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Dielectric Relaxation and Molecular Structure. IV. Intermolecular Interaction between Dichloroethane and Benzene

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Dielectric relaxation times (τ) and dipole moments (μ) of 1, 2-dichloroethane were measured in non-polar solvents with following results. Solvent: benzene τ 3.69 p. sec, μ 1.80D; *p*-xylene τ 4.53 p. sec, μ 1.63D; carbon tetrachloride τ 2.15 p. sec, μ 1.38D; cyclohexane τ 2.16 p. sec, μ 1.39D; and hexane τ 1.31 p. sec, μ 1.35D. High relaxation times in aromatic solvents indicate that rotation of the polar (*gauche*) isomers is hindered by interaction with solvent molecules. The effect of molecular interaction may be estimated by an increase in the activation free energy of rotation which amounts to 400—540 cal/mol. The *gauche* molecules appear to be more stabilized than the *trans* molecules in the medium of aromatic solvent. Weak interaction, believed to involve hydrogen bonding, occurs in the systems of benzene + 1, 2-dichloroethane and *p*-xylene + 1, 2-dichloroethane.

The dipole moment of 1, 2-dichloroethane in benzene is exceptionally high and even independent of temperature. This makes a sharp contrast to the results obtained in other non-polar solvents and has been considered an anomaly exhibited by the aromatic solvent. Early in the '30s Snoek and van Arkel⁽¹⁾ presumed that this anomaly might be due to the presence of the double bonds in a benzene molecule which was soon refuted by Higasi.⁽²⁾ Müller⁽³⁾ proposed the formation of a loose complex with high polarity in which two chlorine atoms approach to the *cis* position (Fig. 1).

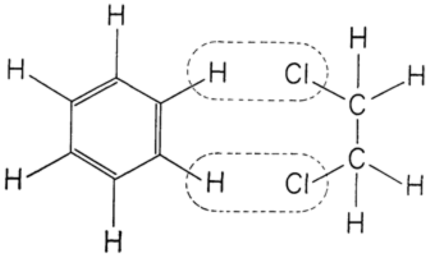

Fig. 1. Müller's complex.

Kubo⁽⁴⁾ confirmed the formation of a 1 : 1 complex, but no information was obtained concerning the geometrical configuration of the complex. Recently, from the viewpoint of donor-acceptor-

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1) J. L. Snoek and A. E. van Arkel, *Z. Physik. Chem.*, **B 18**, 159 (1932).

2) K. Higasi, *Bull. Inst. Phys. Chem. Res. Tokyo*, **13**, 186 (1934).

3) H. Müller, *Physik. Z.*, **34**, 689 (1933).

4) M. Kubo, *Bull. Inst. Phys. Chem. Res. Tokyo*, **13**, 1221 (1934).

complex Neckel and Volk[5] considered that protons of 1, 2-dichloroethane play more important role in the complex formation than the chlorine atoms of the same molecule.

During the development of intensive studies on the rotational isomerism[6] attentions have been directed to the estimation of the numbers of the *gauche* and the *trans* molecules in the medium of benzene. It was discovered that the intensity of the Raman line of 654 cm^{-1} arising from the stretching vibrations of the C–Cl bonds in the *gauche* isomers considerably increases in benzene (compared with hexane) while the corresponding Raman line 754 cm^{-1} due to the *trans* isomers becomes weaker.[7,8] It was made clear through this series of research that the concept of Müller's complex is no longer valid since the *cis* structure of dichloroethane is most unstable and that the formation of a complex between dichloroethane and benzene is not so strong as to cause observable shifts of vibration frequencies of the C–Cl bonds. However, it has never been made clear why the *gauche* structure should be more stabilized in the aromatic solvent than in other aliphatic solvents.[8]

Measurements were made in the present work of the dielectric relaxation times of 1, 2-dichloroethane in a variety of non-polar solvents. Relaxation times are able to provide useful data on the interaction energy between the solvent and the solute.[9] Since a number of physical properties[10,11] of the mixture of 1, 2-dichloroethane and benzene have been well studied, it is hoped that dielectric relaxation would throw a new light on this old problem.

Experimental

Dielectric constants and losses are measured at room temperature by the use of four frequencies, 1 Mc/sec, 9.33 Gc/sec, 24.15 Gc/sec and 48.00 Gc/sec. Description of the apparatus was given in the preceding paper.[9]

The dielectric constant, ε' and loss, ε'', of dilute solutions of polar molecules in a non-polar solvent can be expressed by linear functions of concentration,

$$\varepsilon' = \varepsilon_1' + a'c_2 \text{ and } \varepsilon'' = a''c_2 \tag{1}$$

where c_2 is the gram fraction of the solute, and the subscripts 1 and 2 refer to solvent and solute, respectively.

Table 1. Slopes for dependence of dielectric constant and loss upon concentration (gram fraction) at 20°C

Frequency/sec	a'	a''
1, 2-Dichloroethane - Benzene		
1 Mc	3.602	
9.33 Gc	3.376	0.745
24.15 Gc	2.430	1.335
48.00 Gc	1.650	1.473
1, 2-Dichloroethane - Carbon tetrachloride		
1 Mc	4.000	
9.33 Gc	3.98_2	0.589
24.15 Gc	3.39_0	1.265
48.00 Gc	2.61_0	1.723
1, 2-Dichloroethane - *n*-Hexane		
1 Mc	1.448	
9.33 Gc	1.416	0.118
24.15 Gc	1.310	0.275
48.00 Gc	1.192	0.427
1, 2-Dichloroethane - Cyclohexane		
1 Mc	1.813	
9.33 Gc	1.775	0.184
24.15 Gc	1.646	0.399
48.00 Gc	1.274	0.668
1, 2-Dichloroethane - *p*-Xylene		
1 Mc	2.940	
9.33 Gc	2.630	0.660
24.15 Gc	1.750	1.070
48.00 Gc	1.176	1.008

Coefficients in Eq. (1), a' and a'', which are called "slopes," represent dependence of dielectric constant and loss upon concentration. The value of a slope is obtained usually from several solutions (c_2=0.01—0.05). There are relations[12] for the system with a single relaxation time τ:

$$\frac{a' - a_\infty}{a_0 - a_\infty} = \frac{1}{1 + w^2\tau^2} \tag{2}$$

$$\frac{a''}{a_0 - a_\infty} = \frac{w\tau}{1 + \omega^2\tau^2} \tag{3}$$

where ω is the angular frequency. For the system with multi-relaxation times which obey the Cole-Cole distribution rule

$$\frac{(a' - ia'') - a_\infty}{a_0 - a_\infty} = \frac{1}{1 + (i\omega\tau_0)^{1-\alpha}} \tag{4}$$

in which $i=\sqrt{-1}$, τ_0 is the average relaxation time and α is the Cole-Cole parameter of distribution.[12] By plotting values a' and a'' in a complex plane one can obtain τ_0 and α in the usual manner.

The value a_∞ which is defined by

$$\varepsilon_\infty = \varepsilon_{1\infty} + a_\infty c_2 \tag{5}$$

is not obtainable with accuracy. One may venture to assume that a_∞ is approximately equal to a_D which is given by

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[5] A. Neckel and H. Volk, *Z. Elektrochem.*, **62**, 1104 (1958).

[6] S. Mizushima, "Structure of Molecules and Internal Rotation," Academic Press, New York (1954).

[7] S. Mizushima, Y. Morino and K. Higasi, *Sci. Pap. Inst. Phys. Chem. Res. Tokyo*, **25**, 159 (1934); see, also, I. Watanabe, S. Mizushima and Y. Morino, *ibid.*, **39**, 401 (1942).

[8] A. Wada and Y. Morino, *J. Chem. Phys.*, **22**, 1276 (1954).

[9] K. Chitoku and K. Higasi, This Bulletin, **39**, 2160 (1966).

[10] K. Amaya and R. Fujishiro, *ibid.*, **31**, 90 (1958); R. Fujishiro and K. Kimura, *ibid.*, **32**, 1237 (1959)).

[11] R. J. Fort and W. R. Moore, *Trans. Faraday Soc.*, **62**, 1112 (1966).

[12] K. Higasi, This Bulletin, 39, 2157 (1966).

$$n^2_D = n^2_{1D} + a_D c_2 \tag{6}$$

On the bold supposition there would be no significant contribution from the atomic polarization. In the studies of internal rotation[6,7] it has been usually assumed for 1, 2-dichloroethane that $P_E+P_A=23.9$ cc — if $P_E=21.0$ cc, $P_A/P_E=13.8\%$. In view of this large P_A/P_E ratio it seems to be necessary to make some allowance for P_A in the estimation of a_∞ from a_D.

There is a relation between a small change of P_E and the corresponding change of n^2:

$$\frac{\Delta P_E}{P_E} = \frac{3}{(n^2+2)(n^2-1)}\Delta n^2 \tag{7}$$

Putting $n^2=2.10$ we find the term $(n^2+1)(n^2-1)/3$ to be 1.503. The value of slope a_D is equal to $\bar{n}_2{}^2-n_1{}^2$ in which $\bar{n}_2$ is the value for the solute extrapolated to the concentration $c_2=1$ from the slope in the dilute region. We find $\bar{n}_2$ for 1, 2-dichloroethane in non-polar solvents between 1.95 and 2.12 (Table 2) while $n_2{}^2$ for the pure liquid dichloroethane is 2.10. Inclusion of the atomic polarization would increase these $\bar{n}_2$ values. We do not know exactly how this increase can be determined with accuracy. However, we may take very tentatively the following procedure:[13] the increase $\Delta\bar{n}_2{}^2$ with ΔP_E would parallel to each other and be roughly estimated by Eq. (7). Putting $\Delta P_E/P_E=13.8\%$ we find $\Delta\bar{n}_2{}^2$ to be 0.208 for the solute in benzene and hence, $a_\infty=a_D+0.208=0.059$. In Table 2 are shown the values of a_D and a_∞ thus estimated together with $n_1{}^2$ and $\bar{n}_2{}^2$ values.

Plots of a'' and a' are made for 1, 2-dichloroethane in five non-polar solvents and both a_D and a_∞ estimated by the above procedure are recorded in the same figure (Figs. 2 and 3). The average relaxation time τ_0 and the parameter α are obtained for three cases using three Cole-Cole semi-circles: one circle crosses the abscissa line through point a_D, the second through a_∞ and the third through an intermediate point between a_D—a_∞. The results are collected in Table 3.

TABLE 2. ESTIMATION OF VALUES a_∞ FOR 1, 2-DICHLOROETHANE IN NON-POLAR SOLVENTS

Solvent	$n_1{}^2$	$\bar{n}_2{}^2$	a_D	a_∞
Benzene	2.2500	2.1010	−0.149	0.059
p-Xylene	2.233_2	2.118_2	−0.115	0.097
Carbon tetrachloride	2.1313	1.9783	−0.153	0.026
Cyclohexane	2.0315	2.0440	0.125	0.207
Hexane	1.8992	1.9502	0.051	0.224

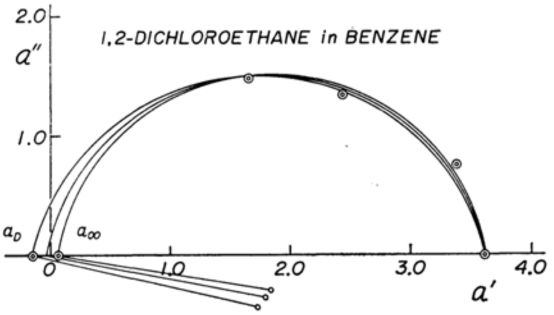

Fig. 2. Arc plot for 1, 2-dichloroethane in benzene at 20°.

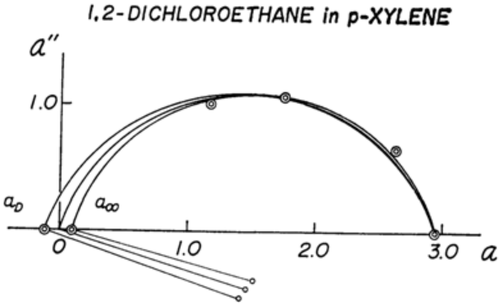

Fig. 3. Arc plot for 1, 2-dichloroethane in *p*-xylene at 20°.

TABLE 3. AVERAGE RELAXATION TIMES τ_0 (p. sec) AND COLE-COLE PARAMETER α OF 1, 2-DICHLOROETHANE

Solvent	a_D		a_∞		Intermediate	
	τ_0	α	τ_0	α	τ_0	α
Benzene	3.61	0.14	3.86	0.11	3.69	0.13
p-Xylene	4.50	0.21	4.86	0.17	4.53	0.19
Carbon tetrachloride	2.14	0.07	2.21	0.06	2.15	0.07
Cyclohexane	2.07	0.12	2.32	0.08	2.16	0.10
Hexane	1.27	0.12	1.44	0.08	1.31	0.10

By the use of static dielectric constant (1 Mc/sec) and the measured density data the solute polarization P_∞ is calculated on Halverstadt and Kumler's approximation.[14] The dipole moment of 1, 2-dichloroethane is calculated by $\mu=0.0128\sqrt{(P_\infty-23.9)T}$

TABLE 4. DIPOLE MOMENTS OF 1, 2-DICHLOROETHANE IN NON-POLAR SOLVENTS (20°C)

Solvent	Present work	Literature
Benzene	1.80	1.68[a], 1.71[b], 1.76[c]
p-Xylene	1.63	(toluene 1.68[e])
Carbon tetrachloride	1.38	1.37[f], 1.38[d]
Cyclohexane	1.39	1.37[f]
Hexane	1.35	1.37[g]

a) A. L. McClellan, Tables of Experimental Dipole Moments, Freeman and Co., San Francisco (1963).
b) K. Higasi, *Bull. Inst. Phys. Chem. Res. Tokyo*, **13**, 186 (1934).
c) A. Neckel und H. Volk, Ref. 5.
d) Calculated from M. Kubo, Ref. 4.
e) Value at 30°C by S. Mizushima *et al.* Ref. 7.
f) A. E. Stearn and C. P. Smyth, *J. Am. Chem. Soc.*, **56**, 1667 (1934).
g) Value at 25°C in Ref. a.

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[13] K. Higasi, K. Chitoku and S. Ogata, *Bull. Inst. Appl. Elec., Hokkaido Univ.*, **18**, 147 (1966).

[14] I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 2988 (1942).

on the assumption of $P_E+P_A=23.9$ cc. The results of the present work are in agreement with literature values (Table 4); some of these values were calculated using different assumptions and methods.⁵⁾

In a preliminary experiment with cyclohexane purified in the usual manner both the dipole moment and the relaxation time were found to be slightly high: 1.48D and 2.51 p.sec, respectively. On examination with an ultraviolet spectrometer the same solvent showed small peaks of benzene. After this discovery special care was taken concerning the purification of solvents especially on cyclohexane.

Purification of Materials. 1, 2-Dichloroethane obtained from Wako (special grade) was purified by the standard method, dried over phosphorus pentoxide and fractionally distilled. Bp 83.5°C, n_D^{20} 1.4440. Benzene, carbon tetrachloride and *n*-hexane were dried and distilled before use. Cyclohexane obtained from Wako (special grade) was purified by use of a chromato-column filled with Wago-gel Q 23 and fractonally distilled over phosphorus pentoxide; no trace of benzene was detected in the UV spectrum. Bp 80.75—8°C, n_D 1.4257.

Discussion

Three different relaxation times, τ_0, are evaluated for 1, 2-dichloroethane in each solvent (Table 3). Since there is no good reason to decide which is the best of all, we shall choose the intermediate one recorded in the last column-that is obtained from a semi-circle crossing the abscissa at a point between a_D and a_∞.

In Table 5 the mean relaxation times thus selected are recorded in the order of increasing viscosity of the solvent. It will be seen that the values observed for two aromatic solvents (τ_0 3.69 p. sec in benzene and τ_0 4.53 p. sec in *p*-xylene) are much higher than that to be expected from viscosities of the media. As the viscosities of these aromatic solvents are intermediate between hexane and the last two solvents, one would expect that the relaxation times would be perhaps of the order of 1.73 p. sec (a mean of τ_0 values of hexane and carbon tetrachloride or cyclohexane).

As a modification of Debye-Stokes' equation for dielectric relaxation, we may assume that[15,16]

$$\tau = A\eta^x \qquad 0 < x \leqslant 1 \qquad (8)$$

where τ is the relaxation time, η is the viscosity of the medium, A is a constant and x is a parameter which is dependent upon the shape of the solvent and other factors. It is evident at inspection at the 4th and 5th columns of Table 5 that the condition $x=1$ is not applicable here. A choice of $x=1/2$, however, gives a more satisfactory result reproducing τ/τ_{HX} values of the last two solvents with fair accuracy. (Compare the 4th with the 6th column.) Using this value of x we can estimate τ for benzene due to the viscosity to be 1.31×1.46 p. sec $=1.91$ p. sec and similarly for *p*-xylene $\tau\simeq 1.89$ p. sec. As a conclusion we may say with good reason that 1, 2-dichloroethane would have a much lower relaxation time in the range of 1.71—1.9 p. sec than the observed values 3.69—4.53 p. sec, if its dipole rotation were hindered only by the viscous resistance of the solvent.

We shall call the hypothetical relaxation time due to the viscosity effect alone τ_1 and the observed relaxation time τ_2. A mean value 1.8 p. sec will be used for τ_1, and τ_2 will be 3.69 p. sec, and 4.53 p. sec, respectively.

From Eyring's equation of rate processes we can write⁹⁾

$$\frac{\tau_2}{\tau_1} = \exp\left(\frac{\Delta F_2^{\ddagger} - \Delta F_1^{\ddagger}}{\boldsymbol{R}T}\right) = \exp\left(\frac{\Delta\Delta F^{\ddagger}}{\boldsymbol{R}T}\right) \qquad (9)$$

in which $\boldsymbol{R}$ is the gas constant, T is the absolute temperature and $\Delta F_1^{\ddagger}$ and $\Delta F_2^{\ddagger}$ are the free energies of activation for dipole rotation under different conditions, 1 and 2. The excess activation energy, that is, the difference in two activation free energies, $\Delta\Delta F^{\ddagger}$, is estimated as 419 cal/mole and 540 cal/mole, respectively.

In Table 6 the dipole moments of 1, 2-dichloroethane are recorded in the order of increasing dielectric constant of the solvent employed for measurements. The molecule of dichloroethane is provided with a high value of dipole moment in aromatic solvent, especially in benzene. This fact is currently believed to indicate that the *gauche* form with strong polarity becomes stabilized in benzene from some unknown cause.⁸,¹⁰⁾ In fact,

TABLE 5. RELAXATION TIME OF 1, 2-DICHLOROETHANE AND VISCOSITY OF SOLVENT

Solvent	τ_0 (p. sec)	η (cp)	τ/τ_{HX}	η/η_{HX}	$(\eta/\eta_{\mathrm{HX}})^{1/2}$
Hexane	1.31	0.308	1.00	1.00	1.00
p-Xylene	4.53	0.638	3.46	2.07	1.44
Benzene	3.69	0.652	2.82	2.12	1.46
Carbon tetrachloride	2.15	0.965	1.64	3.13	1.77
Cyclohexane	2.16	0.965	1.65	3.13	1.77

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15) K. Chitoku and K. Higasi, This Bulletin **36**, 1064 (1963).

16) K. Higasi, "Dielectric Relaxation and Molecular Structure," (R. I. A. E., Hokkaido University), 1961.

TABLE 6. ENERGY DIFFERENCE BETWEEN GAUCHE AND TRANS ROTATIONAL ISOMERS

Solvent	ε	μ (D)	$\Delta\mu$ (D)	x_g	ΔE cal/mol
Hexane	1.901	1.35	—	0.276	940
Cyclohexane	2.026	1.39	0.04	0.292	895
p-Xylene	2.233	1.63	0.28	0.402	606
Carbon tetrachloride	2.237	1.38	0.03	0.289	902
Benzene	2.284	1.80	0.45	0.491	398

the intensity of Raman lines corresponding to the *gauche* form increases in solution of benzene.[7,8]

If the solute molecules are either of the *gauche* or of the *trans* rotational isomers and in no other configuration, the observed dipole moment will be caluclated as an average of moments of *trans* and *gauche* forms.[6]

$$\mu^2 = x_t\mu_t^2 + x_g\mu_g^2 \tag{10}$$

where x_t and μ_t are the mole fraction and dipole moment of the *trans* molecules and x_g and μ_g are the corresponding ones in the *gauche* molecules.

Further, there is a relation for mixtures in equilibrium

$$\frac{x_g}{x_t} = w\exp\left(\frac{\Delta E}{\boldsymbol{RT}}\right) \tag{11}$$

where ΔE is the energy difference between those of the *gauche* and the *trans* forms. Using $\mu_t=0$ and $\mu_g=2.57$ D we can calculate x_g from the observed values μ (see the values x_g in the 5th column of Table 6). Neckel and Volk[5] obtained $x_g=0.476$ in benzene and $x_g=0.289$ in cyclohexane from a similar analysis on their dipole moment data—the results are in agreement with x_g values in the present work.

Since the values of w at different temperatures have been calculated exactly by use of the spectroscopic data, we shall use $w=1.91$ at 20°C from Mizushima's calculation.[6] The energy difference ΔE calculated from Eq. (11) is shown in the last column of Table 6. ΔE 398 cal/mol for benzene and ΔE 895 cal/mol for cyclohexane are also near Neckel and Volk's values (ΔE 430 cal/mol for benzene and ΔE 897 cal/mol for cyclohexane).

The electrostatic stabilization energy E_r defined by[17]

$$E_r = \frac{2(\varepsilon-1)}{2\varepsilon+1}\frac{\mu^2}{a^3} \tag{12}$$

will predict that ΔE will decrease with increasing dielectric constant of the medium, since the *gauche* molecule has a large moment, 2.57 D, while the *trans* molecule is non-polar, the radius a being the same for the two isomers. Since the non-polar solvents have similar dielectric constants in the narrow range of $\varepsilon=1.9$—2.3, one would expect that all the ΔE values would not be essentially different—actually this prediction is fulfilled in Table 6 excepting those for aromatic solvents. The value ΔE in benzene is found to be only half of ΔE's in any of the non-aromatic solvents. If one takes $\Delta E=900$ cal/mol (a mean value for carbon tetrachloride and cyclohexane) to be a probable value for benzene due to the electrostatic stabilization alone, the difference between the probable and the observed values would be an extra energy of stabilization. This extra energy of about 500 cal/mol for the case of 1, 2-dichloroethane dissolved in benzene is of the same order of magnitude with the excess activation energy $\Delta\Delta F^{\ne}$ 400 cal/mol obtained previously.

It is interesting to note that the extra energy in *p*-xylene is only 300 cal/mol while $\Delta\Delta F^{\ne}$ estimated is even larger in this solvent than in benzene. Recently the dipole moments of 1, 2-dichloroethane have been measured in toluene and also in mixtures of naphthalene and carbon tetrachloride.[18] The apparent moments of dichloroethane in these solvents are always larger than in the aliphatic solvent which seems to give further evidence that aromatic molecules interact with dichloroethane molecules; however, it is not certain whether the state of interaction can always be described on the basis of the *trans* and the *gauche* mixtures.

According to the hydrogen-bonding mechanism[5,19] the aromatic molecules behave as donor molecules and 1, 2-dichloroethane as acceptor molecules. In support of this mechanism Neckel and Volk[5] detected shifts in the C–H stretching frequencies of dichloroethane upon the addition of benzene—this was confirmed also in the present work. As the strengths of bases are of the order of *p*-xylene > toluene > benzene, the higher τ value in *p*-xylene than in benzene may be attributable to the difference in attractive forces acting between the acceptor and the donor molecules.

Similar shift of the C–H frequencies[19] and related increase in the relaxation time[20] are observed for the system of chloroform with benzene which has been explained as due to the formation of hydrogen bonds. However, there is a question whether and why the *gauche* molecules are more stabilized in complexes than the *trans* molecules.

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[17] S. Mizushima, *loc. cit.*, p. 42.

[18] K. Uchiyama and K. Higasi, to be published.

[19] M. Tamres, *J. Am. Chem. Soc.*, **74**, 3375 (1952).

[20] A. A. Antony and C. P. Smyth, *ibid.*, **86**, 152 (1964).

Preliminary infra-red studies were made in this laboratory in a hope that the shifts of vibration lines on benzene addition may be discriminated by *gauche* and *trans* isomers.[21] No evidence has been found so far to support that the hydrogen bond formation is only or mainly through the *gauche* isomers. The observed shift in 2957 cm^{-1} is related to both isomers.

If a complex is formed between a polar solute and a non-polar solvent molecules, the complex will be further stabilized by a gain of electrostatic energy through forces acting between the dipole and induced dipoles. This stabilization energy E_s will be estimated by

$$E_s = \frac{1}{2}\frac{\mu^2}{r^6}(3\cos^2\theta - 1)^2\alpha \tag{13}$$

where μ is the dipole moment of the solute, α is the polarizability of the solvent, r is the distance between the point dipole and the point of polarization in the solvent and θ is the angle between r and μ. If one assumes $\mu=2.57$ D or zero and uses $r=3.75$ Å, $\theta=0$ and $\alpha=b_3=7.33\cdot10^{-24}$ cc,[22] E_s will be estimated as 500 cal/mol or zero. The above estimation of E_s values illustrates one possibility[*1] that the *gauche* isomer becomes more stabilized in the complex by the necessary amount to account for large x_g values (Table 5) than the *trans* isomer. However, the same mechanism will result in a high induced moment 0.88 D in benzene[23] and, hence, the complex will have a dipole moment different from the *gauche* isomer. Eq. (10) should be amended accordingly.

The validity of Eq. (10) rests on the premise that no appreciable charge redistribution takes place on the complex formation of the *gauche* molecule with the aromatic solvent. Indeed, the polarity of the 1 : 1 complex between benzene and 1, 2-dichloroethane is estimated from Kubo's measurements[4] to be identical with the *gauche* moment. This coincidence is encouraging and it may also suggest that the bonding of the solute with the solvent is made probably through protons of the C–H bonds, because redistribution of charge would be less apparent than in the alternative case when chlorine atoms of the C–Cl bonds are concerned with the complex formation.[*2]

If there are two polar species of rigid molecular structure, the dielectric system of the mixture will be provided with two relaxation times. The Cole-Cole parameter for the system of dichloroethane and benzene amounts only to 0.11—0.14 in contrast to 0.07—0.12 of other systems, while the system with *p*-xylene has a somewhat appreciable α value between 0.17 and 0.21. However, no serious attempt was made in the present work to separate the observed absorption into two different absorption peaks. The actual situation may possibly be described in the first approximation by a picture of rotating *gauche* molecules in the viscous medium with additional hindrance due to loose-formation of complexes with the solvent molecules.

The writers wish to express their sincere thanks to Professors M. Kimura and H. Baba for helpful discussions and also to Mr. K. Uchiyama for measurements of dipole moments.

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21) T. Shimanouchi, "Bunshi-nai-Kaiten," Iwanami Koza VI. C. (1956).

22) C. G. Le Fevre and R. J. W. Le Fevre, *Rev. Pure Appl. Chem.*, **5**, 261 (1955).

[*1] An alternative possibility is that three protons of the *gauche* isomer accept electrons from the donor molecule while only two protons can do so in the case of the *trans* isomer. This explanation is based on the assumption that edges of the aromatic donor are the places of making hydrogen bonds with the acceptor molecule. (*Cf.* Z. Yoshida *et al.*, Abstracts of papers read at the Symposium on Molecular Structure, Osaka, Oct. 14 (1966); *J. Am. Chem. Soc.*, **87**, 1467 (1965)).

[*2] Even the alternative case may not produce drastic redistribution of charge.[24] For example, hexafluorobenzene forms a 1 : 1 complex with aromatic solvent; these complexes have non-zero but very small dipole moments of 0.3—0.4D.[25]

23) R. P. Young, A. Hott and S. Walker, *Tetrahedron*, **20**, 2351 (1964).

24) W. A. Duncan and F. L. Swinton, *Trans. Faraday Soc.*, **62**, 1082 (1966).

25) W. A. Duncan, J. P. Sheridan and F. L. Swinton, *ibid.*, **62**, 1090 (1966).