Table VI. The Relative Quenching of Phosphorescence of Acetone by Various Additives

Compound	k_q	Compound	k_q
Ethanal	0.95	Oxygen	140
Propanal	1.9	Nitric oxide	380
1-Butanal	2.7	Sulfur dioxide	500
3-Methylpentanal	5.9	Styrene	4800
2-Butenal	100[a]		

[a] 2-Butenal is arbitrarily taken as 100.

3-methylpentanal changes as expected. Similar changes occurred in the direct and benzene-sensitized photolysis. However, at 148° the distribution of the butenes from the acetone-sensitized photolysis corresponds to the direct photolysis at 3340 A. This is in contrast to the results of the acetone-sensitized experiments at 27° in which the distribution corresponds to the direct photolysis at ~3500 A. This difference in results at the two temperatures may be caused by secondary reactions since a greater number of free radicals are present at the higher temperature in the photolysis of acetone. In agreement with this it is to be noted that a 15-fold reduction in intensity causes a change in the butene distribution at 148°, while it has essentially no effect at 27°. Likewise, the results for the benzene-sensitized photolysis at 27 and 151°, at which temperatures the concentration of free radicals must be very low, are consistent with a triplet–triplet energy transfer of 84 kcal at both temperatures.

The similarity in the curves (Figure 4) for the decrease in the phosphorescence of acetone (left-side ordinate) and the increase in the quantum yield of the butene (right-side ordinate) *vs.* aldehyde pressure gives further evidence that a triplet–triplet energy-transfer reaction produces the butene in the acetone-sensitized photolysis. Finally, it must be emphasized that, although the results give further evidence that the intramolecular rearrangement reaction proceeds through a triplet excited state, irrespective of the nature of the excited state, the butene distribution depends only on the amount of energy given to the aldehyde whether by the direct or by the sensitized photolysis.

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Evidence for an Inversion Degree of Freedom of *cis*-5,10-Thianthrene Dioxide

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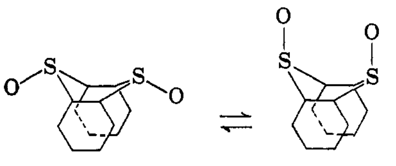
Contribution from the Department of Chemistry, Wake Forest College, Winston-Salem, North Carolina. *Received October 3, 1966*

Abstract: A study of the temperature dependence of the proton resonance of *cis*-5,10-thianthrene dioxide in 1,1,2,2-tetrachloroethane and chloroform has shown the occurrence of an inversion degree of freedom for this molecule. The solvent chloroform appears to appreciably hydrogen bond to the phenyl π electrons. The inversion rate may be placed at greater than 100 sec^{-1}.

Thianthrene and its oxides have been studied by ultraviolet,[1] infrared,[2] and polarizability[3] techniques, and the radical cations and anions have been examined by electron spin resonance.[4,5] In addition, the crystal structures[6] of most members of this class of compounds have also been determined. Some of these studies[2,3] have led to conflicting conclusions regarding the occurrence of a "flapping" or inversion degree of freedom for the *cis*-5,10-thianthrene dioxide.



In the crystal the dihedral angle of the *anti* isomer has been found[6d] to be 123°. Polarizability studies[3] in benzene suggest that a rapid inversion occurs in solution, while solvent-effect studies[2] by infrared were interpreted as negative evidence for the occurrence of inversion at room temperature. There seems to be no obvious reason to expect a lack of inversion for this molecule. On the contrary, molecular models show that inversion is possible with very little strain on the σ framework; neither does it seem likely that C–S π bonding could create a high barrier to inversion. In fact, approximate molecular orbital calculations[7] for thianthrene place the energy of activation for inversion at only ~6 kcal/mole, and an SCF calculation[8] for thiophene indicates very little C–S π bonding.

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Table I

Compound	Solvent	Temp, °C	$\nu_\alpha{}^a$	$\nu_\beta{}^a$	$J_{\beta\beta}{}^a$	$J_{\alpha\beta}{}^a$	$J_{\alpha\beta}{}'^a$
Thianthrene	$C_2H_2Cl_4$	40	−90.6	−78.2	6.2	8.0	1.4
		100	−90.6	−78.2			
trans	$C_2H_2Cl_4$	40	−126.6	−101.4	8.0	7.4	1.2
		100	−126.8	−101.2			
cis	$C_2H_2Cl_4$	−40	−119.7	−104.3	6.6	7.6	1.3
		−20	−120.9	−104.1			
		100	−125.2	−104.0			
		160	−127.0	−104.5			
Thianthrene	$CHCl_3$	40	−14.4	+1.0			
		90	−13.3	+1.7			
cis	$CHCl_3$	−20	−47.2	−28.0			
		100	−48.6	−25.4			

[a] In cps, and the chemical shifts are relative to the solvent.

Experimental Section

These studies were carried out in the solvents chloroform-*d* (Merck Sharp and Dohme) and distilled (middle cut) 1,1,2,2-tetrachloroethane (Baker Practical). Proton magnetic resonance spectra were recorded on a Varian A-56/60 spectrometer equipped with a Varian V-6040 variable-temperature controller.[9] Spectra of the *cis* dioxide were recorded from −40 to 160° in tetrachloroethane and from −20 to 100° in chloroform-*d* at 20° intervals. The choice of solvents for these studies was severely limited by the need for a wide liquid range of the solutions, high solute solubility, and isolated solvent proton resonance. Tetramethylsilane was not used as an internal reference because of boiling at the higher temperatures.

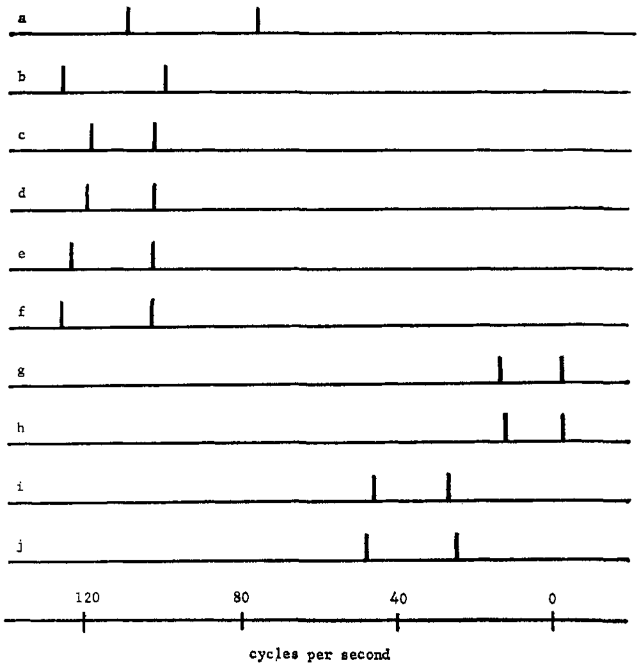

Figure 1. Proton resonances of thianthrene, *cis*-5,10-thianthrene dioxide, and *trans*-5,10-thianthrene dioxide. In tetrachloroethane: (a) thianthrene, 40 and 100°; (b) *trans*, 40 and 100°; *cis* at (c) −40°; (d) −20°, (e) 100°, (f) 160°. In chloroform: thianthrene at (g) 40°, (h) 100°; *cis* at (i) −20°, (j) 100°. All chemical shifts are relative to the solvent at 0 cps.

cis-**5,10-Thianthrene Dioxide.** Chlorine gas (Matheson) was bubbled through a slurry of 10 g of thianthrene (Eastman) in 100 ml of benzene and 20 ml of water until reaction ceased. A ~50% yield of pure compound was obtained after recrystallizing the crude product once from 150-ml of glacial acetic acid and a second time from 100 ml of glacial acetic acid. After drying 12 hr under vacuum over KOH, the compound melted at 281–282° (lit.[10] 284°). The infrared spectrum showed the absence of the *trans* isomer.

trans-**5,10-Thianthrene Dioxide.** The *trans* isomer was isolated from the supernatant liquids from the *cis* isomer by five recrystallizations from glacial acetic acid, one from 50% acetic acid–water, one from benzene, and two from absolute ethanol. Its purity was confirmed by its melting point[6c] and infrared spectrum[2] in KBr.

Thianthrene. This compound was pure as received from Eastman and was not further purified (mp 153°; lit.[11] 154°).

Results

The spectra of all the compounds in both solvents at all temperatures are those of A_2B_2 systems of spins. The spectra were analyzed by the procedure used for naphthalene.[12] The chemical-shift values for each compound in the two solvents for at least two temperatures are displayed in Figure 1. The coupling constants are solvent and temperature independent and are given in Table I along with the chemical-shift values. We note that the value calculated for J_β is only approximate since J_α is assumed to be zero.

With tetrachloroethane as solvent and internal reference, the spectrum of thianthrene is temperature independent. In this same solvent the spectrum of the *trans* compound is also independent of temperature within experimental error. The *cis* compound, however, exhibits a temperature dependence in that the downfield resonance shifts further downfield while the upfield resonance *does not shift* over a 200° range.

With chloroform as the solvent quite different behavior is noted. Both proton resonance energies of thianthrene are seen to shift upfield and essentially equally with the solvent as reference on going from 40 to 90°. The *cis* compound in chloroform exhibits a diamagnetic shift of the upfield resonance and a smaller paramagnetic shift of the downfield portion of the spectrum.

No line broadening with temperature occurs for any of the molecules in this study.

Discussion

We begin by noting that the lack of line broadening for the *cis* and *trans* compounds as the temperature is varied implies either a lack of inversion in these temperature ranges or alternatively that inversion is rapid at all these temperatures.

We have assigned the downfield resonances in the three compounds to the protons α to the sulfur atoms

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and the higher field resonances to the β protons. This was done by analogy with naphthalene[12] and anthracene,[13] and the same arguments for assignment should apply here. The temperature-dependent behavior observed with the *cis* compound is consistent with this assignment, as will be shown.

We will consider the data with tetrachloroethane as solvent first. In this solvent the thianthrene spectrum is seen to be temperature independent, a fact which is somewhat surprising since the chemical shift (relative to TMS) of the solvent protons has been reported[14] to move upfield ~4 cps for a 60° temperature change. We will return to this point later, but it is very important to note at this point that $\nu_\alpha - \nu_\beta$ is temperature independent and, therefore, even though the solvent reference may shift, the relative magnetic environments of the two protons do not change. The same behavior for the *trans* compound is also to be noted. Very important in this case is the fact that the spectrum is that of an A_2B_2 spin system. This alone is very good evidence for a rapid inversion of these molecules since the no-inversion case should exhibit *two* α-proton resonances. This latter statement stems from the expectation of different magnetic environments for an α proton when it is adjacent to a down sulfoxide group or an up sulfoxide group. The difference is expected to be similar to that observed[15] for the N-methyl groups of amides.

Considering the temperature dependence of the *cis* compound we are now left to explain the paramagnetic shift with increasing temperature of the α protons while the β resonance remains essentially constant. Recalling the temperature independence (particularly of $\nu_\alpha - \nu_\beta$) of the thianthrene and *trans* dioxide spectra we cannot ascribe this to a solvent effect. The phenomenon is intramolecular in origin, and we believe the only reasonable explanation consistent with all our data lies in a rapid inversion between the *anti* and *syn* forms with a temperature-dependent population of these forms. We conclude that the sulfoxide group (with probable S=O π bonding) anisotropy is responsible for the change in magnetic environment at the α protons as the molecule inverts and the sulfoxide–α-proton distance changes. It is interesting to note in this connection that the shielding effect of the carbonyl group in amides is also diamagnetic when a proton finds itself alongside the carbonyl bond. With regard to a lack of β-proton resonance temperature shift, apparently these protons are too far removed from the sulfoxide to experience this anisotropy.

While the results obtained with chloroform appear to be at odds with those from tetrachloroethane, a very simple rationalization based on solvent hydrogen bonding in this case brings the results in the two solvents into excellent agreement. Chloroform (which is more acidic than tetrachloroethane) is known[16] to form a hydrogen-bonded complex with π electron donors like benzene. The effect of this interaction is that of shielding of the chloroform proton rather than the customary deshielding effect of hydrogen-bond formation.[17] As a solution of chloroform in an aromatic solvent is diluted with chloroform or the temperature is raised, the aromatic hydrogen-bonded complex is destroyed and the proton resonance of chloroform shifts downfield. We might expect the same phenomenon to be observed with the aromatic compounds in this study. In fact, the upfield shift of the α and β protons of thianthrene as the temperature is increased is most likely due to this downfield shift of the solvent–reference rather than a shift in α- and β-proton resonances. For a 50° temperature change the shift is 1.0 cps. We further note that a temperature of 120° would yield a shift of approximately 2.4 cps.

Upon examining the *cis* spectrum in chloroform we note that over the 120° temperature range −20 to 100°, the β protons shift upfield by 2.6 cps, while the α protons shift in the opposite direction by 1.4 cps. The high-field shift of the β protons of 2.6 cps is what is to be expected if the shift were in fact really due to a solvent reference shift as discussed above. Furthermore, correcting the α-proton shift by this same amount results in a shift of 4.0 cps on going from −20 to 100°. This is closely the same value (4.3 cps) obtained for the α protons over the same temperature range in tetrachloroethane. This consistency in data for the two solvents confirms our belief that the α-proton shift in the *cis* dioxide is intramolecular in origin and is due to molecular inversion. At the same time it appears that the explanation based on hydrogen bonding of chloroform is correct. One might prefer to examine the temperature dependences on the basis of $\nu_\alpha - \nu_\beta$ in which case the β-proton resonance is taken as the reference signal. The conclusions are, nevertheless, the same.

With regard to the rate of inversion and the barrier to inversion, we can only place limiting values on these quantities. A lower limit may be placed on the rate of inversion by noting that ν_α of the *trans* dioxide and ν_α of the *cis* at 160° are closely the same. In the *trans* compound, this value arises from the time-average field at the α proton of an up sulfoxide and a down sulfoxide with equal population of these two environments during a nuclear spin lifetime. Therefore, we may say, approximately, that the *cis* compound at 160° has nearly equal populations of the *syn* and *anti* forms. Taking the low-temperature (−40°) ν_α as the limiting ν_α for the *anti* form, the chemical-shift difference between an α proton next to a down sulfoxide and an up sulfoxide is >14.6 cps. This implies, since only time-averaged spectra are observed, that the lower limit on the rate of inversion may be placed at 100 sec^{-1}.

The barrier to inversion may be estimated at 1 kcal/mole or less after comparison with data in the literature on barriers to inversion and rotation. It appears that a barrier of 1 kcal/mole or less corresponds to exchange-averaged spectra at temperatures as low as −40° and less.

We turn now to a discussion of the effect of a pure solvent resonance shift with temperature that is due to solvent hydrogen bonding with itself and internal rotation in the case of tetrachloroethane. Over a 60° (120°) temperature range chloroform is reported[14] to shift ~3 (5) cps and tetrachloroethane ~4 (8) cps

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relative to TMS. In our studies (*cf.* thianthrene and *trans* dioxide) these shifts were not observed which, if these solvent shifts can be applied to our solutions, means that the α and β protons of thianthrene and the *trans* dioxide both shift to high field as the temperature is raised by the same amount as the solvent! We hasten to note that whatever the origin of this effect, the α and β protons are equally affected in *both the thianthrene and the trans dioxide.* We, therefore, expect no change in $\nu_\alpha - \nu_\beta$ in the *cis* compound either, and our conclusions regarding the existence of inversion in these molecules are still valid.

Summary

In conclusion we can summarize those points which lead us to conclude that thianthrene and its derivatives undergo rapid inversion in solution. (1) There is no apparent reason for a high barrier to inversion. (2) The spectrum of the *trans* dioxide is that of an A_2B_2 system of spins. (3) Only the α protons of the *cis* dioxide exhibit a temperature-dependent resonance energy. (4) This temperature dependence is the same for the two solvents tetrachloroethane and chloroform when a correction for chloroform hydrogen bonding to an aromatic ring is applied. (5) The chemical-shift difference of α and β protons is temperature independent for both thianthrene and the *trans* dioxide. (6) The direction of the α resonance shift indicates the same shielding effect of an adjacent sulfoxide group as for a carbonyl group in N-methylamides.

Acknowledgment. We wish to thank a referee for some particularly useful comments.

Hydration of Ions in Acetonitrile[1]

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Contribution from the School of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455. *Received November 25, 1966*

Abstract: Equations have been derived which permit the calculation of the hydration constants from the solubility product of the slightly soluble salt and the total ionic solubility in the presence of varying concentrations of water. From the experimentally determined total ionic solubility the hydration constant(s), $K^{\mathrm{f}}{}_{1_{x\mathrm{w}}}{}^{\pm}$, of the following monovalent cations, Li^+, Na^+, K^+, and Cs^+, and of the monovalent anions, perchlorate, periodate, methanesulfonate, nitrate, 3,5-dinitrobenzoate, salicylate, picrate, and 3,5-dinitrophenolate, were determined in acetonitrile at 25°. For K , Cs , IO_4^-, ClO_4^-, and picrate, $x = 1$. For the other ions x is equal to 1 and to 2. The values of the constants are listed in Table I. The total ionic solubility has been estimated from the electrical conductance of the saturated solutions, making assumptions specified in the paper. The individual hydration constants of the 3,5-dinitrophenolate ion have been determined by the above method and also by an independent spectrophotometric method. The $K^{\mathrm{f}}{}_{1_{\mathrm{w}}}{}^{\pm}$ values by both methods were found to be in satisfactory agreement.

Upon addition of water to a solution of an ionized salt in acetonitrile (AN), an interaction between the ions and water with the formation of partially hydrated ions may be expected (eq 1) in which $I_s^{\pm}$ is a solvated (or

$$I_s^{\pm} + xH_2O \rightleftharpoons I_{x\mathrm{w}}^{\pm} \tag{1}$$

unsolvated) monovalent cation or anion. In addition hydration of the undissociated salt may also occur; this will be considered in a subsequent paper.

Infrared spectra of water in carbon tetrachloride show the antisymmetric (ν_3) and symmetric (ν_1) -OH stretching bands at 3700 and 3610 cm^{-1}, respectively, which, upon addition of AN,[2] are replaced by ν_3 and ν_1 bands at 3640 and 3545 cm^{-1}, respectively, which are attributed to a hydrogen-bonded complex involving two molecules of AN to one of water. Identical spectra have been observed in 0.045 *M* solutions of water in AN as solvent;[3] apparently, the species designated as H_2O in reaction 1 has the structure $CH_3C{\equiv}N\cdots HOH\cdots N{\equiv}CCH_3$, suggesting that water is monomeric in AN.

In the present paper the equilibrium constant (or constants) of reaction 1 has been determined for several monovalent cations and anions. This was done by measuring conductometrically the ionic solubility of a slightly soluble salt in AN in the presence of known concentrations of water. The mode of calculation of the constant (or constants) is presented in the following section. It was desirable to determine the constant of reaction 1 by an independent method. In previous work[4] it was found that the red 3,5-dinitrophenolate ion (I_s^-) heteroconjugates with water with the formation of a yellow ion $I_{m\mathrm{w}}^-$. The equilibrium constants have been measured spectrophotometrically, m being equal to 1 and 2. From solubility measurements of potassium 3,5-dinitrophenolate, the individual "hydration" constants of the cation and the anion were found. From the independently determined constant for the phenolate ion a check of the reliability of the solubility method was obtained.

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[1] This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Grant AF-AFOSR-28-63.

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