Effect of solvent and temperature upon the rotationally averaged vicinal coupling constants of some substituted 1,2-dibromoethanes

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The solvent dependence of vicinal coupling constants has been investigated for (1,2-dibromoethy)benzene and three of its 4-substituted derivatives and for threo- and erythro(1,2-dibromopropy)benzene. The temperature dependence of the vicinal coupling constants of three of the compounds has also been investigated. The difference between the two vicinal coupling constants of (1,2-dibromoethy)benzene is dependent upon solution dielectric constant (in non-aromatic solvents) while the sum of coupling constants remains constant. The relative stabilities of its three rotamers are deduced from this information. A polar substituent in the 4-position does not affect the rotational equilibrium in any predictable manner. The vicinal coupling constant of three(1,2-dibromopropy)benzene is strongly solvent dependent. The relative stabilities of its three rotamers are deduced from the observation that the vicinal coupling constant is temperature independent. The most stable rotamer of erythro(1,2-dibromopropy)benzene is deduced from the observation that the vicinal coupling constant is large and independent of solvent. Factors affecting conformational preference are deduced. It is concluded that dipolar interactions are as important as steric interactions.

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Introduction

Rotational isomerism in substituted ethanes has been widely investigated by nuclear magnetic resonance (n.m.r.) spectroscopy (1). In the most commonly applied technique (2), energy differences, ΔE , between rotational isomers (rotamers) are estimated from the temperature dependence of averaged vicinal coupling constants, $\langle J_{ii} \rangle$, and chemical shifts. Values of ΔE and the coupling constants for the "frozen" rotamers are determined by a least squares fitting technique. However, it has recently been shown that the value of ΔE and coupling constants for the frozen rotamers of 1,1,2,2-tetrabromofluoroethane measured directly at low temperatures are much different than those obtained from $\langle J_{\rm HF} \rangle$ at high temperatures (3). This was attributed to the insensitivity of the least squares fitting technique. It has also been pointed out that the values of ΔE are temperature dependent (4). Consequently, the above-discussed technique is of doubtful accuracy.

It is well established that for substituted ethanes containing two or more polar groups, the more polar rotamers increase in fractional population upon going from the gas phase to a polar medium (5). Solvent dependent changes in rotationally averaged coupling constants have been noted and interpreted in terms of population changes with change in solvent dielectric constant (6). Recently, Abraham and co-workers have developed a theory which allows one to predict the change in energy difference between rotamers upon going from the gas phase to a solution of dielectric constant ε (4). Then if ΔE is known in the gas phase, ΔE can be determined in the liquid phase. This approach has been successfully applied to a number of simple substituted ethanes (7) and has been extended to include compounds containing three or more polar groups (8).

It is much more difficult to apply this technique quantitatively to the investigation of conformational preference in complex substituted ethanes. Firstly, one generally has no knowledge of the energy differences either in gas phase or in solution; in fact, this is the information one would like to obtain. Secondly, one must also know the molecular volume, polarizability, etc. These quantities are often unavailable. However, it was decided to investigate whether at least semiquantitative information concerning conformational preference could be obtained from an investigation of the effect of ε and, where necessary, temperature upon $\langle J_{ij} \rangle$ for complex substituted ethanes.

A previous investigation of this type had been carried out by Snyder (9). He investigated the effect of a limited number of solvents upon chemical shifts and coupling constants of 12 trisubstituted ethanes (9a). He also developed semiempirical relationships which allowed one to estimate ΔE from $\langle J_{ij} \rangle$ (9c). It was concluded that changes in energy differences between rotamers were only weakly related to the solvent dielectric constant. However, we felt that this conclusion might be incorrect because it was based upon results in a limited number of solvents and because the solutions investigated were very concentrated (40 wt./vol. %).

The initial compounds chosen for this investigation were (1,2-dibromoethyl)benzene and three 4-substituted (1,2-dibromoethyl)benzenes. These compounds were chosen for two main reasons. Firstly, the most stable rotamer of (1,2-dibromoethyl)benzene had been determined by specific deuteration experiments (9b). Therefore, it was possible to check the conclusions from the solvent effect investigation. Secondly, it was considered important to determine the effect of the remote dipolar groups. 4-Substituted (1,2dibromoethyl)benzenes were chosen since the effect of a remote dipole could be determined by direct comparison with the results for the parent compound. In addition, the orientation of the remote dipole with respect to the substituted ethane group would be unaffected by rotation about the carbon-phenyl bond and no additional steric hindrance would be added to the system.

Erythro- and threo(1,2-dibromopropyl)benzene were investigated as examples of substituted ethanes in which there is only one vicinal coupling constant.

In this paper, results are presented for the six compounds mentioned above.

Experimental

(1,2-Dibromoethyl)benzene was prepared by the bromination of styrene in methylene chloride. The corresponding 4-substituted derivatives were prepared by bromination of 4-substituted styrenes in carbon tetrachloride. Erythro(1,2-dibromoethyl)benzene was prepared by bromination of trans-propenylbenzene in methylene chloride while the threo isomer was prepared by bromination of cis-propenylbenzene in carbon tetrachloride. All reactions were carried out in the dark. The starting materials were obtained commercially and were used without purification. Solid products were purified by recrystallization from methanol-water. The only liquid product, threo(1,2-dibromopropyl)benzene, contained approximately 20-25% of the erythro isomer as an impurity. Attempts to purify this compound by vapor phase chromatography and by low temperature recrystallization were unsuccessful and it was used unpurified.

Spectra were recorded on a Varian HA-100 spectrometer operating in frequency sweep mode at a probe temperature of 30 °C (except for variable temperature experiments). The variable temperature controller was calibrated using standard calibration samples before each variable temperature experiment. Spectra were recorded at a sweep rate of 0.05 Hz/s. The spectra were recorded twice in each direction for all coupling constant measurements. Spectra were calibrated by measuring the frequency difference between the lock and sweep oscillators, using a Hewlett–Packard 5253B frequency counter in period average mode.

Samples were usually 0.30 M in solute. Samples were deoxygenated by bubbling N₂ through them. Five percent tetramethylsilane was added as a lock and reference signal. Any solvents which were not analytical reagent grade were distilled prior to use.

Solution dielectric constants were measured with a W.T.W. DKO3 dekameter.

Results

Spectral analyses of the ABC spectra of the 1,2-dibromoethyl groups of (1,2-dibromoethyl)benzene and its para substituted derivatives were carried out by the exact method (10), using the computer program EXAN. Iterative analyses were also attempted, using the computer program LAOCN3 (11). The former method was found to be superior for this system. It provided all possible solutions while the iterative method provided only one solution in each case. The latter solution depended upon the choice of approximate input parameters. This is extremely important in this system since in several cases two solutions were obtained with the correct signs for the coupling constant (9b), i.e., with both vicinal coupling constants positive and the geminal coupling constant negative. This can be understood by considering that the spectrum is an approximate ABX spectrum. The AB part consists of two quartets or subspectra (12) (see Fig. 1). The two solutions correspond to the two possible signs of the apparent chemical shift (12) of the nearly collapsed quartet. In most cases, the correct solution was chosen on the basis that the vicinal coupling constant in erythro(1,2dibromoethyl-2-d)benzene has a value of 10.5 to 11.0 Hz (9b). The correct solution for (1,2dibromoethyl)benzene in benzene was chosen on a basis which will be discussed later. Results for (1.2-dibromoethyl)benzene are given in Table I while results for its para substituted derivatives are given in Table II.

The 1,2-dibromopropyl groups of erythroand threo(1,2-dibromopropyl)benzene gave ABC_3 spectra. A complete ABC_3 spectral analysis was carried out for the erythro isomer in carbon tetrachloride, using the computer program LAOCN3. It was found that the doublet splittings of the A proton and the C₃ methyl

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TABLE I

Chemical shifts (in p.p.m. to low field of tetramethylsilane) and coupling constants (in Hz) for (1,2-dibromoethyl)benzene

Solvent	C.						v	c	د	о С С С С С С С С С С С С С С С С С С С	koot-mean- quare error
	5		VAC/	/JBC/	VAC/ + VBC/	$\langle J_{AC} \rangle - \langle J_{BC} \rangle$	OA	Óв	δc	$\delta_{A} - \delta_{B}$	(Hz)
Hexane	1.98	-10.14	10.95	5.03	15.98	5.92	3.859	3.926	4 979	-0.067	0.05*
Cyclohexane	2.07	-10.14	11.04	4.98	16.02	6.06	3.857	3.924	4 974	-0.067	0.05
Carbon tetrachloride	2.30	-10.12	11.07	5.00	16.07	6.07	3.950	4.015	5.055	-0.065	0.00
Benzene	2.31	-10.28	10.53	5.42	15.95	5.11	3.544	3.573	4.685	-0.029	0.03
	+	(-10.28)	(10.95)	(2.00)	(15.95)	(5 95)	(3 546)	(3 571)	(1 685)		(0,03)
Carbon disulfide	2.59	-10.14	10.97	4.96	15 93	6 01	2 018	010.0		(-70.0-)	
Chloroform_d	7 26	10.72	10.00	21.7		10.0	012.0	212.0	010.5	Ton. 0-	20.0
	07.to	C7.01-	06.01	01.0	00.01	5./4	4.007	4.057	5.128	-0.050	0.03
r-Buryl chloride	8.40	-10.26	10.82	5.15	15.97	5.67	3.976	4.017	5.115	-0 041	0 0
Acetone	18.1	-10.33	10.55	5.39	15.94	5.16	4 245	4 191	5 396	+0.054	0.03
Dimethylsulfoxide	42.4	-10.19	10.41	5.62	16.03	4.79	4.358	4.238	5.526	+0.120	0.01
*Poor-mean-too	ation hotmo			-							

*Root-mean-square deviation between experimental and calculated peak positions. †Alternate solution.

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Substituent	Solvent	3	$\langle J_{ m AB} angle$	$\langle J_{ m AC} angle$	$\langle J_{ m BC} angle$	$\langle J_{\rm AC} angle + \langle J_{\rm BC} angle$	$\langle J_{ m AC} angle - \langle J_{ m BC} angle$	δ	δ_B	$\delta_{\mathbf{c}}$	Root-mean- square error (Hz)
4-Chloro	Carbon tetrachloride	2.25	-10.28	11.40	4.80	$ \begin{array}{r} 16.20 \\ 16.08 \\ 15.98 \\ 16.15 \end{array} $	6.60	3.906	4.012	5.030	0.05*
4-Chloro	Benzene	2.28	-10.32	10.94	5.14		5.80	3.388	3.475	4.513	0.01
4-Chloro	t-Butyl chloride	8.50	-10.28	10.87	5.11		5.76	3.940	4.017	5.101	0.05
4-Chloro	Dimethylsulfoxide	†	-10.20	10.59	5.56		5.03	4.368	4.239	5.570	0.02
4-Methoxy	Carbon tetrachloride	2.41	-10.26	11.22	4.90	$ \begin{array}{r} 16.12 \\ 16.03 \\ 16.04 \\ 16.11 \end{array} $	6.32	3.936	4.010	5.065	0.08
4-Methoxy	Benzene	2.38	-10.22	10.75	5.28		5.47	3.616	3.656	4.785	0.01
4-Methoxy	t-Butyl chloride	9.27	-10.17	10.87	5.17		5.70	3.970	4.017	5.132	0.03
4-Methoxy	Acetone	†	-10.21	10.54	5.57		4.97	4.223	4.169	5.389	0.02
4-Nitro	Carbon tetrachloride	2.67	-10.38	11.52	4.74	16.26	6.78	3.962	4.069	5.134	0.02
4-Nitro	Benzene	2.66	-10.35	11.06	5.19	16.25	5.87	3.297	3.397	4.407	0.06
4-Nitro	t-Butyl chloride	9.48	-10.36	11.14	4.88	16.02	6.26	3.991	4.065	5.205	0.03
4-Nitro	Dimethylsulfoxide	46.8	-10.18	10.59	5.45	16.04	5.14	4.435	4.292	5.717	0.01

TABLE II

*Root-mean-square deviation between experimental and calculated peak positions. †Cell malfunction prevented measurement of the dielectric constants of these solutions.

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IsomerSolvent ε $\langle J_{AB} \rangle$ $\langle J_{BC} \rangle$ δ_A δ_B ThreoCarbon tetrachloride2.325.286.815.1904.5391.ThreoBenzene2.385.756.744.8764.2001.ThreoChloroform-d4.335.686.735.2214.5901.ThreoChloroform-d4.335.686.735.2214.5901.Threocis-Dichloroethylene7.955.856.785.1844.5601.Threot-Butyl chloride8.785.66*5.2074.550*ThreoAcetone18.906.156.715.4164.7251.ThreoDimethylsulfoxide†6.136.675.5674.8171.ErythroCarbon tetrachloride2.2310.256.414.9444.5012.ErythroBenzene2.2810.126.514.7094.1971.ErythroChloroform-d4.1810.166.425.0294.5862.Erythrochloroform-d7.8810.186.424.9984.5621.Erythrot-Butyl chloride8.2510.08*5.0194.558*ErythroAcetone18.6010.106.425.3024.8362.ErythroAcetonitrile32.2010.32*5.2334.782*ErythroDimethylsulfoxide† <td< th=""><th></th><th></th><th></th><th></th><th></th><th></th><th></th><th></th></td<>								
ThreeCarbon tetrachloride2.325.286.81 5.19_0 4.53_9 1.ThreoBenzene2.38 5.75 6.74 4.87_6 4.20_0 1.ThreoChloroform-d4.33 5.68 6.73 5.22_1 4.59_0 1.Threocis-Dichloroethylene 7.95 5.85 6.78 5.18_4 4.56_0 1.Threot-Butyl chloride 8.78 5.66 * 5.20_7 4.55_0 *ThreoAcetone18.90 6.15 6.71 5.41_6 4.72_5 1.ThreoDimethylsulfoxide \dagger 6.13 6.67 5.56_7 4.81_7 1.ErythroCarbon tetrachloride 2.23 10.25 6.41 4.94_4 4.50_1 2.ErythroBenzene 2.28 10.12 6.51 4.70_9 4.19_7 1.ErythroChloroform-d 4.18 10.16 6.42 5.02_9 4.58_6 2.Erythror-Butyl chloride 8.25 10.08 * 5.01_9 4.55_8 *Erythror-Butyl chloride 8.25 10.08 * 5.01_9 4.55_8 *ErythroAcetonic 18.60 10.10 6.42 5.00_2 4.83_6 2.ErythroAcetonic 18.60 10.10 6.42 5.00_2 4.83_6 2.ErythroAcetonic 18.60 10.10 6.42 5.00_2 4.83_6 2.Erythro <th>Isomer</th> <th>Solvent</th> <th>3</th> <th>$\langle J_{ m AB} angle$</th> <th>$\langle J_{ m BC} angle$</th> <th>$\delta_{\mathbf{A}}$</th> <th>δ_{B}</th> <th>δ_{c}</th>	Isomer	Solvent	3	$\langle J_{ m AB} angle$	$\langle J_{ m BC} angle$	$\delta_{\mathbf{A}}$	δ_{B}	δ_{c}
ErythroCarbon tetrachloride2.2310.256.41 4.94_4 4.50_1 2.ErythroBenzene2.2810.126.51 4.70_9 4.19_7 1.ErythroChloroform-d4.1810.16 6.42 5.02_9 4.58_6 2.Erythrocis-Dichloroethylene7.8810.18 6.42 4.99_8 4.56_2 1.Erythrot-Butyl chloride8.2510.08* 5.01_9 4.55_8 *ErythroAcetone18.6010.10 6.42 5.30_2 4.83_6 2.ErythroAcetonitrile32.2010.32* 5.23_3 4.78_2 *ErythroDimethylsulfoxide†10.19 6.41 5.48_5 4.99_1 1.	Threo Threo Threo Threo Threo Threo Threo	Carbon tetrachloride Benzene Chloroform-d cis-Dichloroethylene t-Butyl chloride Acetone Dimethylsulfoxide	2.32 2.38 4.33 7.95 8.78 18.90 †	5.28 5.75 5.68 5.85 5.66 6.15 6.13	6.81 6.74 6.73 6.78 * 6.71 6.67	5.19_0 4.87_6 5.22_1 5.18_4 5.20_7 5.41_6 5.56_7	$\begin{array}{r} 4.53_{9} \\ 4.20_{0} \\ 4.59_{0} \\ 4.56_{0} \\ 4.55_{0} \\ 4.72_{5} \\ 4.81_{7} \end{array}$	1.69 ₆ 1.36 ₁ 1.69 ₈ 1.66 ₅ * 1.68 ₅ 1.63 ₅
	Erythro Erythro Erythro Erythro Erythro Erythro Erythro Erythro	Carbon tetrachloride Benzene Chloroform- <i>d</i> <i>cis</i> -Dichloroethylene <i>t</i> -Butyl chloride Acetone Acetonitrile Dimethylsulfoxide	2.23 2.28 4.18 7.88 8.25 18.60 32.20 †	10.25 10.12 10.16 10.18 10.08 10.10 10.32 10.19	6.41 6.51 6.42 6.42 * 6.42 * 6.41	$\begin{array}{c} 4.94_4\\ 4.70_9\\ 5.02_9\\ 4.99_8\\ 5.01_9\\ 5.30_2\\ 5.23_3\\ 5.48_5\end{array}$	$\begin{array}{c} 4.50_1 \\ 4.19_7 \\ 4.58_6 \\ 4.56_2 \\ 4.55_8 \\ 4.83_6 \\ 4.78_2 \\ 4.99_1 \end{array}$	$2.02_{7} \\ 1.72_{1} \\ 2.03_{0} \\ 1.99_{1} \\ * \\ 2.00_{1} \\ * \\ 1.95_{2} \\ \end{bmatrix}$

TABLE III

Chemical shifts (in p.p.m. to low field of tetramethylsilane) and coupling constants (in Hz) for threo- and erythro(1,2-dibromopropyl)benzene

*Interference with solvent peak prevented measurement. †Cell malfunction prevented measurement of the dielectric constants of these solutions.

protons (see Fig. 2) correspond within 0.01 Hz to the calculated values of $\langle J_{AB} \rangle$ and $\langle J_{BC} \rangle$. Consequently $\langle J_{AB} \rangle$ and $\langle J_{BC} \rangle$ were determined by measuring these splittings. Results are given in Table III.

Values of coupling constants for erythro- and threo(1,2-dibromopropyl)benzene are estimated to be accurate within 0.05 Hz. It is more difficult to estimate the accuracy of the coupling constants for the (1,2-dibromoethyl)benzene compounds since the coupling constants do not correspond to first order splittings. "Probable errors" determined by LAOCN3 ranged from 0.01 to 0.1 Hz with the largest errors found when the chemical shift difference of the methylene protons approached zero.

Results of variable temperature experiments are given in Table IV. Results for concentration dependence experiments are given in Table V.

Discussion

A. (1,2-Dibromoethyl)benzene

The three staggered rotamers for (1,2-dibromoethyl)benzene are shown in Fig. 3. There is a bromine-phenyl steric interaction in rotamer 1, a bromine-bromine steric and a dipolar interaction in rotamer 2, and two steric and one dipolar interaction in rotamer 3. On this basis one would expect rotamer 3 to be the least stable. It is difficult to predict the relative stabilities of rotamers 1 and 2. However, one can make certain predictions concerning the effect of the dielectric constant, ε , upon the vicinal coupling constants. The more polar rotamers (2 and 3)should be relatively more stable in solutions of high ε . If rotamer 1 is the most stable rotamer in solutions of low ε , then $\langle J_{AC} \rangle$ should be large but should decrease as ε increases (since protons A and C are *trans* in rotamer 1 and *gauche* in the other rotamers). Correspondingly $\langle J_{\rm BC} \rangle$ should be small but should increase with ε (since protons B and C are gauche in rotamer 1 and trans in rotamer 2), i.e., the difference between the coupling constants should decrease as ε increases. On the other hand, the reverse effect would be noted if rotamer 2 is the most stable rotamer. $\langle J_{\rm BC} \rangle$ should be larger than $\langle J_{\rm AC} \rangle$ and the former should increase and the latter should decrease as ε increases, i.e., the difference in coupling constants should increase as ε increases. In rotamer 3 both coupling constants are gauche. Consequently any increase in the population of rotamer 3 with ε should lead to a decrease in $(\langle J_{AC} \rangle + \langle J_{BC} \rangle)^1$. The fractional population of rotamer 3, p_3 , is expected to increase with increasing ε . However, this increase would be negligible if rotamer 3 is considerably less stable than the non-polar rotamer 1, since p_3 would then be small in all solvents.

¹This and preceding arguments depend upon the assumption that *trans* proton coupling constants are larger than *gauche* proton coupling constants. Small variations of *gauche* or *trans* coupling constants between different rotamers will not significantly affect these arguments.

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TABLE IV

Temperature dependence of vicinal coupling constants (in Hz) for (1,2-dibromoethyl)benzene and threo- and erythro(1,2-dibromopropyl)benzene

		(1,	2-Dibromo	oethyl)benzer	ne	
Solvent	٤*	Temp. (°C)	$\langle J_{ m AC} angle$	$\langle J_{ m BC} angle$	$\langle J_{ m AC} angle + \langle J_{ m BC} angle$	$\langle J_{\rm AC} angle - \langle J_{\rm BC} angle$
Acetone Acetone Acetone	18.1 21.0 23.4	30 0 -25	10.55 10.77 11.05	5.39 5.37 5.26	15.94 16.14 16.31	5.16 5.40 5.79

Three- and erythro(1.2-dibromopropyl)benzene

	, ()	1 10 /		
Isomer	Solvent	*ع	Temp. (°C)	$\langle J_{ m AB} angle$
Threo	Carbon tetrachloride	2.31	+35	5.34
Threo	Carbon tetrachloride	2.32	+30	5.28
Threo	Carbon tetrachloride	2.39	-5	5.19
Threo	Carbon tetrachloride	2.46	-24	5.14
Threo	Chloroform-d	4.33	+30	5.68
Threo	Chloroform-d	4.92	-5	5.73
Threo	Chloroform-d	5.52	-30	5.70
Threo	Chloroform-d	6.09	- 50	5.70
Threo	Acetone	18.9	+30	6.15
Threo	Acetone	22.3	-5	6.29
Threo	Acetone	26.6	- 40	6.41
Ervthro	Chloroform-d	4.18	+30	10.16
Ervthro	Chloroform-d	4.77	-5	10.39
Erythro	Chloroform-d	5.37	-30	10.63
Erythro	Acetone	18.6	+30	10.10
Erythro	Acetone	22.0	- 5	10.46
Erythro	Acetone	26.3	-40	10.73

*Dielectric constant measured at 30 °C and calculated at other temperatures assuming the same temperature dependence of ε as for the pure solvent.

The fractional populations of the three rotamers approach equality if the temperature is increased sufficiently. Therefore, the difference between $\langle J_{AC} \rangle$ and $\langle J_{BC} \rangle$ should decrease with increasing temperature regardless of the relative stabilities of rotamers 1 and 2. Consequently, the temperature dependence of the averaged vicinal coupling constants will not directly give information concerning the relative stabilities of these rotamers. A significant decrease in ($\langle J_{AC} \rangle +$ $\langle J_{BC} \rangle$) with temperature would suggest that the fractional population of rotamer 3 is not negligible.

From the above discussion it can be seen that it should be possible to determine the relative stabilities of rotamers of (1,2-dibromoethyl)benzene and similar tri-substituted, dipolar ethanes from solvent effect studies, while variable temperature experiments should yield limited information unless one uses a complicated and probably insensitive curve-fitting procedure.

As can be seen from Table I and Fig. 4, the difference between $\langle J_{AC} \rangle$ and $\langle J_{BC} \rangle$ is significantly smaller in solutions of high ε than in

solutions of low ε . The results show a slight anomaly for hexane (although this is barely larger than experimental error) and a major deviation for benzene. Otherwise, a very definite trend is noted. The results strongly suggest that rotamer 1 is the most stable rotamer (since $(\langle J_{AC} \rangle - \langle J_{BC} \rangle)$ decreases as ε increases). This is in agreement with the conclusion reached by Snyder and Buza from their specific deuteration experiments (9b). $(\langle J_{AC} \rangle + \langle J_{BC} \rangle)$ remains constant. This indicates that the population of rotamer 3 is small, as expected. It is obvious that measurements of the effect of ε upon averaged vicinal coupling constants can be used to obtain correct predictions of the relative stabilities of the three rotamers of (1,2-dibromoethyl)benzene. Therefore, it is probable that relative stabilities of rotamers of other tri-substituted, dipolar ethanes can be estimated by the same method. A number of compounds of this type are being investigated.

Rotamer 1 will be even more stable with respect to rotamer 2 in the gas phase. The more polar rotamer 2 is apparently significantly more sta-

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erythro(1,2-Dibromopropyl)benzene

FIG. 3. Staggered rotamers of (1,2-dibromoethyl)benzene and erythro- and threo(1,2-dibromopropyl)benzene.

ble in benzene than in carbon tetrachloride. Similar "benzene" effects have been noted by other investigators, both from vicinal coupling constant measurements (7) and from dipole moment measurements (13). It should be noted that the alternate solution (see Results) gives results which are apparently more consistent with other solvents. However, the first solution was chosen because in the 4-substituted derivatives, the change in $(\langle J_{AC} \rangle - \langle J_{BC} \rangle)$ on going from carbon tetrachloride to benzene was 0.8 to 0.9 Hz. This is more consistent with the first than with the alternate solution.

The conclusion of Snyder that energy differences between rotamers of substituted ethanes are only weakly related to ε was based upon results in a limited number of solvents including benzene. For several of the compounds which he investigated, the apparent discrepancies can be rationalized when it is realized that benzene may give anomalous results. We have noted a very good correlation between ε and $(\langle J_{AC} \rangle - \langle J_{BC} \rangle)$ for (1,2-dibromoethyl)benzene in eight nonaromatic solvents. However, it is only fair to



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FIG. 4. Plot of $\langle J_{AC} \rangle + \langle J_{BC} \rangle$ and $\langle J_{AC} \rangle - \langle J_{BC} \rangle$ for (1,2-dibromoethyl)benzene versus the dielectric function ($\epsilon - 1$)/($2\epsilon + 1$). Filled point represents the benzene solutions.

point out that this correlation is probably better than one can normally expect in an investigation of this type. For erythro- and threo(1,2-dibromopropyl)benzene and for the compounds investigated by Abraham and co-workers (4, 7, 8), the variation of vicinal coupling constants with ε is less regular. However, in all cases definite trends can be noticed, provided that enough nonaromatic solvents are used. The most reasonable conclusion appears to be that there is a general relationship between ε and the energy differences of rotamers of substituted ethanes in nonaromatic solvents, but that for any one solvent this relationship may be partially obscured by specific interactions.

The vicinal coupling constants for (1,2-dibromoethyl)benzene are constant over the concentration range 0.15 to 0.60 M in both carbon tetrachloride and dimethylsulfoxide (see Table V). Consequently, the coupling constants are assumed to be very close to their infinite dilution values. However, the coupling constants in carbon tetrachloride, deuterochloroform, and acetone differ significantly from those reported by Snyder for 40 wt./vol. % solutions

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TABLE V

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N_{AC} $\langle J_{AC} \rangle$ $\langle J_{BC} \rangle$ $\langle J_{AC} \rangle$ $\langle J_{AC} \rangle$ $\langle J_{BC} \rangle$ $\langle J_{AC} \rangle$ <th>Concentrat</th> <th></th> <th>ion dependen</th> <th>ce of chen (1,2-Dil</th> <th>nical shifts (ii promoethyl)</th> <th>n p.p.m. to</th> <th>d 4-nitro</th> <th>1 of tetramethyls (1,2-dibromoeth</th> <th>silane) and coupli yl)benzene</th> <th>ing consta</th> <th>unts (in Hz</th> <th></th> <th></th>	Concentrat		ion dependen	ce of chen (1,2-Dil	nical shifts (ii promoethyl)	n p.p.m. to	d 4-nitro	1 of tetramethyls (1,2-dibromoeth	silane) and coupli yl)benzene	ing consta	unts (in Hz		
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{cc} \text{Concentration} \\ \text{Solvent} \\ (\mathcal{M}) \\ \epsilon \\ \langle J \\ \end{array}$	Concentration $\epsilon \langle J \rangle$	on s S	c>	AB	$\langle J_{ m AC} angle$	$\langle J_{ m BC} angle$	$\langle J_{ m AC} angle + \langle J_{ m BC} angle$	$\langle J_{\rm AC} \rangle - \langle J_{\rm BC} \rangle$	δ _A	δ _B	δ _c st	oot-mean- quare erroi (Hz)
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Carbon tetrachloride 0.15 2.21 -10 Carbon tetrachloride 0.30 2.30 -10 Carbon tetrachloride 0.60 2.36 -10	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	111	0.18	11.12 11.07 11.13	4.98 5.00 4.98	16.10 16.07 16.11	6.14 6.07 6.15	3.954 3.950 3.942	4.021 4.015 4.005	5.056 5.055 5.049	0.01 0.02 0.02
131 11.58 4.71 16.29 6.87 3.957 4.070 5.126 0.01 0.36 11.47 4.73 16.26 6.78 3.962 4.069 5.134 0.02 0.18 10.63 5.47 16.20 6.78 3.962 4.068 5.139 0.01 0.18 10.63 5.47 16.04 4.16 4.298 5.771 0.01 0.18 10.65 5.45 16.04 4.16 4.298 5.771 0.01 0.05 5.47 16.04 4.16 4.298 5.771 0.01 0.05 5.47 4.16 4.298 4.296 5.771 0.01 0.05 5.47 4.296 4.296 4.296 5.771 0.01 0.05 5.47 6.41 5.494 4.501 2.025 0.02 10.25 6.41 5.476 4.991 1.952 0.02 10.25 6.41 5.476 4.991 1.952 <	Dimethylsulfoxide 0.15 * -10 Dimethylsulfoxide 0.30 42.4 -10 Dimethylsulfoxide 0.60 * -10	0.15 * -10 0.30 42.4 -10 0.60 * -10	* -10 *2.4 -10 * -10	111	.15	10.38 10.41 10.40	5.63 5.62 5.62	16.01 16.03 16.02	4.75 4.79 4.78	4.368 4.358 4.358	4.245 4.238 4.240	5.533 5.526 5.526	0.02 0.01 0.02
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	Carbon tetrachloride 0.15 2.42 -10 Carbon tetrachloride 0.30 2.67 -10 Carbon tetrachloride 0.45 2.85 -10 Dimethylsulfoxide 0.15 * -10 Dimethylsulfoxide 0.30 46.8 -10	0.15 2.42 -10 0.30 2.67 -10 0.45 * 2.85 -10 0.15 * -10 0.30 46.8 -10	2.42 -10 2.67 -10 2.85 -10 * -10 46.8 -10	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	31 33 18 36 36 37 38	$11.58 \\ 111.52 \\ 111.47 \\ 10.63 \\ 10.59 $	4.71 4.74 5.47 5.47 5.47	16.29 16.26 16.20 16.04	6.87 6.78 5.16 4.16	3.957 3.962 3.964 4.443 4.435	4.070 4.069 4.298 4.298	5.126 5.134 5.139 5.721 5.717	0.01 0.02 0.01 0.01 0.01
on c $\langle J_{AB} \rangle$ $\langle J_{BC} \rangle$ δ_{A} δ_{B} δ_{B} δ_{B} δ_{C} δ_{C} 2.23 10.25 6.41 4.944 4.501 2.025 2.26 10.27 6.38 4.944 4.501 2.025 2.30 10.25 6.49 4.945 4.991 1.955 * 10.15 6.41 5.485 4.991 1.955 * 6.13 6.67 5.567 4.817 1.655 * 6.20 6.64 5.554 4.796 1.954	Eryth	Eryth	Eryth	Eryth	ro- a	nd threo(1,	,2-dibron	lopropy])benzen	e				
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Concentrati Solvent (M)	Eoncentrati ent (M)	Concentrati (M)	centrati (M)	uo	3		$\langle J_{ m AB} angle$	$\langle J_{ m BC} angle$	δ _A		δ _B	δc
* 10.14 6.37 5.47_6 4.97_8 1.95_4 * 6.13 6.67 5.56_7 4.81_7 1.63_5 * 6.20 6.64 5.55_4 4.79_6 1.64_0	Carbon tetrachloride 0.30 Carbon tetrachloride 0.45 Carbon tetrachloride 0.60 Dimethylsulfoxide 0.30 Dimethylsulfoxide 0.30	achloride 0.30 achloride 0.45 achloride 0.60 froxide 0.30 froxide 0.30	0.30 0.45 0.60 0.30 0.45	0.30 0.45 0.60 0.30 45		2.23 2.30 *		10.25 10.27 10.25 10.19	6.41 6.38 6.49 6.41 6.41	4.944 4.944 4.945 5.485 5.485	4444	501 501 899 899 899 899 899 899 899 899 899 89	2.02_{5} 2.025 1.952 1.952
* 6.13 6.67 5.56 , 4.81 , 1.63_5 * 6.20 6.64 5.55_4 4.79_6 1.64_0	Dimethylsulfoxide 0.60	lfoxide 0.60	0.60	0.60 0.60		*		10,14	6.37	5.476	4.	97 <mark>8</mark>	1.954
	Dimethylsulfoxide 0.30 Dimethylsulfoxide 0.60	lfoxide 0.30 lfoxide 0.60	0.30	$0.30 \\ 0.60$		* *		6.13 6.20	6.67 6.64	5.56_{7} 5.55_{4}	44 	81 ₇ 79 ₆	1.63_{5} 1.64_{0}

in the same solvents (9*a*). The value of ε should be significantly different in the more polar solvents and this could lead to population changes. Solute dimerization could also affect the coupling constants at high concentrations. The latter effect has been shown to be important for β -bromopropionitrile at much lower concentrations (7*c*).

 $(\langle J_{AC} \rangle - \langle J_{BC} \rangle)$ decreases with increasing temperature, as expected. $(\langle J_{AC} \rangle + \langle J_{BC} \rangle)$ decreases slightly, suggesting that the population of rotamer 3, while small, is not negligible.

On the basis of the results presented (see Table I), there appears to be a very good correlation between the chemical shift difference for the methylene protons and solvent dielectric constant (except for benzene). However, this is misleading. Measurements were also made in acetonitrile. In this solvent, $(\delta_A - \delta_B)$ is very nearly zero and, therefore, would not fit the above mentioned correlation. The coupling constants had approximately the expected values. However, these results have not been reported in detail since the "probable errors" in the vicinal coupling constants were sufficiently large (0.4 Hz) to make the results meaningless. As previously mentioned, this appears to be characteristic of this system as $(\delta_A - \delta_B)$ approaches zero.

The observed changes in $(\delta_A - \delta_B)$ with solvent appear to be much too large to be explained solely in terms of conformation changes. It appears more probable that they are due to specific solvent effects.

B. 4-Substituted (1,2-Dibromoethyl)benzene

The results for the 4-substituted derivatives are similar to those for the parent compound. The differences between vicinal coupling constants are generally larger in less polar solvents. There is a small but possibly significant concentration dependence for 4-nitro-(1,2-dibromoethyl)benzene. This might be due to the change in solution dielectric constant with solute concentration. Two conclusions can be reached.

Firstly, a remote dipole does not affect relative populations in any predictable fashion. For example, in the case of the 4-nitro derivative, rotamer 1 might be expected to be destabilized with respect to the parent compound, because of an additional dipolar interaction. In fact, the coupling constant difference is larger, indicating an apparent stabilization of rotamer 1. It is quite

possible, however, that the observed difference is due to electronic rather than conformational effects.

Secondly, the remote dipole does not significantly alter the effect of solvent upon rotamer populations. According to the theory for compounds containing three or more polar groups (8), the effect of ε upon energy differences between two rotamers is determined by the difference in net dipole moments and, to a lesser extent, quadrupole moments of the two rotamers. Assuming tetrahedral angles and dipole moments of 4.0 D for the 4-nitro-phenyl group and 2.0 D for C-Br groups, then for the 4-nitro derivative the net dipole moments for rotamers 1 and 2 are, respectively, 4.0 and 2.3 D. Consequently rotamer 1 should be stabilized with increasing ε . In actual fact, the reverse trend is found, suggesting that the remote dipole has little effect². Since the theory assumes a point dipole in the center of a polarizable sphere, a breakdown in the theory for a bulky molecule such as 4-nitro-(1,2-dibromoethyl)benzene would hardly be surprising. The solvent probably tends to solvate the 1,2-dibromoethyl group quite independently of any solvation of the remote dipole, i.e., the effect of ε upon the conformation about the carbon-carbon bond depends only upon the polar groups directly bonded to the carbon atoms.

This conclusion, if correct, considerably extends the usefulness of the technique. For example, it may be possible to investigate conformational preference in low molecular weight polymers which contain many polar groups. It is obviously desirable to determine how close remote dipoles must be before they exert a significant influence. Unfortunately, it is difficult to find a suitable system. 2-Substituted or 3-substituted (1,2-dibromoethyl)benzenes would not be very suitable since the location of the remote dipole would depend upon the orientation of the phenyl group and since a substituent in the 2 or 3 position may cause additional steric hindrance.

²One might attempt to explain these results by suggesting that the quadrupolar term is more important than the dipolar term. However, nearly identical solvent effects upon vicinal coupling constants are noted for (1,2dibromoethyl)benzene and its 4-substituted derivatives, in spite of the large differences in dipole and quadrupole moments for these compounds. Therefore, we feel that the explanation presented above is more logical.

C. Erythro- and Threo(1,2-dibromopropyl)-

benzene

In each of these compounds there are only two protons in the substituted ethyl group and consequently only one vicinal coupling constant which should be solvent dependent owing to conformational changes. It is more difficult to deduce information concerning conformational preference from solvent effect studies on compounds of this type than on compounds with two solvent-dependent vicinal coupling constants. For example, for the threo compound, p_4 and p_6 should increase with increasing ε since rotamers 4 and 6 are polar (see Fig. 3). The protons are trans in rotamer 4 and gauche in the other two rotamers. Consequently $\langle J_{AB} \rangle$ should increase with increasing ε regardless of the relative energies of the three rotamers. Also, one cannot determine the relative populations of rotamers 5 and 6 since the protons are gauche in both rotamers. However, by observing the magnitude of the change in $\langle J_{AB} \rangle$ with ε and temperature, one can deduce much of the desired information.

 $\langle J_{AB} \rangle$ for the threo compound increases irregularly with ε (see Table III and Fig. 5). However, a definite trend is noted. The overall change in $\langle J_{AB} \rangle$ is large (nearly twice as large as the changes in the vicinal coupling constants in (1,2-dibromoethyl)benzene for the same range in ε). From this observation one can only deduce that rotamers 4 and 5 must be relatively close in energy. If rotamer 4 is either very stable or very unstable with respect to rotamer 5, then a small change in ΔE_{4-5} will have little effect upon p_4 (in the limiting case of infinite energy difference there would be no measurable effect). However, if the energy difference is small, then p_4 should be very sensitive to changes in ΔE_{4-5} .

More definite information can be deduced from the variable temperature results (see Table IV). In CDCl₃, J_{AB} is constant over a temperature range from -50 to +30 °C. Since the protons are *trans* in rotamer 4 and *gauche* in the other rotamers, one would expect a change in $\langle J_{AB} \rangle$ if there is any change in p_4 . Conversely, the constancy of $\langle J_{AB} \rangle$ suggests that p_4 remains essentially constant over this temperature range. This fortuitous constancy can only occur if rotamer 4 is intermediate in energy relative to the other two rotamers. In rotamer 4, there are two steric interactions and one dipolar inter-



FIG. 5. Plot of $\langle J_{AB} \rangle$ for erythro- and threo(1,2dibromopropyl)benzene versus the dielectric function $(\epsilon - 1)/(2\epsilon + 1)$. Filled points represent benzene solutions.

action. There are three steric interactions in both rotamers 5 and 6 but only the latter has a dipolar interaction. On this basis it is believed that the energy order $E_6 > E_4 > E_5$ is much more probable than the alternate order $E_5 > E_4 \ge E_6$.

The conclusion that rotamer 4 must be intermediate in energy can be confirmed by simple calculations. For example, if $E_4 - E_5 =$ 150, $E_6 - E_4 = 600$ cal/mole, $J_4 = 12.0$, and $J_5 = J_6 = 1.9$ Hz, then $\langle J_{AB} \rangle = 5.71$ Hz at 30 °C and 5.70 Hz at -50 °C³. A similar result can be obtained even if one allows for a slight temperature dependence of ΔE_{4-5} and ΔE_{5-6} (due to the decrease in ε with increasing temperature) and for the fact that J_5 is probably larger than J_6 (a vicinal coupling constant is believed

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³The normal assumption is made that the entropy difference between rotamers is zero (2). It has been shown that there are small entropy differences between the rotamers of 1,1,2,2-tetrabromo-1-fluoroethane but that if one ignored the entropy difference, one obtained an apparent energy difference between rotamers which is only slightly different from the true energy difference (3).

to be smaller when one of the protons is *trans* to an electronegative group than when it is *gauche* to that group (7, 14)). For example, if ΔE_{4-5} is 275 cal/mole at -30 °C and 300 cal/mole at +30 °C, ΔE_{6-4} is constant at 500 cal/mole, $J_4 = 12.0, J_5 = 3.0, \text{ and } J_6 = 1.5 \text{ Hz}, \text{ then} \langle J_{AB} \rangle = 5.71 \text{ Hz at } -30 \text{ }^\circ\text{C} \text{ and } 5.71 \text{ Hz at}$ +30 °C. One can obtain the same result for other reasonable choices of ΔE and J. It is impossible to determine from the available data which is the correct choice of parameters. However, any choice of parameters in which rotamer 4 is not intermediate in energy would require that the *trans* coupling constant be smaller than at least one of the *gauche* coupling constants. This would be contrary to all evidence concerning the effect of conformation upon vicinal proton coupling constants. The intermediate size of $\langle J_{AB} \rangle$ is also consistent with the conclusion that rotamer 4 is intermediate in energy.

The relative stability of rotamer 5 should be even greater in the gas phase since this rotamer is non-polar. Consequently, the order of energy levels should be the same in deuterochloroform, in solvents of lower ε , and in the gas phase. However, ΔE_{4-5} should decrease with increasing ε and could possibly change sign at high ε . In any case, relative to rotamer 5, rotamer 4 should be less stable in carbon tetrachloride and more stable in acetone than in deuterochloroform. Since p_4 is essentially independent of temperature in deuterochloroform, p_4 and $\langle J_{AB} \rangle$ should decrease with decreasing temperature in carbon tetrachloride and increase with decreasing temperature in acetone. This reversal of the sign of the temperature is actually observed (see Table IV).

The above observations are significant since they strongly suggest that the observed solvent dependence of the vicinal coupling constants is due to changes in energy differences and rotamer populations with ε rather than to reaction field effects upon the coupling constants of the individual rotamers. The latter effect has been shown to be important for the ¹H-¹⁹F coupling constant in 1-fluoro-1,1,2,2-tetrabromoethane (15). However, it is probable that the reaction field effect is more important for ¹H-¹⁹F coupling constants than for ¹H-¹H vicinal coupling constants in substituted alkanes. Previous results support this contention. For example, it has been shown that the averaged vicinal coupling constants for 1-iodo-3,3-dimethylbutane are solvent independent (14). Since this molecule has only one polar group, no change in rotamer population with ε would be expected. Since the coupling constants do not change, it is improbable that there is a significant reaction field effect.

An increased stabilization of rotamer 4 in benzene was noted. It has been suggested that the increased stabilization of the polar forms of 1,2-dihaloethanes in benzene might be due to specific hydrogen bonding of two adjacent benzene protons with the two halogen atoms in a gauche conformation (16). An alternate possibility would involve the interaction of the gauche halogens with the π electron system of benzene. In an attempt to choose between the two possibilities, we ran the threo compound in cis-1,2dichloroethylene. If the specific interaction is of the former type, one might expect it to occur with *cis*-1,2-dichloroethylene as well. Unfortunately, the results are not entirely conclusive. However, $\langle J_{AB} \rangle$ does have approximately the value which one would expect if no specific interaction occurred. Consequently, it appears probable that the specific interaction with benzene involves the π electron system.

 $\langle J_{AB} \rangle$ is, within experimental error, independent of concentration. It was also found that adding pure erythro compound to the impure three compound did not significantly alter $\langle J_{AB} \rangle$. Consequently, it is believed that our results are not affected by the presence of the erythro compound as an impurity.

 $\langle J_{AB} \rangle$ for the erythro compound is independent of ε (see Table III and Fig. 5). There is a considerable scatter of values of $\langle J_{AB} \rangle$ but no trend which could be related to ε . One would expect $\langle J_{AB} \rangle$ to be independent of ε only if one of the rotamers was very much more stable than the other two, or possibly if both rotamers with gauche protons were much more stable than the rotamer with *trans* protons. Since $\langle J_{AB} \rangle$ is large (10.2 Hz), the compound must exist predominantly in the rotamer with trans protons, i.e., rotamer 7 is much more stable than the other two rotamers. The same order should be found in the gas phase since rotamer 7 is non-polar while the other two rotamers are polar. It is impossible to deduce the relative stabilities of rotamers 8 and 9 from the available information.

The above conclusion is not at all surprising since rotamer 7 has only two steric interactions and no dipolar interaction while both other rotamers have three steric interactions and one dipolar interaction.

The temperature dependence of $\langle J_{AB} \rangle$ is similar to the temperature dependence of the vicinal coupling constants in (1,2-dibromoethyl)benzene. This suggests that the compound does not exist entirely in the conformation of rotamer 7. However, this does not necessarily imply that there are appreciable fractional populations for rotamers 8 and 9. Whitesides et al. have noted a similar temperature dependence of averaged vicinal coupling constants for a series of 1substituted 3,3-dimethylbutanes (14). The larger vicinal coupling constant at room temperature had a value of 10.2 Hz for the cyano derivative and 12.9 Hz for the phenyl derivative, while the corresponding calculated values for J_{trans} were 13.9 and 13.7 Hz. Clearly the simple observation of temperature dependence of an averaged vicinal coupling constant does not provide unequivocal information concerning how close this coupling constant is to a pure *trans* coupling constant.

It is informative to consider the difference in the total number of steric and dipolar interactions for the two most stable rotamers for each of the compounds and to compare this with the observed solvent dependence of the vicinal coupling constants. In threo(1,2-dibromopropyl)benzene there is a total of three steric and (or) dipolar interactions for each of rotamers 4 and 5. In (1,2-dibromoethyl)benzene, rotamer 1 has one less (dipolar) interaction than rotamer 2. In erythro(1,2-dibromopropyl)benzene, rotamer 7 has two less interactions than each of the other two rotamers. The changes in coupling constants (using the larger coupling constant for (1,2)dibromoethyl)benzene) upon going from carbon tetrachloride to acetone are respectively 0.83, 0.49, and 0.15 Hz. Provided that the protons were trans in one of the two most stable rotamers, one would expect the largest change in the vicinal coupling constant when the energy difference is smallest and populations are closest to equality. It is apparent that this inverse relationship does exist for the three compounds discussed above. Consequently, it appears that the relative solvent dependence of vicinal coupling constants for a series of closely related

compounds can provide meaningful information about relative conformational preference in these compounds.

The value of $\langle J_{AB} \rangle$ for the erythro compound is significantly smaller than the value of the larger vicinal coupling constant in (1,2-dibromoethyl)benzene. This is surprising. On the basis of the previous discussion, one would expect that erythro(1,2-dibromopropyl)benzene would exist predominantly as rotamer 7 while for (1,2dibromoethyl)benzene there should be appreciable populations of both rotamers 1 and 2. Therefore, one would anticipate that $\langle J_{AB} \rangle$ for the former compound would be larger than $\langle J_{\rm AC} \rangle$ for the latter compound. We believe that the most probable explanation for this apparent discrepancy is that the *trans* coupling constant in the former compound is significantly smaller than in the latter compound. If this is true, then estimates of conformational preference based only upon the size of a single vicinal coupling constant (17) must be regarded as suspect.

D. Factors Affecting Conformational Preference

Snyder believed that it was surprising that rotamer 1 was significantly more stable than rotamer 2 of (1,2-dibromoethyl)benzene (9). He first considered only steric interactions. Since the phenyl group has a much larger "A" factor (18) than the bromo group, he believed that there should be a much greater steric interaction in rotamer 1 than in rotamer 2. He then postulated that the additional stability of rotamer 1 might be due to a stabilizing interaction between the phenyl group and the bromine on the β carbon atom. However, it has since been shown that "A" factors (which were determined from substituted cyclohexanes) are not an accurate measure of steric interactions in substituted ethanes (14). In actual fact, bromine has only a slightly smaller steric effect than a phenyl group in substituted ethanes (the energy differences between gauche and trans rotamers of 1-bromoand 1-phenyl-3,3-dimethylbutane have been estimated as, respectively, 1.30 and 1.70 kcal/mole (14)). The lower stability of rotamer 2 can then be explained as due to the destabilizing effect of the dipolar repulsion of the gauche bromine atoms (if this effect was not important, there would not be any solvent dependence of rotamer population). However, one cannot entirely exclude the possibility of a stabilizing brominephenyl interaction in rotamer 1 although it is no longer necessary to postulate an interaction of this kind. Indirect support for a stabilizing interaction is provided by the observation of stabilization of polar rotamers by benzene.

As previously discussed, the relative stabilities of rotamers for other compounds can also be rationalized if one assumes that dipolar repulsions are as important as steric interactions in solutions of low ε . Once again, conformational preference might also be affected by stabilizing bromine-phenyl interactions.

There should be considerable decrease of dipolar repulsion by the medium even for solutions of low ε . For example, if the dependence of ΔE upon ε has the form $(\varepsilon - 1)/(2\varepsilon + 1)$ (4), then a medium with $\varepsilon = 2$ will decrease dipolar repulsions 40% as effectively as a hypothetical medium of $\varepsilon = \infty$. Since dipolar interactions are apparently still important in solution, they will obviously be of greater importance in the gas phase.

Summary and Conclusions

The relative stability of the rotamers of (1,2dibromoethyl)benzene can be deduced from the dependence of the sum and difference of the two vicinal coupling constants upon solution dielectric constant. It should be possible to deduce the relative stabilities of rotamers of other similar tri-substituted dipolar ethanes by a similar technique. A polar substituent in the 4position of the phenyl group does not affect conformational equilibrium or the effect of solvent upon conformational equilibrium in any predictable manner.

It was not possible to develop a general procedure to deduce the relative stabilities of rotamers of erythro- and threo(1,2-dibromopropyl)benzene. These are examples of substituted ethanes with only one vicinal coupling constant. However, much of the desired information could be determined by specific observations of the sign and magnitude of the change of the coupling constant with solvent and temperature. There appears to be a definite relationship between the magnitude of change of vicinal coupling constants with solvent and the expected energy difference between the two most stable rotamers for a series of closely related substituted dipolar ethanes.

It is possible to rationalize the deduced relative

stability of rotamers for the compounds investigated if one assumes that both dipolar and steric interactions determine energy differences. The former appears to be at least as important as the latter in solution and is probably of greater importance in the gas phase.

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