ture of products (formaldehyde 2,4-dinitrophenylhydrazone and indole-3-acetaldehyde 2,4-dinitrophenylhydrazone) was filtered, washed with water, and dried. They were separated into pure components by fractional crystallization from light petroleum ether–benzene in which the latter was insoluble.

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Intramolecular Hydrogen Bonding in *cis*-2-Phenylmercaptoindanol

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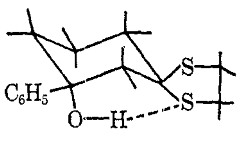
The *cis*- and *trans*-2-phenylmercaptoindanols exhibit some interesting differences in their physical and chemical properties which can be attributed to the existence of an intramolecular hydrogen bond in the *cis* isomer.

The participation of a sulfide function in intramolecular hydrogen bonding has been demonstrated in a relatively small number of situations and apparently it is very sensitive to structural factors. Thus, while compound I is known[2] to give a strong intramolecular hydrogen bond, none is reported,[3,4] for example, in the structures IIa and IIb. On the other hand, intramolecular hydrogen bonding is known to affect conformational equilibria in 1,3-dithianes.[5] In connection with the determination of the structures of the four isomeric 2-phenylsulfinylindanols[6] we had occasion to prepare the corresponding *cis* and *trans* sulfides as well as the sulfones, and, in view of the clear-cut demonstration of an intramolecular hydrogen bond in the *cis* compounds, we have at hand an opportunity to compare the behavior of the sulfide, sulfoxide, and sulfone groups in a related family of structures.



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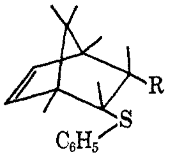

IIa, R=CO_2H
IIb, R=CH_2OH

Experimental Section

Determination of Infrared Spectra.—The infrared spectra of the *cis*- and *trans*-2-phenylmercaptoindanols,[6] mp 71.5 and 101°, respectively, were determined in a variable-path cell by means of a Perkin-Elmer Model 237 spectrophotometer. Carbon tetrachloride was employed as solvent and the concentrations were varied between 0.00625 and 0.100 *M*. The temperature range of the measurements was $25 \pm 2°$. The absorbances of the "free" O–H stretching frequency were measured at 3600 cm^{-1} in the case of both isomers. As will be shown below, the "free" OH band is actually believed to be a "π-bonded" OH association. The absorbances of the "sulfide-bound" OH were determined at 3470 cm^{-1} in the case of the rather simple band of the *cis* compound, and at 3510 cm^{-1} for the *trans* isomer. The results of these measurements are listed in Table I. The infrared spectra of the two isomers were also examined at a single concentration of 0.005 *M* in carbon tetrachloride using a 1-cm cell and a Perkin-Elmer Model 521 spectrophotometer,[7] and the bands, together with those of the corresponding sulfoxides and sulfones, are listed in Table II.

TABLE I

CONCENTRATION DEPENDENCE OF THE ABSORBANCE OF THE OH BANDS IN *cis*- AND *trans*-2-PHENYLMERCAPTOINDANOLS

	Cell path,	Absorbance of OH			
		cis isomer		*trans* isomer	
Concn, *M*	mm	π bonded	S bonded	π bonded	S bonded
0.00384	5.00	0.013	0.067	...	...
0.00625	3.20	0.022	0.070	0.120	0.002
0.0125	1.600	...	...	0.144	0.009
0.025	0.800	...	...	0.135	0.014
0.050	0.400	0.017	0.070	0.120	0.015
0.100	0.200	0.016	0.076	0.110	0.041
0.800	0.025	...	0.067	...	...

TABLE II

HIGH-RESOLUTION H–O STRETCHING FREQUENCIES (CM^{-1}) OF *cis*- AND *trans*-2-PHENYLMERCAPTOINDANOLS AND RELATED COMPOUNDS

	Band Assignment of OH	
Compd	π bonded	S bonded
cis sulfide	3596	3500
trans sulfide	3607	...
cis-anti sulfoxide[6]	3564	3334
cis sulfone	3559	3494
trans sulfone	3587	...

Determination of Ultraviolet Spectra.—The ultraviolet spectra were determined by means of a Zeiss PMQ II spectrophotometer using 1-cm cells, and spectroquality cyclohexane and purified 95% ethanol as solvents. The spectra exhibited one strong band at 253–258 mμ, and peaks of a weaker and partially hidden band at 272 mμ. These results are summarized in Table III.

Spontaneous Decomposition of *cis*-2-Phenylmercaptoindanol.—On several occasions it was noted that a sample of *cis*-2-phenylmercaptoindanol, purified satisfactorily by crystallization from ethanol or hexane, decomposed upon standing with the production of a strong thiophenol-like odor. In order to ascertain the nature of this decomposition a 0.292-g sample of pure compound was kept for 2 months in a closed container. At the end of this period the crystals became oily and there was noted a strong thiophenol-like odor. The mixture was carefully chromatographed on a silica gel column using chloroform as eluent. The eluted material consisted of at least two components, approximately 180 mg of unchanged starting material, and approximately 90 mg of a material, the infrared spectrum of which showed an absence of the hydroxyl function and strong absorption at 1700 cm^{-1} characteristic of a ketone. The material also showed other bands at 1605 and 1585 cm^{-1} characteristic of the 1-indanone spectrum. The material gave a 2,4-dinitrophenylhydrazone of mp 255–258° which did not depress the melting point of an

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[1] From the M.S. Thesis of J. J. R., University of Puerto Rico, 1965.

[2] M. P. Mertes, *J. Org. Chem.*, **26**, 5236 (1961). This paper lists other references pertinent to the subject.

[3] S. Ghersetti, H. Hogeveen, G. Maccaguani, F. Montanari, and F. Taddei, *J. Chem. Soc.*, 3718 (1963).

[4] H. Hogeveen and F. Montanari, *ibid.*, 4864 (1963).

[5] R. J. Abraham and W. A. Thomas, *ibid.*, 335 (1965).

[6] H. H. Szmant and J. J. Rigau, *J. Org. Chem.*, **31**, in press.

[7] We thank the Department of Chemistry of the University of Pennsylvania for this courtesy, and Mr. E. J. Leopold for technical assistance.

TABLE III

ULTRAVIOLET ABSORPTION SPECTRA OF *cis*- AND *trans*- 2-PHENYLMERCAPTOINDANOLS

Compd	Band A[a]		Band B[a]	
	Cyclohexane	Ethanol	Cyclohexane	Ethanol
cis isomer	272.0 (2700)	272.0 (3500)	253.0 (7900)	256.5 (8400)
trans isomer	272.5 (3900)	272.0 (3900)	258.0 (7100)	257.5 (7600)

[a] Absorption maxima are given in millimicrons and molar absorptivities parentheses are reported in ϵ values.

authentic sample of the 2,4-dinitrophenylhydrazone of 1-indanone, and the infrared spectra of both (KBr pellet) samples were identical.

Results and Discussion

The formation of intermolecular hydrogen bonds between hydroxylic compounds and sulfide functions falls into the category of well-recognized interactions between hydroxyl groups and almost any systems containing π or nonbonding electrons.[8] In a recent study of the donor properties of sulfur compounds, the association of phenol and phenyl methyl sulfide is reported[9] to produce a 170-cm^{-1} shift in the O–H stretching frequency and to be accompanied by an enthalpy of formation of -3.4 kcal/mole. At first sight it is surprising that in spite of the common participation of sulfides in intermolecular hydrogen bonds, the formation of intramolecular associations is so much more elusive. The reason for this difference must lie in the relatively negative entropy of the intramolecular S$\cdots$HO bond when compared to the intermolecular association. In the latter case the hydroxylic compound of relatively simple structure is highly associated, to start with, and the formation of an intermolecular complex takes place with a simultaneous partial breakdown of the initial hydroxylic aggregate. In the intramolecular hydrogen bonding, the more complex structure, *ipso facto*, participates less in intermolecular associations, and, thus the formation of the intramolecular hydrogen bond imposes a relatively negative entropy change. This argument leads us to conclude that a part of the required interatomic distance between the interacting functions, intramolecular hydrogen bonding involving sulfide functions (and probably other donors that are weak toward a "hard acid" like a proton), takes place in structures which are not apt to form highly organized aggregates.

The *cis*-2-phenylmercaptoindanol structure appears to be very favorable for intramolecular hydrogen bonding as shown by the infrared data and the greater than 100-cm^{-1} displacement of the "free" O–H stretching frequency. The high-resolution spectra reveal (Table II) that the two conformations of the *cis* isomer in equilibrium are those in which the hydroxyl group interacts either with the sulfur electrons or with the π cloud of the indane ring system. This conclusion is based on the fact that 1-indanol and 2-indanol exhibit,[10] under equivalent experimental conditions, a truly "free" band at 3620 and 3622 cm^{-1}, respectively, and a π-bonded band at 3600 and 3593 cm^{-1}, respectively. Similarly, in the case of compound I, there are observed[2] two concentration-independent bands at 3581 and 3446 cm^{-1}, respectively, which correspond to the π-bonded and sulfide-bonded hydroxyl groups. Thus, none of the compounds under discussion has a "free" hydroxyl bond, and the equilibria involve the interaction of the hydroxyl group with either the sulfur function, or with the π electrons of the indane ring system. Assuming that the latter is not strongly affected by the nature of the sulfur substituent at the relatively remote 2 position, we have an opportunity to compare the magnitude of a sulfide, sulfoxide, and sulfone function as a donor in intramolecular hydrogen bonding. The relative displacements of the "bound" hydroxyl absorption (from the hypothetical band at 3620–3622 cm^{-1} in a truly "free" bond) tell us that this order is sulfoxide $\gg$ sulfone $>$ sulfide. In line with the arguments exposed above, it is our belief that a comparison of relative strength in intramolecular hydrogen bonding is more reliable than a comparison of intermolecular associations since the entropy effect is more nearly eliminated in the former. The magnitude of the frequency displacement is proportional to the free energy of association and is thus strongly influenced by entropy differences in the variety of families under comparison. The sulfoxides are especially prone to auto-associate[11] and this could easily distort any conclusions based on frequency shifts in intermolecular hydrogen bonding.

The results listed in Table I reveal that the absorbances of the *cis* sulfide are independent of concentration within the upper concentration limit examined here (0.100 *M*). This is so, of course, because under our experimental conditions the total number of solute molecules remains constant, and thus there results an average absorbance of 0.017 and 0.070 for the π-bonded and sulfide-bonded hydroxyl bands. We can make an estimate of the equilibrium constant

$$\pi\text{-bonded OH} \rightleftharpoons \text{sulfide-bonded OH}$$

by assuming that the molar absorptivity of the π-bonded OH is alike in the related *cis* and *trans* sulfides, and that the latter is unassociated at the concentration of 0.00625 *M*. Using the data of Table I we calculate the $\epsilon_{\pi\ \text{bonded}}$ to be 60, and then employ this value to calculate the concentration of π-bonded conformer in the *cis* isomer. Subtracting this concentration from the total known concentration of the *cis* sulfide, we obtain the concentration of the sulfide-bonded conformer, and this gives us a value of π bonding/sulfide bonding of approximately 6. We can also calculate the molar absorptivity of the sulfide-bonded hydroxyl group and this turns out to be *ca.* 41. The equilibrium constant of 6 points to a free-energy difference of about -1.0 kcal/mole. The free-energy difference in favor of the sulfur-bonded hydroxyl group in 2,2-dimethyl-5-hydroxy-1,3-dithian is reported[5] to be -0.8 kcal/mole.

At the very high concentration of 0.800 *M* of the *cis* sulfide we note (Table I) that the absorption of the π-bonded hydroxyl band is totally suppressed. The

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(8) (a) A. W. Baker and A. T. Shulgin, *J. Am. Chem. Soc.*, **80**, 5358 (1958); (b) E. Osawa, Ph.D. Thesis, Kyoto University, Kyoto, Japan, 1965.

(9) R. J. Niedzielski, R. S. Drago, and R. L. Middaugh, *J. Am. Chem. Soc.*, **86**, 1696 (1964).

(10) E. L. James, Ph.D. Thesis, University of Pennsylvania, 1963.

(11) R. Figueroa, E. Roig, and H. H. Szmant, *Spectrochim. Acta*, in press.

molecules are sulfide bonded, therefore, either by intra- or intermolecular associations.

The comparison of the ultraviolet spectra of the *cis*- and *trans*-2-phenylmercaptoindanols shows (Table III) a relatively weak, solvent-insensitive band at 272 mμ in both compounds. This band is the forbidden ^1L_b transition[12] also observed in phenyl methyl sulfide at 275 mμ (log ε 3.15).

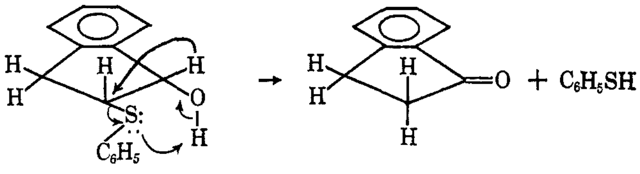
The stronger absorption at 253–258 mμ is of greater interest because it is presumed to be a polar ^1L_a transition[12] in which the benzene electrons are perturbed by the adjacent sulfur atom. A sulfur atom, however, can theoretically perturb the benzene electrons by an interaction of the latter with its d orbitals, or with its nonbonding electrons. The examination of the solvent effect in the case of the *cis*- and *trans*-2-phenylmercaptoindanols allows us to make a rather unambiguous distinction between these two interactions. We note that the 258-mμ band is almost solvent independent in the case of the *trans* isomer, while there exists a distinct hypsochromic shift in the case of the *cis* isomer when the latter is examined in cyclohexane. We take this to mean that the strong intramolecular association between the hydroxyl group and the nonbonding sulfur electrons is responsible for the 5-mμ blue shift, and this implies that the transition is of the n–π* type. The *trans* sulfide suffers only a slight (0.5 mμ) hypsochromic shift of the 258-mμ band when we change from cyclohexane to ethanol. This is in line with the expectation that solvent–solute interactions are predominant at the hydroxyl group and relatively weak at the sulfur atom. The hypsochromic shift in the case of the *cis* isomer is distinctly greater (1.5 mμ) than that suffered by the *trans* isomer (0.5 mμ), and this may mean that the intermolecular association of the sulfide and ethanol is aided by the *cis*-oriented hydroxyl group through the formation of a chelated complex with ethanol. The strength of this intermolecular interaction does not compare, however, with that of the intramolecular hydrogen bond (in cyclohexane) since the latter causes the above-mentioned large hypsochromic shift of 5 mμ.[13]

These interesting solvent interactions at the sulfide atom of the phenylmercapto chromophore can thus be arranged in accord with the magnitude of the observed inhibition in the n–π* transition as shown in Table IV.

TABLE IV

Group	λ_{max}, mμ	Blue shift, mμ	Spectrum of
$C_6H_5\overset{\vert}{\underset{\cdot\cdot}{S}}:$	258.0	. . .	*trans* sulfide in cyclohexane
$C_6H_5\overset{\vert}{\underset{\cdot\cdot}{S}}:\cdots\underset{\underset{C_2H_5}{\vert}}{HO}$	257.5	0.5	*trans* sulfide in ethanol
$C_6H_5\overset{\vert}{\underset{\cdot\cdot}{S}}:\cdots\underset{\underset{C_2H_5}{\vert}}{HO}\cdot\cdot\overset{\vert}{HO}$	256.5	1.5	*cis* sulfide in ethanol
$C_6H_5\overset{\vert}{\underset{\cdot\cdot}{S}}:\cdots\overset{\vert}{HO}$	253.0	5.0	*cis* sulfide in cyclohexane

Finally, we wish to discuss briefly the unexpected tendency of *cis*-2-phenylmercaptoindanol to undergo spontaneous decomposition. In view of the comparative stability of the analogous *trans* isomer, we are led to conclude that the above-mentioned intramolecular hydrogen bond is responsible for the peculiar behavior of the *cis* compound. The formation of 1-indanone and of phenyl mercaptan suggest a mechanism in which the *cis* elimination of phenyl mercaptan is accompanied by a hydride shift. At this time, it is impossible to decide whether both processes are concerted, or whether the elimination of phenyl mercaptan precedes the hydride migration. We hope to examine more closely this novel decomposition reaction of a β-hydroxylethyl phenyl sulfide in the near future.



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[12] H. H. Jaffé and M. Orchin, "Theory and Application of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, pp 474–497.

[13] *In this range of the spectrum a 5-mμ shift represents a difference in the energy of excitation of approximately 2.5 kcal/mole.*