Application of Dipole Moment, NMR, and Infrared Data to Configurational Studies on p-Tolylmercapto- and p-Tolylsulfonylalkenes[1]

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The efficacy of dipole moments for determining configurations of a series of p-tolylmercapto- and p-tolylsulfonylethenes was examined. The infrared spectra of these compounds were correlated with their structure. Values for the proton spin-spin coupling constants of certain members of this series were in agreement with their assigned geometry.

Dipole moments usually offer unambiguous configurational proof for symmetrically-substituted olefins if the substituents consist either of polar atoms or polar groups whose moments are colinear with the bond joining them to the double bond.[2] However, if these pendant groups are angular and the possibility of their free rotation exists, dipole moment measurements may not always show a distinct difference between cis and trans isomers. Certain p-tolylmercapto- and p-tolylsulfonylethenes, and their chlorinated derivatives, fall into the latter category, and it was of interest to determine whether the geometry of these molecules could be elucidated from dipole moment data. The wide variety of compounds prepared for the dipole moment study also allowed evaluation of infrared and NMR spectroscopy as configurational proofs.

EXPERIMENTAL

Materials. Phillips Research Grade[3] (99.93 mole%) or Eastman Spectroscopic Grade benzene was distilled through a glass helix-packed Todd column and stored over sodium; n_D^{25} 1.4979 and 1.4978, respectively; lit.[4] n_D^{25} 1.4981. Matheson-Coleman-Bell Spectroquality dioxane was similarly distilled and stored; n_D^{25} 1.4199; lit.[5] n_D^{25} 1.4203. Compounds studied, their physical constants, and references to the method of preparation are summarized in Table I. All liquids were rectified through a spinning band column; solids were recrystallized from a variety of solvents to a constant melting point.

(1) Taken from Dr. Groten's Ph.D. thesis.
(2) C. P. Smyth, *Dielectric Behavior and Structure*, McGraw-Hill Book Company, Inc., New York, N. Y., 1955, Chap. VIII, *et seq.*
(3) The authors wish to thank the Phillips Petroleum Co. for a gift of this reagent.
(4) International Critical Tables, McGraw-Hill Book Co., Inc., New York, N. Y., 1930, Vol. VII.
(5) C. P. Smyth and W. S. Walls, *J. Am. Chem. Soc.*, 53, 2115 (1931).
(6) W. E. Truce and M. M. Boudakian, *J. Am. Chem. Soc.*, 78, 2748 (1956).
(7) W. E. Truce and R. McManimie, *J. Am. Chem. Soc.*, 76, 5745 (1954).
(8) W. E. Truce and R. Kassinger, *J. Am. Chem. Soc.*, 80, 1916, 6450 (1958).
(9) E. Fromm and E. Seibert, *Ber.*, 55B, 1014 (1922).
(10) J. F. Arens, *Rec. trav. chim.*, 76, 853 (1957).
(11) F. Montanari, *Tetrahedron Letters*, 4, 18 (1960).
(12) E. H. Huntress, *Organic Chlorine Compounds*, John Wiley and Sons, Inc., New York, N. Y., 1948.

Apparatus, procedure, and calculations. The dielectric constants were measured by means of a commercial apparatus: the Dipolemeter, model DMO1, manufactured by Wissenschaftlich-Technische Werkstatten, Weilheim (Obb.), Germany. The equipment employed the heterodyne beat principle and operated at a frequency of two megacycles. The cell, model DFL-1, connected directly into a socket in the side of the Dipolemeter, and was thus well shielded from the extraneous capacitances often encountered with cables and connectors. The outer part of the cell, which contained the thermostat jacket, was also the outer electrode. The inner electrode, mounted through the side wall, was insulated from the assembly by means of a ceramic plug. The entire surface of both electrodes was gold plated. The removable lid of the cell was provided with a Teflon gasket making the entire unit vacuum tight. Ground glass joints were press-fitted into both the lid and base of the cell. The volume of the inner chamber was 20 ml. and the effective capacitance was given by the manufacturer as 35 pF. In practice, however, we have consistently found the effective capacitance to be nearer 24 pF. The cell temperature was maintained at 25° ± 0.03° by means of a recirculating water bath.

A glass reservoir and mixing chamber was connected to the lower joint of the cell. A Teflon gasket in this joint, and a Teflon stopcock in the stem, obviated the need for stopcock greases, most of which were soluble in the dipole solvents. An air line, previously led through a potassium hydroxide/Drierite drying tower, was also connected to the reservoir. With this arrangement, liquid could be forced from the reservoir into the cell by air pressure, and allowed to return to the reservoir by gravity.

A capacitance reading was first taken for dry air, then for pure solvent, and finally for a series of solutions in which the concentration of solute was gradually increased (maximum concentration less than approximately 0.04 mole fraction solute). Refractive index and density measurements were performed on the final solution; the latter done in duplicate using modified Sprengel-Ostwald pycnometers of *ca.* 5 cc. capacity.

A plot of dielectric constant versus mole fraction solute was linear in each case; slopes ($\Delta\epsilon/f_2$) were calculated by the

(13) Unpublished work from this laboratory. This compound arose from attempted oxidations of $(ArS)_2C=CHSAr$ and $(ArS)_2C=C(SAr)_2$ to the corresponding tri- and tetrasulfones, respectively, by means of hydrogen peroxide in acetic acid; this contrasts with an earlier claim to the formation of the trisulfone.[8]
(14) R. Leuckart, *J. prakt. Chem.*, [2] 41, 179 (1890).
(15) E. Fromm, A. Forster, and B. Scherschewitzki, *Ann.*, 394, 348 (1912).
(16) J. L. Jones and R. L. Taylor, *J. Am. Chem. Soc.*, 62, 3480 (1940).
(17) W. E. Truce et al., *J. Am. Chem. Soc.*, 82, 3799 (1960).
(18) Analyses were performed by Dr. C. S. Yeh and Mrs. B. Groten of the Purdue Microanalytical Laboratory.

TABLE I

PHYSICAL PROPERTIES OF SUBSTITUTED ETHEMES[18]

	M.P.	B.P. (Mm.)	n_D^{20a}	Reference
ArSCH=CH$_2$		42–3 (0.8–1.0)	1.5729	6
cis-ArSCH=CHSAr	91–92			6,7
trans-ArSCH=CHSAr	55.5–56.5			7
(ArS)$_2$C=CH$_2$	62–3			10
(ArS)$_2$C=CHSAr	60.5–61.5[b]			8
(ArS)$_2$C=C(SAr)$_2$[c]	197–198[d]			8
(ArS)$_2$CH—CH$_2$SAr	62–63			9, 10
ArSC≡CSAr	101–101.5			8
cis-ArSCH=CHCOOH	143–144.5			11, 17
trans-ArSCH=CHCOOH	134.5–135.5			11, 17
cis-ArSCH=CHCOOC$_2$H$_5$	47–48			11, 17
trans-ArSCH=CHCOOC$_2$H$_5$		134–136 (1.4–1.5)	1.5710 (25)	11, 17
cis-ClCH=CHCl		60 (760)	1.4435 (25)	16
Cl$_2$C=CHCl		87 (760)	1.4742 (25)	12
cis-(ArS)ClC=CCl(SAr)	101–102			8
trans-(ArS)ClC=CCl(SAr)	81–82			8
cis-(ArSO$_2$)CCl=CCl(SO$_2$Ar)	185–186			8
trans(ArSO$_2$)CCl=CCl(SO$_2$Ar)	151–152			8
trans-(ArS)ClC=CHCl[d]		70–1.5 (0.5)	1.5964	8
trans-ArSCH=CHCl		104–5.5 (4.0)	1.5918	6
cis-ArSO$_2$CH=CHCOOC$_2$H$_5$	47.5–49			11
trans-ArSO$_2$CH=CHCOOC$_2$H$_5$	86–87			11
(ArSO$_2$)$_2$CH$_2$	136–137			13, 15
ArSSAr	45–46			14
trans-ArSO$_2$CH=CHSO$_2$Ar[c]	227–229			7

[a] Temperatures other than 20° given in parentheses. [b] An isomorphic form, m.p. 56–57°, was also found. [c] Dipole moment could not be obtained because of insufficient solubility. [d] *trans* refers to the relative positions of the chlorine atoms.

method of least squares.[19] The polarization of the solute ($P_{2\infty}$) was obtained by means of a limiting form of the Hedestrand equation[20,21] and total distortion polarization was assumed equal to the molecular refraction measured at the sodium D line. In cases where the compounds were liquids available in sufficient quantities, P_e was also determined from density and refractive index measurements on the pure liquid. These values were in good agreement with the solution data.

Infrared. Three different Perkin-Elmer double beam instruments were used; the models 21, 221, and 137B, all equipped with sodium chloride optics. Solution spectra were taken in cells of 0.095 (sample) and 0.099 (solvent) mm. thickness. Although concentrations were not absolutely constant, most of the solution spectra are in the range of 5–15% solute.

NMR.[22] The equipment consisted of a Varian V4311 spectrometer operating at a frequency of 60 mc./sec. Samples were run in either carbon disulfide or carbon tetrachloride, and the spectra were calibrated by the usual side-band technique.

DISCUSSION

Dipole moments. Although the calculated values for the dipole moments of the *cis/trans* pairs shown in Table II are close, the differences are of significant magnitude, and, as calculated value for the *cis* isomer is always higher, the method had potential as

a configurational proof provided both isomers were compared. The theoretical figures were obtained by known methods[23] using the measured moment of vinyl *p*-tolyl sulfide, 1.73 D., as the moment for the Ar—S—C= group. Since the vinylic C—H bond has negligible polarity,[24] this approach should give more accurate values than the use of an estimated 1.65 D., derived from the moments of divinyl sulfide[25] and di-*p*-tolyl sulfide,[26] assuming the sulfur bond angle to be 109° 30′.[27,28] The possible sources of the deviations of other measured values in Table II will now be discussed.

The outstanding agreement between the experimental values for *trans*-1,2-bis(*p*-tolylmercapto)-ethene, 2.37 D., bis(*p*-tolylmercapto)ethyne, 2.39 D., and the theoretical value of 2.36 D. calculated for two *p*-tolylmercapto groups with axes of rotation 180° apart, is a very strong indication that in these compounds, there is indeed *fully free rotation of the arylmercapto units.*[29] The experi-

(19) C. A. Bennett and N. L. Franklin, *Statistical Methods in Chemistry and the Chemical Industry*, John Wiley and Sons, Inc., New York, N. Y., 1954.

(20) G. Hedestrand, *Z. physik. Chem.*, B2, 428 (1929).

(21) P. Brown and T. DeVries, *J. Am. Chem. Soc.*, 73, 1811 (1951).

(22) The authors wish to thank Mr. W. Baitinger for the actual determination of these spectra.

(23)(a) O. Fuchs, *Z. physik. Chem.*, 14B, 339 (1931). (b) K. B. Everard and L. E. Sutton, *J. Chem. Soc.*, 16, (1951).

(24) J. W. Smith, *Electric Dipole Moments*, Butterworths Scientific Publications, London, 1955, p. 124.

(25) N. B. Hannay and C. P. Smyth, *J. Am. Chem. Soc.*, 68, 1005 (1946).

(26) E. C. Hunter and J. Partington, *J. Chem. Soc.*, 2822 (1932).

(27) C. W. N. Cumper and S. Walker, *Trans. Faraday Soc.*, 52, 193 (1956).

(28) C. W. N. Cumper and A. I. Vogel, *J. Chem. Soc.*, 3521 (1959).

TABLE II
Dipole Moments

Structural Formula[a]	f_2	$P_{2\infty}$	Pe	μ[b]	μ (Calcd.)
ArSCH=CH$_2$	0.0066	111.77	50.52	1.73	1.65
cis-ArSCH=CHSAr	0.0174	226.10	87.48	2.61	2.49
trans-ArSCH=CHSAr	0.0080	211.08	96.11	2.37	2.36
(ArS)$_2$C=CH$_2$	0.0071	226.37	102.76	2.46	2.40
(ArS)$_2$C=CHSAr	0.0057	247.75	128.30	2.38	2.92
ArSC=CSAr	0.0077	216.17	97.29	2.39	2.36
cis-ClCH=CHCl	0.0377	88.86	19.79	1.84	2.42
Cl$_2$C=CHCl	0.0336	44.52	24.97	0.99	1.44
cis-ArSCCl=CClSAr	0.0050	220.17	102.64	2.39	3.04
trans-ArSCCl=CClSAr	0.0045	260.09	121.92	2.60	2.36
trans-ArSClC=CHCl	0.0083	127.02	55.58	1.87	1.73
trans-ArSCH=CHCl	0.0092	140.02	46.93	2.13	1.93
cis-ArSO$_2$CCl=CClSO$_2$Ar	0.0018	769.95	140.09	5.55	6.50
trans-ArSO$_2$CCl=CClSO$_2$Ar	0.0021	477.12	133.50	4.10	6.47
cis-ArSCH=CHCOOH	0.0070	184.58	61.74	2.44	2.43
trans-ArSCH=CHCOOH	0.0037	213.45	56.65	2.77	2.30
cis-ArSCH=CHCOOC$_2$H$_5$	0.0054	213.69	88.53	2.47	2.59
trans-ArSCH=CHCOOC$_2$H$_5$	0.0109	215.38	73.20	2.64	2.44
cis-ArSO$_2$CH=CHCOOC$_2$H$_5$	0.0025	517.60	103.54	4.50	5.18
trans-ArSO$_2$CH=CHCOOC$_2$H$_5$	0.0040	634.62	116.41	5.03	5.00
(ArS)$_2$CH—CH$_2$SAr	0.0013	371.82	129.74	3.44	
(ArSO$_2$)$_2$CH$_2$	0.0007	1140.1	374.61	6.12	6.30
ArSSAr	0.0077	215.69	87.17	2.51	2.36

[a] Ar = p-tolyl. [b] ±0.03 D., or less.

mental value for cis-1,2-bis(p-tolylmercapto)ethene, 2.61 D., on the other hand, does not agree as well with its calculated value (2.49 D.), and the explanation probably lies in the steric interference to free rotation caused by the proximity of the two bulky substituents. The measured moment of 1,1-bis(p-tolylmercapto)ethene, 2.46 D., shows a slightly smaller deviation from its theoretical 2.40 D. This would be expected, if steric influences are important, as the axes of rotation of the two arylmercapto groups are 120° apart in the 1,1 isomer as compared to 60° apart in the cis-1,2 compound.[30] The direction of these deviations is also significant, since both of these compounds exhibit higher moments than calculated. Molecular models, or a simple vector diagram, show that the conformations which are sterically prohibited are those in which the moment would tend to be low, hence the hindrance tends to increase the over-all statistical moment.

The substitution of chlorine for hydrogen in the arylmercapto ethylenic system complicates interpretation of the moments somewhat, since both the inductive and resonance effects of the chlorine will modify the simple considerations discussed above.

cis-Dichloroethylene, which was one of the first structures studied by means of dipole moments, gave an experimental moment of 1.84 D., which is

in excellent agreement with the literature value of 1.85 D.[31] However, a theoretical calculation gives the moment of this compound as 2.42 D., using the moment of vinyl chloride, 1.44 D., as the group moment of the C—Cl unit. The classical explanation for the lowering of the observed moment is based on the mutual induction of the two C—Cl groups.[2] Trichloroethylene should have the same theoretical moment as vinyl chloride, 1.44 D., since the two trans chlorines effectively cancel one another. However, the measured moment, 0.99 D., which is in excellent agreement with the literature value of 0.94 D.,[31] is low, again presumably because of mutual induction. The moment of trans - 1,2 - dichloro - 1 - (p - tolylmercapto)ethene is found to be 1.87 D., which is slightly higher than anticipated.[32] Also, the moment of trans-1,2 - bis(p - tolylmercapto) - 1,2 - dichloroethene, 2.60 D., is slightly higher than the calculated 2.36 D. cis-1,2-Bis(p-tolylmercapto)-1,2-dichloroethene exhibits a moment of 2.39 D., which is lower than the theoretical 3.04 D., and finally, trans-1-(p-tolylmercapto)-2-chloroethene has a moment, 2.13 D., again somewhat higher than theoretical (1.93 D.). In all of these cases, there is insufficient justification for assigning the deviations to either mutual induction or to steric inhibition of rotation alone, since, in all probability, both effects operate simultaneously. There is still another potential

(29) Everard and Sutton (ref. 23b) have shown that the calculated moments for quinol dimethyl ethers, which are geometrically analogous to these compounds, are the same for freely rotating substituents or for a mixture of equally probable "cis" and "trans" forms.

(30) Molecular models support this statement, despite the greater linear separation in the 1,2-isomer.

(31) L. G. Wesson, Tables of Electric Dipole Moments, Technology Press, Cambridge, Mass., 1948.

(32) By simply replacing a chloro group in trichloroethylene with a p-tolylmercapto group, the resulting moment would be expected to approximate that of vinyl-p-tolyl sulfide (1.73 D.).
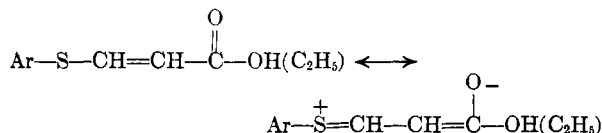
source of perturbation which arises from resonance forms made possible by expansion of the sulfur and chlorine octets:[24,33,34] In the case of

$$Ar—S—CH=CH—Cl \longleftrightarrow Ar—\overset{-}{S}=CH—CH=\overset{+}{Cl} \longleftrightarrow$$
$$Ar—\overset{+}{S}=CH—CH=\overset{-}{Cl}$$
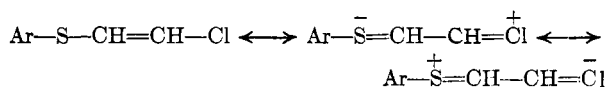
trans-1-(*p*-tolylmercapto)-2-chloroethene, steric hindrance is hardly likely, and the enhanced moment is most probably explained by the resonance possibilities pictured above.

Much of the foregoing discussion is also applicable to the substituted acrylic acids and esters, since the carboxyl and carbethoxyl groups are electron-withdrawing, capable of resonance interaction across the double bond, and possess considerable steric requirements.

The experimental values for *trans*-β-(*p*-tolylmercapto)acrylic acid, 2.77 D., and its ethyl ester, 2.64 D., are both higher than their respective theoretical values of 2.30 D., and 2.44 D. Since the two substituents in each of these compounds are separated by a considerable distance, steric interactions should be negligible, and the cause of the deviations is very likely *not* attributable to inhibition of rotation of either group. Most probably, the enhancement is largely due to the following resonance interactions:

$$Ar—S—CH=CH—\overset{\overset{\displaystyle O}{\|}}{C}—OH(C_2H_5) \longleftrightarrow$$
$$Ar—\overset{+}{S}=CH—CH=\overset{\overset{\displaystyle O-}{|}}{C}—OH(C_2H_5)$$

Rogers[35] showed that *p*-methoxybenzoic acid and its analogs had higher moments than those calculated by vector addition of their individual groups. He attributed this increment to the following resonance forms:
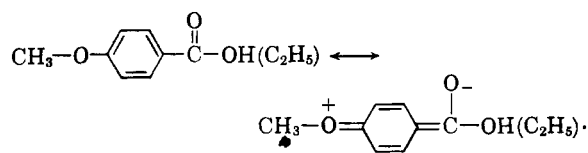
The similarity between these aromatics and the arylmercaptoacrylic acids and esters is obvious, and even the size of the disparity in moments is of approximately the same magnitude. An additional indication that this type of resonance interaction occurs is the fact that the moment of *trans*-ethyl-β-(*p*-tolylsulfonyl)acrylate, 5.03 D., agrees within experimental error with its theoretical value of 5.00 D. Since sulfones cannot resonate in the manner shown above,[36] the calculated moment reduces to simple vector addition of the two ethylenic substituents.

The theoretical moment for *p*-tolyldisulfide, ArS—SAr, should be identical to that computed for bis(*p*-tolylmercapto)ethyne, since, in both cases, the moment results from two freely rotating arylmercapto groups 180° apart. The main difference between these two compounds is the linear separation of the sulfur atoms. Rotation appears to be completely free in the acetylenic compound (as well as in the *trans*-disubstituted ethylene), but there is apparently some degree of restriction in the case of the disulfide, since its measured moment of 2.51 D. is slightly high. It has been shown that steric repulsions do exist for a number of peroxides and disulfides,[37-39] and that the exhaltation of the moment can be correlated with the steric requirements of the two groups on the S—S backbone.

Infrared studies. Although the relation of infrared absorption to geometrical configuration about the olefinic double bond has been extremely well documented for hydrocarbons,[40-43] and for olefins containing certain polar substituents,[40,43-53] the literature is comparatively sparse with respect to unsaturated sulfur compounds.[54-61] Moreover,

(37) Y. Morino and S. Mizushima, *Sci. Papers Inst., Phys. Chem. Research (Tokyo)*, **32**, 220 (1937).

(38) E. Bergmann and M. Tschudnowsky, *Z. physik. Chem.*, **17B**, 107 (1932).

(39) M. T. Rogers and T. Campbell, *J. Am. Chem. Soc.*, **74**, 4742 (1952).

(40) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Methuen, London, 2nd ed., 1959.

(41) N. Sheppard and D. M. Simpson, *Quart. Revs.*, **6**, 1 (1952).

(42) R. S. Rasmussen and R. R. Brattain, *J. Chem. Phys.*, **15**, 120, 131, 135 (1947).

(43) R. C. Lord and F. A. Miller, *Appl. Spectroscopy*, **10**, 115 (1956).

(44) W. H. T. Davison and G. D. Bates, *J. Chem. Soc.*, 2607 (1953).

(45) J. L. H. Allan, G. D. Meakins, and M. C. Whiting, *J. Chem. Soc.*, 1874 (1955).

(46) R. E. Kitson, *Anal. Chem.*, **25**, 1470 (1953).

(47) R. Heilman, G. de Gaudemaris, and P. Arnaud, *Bull. soc. chim. France*, 119 (1957).

(48) H. J. Bernstein and J. Powling, *J. Am. Chem. Soc.*, **73**, 1843 (1951).

(49) L. Schmerling and J. P. West, *J. Am. Chem. Soc.*, **71**, 2015 (1949).

(50) G. D. Meakins, *J. Chem. Soc.*, 4170 (1953).

(51) M. S. C. Flett, *J. Chem. Soc.*, 962 (1951).

(52) T. Katsumoto, *Bull. Chem. Soc. Japan*, **33**, 1376 (1960).

(53) P. Joyner and G. Glockler, *J. Chem. Phys.*, **20**, 302 (1952).

(54) D. E. Jones, *et. al.*, *J. Chem. Soc.*, 2349 (1960).

(55) H. J. Boonstra and L. C. Rinzema, *Rec. trav. chim.*, **79**, 962 (1960).

(56) H. J. Boonstra and J. F. Arens, *Rec. trav. chim.*, **79**, 866 (1960).

(57) J. Cymerman and J. B. Willis, *J. Chem. Soc.*, 1332 (1951).

(58) C. C. Price and R. G. Gillis, *J. Am. Chem. Soc.*, **75**, 4747, 4750 (1951).

(59) W. E. Truce and M. M. Boudakian, *J. Am. Chem. Soc.*, **78**, 2748 (1956).

(60) R. A. Nyquist and W. J. Potts, *Spectrochim. Acta*, **7**, 514 (1959).

(33) G. Cilento, *Chem. Revs.*, **60**, 147 (1960).

(34) J. Hine, *Physical Organic Chemistry*, McGraw-Hill Book Company, Inc., New York, N. Y., 1956.

(35) M. T. Rogers, *J. Am. Chem. Soc.*, **77**, 3681 (1955).

(36) S. C. Abrahams, *Quart. Revs. (London)*, **10**, 407 (1956).

in the few studies of organosulfur compounds that are available, emphasis has been placed primarily on the lower alkanethiols and sulfides.[57,62,63] Outside of the work in this laboratory,[59] there have been no detailed studies made on olefinic compounds with arylmercapto or arylsulfonyl residues attached to the double bond. One need only to try to interpret some of these spectra to see why the literature is so barren.

The traditional sources of information concerning olefinic configuration are: (a) the relative position of the C=C stretching frequency, and (b) the —C—H in-plane and out-of-plane deformation frequencies. In certain α,β-unsaturated ketones, acids and esters, the position of the carbonyl frequency has occasionally been used to elucidate cis/trans isomers.

The compounds in this study present two major difficulties when attempting to find information in the above listed regions. The first difficulty is that the aromatic rings have both C=C stretching and =C—H bending absorptions in regions which are very close to those of the olefin. This is particularly troublesome when the extent of the frequency shifts of the olefinic absorptions, due to the pendant sulfide (or sulfone) group, are not well known. The other major difficulty arises from the large number of spurious bands in the =C—H deformation regions. The sources of these bands have been attributed to either =C—S stretching modes,[60] or to ubiquitous skeletal vibrations.

The correlation between the spectra in the present study and the tables of skeletal vibrations for *alkyl* sulfides is poor.[55,62,63] Table III lists the frequencies common to most of the spectra containing the *p*-tolylmercapto and *p*-tolylsulfonyl residues. No attempt has been made to allocate these bands to particular modes of absorption, although some of the assignments are fairly obvious, because such an analysis would not contribute to the elucidation of geometry. There are additional "skeletal" vibrations in the β-substituted acrylic acids and esters; these will be discussed later.

Substituted ethenes. The problem of locating pertinent bands among the plethora of skeletal vibrations common to most of these compounds is extremely hazardous, since a few of the extraneous absorptions do not always appear in exactly the same place, and, indeed, some may not occur at all in every compound.

The C=C stretching frequency, which for an enormous variety of substituted ethenes,[40,44,64] appears between 1620 and 1660 cm.$^{-1}$ (6.0–6.2 μ),

(61) D. Barnard, J. M. Fabian, and H. P. Koch, *J. Chem. Soc.*, 2442 (1949).

(62) A. Menefee, D. O. Alfred, and C. B. Scott, *J. Org. Chem.*, 22, 792 (1957).

(63) D. W. Scott and J. P. McCullough, *J. Am. Chem. Soc.*, 80, 3554 (1958).

(64) A. R. Katritsky, J. M. Lagowski, and J. A. T. Beard, *Spectrochim. Acta*, 16, 964 (1960).

TABLE III

ABSORPTIONS COMMON TO *p*-TOLYLMERCAPTO AND *p*-TOLYL-SULFONYL ETHENES

Frequency^a (μ)	Intensity^b	Notes
3120 (3.19)	W-M	Not present in sulfones; shoulder on 3085
3085 (3.24)	M-S	
2980 (3.34)	M	Variable in sulfones; shoulder on 3085
2930 (3.42)	W	Shoulder on 2980
2790 (3.61)	vW	Variable in sulfones
2620 (3.81)	vW	Medium in *p*-toluenethiol
2340 (4.29)	vW	
1920 (5.22)	W	Medium in *p*-toluenethiol
1805 (5.53)	vW	
1650 (6.08)	W	vW shoulder or absent in sulfones
1610 (6.20)	V	M-S in sulfones
1580 (6.32)	V	Absent in sulfones
1500 (6.65)	vS	Weak in sulfones
1460 (6.84)	W-M	
1410 (7.10)	M	
1385 (7.20)	W-M	Variable or absent in sulfones
1305 (7.60)	W-M	May shoulder on adjacent sulfone band
1185 (8.40)	V	May shoulder on adjacent sulfone band
1120 (8.90)	V	
1100 (9.05)	vV	Usually medium to strong; shoulder often
1025 (9.77)	S	W-M in sulfones
800–820 (12.2–12.5)	vS	Occasionally broad doublet
685–705 (14.1–14.6)	W-M	Usually broad

^{a} Approximately ± 0.05 μ. ^{b} Based on peak height: S. Strong; M, Medium; W, Weak; V, Variable; v, very.

occurs in the present study as a band of variable intensity (though never more than medium) in the region 1550 ± 25 cm.$^{-1}$ (6.44 μ). This remarkably low C=C frequency is corroborated in a study of alkylmercaptoethenes[55] where the C=C absorption was found in the range 1535–1560 cm.$^{-1}$ (6.4–6 μ).[65] However, the C=C absorption does not always appear, and since its exact location does not correlate with the geometry of the olefin, this band *cannot* be used for configurational assignments.

Another series of absorptions commonly employed for configurational information are the =C—H in-plane deformations. For *cis* and *trans* hydrocarbons, these appear at 1290–1310 cm.$^{-1}$

(65) However, these authors state further that, "In all 1,2-bis-*S*-substituted *trans* compounds this band is absent because of symmetry." This statement shows an apparent misconception, which was originally advanced in an earlier publication, that *trans* ethylenes of this sort have a zero dipole moment. As we have shown, these *trans* olefins have appreciable moments; furthermore, comparison of the spectra of *cis* and *trans*-1,2-bis(*p*-tolylmercapto)ethenes reveals a C=C stretching frequency in *both* compounds, at virtually the same place (1550 cm.$^{-1}$). In addition, the spectrum of *bis*(*p*-tolylmercapto)ethyne exhibits a C≡C band at 2100 cm.$^{-1}$. Although it is a weak absorption, its very appearance in the infrared again demonstrates the presence of a dipole moment in a supposedly symmetrical compound.

(7.62-7.73 μ) and near 1405 cm.$^{-1}$ (7.1 μ), respectively.[40,41,66] However, their utility is diminished because the location of the latter band is somewhat uncertain, and because both bands often show large variations in intensity. In addition, as might be expected, the presence of polar substituents on the double bond shifts these bands appreciably. The specific locations of these bands in a series of mercaptoethenes has been given as 1180–1200 cm.$^{-1}$ (8.36–8.49 μ) (*trans*) and 1285–1310 cm.$^{-1}$ (7.62–7.80 μ) (*cis*);[55,59] however, of the compounds in the present study, only the acrylics can be correlated in these regions. The spectra of both *cis-* and *trans*-1,2-bis(*p*-tolylmercapto)ethene have identical structures throughout the entire 1000–1500-cm.$^{-1}$ (6.6–10.0 μ) region. Their two corresponding sulfones do exhibit a slight difference, since the *cis* isomer, alone, has a band at 1310 cm.$^{-1}$ (7.63 μ). However, this band also occurs in other sulfones, such as the 1,2-bis(*p*-tolylsulfonyl)-1,2-dichloroethenes and bis(*p*-tolylsulfonyl)methane, and cannot, therefore, be assigned to the =C—H in-plane bending mode. This 1310 cm.$^{-1}$ band shoulders on the adjacent strong sulfone absorption, and may actually represent "splitting" of the sulfone band, a phenomenon which has previously been reported.[40,61,67] In all probability, then, the =C—H in-plane bending vibrations in this series of compounds are either masked by skeletal bands (Table III) or are just of insufficient strength to appear.

In contrast with the in-plane modes, which occur in a normally crowded portion of the spectrum, the —C—H out-of-plane deformations are located in a region comparatively free of other bands, and the latter absorptions are therefore efficacious in configurational assignments. The range in which they appear is 895–950 cm.$^{-1}$ (10.5–11.2 μ), which is somewhat lower than the 960–970 cm.$^{-1}$ (10.3–10.4 μ) range usually given for hydrocarbons.[40,41,45,64] However, the position agrees with that given for alkylmercaptoethenes (895–920 cm.$^{-1}$; 10.9–11.21 μ),[55] and the direction and magnitude of the shift correspond well with analogous displacements noted for chlorinated ethylenes.[44,46,68] Although this particular absorption is satisfactory for *cis/trans* proof, the actual presence of 1,2-bis(arylmercapto) (or arylsulfonyl)-ethene must be shown independently, since other bands do occur in this region in some of the chlorinated arylmercapto and arylsulfonylethenes, as well as in certain nonolefinic arylmercapto compounds.[69]

Substituted acrylic acids and esters. The spectra of these compounds are similar to the ethenes dis-

cussed above, but the manner in which they correlate with *cis/trans* geometry is somewhat different.

The four sulfides in this series all exhibit moderate to strong absorptions in the 1550–1600-cm.$^{-1}$ (6.25–6.45 μ) and 1650–1720-cm.$^{-1}$ (5.80–6.06 μ) regions. These may be assigned to the C=C and C=O stretching modes, respectively, but they show little consistency in either position or intensity, and are therefore valueless for the purpose of configurational assignment.

The =C—H out-of-plane deformation region, 930–975 cm.$^{-1}$ (10.25–10.73 μ), contains absorptions for *all* six of the acrylic compounds. Extraneous absorptions have been reported in this region for both a series of carboxylic acids,[51] and for phenyl vinyl sulfide and its corresponding sulfone[58]; therefore, the assignment of the *trans* =C—H deformation can be made only when the spectra of both isomers are available. *trans-β*-(*p*-Tolylmercapto)acrylic acid, its ethyl ester, and its corresponding sulfone exhibit the =C—H out-of-plane deformation at 972 (10.27 μ), 949 (10.53 μ), and 968–969 (10.31 μ) cm.$^{-1}$, respectively.

The =C—H in-plane bending, which was ineffectual in the ethenes described above, has been valuable for configurational assignments in the acrylic series. In *cis-β*-(*p*-tolylmercapto)acrylic acid and its ethyl ester, as well as in the sulfone of the latter compound, this mode appears as a band of at least medium intensity in the narrow range of 1346–1350 cm.$^{-1}$ (7.40–7.42 μ). This absorption, however, occurs in a normally crowded portion of these spectra, and its presence or absence ought to be confirmed by comparison of both geometrical isomers.

NMR studies. The method commonly used to obtain olefinic configurational information from NMR involves measurement of the spin-spin coupling between the various protons on the double bond.[70–75] The intrinsic requirement that both protons, in a *cis* or *trans* disubstituted ethene, exist in different environments, has limited the

(66) G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules*, D. Van Nostrand Company, Inc., New York, N. Y., 1945.

(67) L. J. Bellamy and R. L. Williams, *J. Chem. Soc.*, 863 (1957).

(68) H. J. Bernstein and D. A. Ramsay, *J. Chem. Phys.*, 17, 556 (1949).

(69) It is claimed (ref. 55) that the spectrum of *cis* or *trans*-1,2-bis(ethylmercapto)ethene compares very well with the spectrum of *cis* or *trans*-dichloroethylene upon which the spectrum of ethyl disulfide is superimposed. An analogous composite spectrum of *p*-tolyl disulfide and *cis*-dichloroethylene shows *moderate* agreement with *cis*-1,2-bis(*p*-tolylmercapto)ethene, but so do many other spectra in this series.

(70) J. D. Roberts, *Nuclear Magnetic Resonance*, McGraw-Hill Book Co., Inc., New York, 1959.

(71) J. A. Pople, W. G. Schneider, and H. J. Bernstein, *High Resolution Nuclear Magnetic Resonance*, McGraw-Hill Book Company, Inc., New York, N. Y., 1959.

(72) L. M. Jackman, *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, Pergamon Press, New York, N. Y., 1959.

(73) M. Karplus, *J. Chem. Phys.*, 31, 1278 (1959).

(74) C. N. Banwell, N. Sheppard, and J. J. Turner, *Spectrochim. Acta*, 16, 794 (1960).

(75) C. N. Banwell and N. Sheppard, *Molec. Phys.*, 3, 351 (1960).

application of NMR in the present study to the acrylic series of compounds. The coupling constants found for four sulfides and one sulfone are given in Table IV. The *cis* isomer of β-(*p*-tolylsulfonyl)acrylic acid was not sufficiently soluble in any suitable solvent for its NMR spectrum to be determined. It should be noted that the single value found, while somewhat indicative of *trans* configuration, is not at all conclusive without the J_{cis} value.

Banwell and Sheppard[75] give the following ranges for proton coupling constants, as determined by a study of a large number of variously substituted olefins: J_{cis} = 5–11 c.p.s.; J_{trans} = 13–18 c.p.s.; J_{gem} = 2 c.p.s.; the mean values are: J_{cis} = 7.3 c.p.s.; J_{trans} = 14.9 c.p.s.; J_{gem} = 2 c.p.s. Most other published constants are in agreement with these figures. Although the data in Table IV support the proposed geometrical configurations very well, they do so only because both isomers of each pair were available. Once again, as in the infrared studies, *both forms must be compared* in order to obtain truly unambiguous proof.

TABLE IV
Proton Coupling Constants

Compound	J_{HH}, c.p.s.
cis-ArSCH=CHCOOH	9.7
trans-ArSCH=CHCOOH	15.4
cis-ArSCH=CHCOOC$_2$H$_5$	10.4
trans-ArSCH=CHCOOC$_2$H$_5$	14.9
trans-ArSO$_2$CH=CHCOOH	12–13

Because of their identical environment, the vinylic proton peaks for *cis*- and *trans*-1,2-bis(*p*-tolylmercapto)ethene do not split. However, certain symmetrically disubstituted ethenes have shown chemical shift differences as high as 0.5 p.p.m.[76,77] Measurements on our compounds, however, did *not* show any significant variation in location of the vinylic proton peaks.

Summary. Uncertainties resulting from steric, inductive, and resonance effects prevent dipole moment measurements from clearly indicating geometry in *p*-tolylmercapto- and *p*-tolylsulfonylethenes. The appreciable moments of the *trans*-ethenes, resulting from rotation of the pendant sulfide groups, are too close to the values for the *cis* isomers to allow valid assignments to be made.

The utility of infrared as a configurational proof is reduced because of the complexity of these spectra. The intricacy arises from: (a) the presence of the various absorptions of the aromatic ring, and (b) the frequency shifts of useful bands whose positions are known mainly for hydrocarbons. Although the =C—H deformation modes *can* be used successfully for geometrical assignment, varying amounts of supplementary information for any particular compound under examination are necessary.

NMR coupling constants give unambiguous information regarding geometric isomerism, but they are limited to ethenes that contain two different substituents attached to the double bond. For absolute certainty, though, the constants of *both* members of any *cis/trans* pair should be compared.

(76) L. M. Jackman and R. H. Wiley, *J. Chem. Soc.,* 2870, 2881, 2886 (1960).
(77) D. E. Jones *et al., J. Chem. Soc.,* 2349 (1960).