presence of *tert*-butyl alcohol and chlorotoluene. From the solids remaining *p*-nitrobenzoic acid and methyl *p*-nitrobenzoate were identified.

PCA (503 mg) was dissolved in 5 ml of chlorobenzene. The sample was degassed by alternated freezing and melting and was then sealed. The sample was heated at 107° for 24 hr. It was then cooled and opened, and an nmr was taken of the filtered solution. The peaks at δ 1.2 (*tert*-butyl alcohol), 1.83 (acetone), 2.09 (chlorotoluene), and 3.71 (methyl *p*-nitrobenzoate) and an unidentified peak at 1.11 were integrated. The peak at δ 1.11 was shown not to be *tert*-butyl *p*-nitrobenzoate, *tert*-butyl *p*-nitroperbenzoate, or the dimethyl ketal of acetone. This is the procedure of Hideya, *et al.*[9]

The solvents were removed and the residue was dissolved in ether and extracted with 2% NaOH solution. The ether was dried and removed under vacuum. Fairly pure (ir, mp 78–89°) methyl *p*-nitrobenzoate (148 mg) remained. The NaOH was neutralized with concentrated HCl, and the precipitate was collected. After drying the *p*-nitrobenzoic acid weighed 149.4 mg.

Decomposition in Undegassed Sealed Tubes.—Two 100-mg. samples of PCA were dissolved in 1-ml portions of chlorobenzene. The solutions were sealed in unevacuated tubes without degassing, and the samples were heated for 24 hr at 107°. (One sample turned dark while the other remained light.) The samples were opened and nmr spectra were taken as in the previous case. The spectra were similar to those of the degassed samples except that the dark sample had less *tert*-butyl alcohol and more of the material with the peak δ 1.11. The solid that crystallized out was examined and found to be *p*-nitrobenzoic acid. No evidence was obtained for the presence of *p*-nitrobenzoic anhydride.

Registry No.—2, 38401-55-7; *tert*-butyl hydroperoxide, 75-91-2; *p*-nitrobenzoyl chloride, 122-04-3; methyl *p*-nitrobenzoate, 619-50-1.

Correlation between Nuclear Magnetic Resonance and Infrared Studies of Conformational Preferences in Chloro Sulfides

GARY M. UNDERWOOD, C. T. WATTS, AND CHARLES A. KINGSBURY*

Department of Chemistry, University of Nebraska, Lincoln, Nebraska 68508

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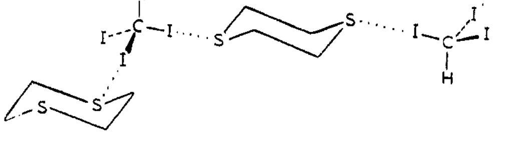
Nmr and ir methods of determining conformational preferences in alkyl substituted 1-chloro-2-ethyl 2,4-dinitrophenyl sulfides are in fair agreement. For *erythro*-2-chloro-3-butyl 2,4-dinitrophenyl sulfide, a preference for gauche chlorine–sulfur groups is evident. However, the study of model compounds shows that the chlorine–sulfur interaction is probably slightly repulsive. A very unusual preference for a conformer having gauche hydrogens is noted in both isomers of the above compound.

Conformational reasoning has been deeply affected by the early work on butane and on cyclohexane systems.[1,2] This work led to the idea that alkyl groups, and presumably other large groups, prefer a trans orientation in order to minimize repulsive nonbonded interactions.[3] In recent years, there has been a growing realization that many groups, some sizable, have attractive rather than repulsive interactions. In substituted propanes, $XCH_2CH_2CH_3$, the conformer having X gauche to methyl is slightly more stable or of equivalent stability to the trans conformer where X is F, Cl, Br, CN, NC, C≡CH, and OH.[4] A slight dipolar attraction is presumed to overcome steric repulsions. Notable among other interections that are considered attractive in nature are the interactions of oxygen-containing groups,[5,6] cyano–cyano groups,[7] mercury–amine,[8] sulfoxide–hydrogen,[9] and chlorine–hydrogen.[10] Halogen–halogen interactions are complex, and these may vary from compound to compound depending upon bond angle and internuclear distance.[11] However, it is noteworthy that, in a large variety of dihaloethylenes, the cis isomer is the more stable.[11c] In acyclic compounds capable of internal rotation, the gauche X–X conformer is stabilized in solvents of high dielectric constant, since the solvent effect counteracts the repulsive effects of the halogen dipoles.[6a,7,12] The list of attractive interactions is diverse enough so as to suggest that the phenomenon is widespread, though many times rather weak.

The present work is an inquiry into the possibility of an attractive interaction between sulfur and halogen. Precedent for considering this interaction as attractive exists in the work of Bjorvatten and Hassel,[13] who observed the alignment of molecules shown in (1) by X-ray analysis. The tendency for halogens to complex with sulfides is well known,[14] though this



(1)

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[1] D. H. R. Barton, *Experientia*, **23**, 316 (1950).

[2] S. Mizushima, "Structure of Molecules and Internal Rotation," Academic Press, New York, N. Y., 1954.

[3] E. L. Eliel, N. Allinger, J. Angyal, and G. Morrison, "Conformational Analysis," Interscience, New York, N. Y., 1965, pp 5–22.

[4] E. B. Wilson, *Chem. Soc. Rev.*, **1**, 293 (1972).

[5] (a) E. L. Eliel and M. Kaloustian, *Chem. Commun.*, 290 (1970); (b) R. J. Abraham and K. Pachler, *Mol. Phys.*, **7**, 165 (1963).

[6] (a) A. A. Bothner-By and C. Naar-Colin, *J. Amer. Chem. Soc.*, **84**, 743 (1962); (b) F. A. L. Anet, *ibid.*, **84**, 747 (1962).

[7] (a) L. I. Peterson, *ibid.*, **89**, 2677 (1967); (b) J. P. Aycard, H. Bodot, R. Garnier, R. Lauricella, and G. Pouzard, *Org. Magn. Resonance*, **2**, 7 (1970).

[8] (a) E. F. Kiefer, W. L. Walters, and D. A. Carlson, *J. Amer. Chem. Soc.*, **90**, 5127 (1968); (b) E. F. Kiefer and W. Gericke, *ibid.*, **90**, 5131 (1968).

[9] (a) C. R. Johnson and D. McCants, Jr., *ibid.*, **87**, 110 (1965); (b) N. L. Allinger, J. Hirsch, M. Miller, and I. Tyminski, *ibid.*, **91**, 337 (1969).

[10] (a) R. J. Abraham and K. Parry, *J. Chem. Soc. B*, 539 (1970); (b) B. Hawkins, W. Bremser, S. Borcic, and J. D. Roberts, *J. Amer. Chem. Soc.*, **93**, 4472 (1971), and references cited therein.

[11] (a) A. Berlin and F. Jensen, *Chem. Ind.* (*London*), 998 (1960); (b) R. A. Pethrick and E. Wyn-Jones, *Quart. Rev. Chem. Soc.*, **23**, 301 (1969); (c) H. Viehe, J. Dale, and E. Franchimont, *Chem. Ber.*, **97**, 244 (1964), and many related papers.

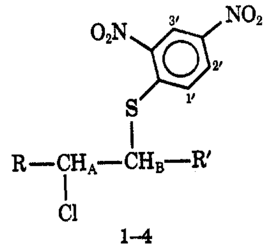
[12] G. Hamer, W. F. Reynolds, and D. Wood, *Can. J. Chem.*, **49**, 1755 (1971).

[13] T. Bjorvatten and O. Hassel, *Acta Chem. Scand.*, **15**, 1429 (1961).

[14] (a) J. D. McCullough, G. Chao, and D. Zuccaro, *Acta Crystallogr.*, **12**, 815 (1959); (b) M. Good, A. Major, J. Nag-Chaudhuri, and S. McGlynn, *J. Amer. Chem. Soc.*, **83**, 4329 (1961).

TABLE I

NMR PARAMETERS[b] (60 MHz) OF 1–4



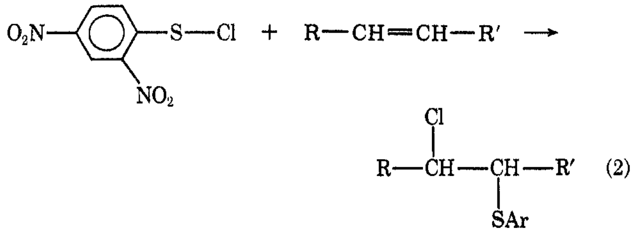
1–4

			Coupling constants, Hz			Chemical shifts, ppm						
Compound	R	R′	J_{AB}	$J_A[\mathbf{C}\mathbf{H}(CH_3)_2]$	$J_B[\mathbf{C}\mathbf{H}(CH_3)_2]$	A	B	1′	2′	3′	R	R′
erythro-**1**	CH_3	CH_3	4.0[b] (3.5)[c]			4.44	3.89	7.77	8.42	8.95	1.69	1.58
threo-**1**	CH_3	CH_3	3.2 (3.6)			4.34	3.90	7.72	8.47	9.03	1.60	1.57
erythro-**2**	CH_3	$CH(CH_3)_2$	7.3 (7.4		5.7	4.36	3.54	7.83	8.33	8.87	1.62	*a*
threo-**2**	CH_3	$CH(CH_3)_2$	4.2 (3.7)		6.7	4.51	3.52	7.83	8.40	8.94	1.72	*a*
erythro-**3**	$CH(CH_3)_2$	$CH(CH_2)_2$	10.5 (10.5)	2.2	3.1	4.04	3.67	7.82	8.43	8.95	*a*	*a*
threo-**3**	$CH(CH_3)_2$	$CH(CH_3)_2$	5.6 (~6)	5.2	6.3	4.16	3.72	7.98	8.47	8.93	*a*	*a*
erythro-**4**	CH_3	$C(CH_3)_3$	2.6 (2.7)			4.83	3.79	8.02	8.34	8.90	1.72	1.17
threo-**4**	CH_3	$C(CH_3)_3$	1.3 (1.3)			4.72	3.44	7.79	8.36	8.88	1.65	1.19

[a] Complex nonequivalent resonances of the methyls were observed. [b] *Ca.* 10% w/v solution in $CDCl_3$. [c] The data in parentheses refer to 10.0% w/v solutions in DMSO as solvent observed at 100 MHz.

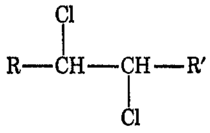
type of interaction may have a different origin from that present in the compounds of this study.

The present work concerns certain chloro sulfides having nitro substitutents in the aromatic ring (eq 2). The inductive effect of the nitro groups renders sulfur somewhat electron deficient. Thus, attempted observation of pseudocontact shifts using Eu(fod)$_3$ showed little or no displacement of the alkyl resonances in the nmr spectrum, although the aromatic resonances were shifted slightly.[15,16] The electron deficient nature of the sulfur should increase the probability of an attractive gauche interaction with the electron-rich chlorine.



(2)

1–4



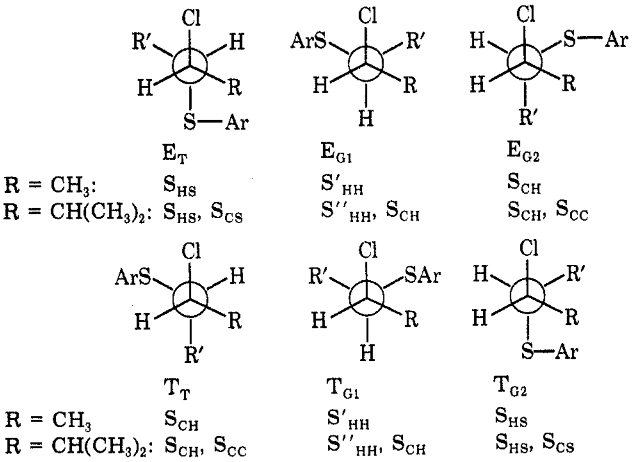
$$R-CH(Cl)-CH(Cl)-R'$$

5

The chloro sulfides were synthesized as shown in eq 2.[17] In this study, nmr and ir methods of determining conformational preferences will be compared. In addition to **1–4**, certain analogous dichlorides, **5**, will also be considered.

The nmr data for compounds in which R and R′ are alkyl groups are listed in Table I. The conformational preferences are approximated from vicinal nmr coupling constants (J_{AB}).[18] Large values for J_{AB} (10–13 Hz) are taken as indicative of predominately trans hydrogens, whereas small values for J_{AB} (1–4 Hz) indicate predominately gauche hydrogens. Intermediate values are thought to reflect weighted averages of the above conformations. Other work[19] has suggested that every conformer of every compound has distinct and separate values for J_{AB} (although these values are usually within the above ranges). Only a qualitative interpretation of the data will be attempted, in terms of the conformers shown in Scheme I. The infrared spectroscopic designations of the bands expected for each conformer are also given in Scheme I.

SCHEME I



For *erythro*-**1**, a quite small value for J_{AB} (4.0 Hz) is noted. This value is substantially smaller than that found for the analogous dichloride (7.4 Hz), which suggests that the conformers having gauche heteroatoms, E_{G1} and/or E_{G2}, are more highly populated for **1** than for the dichloride.

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[15] (a) C. C. Hinckley, *J. Amer. Chem. Soc.*, **91**, 5160 (1969); (b) P. DeMarco, T. Elzey, R. Lewis, and E. Wenkert, *ibid.*, **92**, 5734, 5737 (1970); (c) J. Sanders and D. Williams, *Chem. Commun.*, 422 (1970).

[16] Private observations have shown highly delocalized electron pairs do not complex well with Eu(dpm)$_3$.

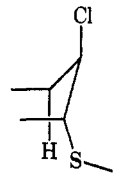
[17] (a) N. Kharasch, *J. Chem. Educ.*, **33**, 585 (1956); (b) W. H. Mueller and P. E. Butler, *J. Amer. Chem. Soc.*, **90**, 2075 (1968); (c) G. H. Schmid and V. M. Csizmadia, *Can. J. Chem.*, **44**, 1338 (1966); (d) G. H. Schmid, *ibid.*, **46**, 3757 (1968).

[18] (a) M. Karplus, *J. Amer. Chem. Soc.*, **85**, 2870 (1963); (b) E. Garbisch, Jr., and M. Griffith, *ibid.*, **90**, 6543 (1968).

[19] (a) R. J. Abraham and G. Gatti, *J. Chem. Soc. B*, 961 (1969); (b) R. J. Abraham, L. Cavalli, and K. Pachler, *Mol. Phys.*, **11**, 471 (1966).

In studies on a considerable number of chlorine compounds, Mizushima and coworkers have developed,[20] and others have expanded, a correlation between ir absorption and conformation.[21] According to Altona,[21] the three types of ir absorption applicable to **1** are termed S_{HS}, S'_{HH}, and S_{CH}, which can be correlated with conformers E_T, E_{G1}, and E_{G2}, respectively (Scheme I).

These three absorptions are found at 701, 632, and 666 ± 20 cm^{-1}, respectively. The designation S_{HS} refers to an ir band expected from a secondary chlorine that is simultaneously trans to a sulfur atom and to a hydrogen (*i.e.*, structure a).



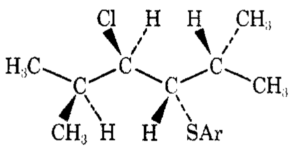
a

For *erythro*-**1** in CS$_2$ solution, absorptions at 714 (m) and at 653 (s) were observed. In the solid phase (KBr pellet), the latter band was also prominent. A strong band at 670–685 cm^{-1}, possibly an aromatic absorption, interferes with the S_{HS} or S_{CH} absorption in certain cases; so the identification of a band is not always straightforward. The strongest band (653 cm^{-1}) is closest to the region expected for the S_{CH} absorption, which suggests that the predominant conformer is E_{G2}. No ir band is noted near 632 cm^{-1}. Although this absence would seem to indicate that conformer E_{G1} is unpopulated, we feel that this indication is open to question.[22]

The temperature effect on the spectrum of *erythro*-**1** was quite normal.[23] In benzonitrile solution, J_{AB} increased monotonically from 3.7 at *ca.* 40° to 4.7 at 130°. Unlike certain dihalides,[12] a change to a more polar solvent (DMSO) had little effect on the coupling constants of these chloro sulfides (Table I).

Moving from *erythro*-**1** to *erythro*-**2** involves a change in R′ from methyl to isopropyl. A corresponding change in J_{AB} to 7.3 Hz is observed, indicating an increased importance of E_T. However, the ir spectrum shows only a weak band at 711 cm^{-1} that can be correlated with E_T, in addition to a strong S_{CH} band, which is correlated with E_{G2}. A preference for E_{G2} rather than E_{G1} is more reasonable in this case, since the largest group (isopropyl) would be very hindered in E_{G1}. If one assumes the nmr evidence to be the more compelling, the growing preference for E_T is consistent with observations in other erythro isomers, in which the two alkyl groups seek a maximally separated orientation. The preference for E_T is stronger in the analogous dichloride (J_{AB} = 9.2 Hz), in which the chlorines probably also repel each other.

For *erythro*-**3**, R and R′ are both isopropyl. The very large J_{AB} (10.5 Hz) indicates a strong preference for conformer E_T, in which these groups are trans. The very small coupling constants for the isopropyl methine H_A and methine H_B protons (*ca.* 3 Hz), in contrast to J_{AB}, provides another illustration of the alternation of coupling constants. The alternation is the result of a preference for the conformation in which 1,3 interactions are minimized (structure b).



b

Thus, a large group at a given carbon is eclipsed only by a small group (hydrogen) at the carbon two atoms away.

The ir spectrum indicates a strong S_{HS} absorption, as expected for E_T. The ir spectrum also shows a S_{CS} band at 758 cm^{-1} (alternatively, this could be an S_{CC} absorption), which is consistent with conformer E_T but not consistent with structure b, since the S_{CS} absorption requires the sulfur to be eclipsed with carbon. At one time it was believed that such eclipsed conformations were highly improbable (by analogy to the *ca.* 3.5 kcal destabilization of eclipsed 1,3-diaxial groups in a cyclohexane system),[1-3] but recent force-field calculations have shown that 1,3-oxygen–carbon eclipsing interactions were indeed unfavorable, but not grossly so.[24] Nevertheless, structure b probably represents the major conformer.

In the series **1** → **2** → **3**, a progressive upfield shift of the nmr resonance for H_A is noted (Table I). Models show that the aromatic group is preferentially situated so that its face lies over H_A, particularly in conformer

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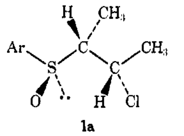
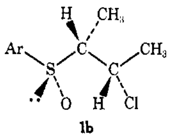
[20] S. Mizushima, T. Shimanouchi, K. Nakamura, M. Hayashi, and S. Tsuchiya, *J. Chem. Phys.*, **26**, 970 (1957).

[21] (a) C. Altona, *Tetrahedron Lett.*, 2325 (1968); (b) J. J. Shipman, V. Folt, and S. Krimm, *Spectrochim. Acta*, **18**, 1603 (1962); (c) P. N. Gates, E. Mooney, and H. Willis, *Spectrochim. Acta, Part A*, **23**, 2043 (1967).

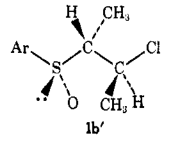
[22] It is instructive to consider the sulfoxides and the sulfone derived from the sulfide **1**. The sulfoxide **1a**, mp 139°, showed a lower vicinal coupling constant (3.2 Hz) than the original sulfide. The highly deshielded chemical shift for H_A (δ 4.73) suggests the configuration and conformation shown in structure **1a** in which the SO group is eclipsed with H_A. The second sulfoxide **1b** (an oil) showed a J_{AB} value of 6.9 Hz, indicative of mixed conformers. In conformer **1b**, dipolar and steric repulsions exist between oxygen and chlorine. In the alternate conformer **1b**, no 1,3 interactions exist, but the largest groups, methyl and sulfinyl, are gauche not trans. The chemical shift of H_A is less extreme (δ 4.5). The sulfone **1c** showed a J_{AB} value of 3.3 Hz. Thus, the progressive increase in size of the sulfur function in the series **1** → **1a** → **1c** involves a general strengthening of the preference for a conformer having gauche hydrogens (although part of the change in J_{AB} is due to an electronegativity effect). It is difficult to believe that the sulfone will tolerate a congested position as in conformer E_{G2}. More likely the sulfoxide and sulfone prefer conformer E_{G1}, in which the largest groups (ArSO$_2$ and CH$_3$) can be trans to one another. In the parent sulfide **1**, the general conformational purity is lower, but by analogy to **1a** and **1c** it seems likely that E_{G1} should have a significant population (the aromatic group is less hindered in E_{G1} than in E_{G2}). It is possible that the ir band at 653 cm^{-1} is a combination of S_{CH} and S'_{HH}, bands. It is also noteworthy that **1** is more complicated than the molecules used to establish the position of these bands. The referee is thanked for suggesting the study of the sulfone.



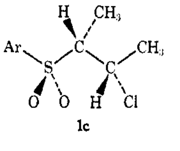
1a



1b



1b′



1c

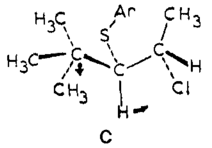
[23] J. R. Cavanaugh, *J. Amer. Chem. Soc.*, **89**, 1558 (1967), and later papers, reports an "abnormal" temperature effect. The energy difference between conformers was found to be temperature dependent.

[24] (a) C. Altona and J. Hirschmann, *Tetrahedron*, **26**, 2173 (1970); (b) see also N. L. Allinger, J. Hirsch, M. Miller, I. Tyminski, and F. Van-Catledge, *J. Amer. Chem. Soc.*, **90**, 1199 (1968).

E_T. The ring current of the aryl group thus shields H_A.[25]

Like many *tert*-butyl compounds, *erythro*-**4** appears to occupy a grossly different conformation from *erythro*-**2**. The chemical shift of H_A in **4** is 0.47 ppm *downfield* from that in **2**. The very low J_{AB} suggests a preference for one of the gauche conformers. The strong S_{CH} ir band (CS_2 solution) suggests that the major conformer is E_{G2}. X-Ray structures of certain *tert*-butyl compounds by Altona and Faber have shown that the bond to the *tert*-butyl group is quite long compared to the normal C–C single bond.[26] Of greater importance is the spreading of the $C–C–C(CH_3)_3$ bond angle, which also tends to minimize the steric interactions of the *tert*-butyl group with other large groups.[26,27]

In *erythro*-**4**, the hydrogen at C_2 (structure c) would be expected to move toward C_1 as the $C–C–C(CH_3)_3$ angle spreads.[26] In conformation E_{G2}, this inward motion would be relatively facile since the hydrogen in question would approach the two smallest groups substituted at C_1, namely hydrogen and chlorine. In conformer E_T, which is less highly populated, the hydrogen at C_2 would approach methyl and chlorine upon moving inward, which should be more difficult. This deformation of the ethanic backbone would probably lead to abnormally low coupling constants, as, in fact, are observed for many *tert*-butyl compounds (*cf.* *threo*-**4**). Deviation of dihedral angles from 60°, which is an idealized value, seldom found, may also be *quite* pronounced in **4** in order that the most comfortable fit of groups may be achieved. This would also tend to lower the observed coupling constant.



c

The underlying causes for the conformations of compounds having the threo configuration is harder to evaluate, since these conformations frequently are the result of a balance between opposing effects. *threo*-**1** (R′ = CH_3) shows a very low value for J_{AB} (3.2 Hz) that is consistent with a preference for T_{G1} and/or T_{G2}.[28] The analogous dichloride shows a similarly low coupling constant. The dipole moment of the dichloride[29] indicates that the conformer with gauche chlorines, *i.e.*, T_{G1}, is quite important. However, for *threo*-**1**, the ir spectrum shows a sizable S_{HS} absorption, which suggests that T_{G2} is preferred. Oxidation of *threo*-**1** gave a sulfone having a J_{AB} of 4.7 Hz. This higher value for J_{AB} suggests that T_T has become more important, probably because the bulkiest groups ($Ar–SO_2$ and CH_3) are trans in this conformer. However, it is surprising that T_T is not the major conformer. *erythro*- and *threo*-**1** and their respective sulfones[22] are an unusual class of compounds in that a preference exists in both isomers for a conformer having gauche hydrogens (*cf.* Allinger's rationale).[24b]

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(25) F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy," Academic Press, New York, N. Y., 1969, pp 66–70. The referee suggests that the effect of the nitro group or C–C bond anisotropies are alternative ways of explaining the shielding effect.

(26) C. Altona and D. Faber, *Chem. Commun.*, 1210 (1971).

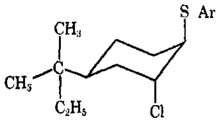
(27) C. Kingsbury and D. C. Best, *J. Org. Chem.*, **32**, 6 (1967). This paper states on the basis of $^{13}C–H$ coupling constants that angle spreading probably was not important on the basis of "normal" $^{13}C–H$ coupling constants. The $J_{^{13}C–H}$ values are no longer considered to be conclusive.

(28) The referee requested studies on cyclic molecules in order to more closely define the effects that determine conformation. Addition of 2,4-dinitrobenzenesulfenyl chloride to cyclic alkenes yields trans adducts, which are analogous to the threo diastereomers discussed above. We were unsuccessful in the synthesis of cis cyclic chloro sulfides. Addition of the sulfenyl chloride to 4-(1,1-dimethylpropyl)cyclohexene gave a mixture of **6** and **7** which resisted separation. It was possible to decouple H_A from all protons except H_B. Under these conditions, one compound, presumably **7**, showed a line separation for H_A that was independent of the exact decoupling frequency. This line separation (2.1 Hz) is probably close to the true coupling constant for gauche (equatorial–equatorial) hydrogens [see E. Garbisch, Jr., and M. Griffith, *J. Amer. Chem. Soc.*, **90**, 6543 (1968)]. The spectrum of the other compound could not be adequately decoupled, but it was clear that J_{AB} must be of similar magnitude. The conformationally mobile compound, **8**, which is analogous to *threo*-**1**, showed a J_{AB} of 7.2 Hz. The difference between *threo*-**1** (J_{AB} = 3.2 Hz) and **8** is partly due to the fact that one conformer having a low coupling constant, *i.e.*, T_{G1}, is impossible for the cyclic compound. More important, the other conformer having a low coupling constant, T_{G2}, is less probable for the cyclic compound because Cl and S–Ar are axial. Each of these axial groups is gauche to two carbon atoms, whereas if *threo*-**1** populates T_{G2}, Cl and S–Ar are each gauche to but one carbon atom.

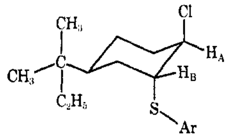
Slight deviations from dihedral angles of 60° are common so that compounds may achieve the most comfortable fit of groups.[24] These deviations are very likely quite different in cyclic and acyclic compounds. Thus, in T_{G2} repulsions between R and R′ would tend to force these groups apart in acyclic molecules, but in cyclohexanes these "groups" move toward one another because of a slight flattening of the ring. Thus, a rigid, cyclic molecule is not necessarily a good model for an acyclic system.

However, the cyclic molecule **9**, mp 157°, shows a J_{AB} value (3.2 Hz) that is *smaller* than that of its open-chain analog, *threo*-**2**. The preference for **9** over **9′** strongly suggests that the Cl–S–Ar interaction cannot be strongly attractive and is probably repulsive. If a limiting value of *ca.* 12 Hz is assumed for a conformer having purely trans vicinal hydrogens, the conformational equilibrium may be calculated to be roughly 85% **9** and 15% **9′**. Using Hirsch's "best values" for conformational energies [*Top. Stereochem.*, **1**, 199 (1967)], and assuming no interaction of Cl and S–Ar, the equilibrium mixture is calculated to be roughly 70% **9** and 30% **9′**. The greater preference for **9** over **9′** that is observed may be ascribed to a roughly 0.5-kcal repulsion of gauche Cl and S–Ar groups.

An attempt was made to synthesize a compound, *i.e.*, **10**, in which Cl and S–Ar would be almost completely equatorial. In spite of the 1,3-diaxial interaction present in **10′**, this conformer is substantially populated as shown by the fairly low J_{AB} value of 10.8 Hz. Compound **11** was synthesized to serve as an analog of *threo*-**3**. A J_{AB} value of 7.6 Hz was observed, which also suggests that **11′** has a surprisingly large population (*ca.* 40%). Thus, not only does chlorine readily tolerate an axial conformation [E. L. Eliel and R. Haber, *J. Amer. Chem. Soc.*, **81**, 1249 (1959)], but 1,3-diaxial interactions between chlorine and methyl groups appear to be much less repulsive than methyl–methyl interactions in these particular cases.

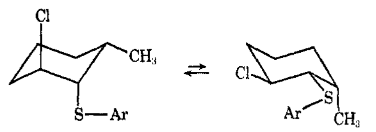


6

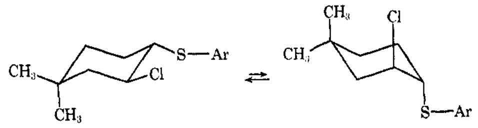


7

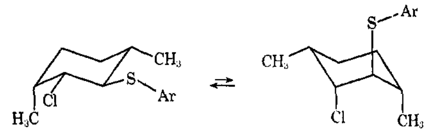
8



9 **9′**



10 **10′**

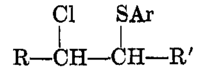


11 **11′**

(29) A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman, San Francisco, Calif., 1963, p 251.

TABLE II

INFRARED BANDS OF SULFIDE CHLORIDES 1–4 IN CS_2 SOLUTION AND AS A KBR PELLET



$$R{-}\overset{\overset{\large Cl}{|}}{C}H{-}\overset{\overset{\large SAr}{|}}{C}H{-}R'$$

Compound	R	R′	S'_{HH} (632)[a]	S''_{HH} (685)	S_{CH} (666)	S_{CC} (742)	S_{HS} (700)	S_{CS} (765)
erythro-**1**	CH_3	CH_3		*b*	653, m	*b*	711, m	*b*
				(*b*)	(666, m)	(*b*)	(704, m)	(*b*)
threo-**1**	CH_3	CH_3		*b*	658, m	*b*	708, m	*b*
			(613 w)	(*b*)	(667, m)	(*b*)	(716, s)	(*b*)
erythro-**2**	CH_3	$CH(CH_3)_2$		*b*	653, s	*b*	711, w, sh	*b*
				(*b*)	(669, s)	(*b*)		(*b*)
threo-**2**	CH_3	$CH(CH_3)_2$	626, m	*b*	658, s	*b*	708, vw	*b*
			(623, s)	(*b*)	(664, s)	(*b*)		(*b*)
erythro-**3**	$CH(CH_3)_2$	$CH(CH_3)_2$	*b*	(694, s)[e]	650, w, sh	*d*	*e*	758, m[d]
			(*b*)	(696, s)[e]	(663, s)	(*d*)	*e*	(755, m)
threo-**3**	$CH(CH_3)_2$	$CH(CH_3)_2$	*b*	692, m[e]	667, sh	758, m	710 (w)	780, m
			(*b*)	(685, m)[e]	(*c*)		(*e*)	(783, m)
erythro-**4**	CH_3	t-C_4H_9		(*b*)	664, s, sh	*b*		*b*
				(*b*)	(663, m)	(*b*)	(691, s)	(*b*)
threo-**4**	CH_3	t-C_4H_9	636, s	*b*	658, w	*b*		*b*
			(633, m)	(*b*)	(665, s)	(*b*)		(*b*)

[a] The figures in parentheses refers to the expected position of the band (±20 cm^{-1}). [b] Not applicable. [c] Either superimposed on other absorptions or absent. [d] The assignment of the band at *ca.* 755 as S_{CS}, not as S_{CC}, is arbitrary. [e] The assignment of the band at *ca.* 694 as S''_{HH}, not as S_{HS}, is arbitrary.

threo-**2** (J_{AB} = 4.2 Hz) shows a stronger preference for conformer T_T than *threo*-**1**.[28] An S'_{HH} ir band is apparent for *threo*-**2**, which suggests that T_{G1} has become populated. The analogous dichloride strongly prefers T_{G1} (J_{AB} = 3.7 Hz; μ = 2.4 D).[27]

A further increase in the size of the R group, *i.e.*, going to *threo*-**3**, results in a still larger value for J_{AB} (5.6 Hz). This value is close to the "averaged coupling constant" indicative of no strong conformational preference. The ir spectrum also indicates that a variety of conformations are populated. The increased population of T_T in the sequence **1** → **2** → **3** is unusual, since as the alkyl groups increase in size a growing preference exists for a conformer in which these groups are gauche. Molecular models suggest that the freedom of motion of the S–Ar group about the S–C and S–Ar bonds is severely restricted when R′ *and* R are isopropyl, especially in conformer T_{G1}. Thus, the isopropyl groups are most comfortable in T_{G1}, but the S–Ar is less restricted in T_T, and a mixture of these conformers results.[30]

threo-**4** has a very small J_{AB} (1.3 Hz) indicative of a preference for one of the conformers having gauche hydrogens. The ir spectrum shows a strong S'_{HH} band, consistent with conformer T_{G1}; the extreme size of R appears to be dominate over the preference of S–Ar for an unrestricted position.

In summary, the ir (Table II) and nmr data are in fair agreement. Possible discrepancies have been noted for *erythro*-**1** and -**2**, which points up the need for additional studies of the two methods. No evidence exists for an attractive Cl—S–Ar interaction in these compounds, but this interaction is not strongly repulsive.[28] The Br—S–Ar or I—S–Ar interaction, however, may be quite different, and it is regretable that compounds having these substituents are rather unstable and difficult to study.

Although a preference exists in *erythro*-**1** for a conformer having gauche Cl and S–Ar groups, this preference probably is not the result of an attractive interaction between these groups. In the cyclohexane system[28] and in the threo isomers, no particular tendency for having gauche Cl and S–Ar groups was evident. In *erythro*-**1**, the preference for a conformer with gauche Cl and S–Ar groups probably is the consequence of minimized unfavorable interactions in these conformer(s). However, in the erythro set of compounds, gauche Cl and S–Ar groups are more tolerable than gauche Cl–Cl groups. The dichlorides show a much stronger preference for conformer E_T.

Although it is particularly difficult to pinpoint any one factor as strongly conformationally determinative in **1–4**, the restriction of motion of the S–Ar group seems to be fairly important. This was rather unexpected, since in a cyclohexane system the groups OH, OCH_3, OAc, and OTs have similar conformational preferences, as do SH and S–Ph groups. In the latter case, however, the Ph group is gauche to carbon and to hydrogen in either of the axial or equatorial conformations of sulfur. In an open chain compound, a greater choice of conformation is open to the aromatic group. In the S–Ar group of this study, the greater spatial requirements of the Ar group because of the ortho nitro function are also important.

Experimental Section

Reaction of 2-Butenes with 2,4-Dinitrobenzenesulfenyl Chloride (12).—Into a solution of **12** (7.02 g, 0.03 mol) in dry acetic acid (75 ml) at room temperature was bubbled the appropriate isomer of 2-butene (*trans*-2-butene for the erythro adduct and *cis*-2-butene for the threo adduct). When the gas flow had started, the flask was cooled in an ice bath until the product solidified. The gas flow was then stopped, the flask corked, and the mixture allowed to stand for 2 hr, warming to room temperature. The mixture was then heated on the steam bath for 20 min and removed, and 2-butene again was bubbled into the solution while cooling to solidification. This process was repeated two more times. From the reactions were obtained the erythro adduct (7.91 g, 90%) with mp 75.5–76° (recrystallized from chloroform–pentane) (lit.[15b] 76.5–77.5°) and the threo adduct (6.44 g, 73%) with mp 140.3–149.7° (from chloroform–pentane) (lit.[15c] 128–129°).

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[30] An increase in temperature of *ca.* 100° led to little or no change in vicinal coupling constant, which suggests that little difference in energy exists between the various conformers.

erythro-2-Chloro-3-butyl 2,4-dinitrophenyl sulfide (**1**): ir (KBr) ~1590, ~1530, ~1505, 1448, 1394, 1387, 1381, ~1340, 1290, 1243, 1162, 1134, 1094, 1068, 1050, 983, 963, 916, 849, 833, 747, 735, 703, 676, 665, 605, 547, 518, 494, 416 cm^{-1}.

threo-2-Chloro-3-butyl 2,4-dinitrophenyl sulfide (**1**): ir (KBr) ~1590, ~1520, 1451, 1377, ~1340, 1244, 1156, 1138, 1100, 1052, 1014, 988, 917, 849, 834, 826, 762, 746, 735, 716, 708, 685, 667, 614, 590, 545, 529, 495, 480, 426 cm^{-1}.

Anal. Calcd for $C_{10}H_{11}ClN_2O_4S$: C, 41.31; H, 3.81. Found: C, 41.37, H, 3.88.

Reaction of 4-Methyl-2-pentenes with 12.—To a solution of the appropriate alkene (2.10 g, 0.025 mol) in dry acetic acid (10 ml) was added **12** (6.37 g, 0.027 mol). The reaction yielded 7.21 g (90%) of the erythro adduct (from trans alkene) with mp 89.0–89.5° (from dichloromethane–pentane) and 7.03 g (88%) of the threo adduct (from cis alkene) with mp 92.5–93.0° (from dichloromethane–pentane).

erythro-2-Chloro-4-methyl-3-pentyl 2,4-dinitrophenyl sulfide (**2**): ir (KBr) 1588, ~1520, 1471, 1462, 1451, ~1340, 1297, 1244, 1213, 1151, 1133, 1092, 1050, 1004, 918, 902, 882, 842, 830, 812, 744, 733, 728, 677, 669, 605, 548, 532, 502, 479, 434 cm^{-1}.

Anal. Calcd for $C_{12}H_{15}ClN_2O_4S$: C, 45.21; H, 4.74. Found: C, 45.21; H, 4.71.

threo-2-Chloro-4-methyl-3-pentyl 2,4-dinitrophenyl sulfide (**2**): ir (KBr) ~1585, ~1520, 1450, 1391, 1378, ~1340, 1152, 1135, 1093, 1054, 1045, 991, 957, 912, 895, 831, 820, 805, 754, 740, 732, 684, 664, 623, 595, 579, 549, 540, 522, 483, 472, 433, 413 cm^{-1}.

Anal. Calcd for $C_{12}H_{15}ClN_2O_4S$: C, 45.21; H, 4.74. Found: C, 45.09; H, 4.75.

Reaction of 2,5-Dimethyl-3-hexenes with 12.—To a solution of the appropriate alkene (2.12 g, 0.0190 mol) in dry acetic acid (10 ml) was added **12** (4.90 g, 0.0208 mol). The reactions formed 5.89 g (89%) of the erythro adduct (from trans alkene) with mp 97.5–98.0° (chloroform–pentane) and 5.82 g (88%) of the threo adduct (from cis alkene) with mp 69.5–70.0° (chloroform–pentane).

erythro-3-Chloro-2,5-dimethyl-4-hexyl 2,4-dinitrophenyl sulfide (**3**): ir ~1590, ~1515, 1471, 1460, 1389, ~1340, 1182, 1149, 1137, 1102, 1091, 1051, 615, 837, 831, 804, 760, 755, 740, 731, 696, 675, 664, 601, 548, 531, 520, 498, 471 cm^{-1}.

Anal. Calcd for $C_{14}H_{19}ClN_2O_4S$: C, 48.48; H, 5.52. Found: C, 48.29; H, 5.38.

threo-3-Chloro-2,5-dimethyl-4-hexyl 2,4-dinitrophenyl sulfide (**3**): ir (KBr) 1590, 1515, 1463, 1390, ~1340, 1302, 1244, 1145, 1101, 1052, 918, 913, 832, 820, 783, 742, 732, 685, 667, 612, 601, 536, 515, 475 cm^{-1}.

Anal. Calcd for $C_{14}H_{19}ClN_2O_4S$: C, 48.48; H, 5.52. Found: C, 48.66; H, 5.40.

Preparation of *erythro*-2-Chloro-4,4-dimethyl-3-pentyl 2,4-Dinitrophenyl Sulfide (4).—To a solution of *trans*-4,4-dimethyl-2-pentene (2.0 g, 0.0204 mol) in dry acetic acid (10 ml) was added **12** (5.00 g, 0.0213 mol). The reaction formed 5.51 g (81%) of yellow plates: mp 106.0–106.5° (from chloroform–pentane); ir (KBr) ~1590, ~1520, 1481, 1465, 1459, 1396, 1389, 1375, ~1340, 1251, 1243, 1220, 1146, 1134, 1116, 1098, 1047, 1016, 994, 916, 907, 862, 833, 830, 775, 746, 737, 731, 690, 674, 663, 594, 545, 533, 520, 498, 471, 433, 422, 411 cm^{-1}.

Anal. Calcd for $C_{13}H_{17}ClN_2O_4S$: C, 46.92; H, 5.15. Found: C, 46.83; H, 5.18.

Preparation of *threo*-2-Chloro-4,4-dimethyl-3-pentyl 2,4-Dinitrophenyl Sulfide (4).—To a solution of *cis*-4,4-dimethyl-2-pentene (2.6 g, 0.026 mol) in DMF (10 ml) was added **12** (6.6 g, 0.028 mol). The reaction formed 6.44 g (74%) of yellow plates: mp 107.5–108.0° (from dichloromethane–pentane); ir (KBr) 1596, 1589, 1520, ~1515, 1500, 1488, 1478, 1471, 1463, 1451, 1436, 1242, 1144, 1133, 1094, 1050, 1031, 917, 904, 870, 842, 836, 773, 762, 741, 732, 689, 664, 632, 593, 549, 531, 522, 507, 471 cm^{-1}.

Anal. Calcd for $C_{13}H_{17}ClN_2O_4S$: C, 46.92; H, 5.15; N, 8.42. Found: C, 46.81; H, 5.19; N, 8.22.

The nmr data were taken on a A-60D or XL-100 instrument at normal probe temperature. Coupling constants were determined from the average of two to three traces of 100-Hz expansions of the region in question. The concentration of the samples was *ca.* 10% ($CDCl_3$) or 10.0% (DMSO). The correctness of the nmr parameters was verified by simulation of the spectrum using the LAOCOON III computer program[31] equipped with a California Computer Products plot of the simulation. The parameters were varied until the simulated plot was superimposible on the original spectrum.

The infrared data were determined on Perkin-Elmer 231 or 621 instruments, usually the latter. The spectra were run at a concentration of *ca.* 0.2–0.6% w/v in CS_2 solution. The KBr spectra were run by the usual method. Nmr spectra were run in CS_2 solution at the same concentration as the ir spectra were taken. Only minor differences from the data given in Table I were noted.

Registry No.—*erythro*-**1**, 38434-69-4; *threo*-**1**, 38434-70-7; *erythro*-**2**, 38434-71-8; *threo*-**2**, 38434-72-9; *erythro*-**3**, 38434-73-0; *threo*-**3**, 38434-74-1; *erythro*-**4**, 38434-75-2; *threo*-**4**, 38434-76-3; **12**, 528-76-7; *cis*-butene, 590-18-1; *trans*-butene, 624-64-6; *cis*-4-methyl-2-pentene, 691-38-3; *trans*-4-methyl-2-pentene, 674-76-0; *cis*-2,5-dimethyl-3-hexene, 10557-44-5; *trans*-2,5-dimethyl-3-hexene, 692-70-6; *cis*-4,4-dimethyl-2-pentene, 762-63-0; *trans*-4,4-dimethyl-2-pentene, 690-08-4.

Acknowledgments.—The award of the Texaco fellowship to G. M. U. is gratefully acknowledged. Partial funds for the purchase of the XL-100 nmr instrument were provided by NSF GP-10293, which is gratefully acknowledged.

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[31] S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, **41**, 3863 (1964).