate esters is one in which the R-S-O-R' dihedral angle is approximately 90° and that the S-O bond has therefore a rotational barrier like that of sulfenamides. Although the S-O barrier is calculated to be much lower than the S-N barrier (5.3 kcal/mol for CH_3SOCH_3[8] compared to 12-16 kcal/mol for sulfenamides[5a]), it is a sufficient barrier to give rise to asymmetric induction in chiral sulfenate esters. Thus, sulfenate esters of chiral secondary alcohols should exist in solution as a mixture of diastereomeric conformers in unequal amounts (Figure 1). Four rotamers that should be considered as contributors to this equilibrium, and their likely relative contributions, are shown. If the induced asymmetry around the S-O axis produces an optically active transition of moderate strength at long wavelength, and if that transition does not interact strongly with other transitions in the molecule, the sign of the sodium D line rotations of the 2,4-dinitrobenzenesulfenate esters of chiral secondary alcohols could plausibly be expected to be systematically correlated to the absolute configurations of the original alcohols. Indeed, ORD data previously published suggested the probable existence of such a relationship.[4]

A preliminary test of this hypothesis was made on a variety of optically active secondary alcohols.[10] In most cases, derivatives of alcohols with stereoformula A (where L and M refer to sterically large and medium groups,

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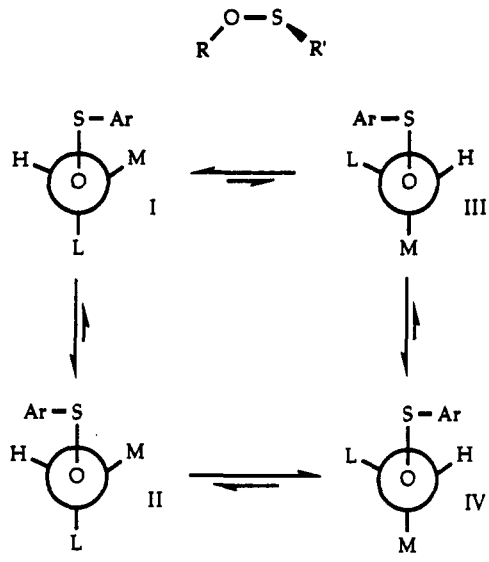
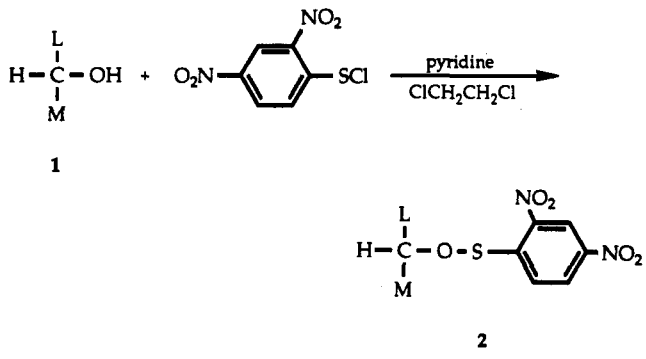


Figure 1. Asymmetric induction by chiral center on sulfenate ester conformation equilibrium.

Scheme I



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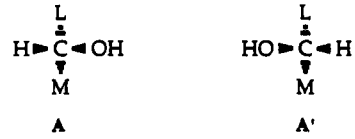
respectively) were dextrorotatory and derivatives of alcohols with stereoformula A′ were levorotatory at 589 nm.



A A′

Although there were a couple of exceptions to this pattern among bicyclic and polycyclic aliphatic alcohols, it was found that the acyclic aliphatic and benzylic alcohols examined followed this pattern without exception and that the rotations for the derivatives of benzylic alcohols were unusually large. We therefore decided to investigate more thoroughly the optical behavior of the 2,4-dinitrobenzenesulfenate esters of these two classes of alcohols.

Results and Discussion

The 2,4-dinitrobenzenesulfenyl derivatives of 11 acyclic aliphatic and 11 benzylic optically active secondary alcohols of known configuration were prepared by Kharasch's method[2a] (Scheme I), and the sodium D line optical rotations of these derivatives and some of their parent alcohols were measured in acetonitrile. The results are summarized in Table I.

Based on previous ORD data in the literature,[4] the 2,4-dinitrobenzenesulfenyl derivatives of alcohols with the stereoformula A were expected to be dextrorotatory, and the derivatives of alcohols with the stereoformula A′ were expected to be levorotatory at the sodium D line. For all alcohols used, stereoformula A corresponds to the *R* configuration and stereoformula A′ corresponds to the *S* configuration at the carbinol carbon. In all cases examined, the rotations of the sulfenate esters did conform to this pattern.

Because the rotations for the benzylic alcohols **2l–r** were unusually large, rotations were taken of **2m** and **2o** at c = 0.5 and of **2n** at c = 0.13 to ascertain that the sign of rotation was correct. The specific rotations for the diluted samples were found to be within 4% of those determined at the concentrations given in Table I. In most cases, differences in the magnitude of rotation between derivatives of enantiomeric alcohols reflect differences in the enantiomeric purity of the starting alcohols, which were used as obtained from commercial sources. For the cyclic benzylic alcohols **2s–v**, the differences reflect problems with solubility and purity of the derivatives. (These derivatives were very unstable, and it was not possible to obtain accurate elemental analyses of them, although their presence was clearly established by ^{1}H NMR and ^{13}C NMR spectral data.) The results for these derivatives are qualitatively accurate but quantitatively unreliable.

To gain further insight into the observed correlation, the UV spectra of derivatives **2a–v** were obtained on 1×10^{-4} M solutions in acetonitrile. Representative UV data are given in Table II. The CD spectra of derivatives **2a–v** were obtained on 4×10^{-4} M acetonitrile solutions. The information from these spectra is summarized in Tables III and IV. In addition, an X-ray crystal structure was obtained from **2m** (Figure 2) to determine the dihedral angle of the sulfenate ester unit and to determine the orientation of groups around the carbinol carbon with respect to the 2,4-dinitrophenyl substituent on sulfur.

The sign of molecular rotation for the 2,4-dinitrobenzenesulfenate esters of alcohols **1a–v** is consistently correlated with the configuration at the carbinol carbon. The direction of shift in rotation of the derivative ($[M]_2 - [M]_1$) is the same as the sign of molecular rotation for the derivative, and in all cases is positive for alcohols with the A (*R*) configuration and negative for alcohols with the A′ (*S*) configuration. Derivatives of enantiomeric pairs of alcohols exhibit oppositely signed rotations of approximately equal magnitude. This result is consistent with the hypothesis that asymmetric induction in the skewness of the C–S–O–C* unit by the chiral carbinol carbon (Figure 1) produces one major conformer and that the induction is of the same magnitude in the sulfenate esters of enantiomeric alcohols. One would therefore expect the ORD spectra of the derivatives of enantiomeric pairs to be approximately enantiomeric.

The molecular rotations of the acyclic benzylic sulfenate esters are 5–20 times greater in magnitude than those of the acyclic aliphatic sulfenate esters. The magnitude of molecular rotation for the cyclic benzylic derivatives is not as large as that of the acyclic benzylic derivatives, but is about 3 times that of the aliphatic acyclic derivatives. Since the optical rotation at the sodium D line results from summation of all the Cotton effects in the ORD spectrum, it is to be expected that additional contributions from optically active transitions associated with the phenyl

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Table I. Sodium D Line Specific and Molecular Optical Rotations of Sulfenate Esters 2[a]

compd	known config (1)	L	M	$[\alpha]_D$ (1)	$[\alpha]_D$ (2)	Δ[M] (2 - 1)	[M]
2a	*R*	C_2H_5	CH_3	−13.0[b]	17.4	57.0	47.4
2b	*S*	C_2H_5	CH_3	12.4	−16.8	−54.9	−45.7
2c	*R*	*n*-C_3H_7	CH_3	−13.0[c]	32.9	105.6	94.2
2d	*S*	*n*-C_3H_7	CH_3	13.0	−33.2	−106.6	−95.1
2e	*S*	*i*-C_3H_7	CH_3	5.0[d]	−52.7	−155.3	−150.9
2f	*R*	*n*-C_4H_9	CH_3	−12.5	40.1	132.9	120.1
2g	*S*	*n*-C_4H_9	CH_3	10.5	−38.5	−126.3	−115.6
2h	*R*	*n*-C_5H_{11}	CH_3	−11.3	43.8	150.8	137.7
2i	*S*	*n*-C_5H_{11}	CH_3	10.7	−45.0	−153.9	−141.5
2j	*R*	*n*-C_6H_{13}	CH_3	−9.4	44.9	159.6	147.4
2k	*S*	*n*-C_6H_{13}	CH_3	9.9	−47.7	−169.5	−156.6
2l	*R*	C_6H_5	CH_3	49.0	317.6	957.6	1017.5
2m	*S*	C_6H_5	CH_3	−41.3[e]	−322.2	−981.6	−1032.1
2n	*R*	C_6H_5	*n*-C_3H_7	55.0[f]	298.9[g]	958.6	1041.2
2o	*S*	C_6H_5	*n*-C_3H_7	−52.0	−293.1	−942.9	−1021.0
2p	*R*	C_6H_5	*i*-C_3H_7	21.0[e]	318.9[g]	1079.6	1111.1
2q	*S*	C_6H_5	*i*-C_3H_7	−38.0	−315.2	−1041.1	−1098.2
2r	*S*	2-napthyl	CH_3	−53.4	−372.5	−1287.7	−1379.7
2s	*R*	1-indanyl		−29.0[h]	157.2[g]	561.4	522.6
3t	*S*	1-indanyl		−2.8	−121.8	−401.1	−404.8
2u	*R*	1,2,3,4-tetrahydro-1-naphthyl		−11.4	96.9[i]	352.5	335.6
2v	*S*	1,2,3,4-tetrahydro-1-naphthyl		32.0[j]	−14.6[g]	−98.0	−50.6

[a] The solvent is acetonitrile, the temperature is 30 °C (±1 °C). The path length is 1 dm, and $c = 1$, except where indicated. [b] Neat (lit. $[\alpha]_D$ = +13.52° neat, Leroux, L. *J. Am. Chem. Soc.* **1951**, *73*, 41. [c] Neat (lit. $[\alpha]_D$ = +12.1° neat, Pickard, R. H.; Kenyon, J. *J. Chem. Soc.* **1911**, *99*, 45). [d] Neat (lit. $[\alpha]_D$ = +4.34°, c = 4.8, EtOH, Pickard, R. H.; Kenyon, J. *J. Chem. Soc.* **1915**, *103*, 1957). [e] Neat. [f] c = 5, $CHCl_3$. [g] c = 0.5. [h] c = 2, $CHCl_3$. [i] c = 0.2. [j] c = 2.5, $CHCl_3$.

Table II. UV Maxima and Molar Absorptivities of Compounds 2b and 2l in Acetonitrile (1×10^{-4} M, Path Length = 1 cm)

compd	λ_{max} (nm)	ε	compd	λ_{max} (nm)	ε
2b	384	3700	**2l**	382	5600
	338	7400		336	11000
	258	6400		258	9600
	212	8400		212	18700
	194	6400		200	16500

Table III. Molar Ellipticities and Molar Dichroic Absorption of the Sulfenate Esters 2a–k of Aliphatic Acyclic Alcohols[a]

compd	λ (nm)	[θ]	Δε	compd	λ (nm)	[θ]	Δε
2a	245	−1637	−0.50	**2b**	243	1450	0.49
	265	1183	0.36		265	−1472	−0.45
	319	383	0.12		304	−808	−0.24
					329	−974	−0.30
2c	244	−2754	−0.84	**2d**	244	2781	0.84
	263	1291	0.39		273	−1601	−0.48
	337	506	0.15		311	−1118	−0.34
					330	−1416	−0.43
				2e	245	4299	1.30
					270	−3461	−1.05
					329	−2012	−0.61
2f	244	−2313	−0.70	**2g**	243	1633	0.59
	269	1633	0.50		266	−1408	−0.43
	324	693	0.21		308	−1153	−0.35
	342	235	0.07		331	−1294	−0.39
2h	242	−2230	−0.68	**2i**	241	2401	0.73
	267	1627	0.49		269	−1551	−0.47
	328	532	0.16		312	−1337	−0.40
					337	−1251	−0.38
2j	242	−2885	−0.87	**2k**	243	2466	0.75
	266	1679	0.51		269	−1506	−0.46
	312	604	0.18		323	−1443	−0.44
	338	267	0.27		341	−1277	−0.39

[a] Spectra were obtained for 4×10^{-4} M solutions in acetonitrile, with a cell path length of 0.5 cm.

chromophore in the benzylic alcohols will be reflected in larger optical rotations for the derivatives of these alcohols.

The correlation between the absolute configuration of the alcohols and the sign of the optical rotation of their 2,4-dinitrobenzenesulfenate derivatives is consistent for

Table IV. Molar Ellipticities and Molar Dichroic Absorption of the Sulfenate Esters 2l–v of Benzylic Alcohols[a]

compd	λ (nm)	[θ]	Δε	compd	λ (nm)	λ [θ]	Δε
2l	214	50570	15.3	**2m**	217	−37203	−11.3
	327	8764	2.66		320	−9235	−2.80
	389	−2206	−0.67		392	1728	0.52
2n	216	54530	16.5	**2o**	218	−41225	−12.5
	278	−278	−0.08		278	254	0.08
	326	9533	2.89		326	−9914	−3.0
	394	−2498	−0.76		399	2108	0.64
2p	216	61045	18.5	**2q**	218	−47610	−14.4
	276	−1673	−0.51		274	1413	0.43
	325	11061	3.35		323	−10741	−3.25
	392	−2897	−0.88		393	2606	0.79
				2r	222	14528	4.4
					237	−19948	−6.04
					262	−6759	−2.05
					324	−14337	−4.34
2s	244	6269	1.90	**2t**	207	11951	3.62
	286	−797	−0.80		247	−5141	−1.56
	388	5906	1.79		287	1267	0.38
					393	−5274	−1.60
2u	210	−3522	−1.07	**2v**	211	13363	4.05
	221	3003	0.91		244	−1158	−0.35
	233	−1811	−0.55		265	−364	−0.11
	249	3424	1.04		336	−646	−0.20
	283	−3276	−0.99				
	399	3640	1.10				

[a] Spectra were obtained for 4×10^{-4} M solutions in acetonitrile, with a cell path length of 0.5 cm.

the alcohols examined. However, the extent to which reliance may be placed on the sodium D line rotation as diagnostic information requires examination of the UV and CD spectra of the derivatives.

In their UV spectra, all derivatives exhibited the shorter wavelength absorption bands between 200 and 300 nm characteristic of compounds containing phenyl rings. However, the band at 258 nm was stronger than the 254-nm band normally associated with benzene rings and is likely to be associated with the conformational asymmetry due to the dihedral angle of the sulfenate ester unit.[11] In addition, two absorption bands exclusively associated with the 2,4-dinitrobenzenesulfenyl chromophore, usually at

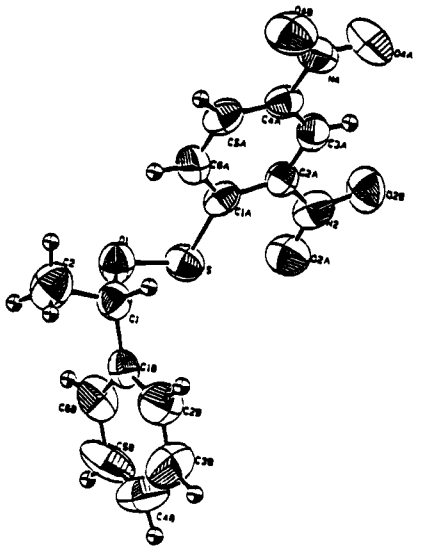

Figure 2. ORTEP drawing of (*S*)-(−)-*sec*-phenethyl 2,4-dinitrobenzenesulfenate (**2m**).

338 and 384 nm, were present in every case. For the derivatives of aliphatic alcohols, **2a–k**, the strongest bands were at 212 and 338 nm, with the former having a slightly higher molar absorptivity. For the benzylic derivatives, **2l–v**, the shorter wavelength absorbances (212 and 196 nm) were dominant, but the 338-nm band also had a large molar absorptivity ($\epsilon > 10\,000$) except in compounds **2u–v**, where the 338-nm band was significantly weaker. In all cases, the 384-nm band appeared as an unresolved shoulder on the 338-nm band. In chloroform, the 338-nm band was bathochromically shifted by 4–6 nm. Spectra in ethanol and dioxane were comparable to the spectra in acetonitrile. Molar absorptivities in acetonitrile were generally slightly lower than in the other three solvents.

The most striking feature of the CD spectra for the sulfenate ester derivatives is the mirror image quality of the spectra of the derivatives of enantiomeric pairs of alcohols. This is true for the derivatives of both aliphatic and benzylic alcohols and probably reflects the dominance of two enantiomeric conformers. However, the spectra of the derivatives of these two classes of alcohols differ in several respects. The UV absorption spectra of the sulfenate esters all exhibit a long-wavelength absorption band at 336–338 nm that is not significantly shifted or changed in magnitude as the substituents of the carbinol asymmetric center are varied. The CD spectra of the derivatives **2a–k** of acyclic aliphatic alcohols contain a weak transition corresponding to this UV absorption band and usually containing two maxima or minima between 308 and 342 nm. Two stronger transitions occur in the 263–273-nm region and in the 241–245-nm region. These are always oppositely signed, the longer wavelength band having the same sign as the weaker transitions in the 308–342-nm region and the sodium D line rotation. The rotatory strength of these transitions increases with increased steric bulk of the large group on the carbinol carbon from ethyl to *n*-propyl to isopropyl. This suggests that asymmetric induction around the S–O bond is affected by the difference in steric bulk between the large and medium groups on the carbinol carbon and that these transitions reflect the predominant skewness of the sulfenate ester conformational unit. Although the rotatory strength of these two transitions is not large, the two bands appear to be diagnostic for the absolute configuration of saturated acyclic aliphatic alcohols.

The CD spectra of the derivatives **2l–q** of acyclic benzylic alcohols contain a transition corresponding to the 338-nm UV absorption band, but hypsochromically shifted by 10–17 nm. This band is broad, without fine features, and is well separated from the only stronger band in the spectrum at 214–218 nm (the ^1L_a region for phenyl rings). Both of these bands have the same sign as the sodium D line rotations. Two much weaker transitions located at 274–278 nm (^1L_b) and 389–399 nm are of opposite sign to the sodium D line rotation. Of these two, the sign of the shorter wavelength band is known to be characteristic for phenylcarbinols in which the phenyl ring is not substituted and is correlated to the absolute configuration of the carbinol, as specified by Brewster's rules of atomic asymmetry.[12] The electronic properties of ring substituents in phenylcarbinols are known to affect the sign of this transition in a predictable manner.[13] However, this band corresponds to a forbidden transition and is weak compared to the band at 320–327 nm. Unless there is coupling between the two transitions involved, the sign of the 320–327-nm transition can be considered a reliable indication of the predominant conformation of the sulfenate ester unit. This transition appears to be strong enough and at sufficiently long wavelength to dominate the sign of rotation at the sodium D line. Whether it is independent of other shorter wavelength transitions can be tested by examining the CD spectra of the derivatives of ring-substituted phenylcarbinols, a study which is currently underway in our lab.

The appearance of the CD spectra of compounds **2l–q** in the 274–327-nm region suggests the possibility that the 2,4-dinitrobenzenesulfenyl and phenyl chromophores in these compounds are coupled through exciton formation, producing a split CD pattern. This is unlikely, however, because effective exciton formation requires highly symmetric chromophores, and the 2,4-dinitrobenzenesulfenyl chromophore is not highly symmetric. Electronic transition moments of ortho- and meta-substituted phenyl chromophores tend to be weaker and their polarization less well defined than in the symmetric para-substituted phenyl chromophores, and thus a strong interaction with transition moments in other chromophores is less likely. Also, the chirality of the interaction of polarization moments in these cases is dependent upon rotational conformations of the chromophores.[14] In the X-ray crystal structure of **2m** (Figure 2), the dihedral angle formed by the planes of the two aromatic rings is 77.4°, which suggests that unless the polarization of the transition is along the long axis of the 2,4-dinitrophenyl ring, there is little interaction if any between the transition moments in the two rings. The possibility of such an interaction can be tested by examining the derivatives of para-substituted 1-phenylethanols.

Compound **2r**, in which the large group is 2-naphthyl, also has a strong transition at 324 nm, corresponding in sign to the sodium D line rotation. Other strong transitions

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of the same sign are present at 262 and 237 nm. Again, unless there is interaction between these transitions and the transition at 324 nm, the latter should dominate the sign of rotation at the sodium D line.

Binding of the alkyl group of secondary aralkylcarbinols into a ring evidently affects the overall conformation of the sulfenate ester in such a manner as to alter significantly the features of the CD spectra of these derivatives. For derivatives **2s–u** of cyclic benzylic alcohols, there is no optically active transition corresponding to the 338-nm UV absorption, but there is a broad band of moderate strength at 388–400 nm, corresponding to the longest wavelength absorption in the UV spectrum. The sign of this band is the same as the sign of the sodium D line rotation. This transition, which is due solely to the 2,4-dinitrobenzenesulfenyl chromophore, does not appear to be affected by any other transitions, and at such long wavelength clearly dominates the sign of rotation at the sodium D line. No useful information was obtained from the very weak spectrum of **2v**.

The X-ray crystal structure of **2m**, which has the *S* configuration at the carbinol carbon, provides evidence to support the proposition that the lowest energy conformation of the sulfenate ester unit is a conformation in which the dihedral angle approaches 90°. For **2m**, this angle is −90.9°. The bond angles and lengths found agree well with those found in the 2-nitrobenzenesulfenate ester of methanol,[9] the only other structure of a sulfenate ester in the literature. Moreover, the arrangement of groups around the chiral carbinol center corresponds to the arrangement depicted in conformation IV in Figure 1, in which M = methyl and L = phenyl. The S–O bond is clearly anti to the methyl group instead of the phenyl group, and the 2,4-dinitrophenyl group is directed away from the phenyl group and toward the hydrogen.

Another significant feature of the conformation revealed in this structure is the rigid geometry into which the two aromatic rings are locked. The S–O bond eclipses the plane of the 2,4-dinitrophenyl ring. This was expected and corresponds to the geometry found for the 2-nitrobenzenesulfenate derivative of methanol.[9] There is an unusually short interatomic distance between the sulfur atom and an oxygen atom on the *o*-nitro group of the 2,4-dinitrophenyl ring that suggests a partial bonding interaction. It may well be that the eclipsing of the ring by the S–O bond and the C–S–O–C* dihedral angle are together responsible for the major chiroptical effects associated with the absorption bands of the 2,4-dinitrobenzenesulfenyl group. This possibility can be examined by varying the derivatizing group. In addition, the plane of the phenyl ring on the carbinol carbon is eclipsed by the carbinol C–H bond. If one assumes these constraints in addition to the C–S–O–C* dihedral angle, examination of models clearly shows less steric interaction between the ortho hydrogens of the two aromatic rings when the molecule assumes conformation IV, in which S is anti to methyl, over conformation II, in which S is anti to phenyl. Examination of models of conformations I and III reveals them to be more sterically crowded than either II or IV. It may be that with some L groups other than phenyl, conformation II would be preferred over conformation IV. This may explain the predictive failure of this method for some bicyclic secondary alcohols and suggests that careful conformational analysis may make it possible to extend the use of this method to such compounds.

Examination of models of derivatives **2s–v** reveals that the eclipsing of the plane of the phenyl ring by the carbinol C–H bond is not possible. The dihedral angle of the two aromatic planes in these compounds thus approaches zero. Examination of the models indicates that conformation IV should still be preferred sterically over conformation II, but this considerable change in geometry is undoubtedly responsible for the very different CD spectra which are observed for these compounds.

Although there is no guarantee that the solution structure of compound **2m** is in agreement with the solid structure, the fact that this chiral compound crystallizes in a conformation that minimizes steric interaction between the *S*-aryl substituent and the large substituent on the carbinol carbon, while maintaining a virtually orthogonal relationship between the O–C* and S–C bonds of the sulfenate ester unit, suggests that there is indeed induction in the sulfenate ester unit by the chiral carbinol center based on steric considerations.

Conclusion

The signs of the sodium D line rotations of the 2,4-dinitrobenzenesulfenate ester derivatives **2a–v** of acyclic aliphatic and benzylic alcohols are consistently correlated with the arrangement of large, medium, and small groups around the carbinol carbon of the original alcohol. The CD spectra of these derivatives all exhibit at least one transition well above 300 nm solely due to the presence of the 2,4-dinitrobenzenesulfenyl chromophore. It is hypothesized that this transition reflects the inductive effect of the chiral carbinol center on the conformation of the sulfenate ester unit, and that the induced asymmetry is consistently correlated with the arrangement of groups around the carbinol carbon. This hypothesis is supported by the geometry of the crystal structure of derivative **2m**. The sign of these CD transitions can be considered diagnostic for the absolute configuration of the original alcohol, and in the case of the benzylic alcohols the sodium D line optical rotation is large enough to be used to identify the absolute configuration of the alcohol.

The ease with which this potential method of determining absolute configurations can be applied makes it highly attractive. The derivative is easily synthesized from readily available starting materials. Moreover, the use of an achiral derivatizing agent eliminates the problem of kinetic resolution that arises when chiral derivatizing reagents are used.

Experimental Section

General Procedures. Commercially obtained 2,4-dinitrobenzenesulfenyl chloride was recrystallized from CCl_4 before use. The optically active alcohols were used as received. HPLC-grade pyridine and ACS-certified 1,2-dichloroethane were distilled from BaO and stored over 4-Å molecular sieves. Melting point ranges were taken on an Electrothermal digital melting point apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a 300-MHz spectrometer from $CDCl_3$ solutions with a TMS internal reference. UV spectra were obtained on a diode-array UV spectrometer. Optical rotations of the sulfenate esters were taken on a Rudolph Autopol III polarimeter, and CD spectra were taken on an AVIV 60DS Circular Dichroism Spectropolarimeter.

Synthesis of 2,4-Dinitrobenzenesulfenate Esters 2a–v. The method of Kharasch[2a] was used to synthesize the sulfenate esters. A typical procedure follows.

Synthesis of (*S*)-3-Methyl-2-butyl 2,4-Dinitrobenzenesulfenate (2e). 2,4-Dinitrobenzenesulfenyl chloride (0.704 g, 3 mmol) was dissolved in dry 1,2-dichloroethane (5 mL) in a 50-mL Erlenmeyer flask. (*S*)-(+)-3-Methyl-2-butanol (**1e**) (0.264 g,

3 mmol) was added to the sulfenyl chloride solution, followed by 5 mL of 1,2-dichloroethane and 0.24 mL (3 mmol) of dry pyridine, respectively. The reaction mixture was swirled and set aside at room temperature for 30 min. The reaction mixture was then vacuum filtered to remove a light yellow precipitate, which was washed with 1,2-dichloroethane (20 mL). The solvent was removed in vacuo, and the remaining oily yellow solid was washed with cold water, filtered, and dried in vacuo, yielding 0.66 g (74%) of the sulfenate ester **2e** as a yellow powder. The crude product was recrystallized from 15 mL of hot ethanol and a trace of benzene, yielding 0.46 g (54%), bright yellow crystals, mp 78.3–79.7 °C.

Solid products were recrystallized from absolute ethanol or from a mixture of ethanol and benzene or purified by column chromatography. Oils were chromatographed on silica gel (240–400 mesh) in 1:1 (v/v) CH_2Cl_2/hexane. The following sulfenate esters have been previously reported in the literature: **2b**, **2k**, **2l**.[4] In addition, the esters of racemic 2-butanol and racemic 1-phenylethanol have been reported.[2a,b] Sulfenate esters **2a**,**c**–**j**,**m**–**v** are reported here for the first time. The IR, ^1H NMR, and ^{13}C NMR spectra are consistent with the proposed structures of these compounds, and the percent composition found (C, H, N, S) for each compound analyzed is within 0.4% of the percent composition calculated.

Optical Rotations and CD Spectra of Sulfenate Esters. The sulfenate esters and selected original alcohols were dissolved in spectrophotometric grade acetonitrile at a concentration of 1 g/100 mL (except where otherwise specified). Optical rotations were taken in a 1-dm microcell at 30 °C (±1 °C) at 589 nm. CD spectra of the sulfenate esters were taken on 4×10^{-4} M solutions in spectrophotometric-grade acetonitrile in a 0.05-dm cell from 600 to 220 nm (aliphatic) or 200 nm (benzylic).

Single-Crystal X-ray Analysis of 2m. Measurements were made on a Rigaku AFC6S diffractometer with graphite monochromated Mo Kα radiation and a 12-kW rotating anode generator. A clear prism of **2m** having approximate dimensions of 0.400 × 0.300 × 0.500 mm was mounted on a glass fiber. Data were collected at 23 ± 1 °C using the ω scan technique. The crystal was found to be monoclinic, of the space group $P2_1$ with cell dimensions a = 5.751 (2) Å, b = 10.647 (4) Å, c = 12.085 (3) Å, V = 739.6 (4) Å^3, β = 91.95 (2)°. The structure was solved by direct methods.[15] Neutral atom scattering factors were taken from Cromer and Waber.[16] Anomalous dispersion effects were included in Fcalc;[17] the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[16] All calculations were performed using the TEXAN crystallographic software package of Molecular Structure Corporation.[18,19]

(*R*)-2-Butyl 2,4-dinitrobenzenesulfenate (2a): yellow crystals, yield 34%; mp 73–73.5 °C (lit.[2a] racemic mp 71–72 °C); IR (KBr) 3108, 2972, 1589, 1521, 1338, 1302, 880, 831, 744, 734 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.13 (d, 1 H, J = 2.2 Hz), 8.48 (dd, 1 H, J = 9.2, 2.2 Hz), 7.99 (d, 1 H, J = 9.2 Hz), 3.84 (m, 1 H), 1.86 (m, 1 H), 1.73 (m, 1 H), 1.40 (d, 3 H), 1.02 (t, 3 H); ^{13}C NMR ($CDCl_3$) δ 127.53, 123.83, 121.13, 85.53 (C–O), 29.53, 19.70, 9.57; UV (acetonitrile) λ_{194} ϵ 3850, λ_{212} ϵ 7620, λ_{258} ϵ 6550, λ_{338} ϵ 8680, λ_{384} ϵ 6780. Anal. Calcd: C, 44.11; H, 4.44; N, 10.29; S, 11.77. Found: C, 44.51; H, 4.57; N, 10.45; S, 12.01.

(*S*)-2-Butyl 2,4-dinitrobenzenesulfenate (2b): bright yellow crystals, crude yield 89%, mp 69.5–71 °C; recrystallized yield 75%, mp 71–73 °C (lit.[4] mp 71–72 °C); IR (KBr) 3113, 2969, 1589, 1515, 1342, 1301, 1085, 1053, 878, 831, 744, 743 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.11 (d, 1 H, J = 2.64 Hz), 8.48 (dd, 1 H, J = 2.64, 9.24 Hz), 8.00 (d, 1 H, J = 9.24 Hz), 3.85 (m, 1 H), 1.80 (m, 2 H), 1.41 (m, 3 H), 1.03 (t, 3 H); ^{13}C NMR ($CDCl_3$) δ 155.9, 145.0, 139.9, 128.1, 124.5, 121.7, 86.2, 30.2, 20.3, 10.1; UV (acetonitrile) λ_{194} ϵ 6460, λ_{212} ϵ 8400, λ_{258} ϵ 6370, λ_{338} ϵ 7420, λ_{384} ϵ 3750.

(*R*)-2-Pentyl 2,4-dinitrobenzenesulfenate (2c): yellow crystals, crude yield 78.1%, mp 62.4–63.4 °C; recrystallized yield 41.3%, mp 67.9–69.1 °C; IR (KBr) 3117, 2972, 2959, 2934, 2876, 1589, 1518, 1340, 1300, 845, 831, 733 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.11 (d, 1 H, J = 2.6 Hz), 8.48 (dd, 1 H, J = 2.6, 8.8 Hz), 8.00 (d, 1 H, J = 8.8 Hz), 3.91 (sxt, 1 H, J = 6.2 Hz), 1.84 (m, 1 H), 1.64 (m, 1 H), 1.47 (m, 2 H), 1.40 (d, 3 H, J = 6.2 Hz), 0.98 (t, 3 H); ^{13}C NMR ($CDCl_3$) δ 155.4, 144.5, 139.3, 127.5, 123.9, 121.1, 84.3, 39.0, 20.3, 18.7, 14.0 ppm; UV (acetonitrile) λ_{194} ϵ 7480, λ_{212} ϵ 9780, λ_{258} ϵ 7450, λ_{338} ϵ 8740, λ_{380} ϵ 4760.

(*S*)-2-Pentyl 2,4-dinitrobenzenesulfenate (2d): light yellow fluffy crystals, crude yield 74.9%; recrystallized yield 52.4%, mp 67.5–69.5 °C; IR (KBr) 3117, 2972, 2959, 2934, 2876, 1589, 1518, 1341, 1300, 845, 831, 733, 712 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.11 (d, 1 H, J = 2.2 Hz), 8.48 (dd, 1 H, J = 2.2, 9.24 Hz), 8.00 (d, 1 H, J = 9.24 Hz), 3.91 (sxt, 1 H, J = 6.2 Hz), 1.85 (m, 1 H), 1.64 (m, 1 H), 1.48 (m, 2 H), 1.40 (d, 3 H, J = 6.2 Hz), 0.98 (t, 3 H); ^{13}C NMR ($CDCl_3$ δ 156.0, 145.1, 139.9, 128.1, 124.5, 121.7, 85.0, 39.6, 20.9, 19.3, 14.6; UV (acetonitrile) λ_{194} ϵ 8910, λ_{212} ϵ 12150, λ_{258} ϵ 9360, λ_{338} ϵ 11020, λ_{382} ϵ 5800. Anal. Calcd: C, 46.15; H, 4.93; N, 9.78; S, 11.20. Found: C, 45.99; H, 4.81; N, 9.66; O, 11.10.

(*S*)-3-Methyl-2-butyl 2,4-dinitrobenzenesulfenate (2e): bright yellow crystals, crude yield 76.4%; recrystallized yield 53.6%, mp 78.3–79.7 °C; IR (KBr) 3107, 2967, 1597, 1585, 1510, 1340, 1302, 1085, 1051, 918, 871, 738 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.10 (d, 1 H, J = 2.64 Hz), 8.46 (dd, 1 H, J = 2.2, 9.24 Hz), 8.01 (d, 1 H, J = 9.24 Hz), 3.75 (m, 1 H), 2.12 (m, 1 H), 1.32 (d, 3 H, J = 6.2 Hz), 1.03 (d, 3 H, J = 7 Hz)), 1.01 (d, 3 H, J = 7 Hz); ^{13}C NMR ($CDCl_3$) δ 156.0, 145.0, 139.8, 128.1, 124.5, 121.7, 89.5, 34.0, 19.1, 17.6, 16.6; UV (acetonitrile) λ_{194} ϵ 5800, λ_{212} ϵ 7450, λ_{258} ϵ 5640, λ_{340} ϵ 6560, λ_{390} ϵ 3140. Anal. Calcd: C, 46.15; H, 4.93; N, 9.78; S, 11.20. Found: C, 46.13; H, 4.83; N, 9.69; S, 11.06.

(*R*)-2-Hexyl 2,4-dinitrobenzenesulfenate (2f): yellow orange oil, crude yield 84.3%, purified yield 71.3%; IR (neat) 3070, 2920, 2850, 1585, 1505, 1335, 1295, 1225, 1145, 1130, 1100, 1080, 1045, 900, 840, 820, 725 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.13 (d, 1 H, J = 2.2 Hz), 8.47 (dd, 1 H, J = 9.2, 2.2 Hz), 7.99 (d, 1 H, J = 9.2 Hz), 3.88 (sxt, 1 H), 1.85 (m, 1 H), 1.67 (m, 1 H), 1.40 (m, 7 H), 0.94 (t, 3 H); ^{13}C NMR ($CDCl_3$) δ 155.4, 144.3, 139.2, 127.5, 123.9, 121.2, 84.6, 36.5, 27.5, 22.6, 20.2, 14.0 ppm; UV (acetonitrile) λ_{194} ϵ 8290, λ_{212} ϵ 11020, λ_{258} ϵ 8420, λ_{338} ϵ 9920, λ_{382} ϵ 5250. Anal. Calcd: C, 47.99; H, 5.37; N, 9.33; S, 10.68. Found: C, 48.23; H, 5.34; N, 9.17; S, 10.57.

(*S*)-2-Hexyl 2,4-dinitrobenzenesulfenate (2g): yellow-orange oil, crude yield 79.16%, purified yield 63.2%; IR (neat) 3100, 2954, 2924, 2854, 1594, 1502, 1453, 1372, 1334, 1298, 1238, 1145, 1129, 1102, 1080, 1042, 1024, 908, 818, 723 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.10 (d, 1 H, J = 2.2 Hz), 8.47 (dd, 1 H, J = 2.2, 9.2 Hz), 7.99 (d, 1 H, J = 9.2 Hz), 3.88 (sxt, 1 H), 1.85 (m, 1 H), 1.66 (m, 1 H), 1.39 (m, 7 H), 0.94 (t, 3 H); ^{13}C NMR ($CDCl_3$) δ 156.0, 145.0, 139.9, 128.2, 124.6, 121.8, 85.2, 37.2, 28.1, 23.3, 20.9, 14.6; UV (acetonitrile) λ_{194} ϵ 7840, λ_{212} ϵ 9460, λ_{258} ϵ 7020, λ_{338} ϵ 7640, λ_{388} ϵ 3910. Anal. Calcd: C, 47.99; H, 5.37; N, 9.33; S, 10.68. Found: C, 48.25; H, 5.40; N, 9.33; S, 10.60.

(*R*)-2-Heptyl 2,4-dinitrobenzenesulfenate (2h): yellow-orange oil, crude yield 80.5%, purified yield 61.5%; IR (neat) 3120, 2960, 2890, 1585, 1500, 1430, 1365, 1323, 1290, 1220, 1137, 1125, 1100, 1069, 1035, 900, 795, 710 cm-11; ^1H NMR ($CDCl_3$) δ 9.12 (d, 1 H, J = 2.2 Hz), 8.47 (dd, 1 H, J = 2.2, 9.2 Hz), 7.99 (d, 1 H, J = 9.2 Hz), 3.88 (m, 1 H), 1.83 (m, 1 H), 1.65 (m, 1 H), 1.40 (d, 3 H, J = 6.2 Hz), 1.34 (m, 6 H), 0.91 (t, 3 H); ^{13}C NMR ($CDCl_3$) δ 156.1, 145.2, 139.9, 128.2, 124.6, 121.8, 85.2, 37.4, 32.4, 25.7, 23.2, 20.9, 14.6 ppm; UV (acetonitrile) λ_{194} ϵ 3520, λ_{212} ϵ 3710, λ_{256} ϵ 2560, λ_{338} ϵ 2560, λ_{388} ϵ 1370. Anal. Calcd: C, 49.67; H, 5.77; N, 8.91; S, 10.20. Found: C, 49.83; H, 5.78; N, 8.86; S, 10.01.

(*S*)-2-Heptyl 2,4-dinitrobenzenesulfenate (2i): yellow-orange oil which eventually solidified, crude yield 84.0%, purified yield 70.4%; IR (neat) 3094, 2920, 2854, 1582, 1500, 1442, 1372, 1335, 1295, 1225, 1142, 1128, 1103, 1077, 1043, 906, 820, 725, 657 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.10 (d, 1 H, J = 2.2 Hz), 8.46 (dd, 1 H, J = 2.2, 9.24 Hz), 7.98 (d, 1 H, J = 9.24 Hz), 3.88 (sxt, 1 H), 1.83

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(17) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781.

(18) TEXAN – TEXRAY Structure Analysis Package, Molecular Structure Corporation (1985).

(19) The author has deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

(m, 1 H), 1.65 (m, 1 H), 1.39 (d, 3 H), 1.34 (m, 6 H), 0.91 (t, 3 H); ^{13}C NMR ($CDCl_3$) δ 155.4, 144.3, 139.2, 127.5, 123.9, 121.1, 84.6, 36.8, 31.7, 25.0, 22.5, 20.2, 14.0; UV (acetonitrile) λ_{194} ε 3970, λ_{212} ε 4680, λ_{258} ε 3380, λ_{338} ε 3780, λ_{388} ε 1900. Anal. Calcd: C, 49.67; H, 5.77; N, 8.91; S, 10.20. Found: C, 49.83; H, 5.80; N, 8.84; S, 10.01.

(*R*)-2-Octyl 2,4-dinitrobenzenesulfenate (2j): yellow-orange oil (lit.[4] enantiomer, oil), crude yield 84.2%, purified yield 72.2%; IR (neat) 3080, 2910, 2850, 1195, 1510, 1455, 1385, 1345, 1300, 1235, 1152, 1138, 1115, 1089, 1055, 910, 839, 830, 735 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 9.12 (d, 1 H, *J* = 2.6 Hz), 8.48 (dd, 1 H, *J* = 9.2, 2.6 Hz), 8.00 (d, 1 H, *J* = 9.2 Hz), 3.89 (sxt, 1 H), 1.85 (m, 1 H), 1.65 (m, 1 H), 1.40 (d, 3 H, *J* = 6.2 Hz), 1.31 (m, 8 H), 0.90 (t, 3 H); ^{13}C NMR ($CDCl_3$) δ 156.1, 145.0, 139.9, 128.2, 124.6, 121.8, 85.2, 37.5, 32.4, 29.9, 26.0, 23.2, 20.9, 14.7 ppm; UV (acetonitrile) λ_{194} ε 5480, λ_{212} ε 6650, λ_{258} ε 4930, λ_{338} ε 5680, λ_{386} ε 2870.

(*S*)-2-Octyl 2,4-dinitrobenzenesulfenate (2k): yellow-orange oil (lit.[4] oil), crude yield 75.47%, purified yield 53.5%; IR (neat) 3096, 2916, 2846, 1591, 1515, 1461, 1379, 1341, 1300, 1233, 1150, 1136, 1112, 1086, 1050, 918, 823, 733, 667 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 9.11 (d, 1 H, *J* = 2.64 Hz), 8.48 (dd, 1 H, *J* = 2.64, 9.24 Hz), 8.00 (d, 1 H, *J* = 9.24 Hz), 3.89 (sxt, 1 H), 1.84 (m, 1 H), 1.65 (m, 1 H), 1.40 (d, 3 H), 1.32 (m, 8 H), 0.90 (t, 3 H); ^{13}C NMR ($CDCl_3$) δ 156.1, 145.0, 139.9, 128.2, 124.6, 121.8, 85.2, 37.5, 32.4, 29.9, 26.0, 23.2, 20.9, 14.7; UV (acetonitrile) λ_{192} ε 3450, λ_{212} ε 4120, λ_{258} ε 3050, λ_{338} ε 3490, λ_{388} ε 1740.

(*R*)-*sec*-Phenethyl 2,4-dinitrobenzenesulfenate (2l): yellow crystals, crude yield 81.1%, mp 105.3 °C (lit.[4] mp 90.5–91 °C); recrystallized yield 38.7%, mp 106.5–108.1 °C; IR (KBr) 3106, 1588, 1512, 1341, 1300, 1134, 1084, 1051, 878, 737, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 9.10 (d, 1 H, *J* = 2.64 Hz), 8.39 (dd, 1 H, *J* = 2.2, 9.23 Hz), 7.87 (d, 1 H, *J* = 9.24 Hz), 7.40 (s, 5 H), 4.78 (q, 1 H), 1.76 (d, 3 H); ^{13}C NMR ($CDCl_3$) δ 155.3, 141.5, 129.6, 129.5, 128.3, 127.1, 124.6, 121.8, 86.8 (C–O), 24.0 ppm; UV (acetonitrile) λ_{200} ε 16 580, λ_{212} ε 18 800, λ_{258} ε 9650, λ_{336} ε 11 030, λ_{382} ε 5590.

(*S*)-*sec*-Phenethyl 2,4-dinitrobenzenesulfenate (2m): yellow crystals, yield 53%, mp 92–94 °C (lit.[2b] racemic, mp 92–93 °C); IR (KBr) 3104, 2981, 1586, 1503, 1339, 1302, 1053, 877, 744, 736, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 9.10 (d, 1 H, *J* = 2.4 Hz), 8.40 (dd, 1 H, *J* = 2.4, 9.0 Hz), 7.87 (d, 1 H, *J* = 9.0 Hz), 7.40 (m, 5 H), 4.78 (q, 1 H), 1.76 (d, 3 H); ^{13}C NMR ($CDCl_3$) δ 129.62, 128.29, 127.13, 124.59, 121.77, 86.79 (C–O), 24.02; UV (acetonitrile) λ_{200} ε 16780, λ_{212} ε 18830, λ_{260} ε 10120, λ_{336} ε 11050, λ_{382} ε 5610. Anal. Calcd: C, 52.50; H, 3.78; N, 8.75; S, 10.01. Found: C, 52.46; H, 3.63; N, 8.46; S, 10.21.

(*R*)-1-Phenylbutyl 2,4-dinitrobenzenesulfenate (2n): yellow crystals, crude yield 94.8%, mp 71.7–78.4 °C; recrystallized yield 49.6%, mp 70–73 °C; IR (KBr) 3086, 3029, 2927, 1589, 1525, 1514, 1453, 1344, 1302, 1085, 1053, 912, 831, 812, 770, 734, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 9.07 (d, 1 H, *J* = 2.6 Hz), 8.34 (dd, 1 H, *J* = 2.2, 9.2 Hz), 7.84 (d, 1 H, *J* = 8.8 Hz), 7.37 (m, 5 H), 4.60 (t, 1 H), 2.19 (m, 1 H), 1.95 (m, 1 H), 1.37 (m, 2 H), 0.96 (t, 3 H); ^{13}C NMR ($CDCl_3$) δ 154.7, 144.5, 139.8, 139.2, 129.0, 128.8, 127.4, 127.1, 124.0, 121.0, 90.5, 39.3, 18.9, 13.9 ppm; UV (acetonitrile) λ_{198} ε 17130, λ_{212} ε 20240, λ_{258} ε 10530, λ_{338} ε 11990, λ_{386} ε 5920.

(*S*)-1-Phenylbutyl 2,4-dinitrobenzenesulfenate (2o): bright yellow crystals, crude yield 87.4%, mp 64.6–75.1 °C; recrystallized yield 22.6%, mp 71–73 °C; IR (KBr) 3087, 2960, 1590, 1517, 1342, 1302, 1052, 912, 734, 699 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 9.07 (d, 1 H, *J* = 2.64 Hz), 8.34 (dd, 1 H, *J* = 2.2, 9.24 Hz), 7.84 (d, 1 H, *J* = 9.23 Hz), 7.37 (m, 5 H), 4.60 (t, 1 H), 2.19 (m, 1 H), 1.95 (m, 1 H), 1.37 (m, 2 H), 0.96 (t, 3 H); ^{13}C NMR ($CDCl_3$) δ 154.8, 144.5, 139.8, 139.3, 129.0, 128.9, 127.4, 127.1, 124.0, 121.0, 90.5, 39.3, 18.9, 13.9 ppm; UV (acetonitrile) λ_{198} ε 17 110, λ_{212} ε 19 750, λ_{260} ε 10 600, λ_{338} ε 11 650, λ_{386} ε 5750.

(*R*)-2-Methyl-1-phenylpropyl 2,4-dinitrobenzenesulfenate (2p): yellow crystals, crude yield 60%, mp 99.5–102.5 °C; recrystallized yield 35%, mp 93–94 °C; IR (KBr) 3106, 2965, 2903, 1589, 1514, 1343, 1302, 897, 799 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 9.06 (d, 1 H, *J* = 2.2 Hz), 8.29 (dd, 1 H, *J* = 2.2, 9.24 Hz), 7.83 (d, 1 H, *J* = 9.23 Hz), 7.32 (m, 5 H), 4.35 (d, 1 H, *J* = 7.92 Hz), 2.36 (m, 1 H), 1.19 (d, 3 H, *J* = 6.6 Hz), 0.841 (d, 3 H, *J* = 6.6 Hz); ^{13}C NMR ($CDCl_3$) δ 155.5, 149.9, 139.2, 129.5, 129.2, 128.3, 128.0, 124.7, 121.7, 96.6, 35.3, 20.1, 19.1 ppm; UV (acetonitrile) λ_{200} ε 17 360, λ_{212} ε 18 990, λ_{260} ε 9870, λ_{338} ε 11 200, λ_{386} ε 5670.

(*S*)-2-Methyl-1-phenylpropyl 2,4-dinitrobenzenesulfenate (2q): yellow crystals, crude yield 81.3%, recrystallized yield 44.1%, mp 98–99 °C; IR (KBr) 3108, 2965, 2905, 1587, 1514, 1342, 1302, 884, 799 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 9.04 (d, 1 H, *J* = 2.2 Hz), 8.28 (dd, 1 H, *J* = 2.2, 8.8 Hz), 7.82 (d, 1 H, *J* = 8.8 Hz), 7.34 (m, 5 H), 4.35 (d, 1 H), 2.36 (m, 1 H), 1.18 (d, 3 H), 0.84 (d, 3 H); ^{13}C NMR ($CDCl_3$) δ 154.8, 144.4, 138.6, 128.8, 128.6, 127.7, 127.3, 124.0, 120.9, 96.0, 34.7, 19.4, 18.4 ppm; UV (acetonitrile) λ_{200} ε 17 340, λ_{212} ε 18 760, λ_{260} ε 10 660, λ_{338} ε 10 990, λ_{386} ε 5580. Anal. Calcd: C, 55.16; H, 4.63; N, 8.04; S, 9.20. Found: C, 55.21; H, 4.57; N, 8.02; S, 9.10.

(*S*)-(α-Methylnaphthyl)methyl 2,4-dinitrobenzenesulfenate (2r): yellow crystals, yield 48%, mp 100.1–100.4 °C dec; IR (KBr) 3098, 3082, 2982, 1599, 1585, 1516, 1345, 1303, 1053, 980, 893, 851, 830, 746 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 9.07 (d, 1 H, *J* = 2.2 Hz), 8.37 (dd, 1 H, *J* = 2.2, 9.2 Hz), 7.91 (d, 1 H, *J* = 9.2 Hz), 7.90 (d, 1 H), 7.86 (t, 1 H), 7.85 (t, 1 H), 7.80 (s, 1 H), 7.53 (m, 3 H), 4.94 (q, 1 H), 1.84 (d, 3 H); ^{13}C NMR ($CDCl_3$) δ 138.21, 128.93, 128.07, 127.80, 127.63, 126.61, 125.89, 123.87, 123.62, 121.06, 86.18 (C–O), 23.44 (CH_3); UV (acetonitrile) λ_{226} ε 29 340, λ_{266} ε 13 160, λ_{336} ε 10 720, λ_{384} ε 5350. Anal. Calcd: C, 58.37; H, 3.81; N, 7.56; S, 8.66. Found: C, 58.18; H, 3.68; N, 7.53; S, 8.72.

(*R*)-1-Indanyl 2,4-dinitrobenzenesulfenate (2s): bright yellow solid, crude yield 88.7%, mp 98.5–98.7 °C; purified yield 75.3%, mp 76.8–85.2 °C; IR (KBr) 3106, 2934, 1596, 1587, 1343, 1303, 1136, 1086, 1050, 885, 791, 759, 733 cm^{-1}; ^{1}H NMR (acetone-d_6) δ 9.03 (d, 1 H, *J* = 2.2 Hz), 8.61 (dd, 1 H, *J* = 2.2, 9.24 Hz), 8.07 (d, 1 H, *J* = 9.24 Hz), 7.66 (d, 1 H, *J* = 7.5 Hz), 7.36 (m, 2 H), 7.24 (m, 1 H), 5.43 (t, 1 H), 3.23 (m, 1 H), 2.84 (m, 1 H), 2.48 (m, 2 H); UV (acetonitrile) λ_{204} ε 24 340, λ_{214} ε 23 230, λ_{260} ε 11 660, λ_{266} ε 11 450, λ_{338} ε 12 430, λ_{382} ε 6910.

(*S*)-1-Indanyl 2,4-dinitrobenzenesulfenate (2t): bright yellow solid, crude yield 83.8%, mp 93.6–94.9 °C dec; purified yield 65.7%, mp 82.5–90.8 °C; IR (KBr) 3107, 2936, 1588, 1504, 1481, 1343, 1302, 1085, 1051, 922, 885, 863, 791, 732 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 9.10 (d, 1 H, *J* = 2.2 Hz), 8.35 (dd, 1 H, *J* = 2.2, 9.24 Hz), 7.79 (d, 1 H, *J* = 9.24 Hz), 7.51 (d, 1 H, *J* = 7.5 Hz), 7.33 (m, 1 H), 7.21 (m, 2 H), 5.31 (m, 1 H), 3.23 (m, 1 H), 2.95 (m, 1 H), 2.45 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 155.5, 145.7, 139.9, 130.7, 127.8, 127.5, 126.2, 126.0, 124.6, 121.6, 91.4, 33.9, 31.0 ppm; UV (acetonitrile) λ_{204} ε 22 870, λ_{212} ε 22 460, λ_{260} ε 11 420, λ_{266} ε 11 240, λ_{338} ε 12 130, λ_{386} ε 6340.

(*R*)-1,2,3,4-Tetrahydro-1-naphthyl 2,4-dinitrobenzenesulfenate (2u): bright yellow solid, crude yield 93.4%, mp 98.1–99.6 °C; purified yield 83.3%, mp 86.4–88.0 °C; IR (KBr) 3100, 2934, 1588, 1515, 1454, 1392, 1336, 1301, 1136, 1052, 916, 823, 758, 732, 675 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 9.09 (d, 1 H, *J* = 2.2 Hz), 8.35 (dd, 1 H, *J* = 2.2, 9.0 Hz), 7.90 (d, 1 H, *J* = 9.0 Hz), 7.39 (d, 1 H), 7.35 (q, 1 H), 7.19 (m, 2 H), 4.87 (t, 1 H), 2.97 (m, 1 H), 2.81 (m, 1 H), 2.42 (m, 1 H), 2.15 (m, 1 H), 2.00 (m, 1 H), 1.92 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 155.7, 145.0, 139.8, 138.6, 134.2, 130.6, 130.2, 129.9, 127.9, 126.7, 124.8, 121.6, 84.3, 29.7, 29.4, 18.6 ppm; UV (acetonitrile) λ_{206} ε 24 950, λ_{256} ε 11 720, λ_{338} ε 5840, λ_{386} ε 2960.

(*S*)-1,2,3,4-Tetrahydro-1-naphthyl 2,4-dinitrobenzenesulfenate (2v): bright yellow solid, crude yield 90.1%, mp 87.5–87.7 °C; purified yield 53.7%, mp 85.3–87.3 °C dec; IR (KBr) 3100, 2934, 1589, 1517, 1341, 1301, 1137, 1085, 1053, 823, 790, 733 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 9.10 (d, 1 H, *J* = 2.2 Hz), 8.35 (dd, 1 H, *J* = 2.65, 9.24 Hz), 7.90 (d, 1 H, *J* = 9.24 Hz), 7.38 (d, 1 H), 7.28 (m, 1 H), 7.17 (m, 2 H), 4.87 (t, 1 H), 2.97 (m, 1 H), 2.81 (m, 1 H), 2.42 (m, 1 H), 2.15 (m, 1 H), 2.02 (m, 1 H), 1.92 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 155.7, 138.6, 134.2, 130.6, 130.2, 129.9, 127.9, 126.8, 124.8, 121.7, 84.3, 29.7, 29.4, 18.6 ppm; UV (acetonitrile) λ_{210} ε 19 360, λ_{254} ε 10 520, λ_{334} ε 1910.

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Supplementary Material Available: ^{1}H and ^{13}C NMR spectra for new sulfenate esters for which elemental analysis is not given (15 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.