Effect of Solvent Upon the Vicinal Proton Coupling Constants of Complex Substituted Ethanes. II. Anomalous Results for 1-Phenyl-1,2,2-trihaloethanes[1]

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The n.m.r. spectra of 11 tetra-substituted ethanes have been obtained in a number of solvents. Changes in the vicinal coupling constants of 1-phenyl-1,2,2-trihaloethanes with solvent do not fit the electrostatic model for solvent effects. It is concluded that the theory breaks down because solute–solvent hydrogen bonding specifically favors the *trans* rotamers of these compounds. The conditions under which the theory would be expected to break down are also discussed in more general terms.

Les spectres r.m.n. de 11 éthanes tetra-substitués ont été obtenus dans un certain nombre de solvants. Des changements, avec le solvant, des constantes de couplage vicinales des phényl-1 trihalo-1,2,2 éthanes ne peuvent être accomodés avec le modèle électrostatique des effets de solvant. Il en est conclu que la théorie ne tient pas parce que des ponts hydrogènes entre le solvant et le soluté favorisent le rotamère *trans* de ces composés. Les conditions où la théorie ne serait pas appropriée sont aussi discutées en termes plus généraux.

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Introduction

For substituted ethanes containing two or more polar groups, the fractional population of the most polar rotational isomer (rotamer) normally increases on going from the gas phase to a polar or polarizable medium (1). Observed differences for the rotationally averaged vicinal n.m.r. coupling constant(s) of the same compound in different solvents have been interpreted as due to changes in rotamer population (2–4). More recently, Abraham *et al.* have developed an electrostatic theory for the solvent reaction field (5), which enables one to calculate the energy difference between rotamers of a disubstituted ethane as a function of solvent dielectric constant, ε, and the energy difference in the gas phase. It can also be used to calculate vicinal coupling constants for the individual rotamers from changes in rotationally averaged vicinal coupling constants with solvent. The theory has been modified to allow for the presence of three or more dipolar substituents (6) and solvent–solute dipole–dipole interactions (7). It has been successfully used to predict differences between rotamer energy levels in a number of simple substituted ethanes in which two of the three rotamers have degenerate energy levels (8).

We have been interested in the problem of estimating relative rotamer energy levels of more complex substituted ethanes where all three rotamers have different energy levels and where gas phase energy differences are generally not known. We have shown that relative rotamer energy levels for 1-phenyl-1,2-dibromoethane can be correctly deduced from changes of vicinal coupling constants with ε and that reasonable values of relative rotamer energy levels for 1-phenyl-1,2-dibromopropanes can be deduced from the variation of vicinal coupling constants with ε and temperature (9). However, this approach will only be valid if the compounds investigated obey the electrostatic theory (5). In order to test the limits of applicability of the theory to more complex substituted ethanes, we have extended our investigation to include a large number of tetra-substituted ethanes, including 1-phenyl-1,2,2-trihaloethanes, 1-phenyl-1,2-dichloropropanes and 1,1,2-trihalopropanes. The results of these investigations are reported here.

Experimental

1-Phenyl-1,2,2-trichloropropane was produced as a by-product (20% yield) during the chlorination of styrene in CH_2Cl_2. It was separated and purified by v.p.c. Similarly, 1-(*p*-tolyl)-1,2,2-trichloroethane was produced from 4-methylstyrene. 1-Phenyl-1,2,2-tribromoethane was prepared by the addition of Br_2 to *trans*-β-bromostyrene in CH_2Cl_2. The solid product (m.p. 34°) was purified by low temperature recrystallization from methanol.

Bromination of *trans*-β-chlorostyrene in CH_2Cl_2 gave a 52–48 mixture of the two isomeric 1-phenyl-1,2-dibromo-2-chloroethanes. The products could not be separated by v.p.c. or fractional distillation because of their very similar physical properties. Therefore the mixture was purified by v.p.c. and n.m.r. data were obtained using the mixture. Chlorination of *trans*-β-bromostyrene

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[1] For Part I, see ref. 9.

TABLE 1. Chemical shifts (δ scale) and vicinal coupling constants (Hz) for 1-phenyl-1,2,2-trihaloethanes

Compound	Solvent	Concentration (M)	ε	J_{AB}	δ_A	δ_B
1-Phenyl-1,2,2-tribromoethane	CCl_4	0.30	2.36	7.35	5.93	5.30
	$CDCl_3$	0.15	4.58	7.39	6.00	5.38
		0.30	4.70	7.39	6.00	5.38
		0.60	4.65	7.37	5.99	5.37
	$(CH_2)_4O$	0.30	6.79	7.77	6.45	5.61
	$(CH_3)_3CCl$	0.30	9.17	7.32	6.05	5.39
	$(CH_3)_2C{=}O$	0.15	19.1	7.83	6.55	5.71
		0.30	18.9	7.81	6.55	5.71
		0.60	17.6	7.72	6.53	5.68
	C_2H_5OH	0.30	23.8	7.41	6.30	5.49
	$CH_3C{\equiv}N$	0.30	33.6	7.69	6.31	5.60
	$(CH_3)_2S{=}O$	0.30	43.1	8.14	6.86	5.88
1-Phenyl-1,2,2-trichloroethane	CCl_4	0.30	2.33	5.98	5.89	5.09
	$CDCl_3$	0.30	4.59	5.86	5.98	5.18
	$(CH_3)_3CCl$	0.30	9.15	5.77	6.03	5.20
	$(CH_3)_2C{=}O$	0.30	18.5	5.93	6.53	5.55
	$CH_3C{\equiv}N$	0.30	33.4	5.80	6.31	5.44
	$(CH_3)_2S{=}O$	0.30	43.6	6.04	6.87	5.75
erythro-1-Phenyl-1,2-dibromo-2-chloroethane	CCl_4	0.21*	2.41	7.86	5.98	5.22
	$CDCl_3$	0.21	4.52	7.84	6.05	5.29
	$(CH_3)_3CCl$	0.21	8.97	7.75	6.11	5.31
	$(CH_3)_2C{=}O$	0.21	18.5	8.15	6.63	5.65
	$(CH_3)_2S{=}O$	0.21	42.2	8.46	6.98	5.85
threo-1-Phenyl-1,2-dibromo-2-chloroethane	CCl_4	0.19*	2.41	6.02	6.03	5.28
	$CDCl_3$	0.19	4.52	6.08	6.09	5.34
	$(CH_3)_3CCl$	0.19	8.97	6.01	6.13	5.37
	$(CH_3)_2C{=}O$	0.19	18.5	6.43	6.61	5.69
	$(CH_3)_2S{=}O$	0.19	42.2	6.71	6.93	5.87
erythro-1-Phenyl-1,2-dichloro-2-bromoethane	CCl_4	0.25*	2.42	5.66	5.93	5.17
	$CDCl_3$	0.25	4.70	5.60	6.00	5.24
	$(CH_3)_3CCl$	0.25	8.87	5.50	6.04	5.25
	$(CH_3)_2C{=}O$	0.25	18.4	5.73	6.53	5.58
	$(CH_3)_2S{=}O$	0.25	42.3	5.88	6.85	5.77
threo-1-Phenyl-1,2-dichloro-2-bromoethane	CCl_4	0.32*	2.43	6.58	5.90	5.14
	$CDCl_3$	0.32	4.67	6.52	5.98	5.23
	$(CH_3)_3CCl$	0.32	8.87	6.47	6.02	5.24
	$(CH_3)_2C{=}O$	0.32	18.4	6.66	6.54	5.57
	$(CH_3)_2S{=}O$	0.32	42.2	6.81	6.87	5.77

*Total solute concentration 0.40 M.

in CH_2Cl_2 gave an 80–20 mixture of the two isomeric 1-phenyl-1,2-dichloro-2-bromoethanes with the major product having the larger coupling constant. The corresponding reaction of *cis*-β-bromostyrene gave a 33–67 mixture of the same products. The isomers could not be separated and the two mixtures were purified by v.p.c. The n.m.r. spectra of both mixtures were recorded for each solvent. In every case, coupling constants for a given compound agreed within experimental error, suggesting that solute–solute interactions were unimportant. Assignment of each pair of isomers as *erythro* and *threo* is considered in the Discussion.

Erythro- and *threo*-1-phenyl-1,2-dichloropropane were prepared by addition of Cl_2 to *trans*-1-phenylpropene in CCl_4. The two liquid products were obtained in nearly equimolar quantities. They were separated and purified by v.p.c. 1,1,2-Tribromo- and 1,1,2-trichloropropane were obtained commercially and purified by v.p.c.

All halogenation reactions were carried out in the dark, using 0.3 M solutions of styrenes. The styrenes used in this investigation were obtained commercially and were used without further purification. All products were characterized by n.m.r. and mass spectra. Solvents were dried with appropriate drying agents and distilled in an N_2 atmosphere before use.

The n.m.r. spectra were recorded on a Varian HA-100 spectrometer operating in frequency sweep mode (ambient temperature 30°). Procedures followed were identical to those reported previously (9).

Solution dielectric constants were measured with a W.T.W. DK03 dielectric constant apparatus with the cell thermostatted at 30°. The v.p.c. purifications were carried out using a Varian Aerograph Autoprep 700 gas chromatograph. Mass spectra were obtained with a C.D.C. 21490 mass spectrometer.

Results

The n.m.r. spectra of the substituted ethyl groups of the various 1-phenyl-1,2,2-trihalo-

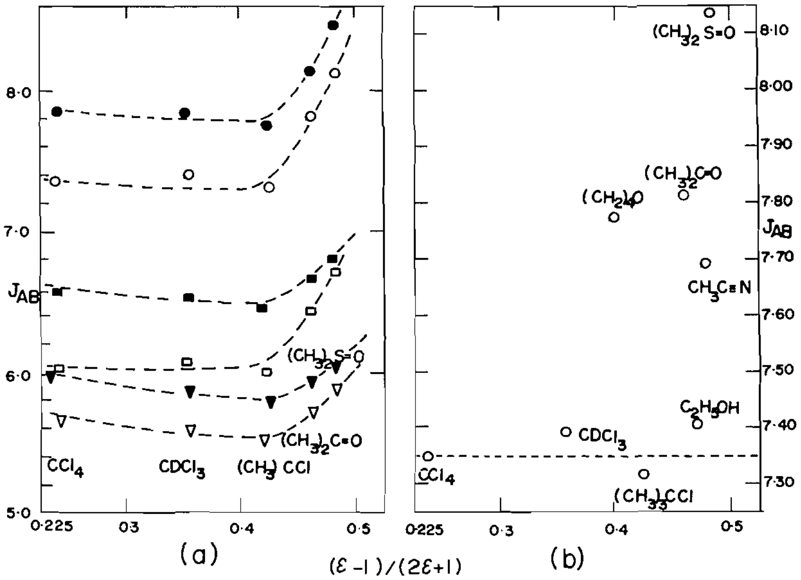

FIG. 1. (*a*) Plot of the vicinal coupling constant, J_{AB}, for 1-phenyl-1,2,2-trihaloethanes in five solvents *vs.* the dielectric function $(\varepsilon - 1)/(2\varepsilon + 1)$. ● *erythro*-1-phenyl-1,2-dibromo-2-chloroethane, ○ 1-phenyl-1,2,2-tribromoethane, ■ *threo*-1-phenyl-1,2-dichloro-2-bromoethane, □ *threo*-1-phenyl-1,2-dibromo-2-chloroethane, ▼ 1-phenyl-1,2,2-trichloroethane, ▽ *erythro*-1-phenyl-1,2-dichloro-2-bromoethane. (*b*) Expanded plot of J_{AB} *vs.* $(\varepsilon - 1)/(2\varepsilon + 1)$ for 1-phenyl-1,2,2-tribromoethane.

ethanes were analyzed as AB spectra. Results for room temperature measurements are given in Table 1 and Fig. 1. Results for variable temperature experiments for 1-phenyl-1,2,2-tribromoethane are given in Fig. 2.

The substituted propyl groups for the 1-phenyl-1,2-dichloropropanes and 1,1,2-trihalopropanes gave ABC_3 spectra. As previously reported (9), the splittings of the A and C protons corresponded, within 0.01 Hz, with $|J_{AC}|$ and $|J_{BC}|$. Therefore, the coupling constants were measured directly from these splittings. Values of the vicinal coupling constants are given in Table 2.

Results for 1-(*p*-tolyl)-1,2,2-trichloroethane are given in Table 3. The AA′BB′ ring proton spectra were analyzed by an AB approximation. Assignment of ortho and meta protons was based upon the observation of greater long range coupling to the protons ortho to the methyl group (10) and was confirmed by a double resonance experiment in which the methyl group was decoupled.

The r.m.s. error for measurements of coupling constants was always less than 0.05 Hz. It is assumed that coupling constants are accurate within this value.

Rotamers for the various compounds included in this investigation are illustrated in Fig. 3.

Discussion

It is difficult to unambiguously assign pairs of *erythro* and *threo* compounds in the 1-phenyl-1,2,2-trihaloethane series. The actual assignments given are based upon the results of empirical energy calculations (11) similar to those of Scott and Scheraga (12). Pairs of compounds were assigned by assuming that the compound with the larger vicinal coupling constant (J_{AB}) corresponded to the compound with the larger fractional population of the *trans* rotamer. The assignments are believed to be correct since they correspond to predominant *cis* addition of chlorine and *trans* addition of bromine to ethylenic bonds, in agreement with previously reported results for the halogenation of 1-phenylpropene (13). It should be emphasized, however, that the following discussion would not be changed even if one or more of the assignments were incorrect since it is concerned with the anomalous solvent dependence of the vicinal coupling constants of these compounds and not primarily with the relative stabilities of rotamers.

(a) Evidence for Breakdown of the Electrostatic Theory

The effect of solvent upon the rotationally

TABLE 2. Chemical shifts (δ scale) and coupling constants (Hz) for 1,1,2-trisubstituted propanes (all solute concentrations 0.30 *M*)

Compound	Solvent	ε	J_{AB}	J_{BC}	δ_A	δ_B	δ_C
1,1,2-Tribromopropane	CCl_4	2.29	3.20	6.53	5.88	4.46	1.90
	$CDCl_3$	4.52	3.20	6.54	5.91	4.50	1.89
	$(CH_3)_3CCl$	8.58	3.19	†	5.94	4.49	†
	$(CH_3)_2C{=}O$	*	3.11	6.51	6.31	4.72	1.85
	$(CH_3)_2S{=}O$	44.3	2.94	6.50	6.54	4.82	1.75
1,1,2-Trichloropropane	CCl_4	2.32	3.60	6.54	5.81	4.29	1.70
	$CDCl_3$	4.65	3.56	6.56	5.85	4.35	1.69
	$(CH_3)_3CCl$	9.14	3.50	†	5.89	4.34	†
	$(CH_3)_2C{=}O$	*	3.24	6.52	6.30	4.58	1.65
	$(CH_3)_2S{=}O$	43.6	3.01	6.52	6.58	4.68	1.57
erythro-1-Phenyl-1,2-dichloropropane	CCl_4	2.30	8.03	6.43	4.80	4.28	1.70
	$CDCl_3$	4.48	7.82	6.44	4.88	4.36	1.70
	$(CH_3)_3CCl$	9.05	7.67	†	4.88	4.34	†
	$(CH_3)_2C{=}O$	18.6	7.63	6.43	5.16	4.59	1.66
	$(CH_3)_2S{=}O$	43.4	7.50	6.47	5.32	4.71	1.60
threo-1-Phenyl-1,2-dichloropropane	CCl_4	2.39	5.58	6.69	4.93	4.32	1.43
	$CDCl_3$	4.51	6.00	6.65	4.97	4.38	1.44
	$(CH_3)_3CCl$	9.28	5.94	†	4.97	4.35	†
	$(CH_3)_2C{=}O$	20.0	6.11	6.59	5.22	4.55	1.46
	$(CH_3)_2S{=}O$	44.4	5.98	6.59	5.39	4.65	1.43

*Cell malfunction prevented measurement.
†Solvent peak interference prevented measurement.

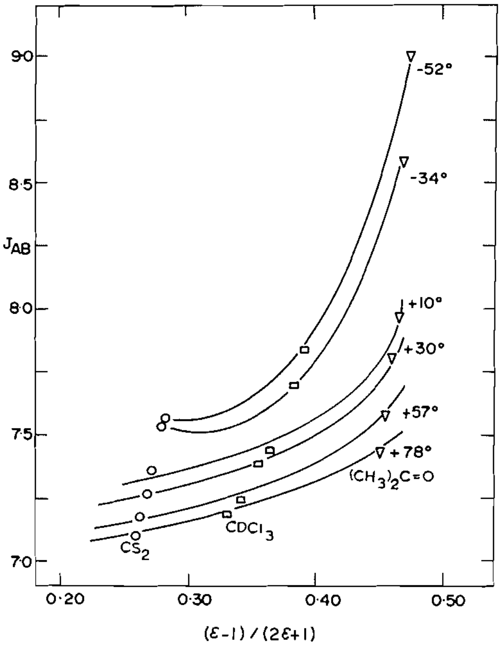

FIG. 2. Plot of J_{AB} for 1-phenyl-1,2,2-tribromoethane in three solvents at different temperatures *vs.* the dielectric function (ε − 1)/(2ε + 1).

averaged coupling constants of 1-phenyl-1,2,2-trihaloethanes is unusual (see Fig. 1*a*). The J_{AB} value decreases slightly or remains essentially constant on changing from solvents of low to intermediate ε but increases significantly in solvents of higher ε (particularly acetone and dimethylsulfoxide). Previous investigations of simpler substituted ethanes have revealed either a regular increase or a regular decrease in vicinal coupling constants with increasing ε for the solvents used in this investigation (8), although anomalous results have been noted for aromatic and hydroxylic solvents. Results of previous investigations have also been in general agreement with predictions of the electrostatic theory. However, as shown below, this theory does not predict the increase of J_{AB} for 1-phenyl-1,2,2-trihaloethanes in polar media.

Assuming staggered conformations for the three rotamers of 1-phenyl-1,2,2-tribromoethane and C—Br, H—C and C—phenyl bond dipole moments of respectively 1.48, 0.4 (14), and 0.35 D,[2] the predicted dipole moments of rotamers **1**, **2**, and **3** (see Fig. 3) are respectively 1.13, 2.08, and 3.11 D. According to the electrostatic theory, rotamer **3** would be stabilized relative to rotamers **1** and **2** by 0.33 and 0.23 kcal/mol respectively on going from the gas phase to carbon tetrachloride solution and by 0.52 and 0.35 kcal/mol on going from carbon tetrachloride to acetone solution (for details of calculations see Appendix). These predictions are not significantly altered if

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[2] Based upon dipole moments for alkylbenzenes (15).

TABLE 3. Chemical shifts (δ scale) and coupling constants (Hz) for 1-(*p*-tolyl)-1,2,2-trichloroethane (all solutions 0.30 *M*)

Solvent	δ_{ortho}*	δ_{meta}	$\delta_{\text{ortho}} - \delta_{\text{meta}}$	J_{AB}	δ_A	δ_B
CCl_4	7.278	7.121	0.156	5.97	5.88	5.04
$(CH_2)_4O$	7.376	7.164	0.212	6.03	6.36	5.37
$(CH_3)_3CCl$	7.307	7.138	0.169	5.81	5.97	5.15
$(CH_3)_2C{=}O$	7.470	7.227	0.243	5.95	6.47	5.48
$(CH_3)_2S{=}O$	7.451	7.209	0.243	6.09	6.83	5.69

*Ortho to trichloroethyl group.

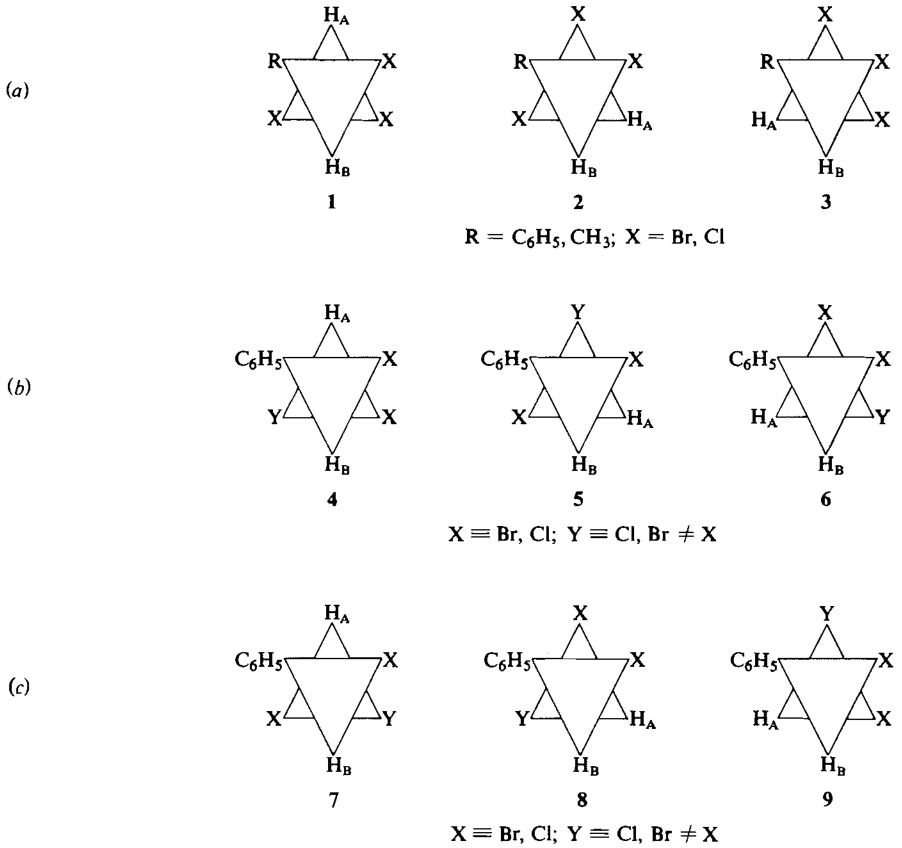

FIG. 3. Possible rotamers for the various tetrasubstituted ethanes which were investigated: (*a*) tribromo- and trichloro-compounds, (*b*) *threo*-1-phenyl-1,2,2-trihaloethanes, (*c*) *erythro*-1-phenyl-1,2,2-trihaloethanes (for *erythro*- and *threo*-1-phenyl-1,2-dihalopropanes see ref. 9).

one considers deviations from staggered conformations of as much as 15° or if one uses only C—Br group dipole moments in place of C—Br, H—C and C—phenyl bond dipole moments. Therefore, according to the electrostatic theory, the fractional population of rotamer **1** should decrease with increasing ε, leading to a decrease in J_{AB}. The same prediction would be made for all of the other 1-phenyl-1,2,2-trihaloethanes included in this investigation since C—Cl and C—Br bond dipole moments are only slightly different.

The electrostatic theory has recently been modified to include solvent–solute dipole–dipole interactions (7). However, inclusion of a term of this type would lead to the prediction of even greater stability of rotamer **3** (and a correspondingly smaller value of J_{AB}) in polar media (an effect of this type has been demonstrated experimentally for 1,1,2-trichloroethane (7)). Therefore, it must be concluded that neither the simple nor the modified electrostatic theory can explain the observed increase of J_{AB} for 1-phenyl-1,2,2-trihaloethanes in acetone and dimethylsulfoxide.

(b) Evidence for Existence of Specific Hydrogen Bonding Interactions

As shown in Table 1, J_{AB} for 1-phenyl-1,2,2-trichloroethane is nearly independent of concentration in chloroform and acetone over a concentration range from 0.15 to 0.60 *M*. Consequently, it is improbable that anomalous results can be explained in terms of specific solute–solute interactions.

An alternate explanation, which we favor, is that specific hydrogen bonding occurs between the protons of 1-phenyl-1,2,2-trihaloethanes (either involving the ethyl protons or phenyl protons, *vide infra*) and strong hydrogen bonding solvents such as acetone and dimethylsulfoxide and that this hydrogen bonding favors the *trans* rotamer relative to the other rotamers. A similar explanation has been offered to account for the failure of the electrostatic theory to predict accurate rotamer energy differences for 1-chloro-1,2-dibromo-1-iodoethane in polar solvents (16).

In order to test the possibility of specific hydrogen bonding, 1-phenyl-1,2,2-tribromoethane was investigated in a number of additional solvents which were chosen because their hydrogen bonding properties did not parallel their dielectric constants. Assuming that CCl_4, $CDCl_3$, and $(CH_3)_3CCl$ are "normal" solvents, the order of magnitude of deviation of J_{AB} is acetonitrile < tetrahydrofuran < acetone < dimethylsulfoxide (see Fig. 1*b*). This parallels the hydrogen bonding abilities of these solvents as measured by association constants with phenol (17, 18), but is totally unrelated to ε. The large value of J_{AB} in tetrahydrofuran is particularly suggestive of hydrogen bonding in view of the relatively low ε for the tetrahydrofuran solution. Ethanol shows no tendency to stabilize the *trans* rotamer. This may indicate that ethanol preferentially hydrogen bonds to the halogen atoms.

Variable temperature measurements for 1-phenyl-1,2,2-tribromoethane in carbon disulfide, chloroform, and acetone provide support for the suggestion of specific hydrogen bonding in acetone. The J_{AB} value has a much larger negative temperature coefficient in acetone than in the other two solvents. When J_{AB} is plotted as a function of ε at different temperatures (Fig. 2), it is seen that J_{AB} increases rapidly with ε at low temperatures but that the plot becomes flatter as the temperature is increased, *i.e.* the solvent dependence of J_{AB} becomes closer to the predictions of the electrostatic theory at higher temperatures.

This is precisely the behavior which one would expect if the *trans* rotamer were being favored by specific hydrogen bonding in acetone. The extent of hydrogen bonding should decrease with increasing temperature. The negative temperature coefficient for J_{AB} in the other solvents is not surprising. Since rotamer **1** has a smaller total of steric and dipolar interactions than the other two rotamers, it should be the most stable rotamer. This is supported by the relatively large value of J_{AB} in all solvents and by empirical energy calculations (11). Consequently, the fractional population of rotamer **1** would be expected to increase with decreasing temperature, leading to an increase in J_{AB}. There will be a compensating change in each solvent due to the increase in ε with decreasing temperature, but the plots of J_{AB} *vs.* $(\varepsilon - 1)/(2\varepsilon + 1)$ at different temperatures indicate that the former effect predominates.

The chemical shift data for 1-phenyl-1,2,2-tribromoethane suggest specific hydrogen bonding to the protons of the substituted ethyl group. In acetone, H_A (see Fig. 3) shifts to high field by approximately 0.34 p.p.m. (relative to internal tetramethylsilane) when the temperature is increased from −52° to +78°. Corresponding shifts in chloroform and carbon disulfide are 0.06 and −0.04 p.p.m. The large shifts in acetone are consistent with hydrogen bond breaking. At room temperature, H_A for 1-phenyl-1,2,2-tribromoethane shifts 0.12 p.p.m. to low field on going from carbon tetrachloride to *t*-butyl chloride but by 0.38, 0.52, 0.62, and 0.93 p.p.m. on going from carbon tetrachloride to acetonitrile, tetrahydrofuran, acetone, and dimethylsulfoxide, respectively. Similar, although smaller, shifts are noted for H_B and for the other compounds investigated (see Table 1).

It can be seen from the above discussion that the chemical shift and coupling constant data for 1-phenyl-1,2,2-tribromoethane are all consistent with the suggestion that basic hydrogen-bonding solvents form hydrogen bonds with 1-phenyl-1,2,2-trihaloethanes, preferentially stabilizing the *trans* rotamers **1**, **4**, or **7**.

(*c*) *General Discussion of Conditions for Breakdown of Electrostatic Theory*

As stated in the Introduction, the primary purpose of this investigation was to establish the limitations of the application of the electrostatic theory to complex substituted ethanes. On the basis of available evidence, it would appear that di- and tri-substituted ethanes (with at least two halogen substituents) obey the simple (5) or modified (7) theory. Our results suggest that the theory may break down in the case of tetra-substituted ethanes in hydrogen-bonding media and should be used with caution in these systems.

One possible explanation for these observations is that in di- and tri-substituted ethanes all rotamers are hydrogen-bonded to a roughly equal extent while in tetra-substituted ethanes the *trans* rotamer is specifically favored by hydrogen bonding to ethyl C—H protons, possibly for steric reasons. The coupling constant data for 1-phenyl-1,2,2-trihaloethanes (Table 1 and Fig. 1) indicate that steric factors may be important in determining preferential stabilization of the *trans* rotamer. For example, the change in J_{AB} on going from *t*-butyl chloride to dimethylsulfoxide is only 0.27 Hz for 1-phenyl-1,2,2-trichloroethane while it is 0.82 Hz for 1-phenyl-1,2,2-tribromoethane. Average values for the bromodichloro and chlorodibromo compounds are respectively 0.36 and 0.71 Hz.

On the basis of the above explanation, one would expect the probability of breakdown of the theory to increase as the number of electron-withdrawing groups increases, due to increased hydrogen bonding. The evidence concerning this point is ambiguous. The electrostatic theory gives at least qualitatively correct predictions for meso-2,3-dibromobutane (7), *erythro*- and *threo*-1-phenyl-1,2-dibromo- (9) and dichloropropanes (Table 2) and 1,1,2-trihalopropanes (Table 2) while it breaks down for 1-phenyl-1,2,2-trihaloethanes. Three 1,1,2,2-tetrahaloethanes have been investigated. In both 1-chloro-1,2-dibromo-1-iodoethane (16) and 1,1,2,2-tetrafluoroethane (19), the electrostatic theory underestimates the stability of the *trans* rotamer in polar solvents. However, in both cases the deviations probably are less than the possible errors in the calculation. The theory gives good results for 1,1,2,2-tetrachloroethane (20). Consequently, it must be concluded that there is conclusive evidence for the breakdown of the electrostatic theory only in the case of 1-phenyl-1,2,2-trihaloethanes.

An alternative explanation involves specific hydrogen bonding of the solvent with phenyl protons. We have obtained some evidence that the phenyl group may be involved in specific hydrogen bonding. In non-polar solvents, the phenyl proton spectrum of each 1-phenyl-1,2,2-trihaloethane was essentially a single peak but in basic hydrogen bonding solvents a two proton multiplet appeared at slightly lower field. In order to investigate this phenomenon, we synthesized 1-(*p*-tolyl)-1,2,2-trichloroethane. The pattern of chemical shifts for this compound (see Table 3) is consistent with hydrogen-bonding to the phenyl protons. The protons ortho to the trihaloethyl group are shifted to a greater extent than the meta protons.

It is possible that hydrogen bonding may favor the *trans* rotamer simply by increasing the effective size of the phenyl group. On the basis of total steric and dipolar interactions, the *trans* rotamer (**1**, **4**, or **7**) and one of the *gauche* rotamers (**2**, **5**, or **8**) should be favored over the other *gauche* rotamer. The phenyl group is in a less sterically hindered environment than the favored *gauche* rotamer (see Fig. 3). Consequently an increase in size of the phenyl group should favor the *trans* rotamer.

However, in view of the bulk of the trihaloethyl group, it is surprising that the solvent should hydrogen bond to a greater extent to the ortho protons than to the meta protons. It has previously been reported that in 1-methyl-4-X-benzenes (where X was a polar group), acetone preferentially hydrogen bonded to the protons ortho to the methyl group (10*a*). Examination of molecular models suggests an alternate, although highly speculative, explanation for the low field shift of the ortho phenyl protons and, in part, for the increased stability of the *trans* rotamer (**1**, **4**, or **7**). In this rotamer, the β proton (H_A) and one of the ortho protons tend to align in a manner which allows them to simultaneously hydrogen bond to the same solvent molecule. No similar arrangement is possible with the *gauche* rotamer (**2**, **5**, or **8**) since the β proton is *trans* to the phenyl group in this rotamer.

It would obviously be useful to determine more conclusively the reasons for the break-down of the electrostatic theory. Low temperature investigations, in which individual rotamers are observed, would be particularly useful in this respect. Our spectrometer cannot, at present, reach sufficiently low temperatures to "freeze out" individual rotamers but it is hoped to modify it to carry out experiments of this type.

In the absence of more definite information, our tentative conclusion is that the electrostatic theory probably breaks down in the case of 1-phenyl-1,2,2-trihaloethanes in polar media because of specific hydrogen bonding to the phenyl groups. However, the possibility that the breakdown is at least in part due to hydrogen bonding to the ethyl C—H protons also cannot be ruled out.

Conclusions

(*1*) Changes in the vicinal coupling constants of 1-phenyl-1,2,2-trihaloethanes with solvent cannot be explained by the electrostatic theory of solvent effects.

(*2*) Chemical shift and coupling data support the postulate that the *trans* rotamers of 1-phenyl-1,2,2-trihaloethanes are preferentially stabilized by hydrogen bonding in basic hydrogen bonding solvents.

(*3*) The preferential stabilization may be due to hydrogen bonding to either ethyl or phenyl protons or to some combination of both effects.

Appendix

The radius of the molecular cavity for 1-phenyl-1,2,2-tribromoethane was estimated by assuming that the difference in molar volume between 1-phenyl-1,2,2-tribromoethane and 1,1,2-tribromoethane was equal to that between 1-phenyl-1-bromoethane and bromoethane. The estimated molar volume and radius of the molecular cavity were respectively 168.4 cm^3 and 4.055 Å. The refractive index, n, was estimated as 1.617, using additive molar refraction parameters (21).

Bond dipole moments used in the calculation of rotamer dipole moments are listed in the discussion. The X—C—C and X—C—X (X ≡ Br or C_6H_5) angles were fixed at 111.5° and H—C—C angles at 109.5°. The following bond lengths (Å) were used: C—C = 1.54, C—C_6H_5 = 1.52, C—Br = 1.94, C—H = 1.11. Due to the completely non-spherical shape of the molecule, the quadrupole moment for each rotamer was calculated choosing the mid-point of the ethyl C—C bond as the origin. Since the calculation should be carried out with the geometrical center of the molecule as the origin, this may have introduced some error, particularly for the *gauche* rotamers (6). However, any significant change in the origin for rotamer **3** would result in an increase in the relatively small value (see below) for the quadrupolar reaction field parameter q_3 and a predicted greater stability for this rotamer.

The calculated values for the dipolar and quadrupolar reaction field parameters (5) are: $k_1 = 0.27_6$, $k_2 = 0.93_5$, $k_3 = 2.08_2$, $h_1 = 1.47_2$, $h_2 = 0.91_2$, $h_3 = 0.24_3$ kcal/mol. These values are generally smaller than previously calculated values for haloethanes (8). This is due to the significantly larger molar volume of this compound and to the use of bond dipole moments in place of group dipole moments.

The above values for k, h, and n lead to eqs. 1 and 2 for the rotamer energy differences (5);

$$[1]\quad \Delta E_{3-1}{}^{s} = \Delta E_{3-1}{}^{g} - [1.806X/(1 - 0.700X)] + [3.687X/(5 - X)]$$

$$[2]\quad \Delta E_{3-2}{}^{s} = \Delta E_{3-2}{}^{g} - [1.147X/(1 - 0.700X)] + [2.007X/(5 - X)]$$

where $\Delta E^{g} \equiv$ energy difference in the gas phase $\Delta E^{s} \equiv$ energy difference in a solution of dielectric constant ε, and $X \equiv (\varepsilon - 1)/(2\varepsilon + 1)$ (5). Insertion of solution dielectric constants into eqs. 1 and 2 yields the energy changes quoted in the discussion.

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