ELSEVIER

Spectrochimica Acta Part A 51 (1995) 1919-1932

SPECTROCHIMICA
ACTA
PART A

# Thermodynamic parameters of conformational equilibrium in 1,2-dichloroethane: influence of medium, benzene and compensation effects

A.A. Stolov [a,*], A.B. Remizov [b]

[a] *Department of Chemistry, Kazan State University, Lenin st. 18, Kazan 420008, Russia*
[b] *Kazan State Technological University, Karl Marx st. 68, Kazan 420015, Russia*

Received 20 September 1994; accepted 13 January 1995

---

## Abstract

The conformational equilibrium of 1,2-dichloroethane (DCE) in 19 different media (vapour phase, liquid, solutions in *n*-hexane, *n*-heptane, carbon tetrachloride, benzene, toluene, ethyl benzene (EB), carbon disulphide, diethyl ether, bromoform, chloroform, dichloromethane, pyridine, acetone, methanol-$d_3$, acetonitrile, glassy polystyrene (PS) matrix and 1:1 mixture of PS and EB) has been studied by IR absorption spectra. The enthalpy differences ($\Delta H_0$) between trans (t) and gauche (g) conformers were determined from the dependencies of $\ln(I_t/I_g)$ upon $T^{-1}$, where $I_t$ and $I_g$ are the integrated intensities of the bands belonging to trans and gauche conformers, respectively. The values of $RT\ln(I_t/I_g)$ and $(R\ln(I_t/I_g)+\Delta H_0/T)$ obtained at 296 K were used as measures of the free enthalpy ($\Delta G_0$) and entropy ($\Delta S_0$) differences of the conformers respectively, when considering their changes with solvent. Good correlations between $\Delta G_0$, $\Delta H_0$ and the function of the dielectric permittivity of the medium $(0.5-(\varepsilon-1)/(2\varepsilon+1))^{1/2}$ were observed for all solvents except methanol-$d_3$ (effect of self-association) and the aromatic solvents (benzene effect). Notwithstanding the similar structures and dielectric permittivities of EB and PS, the former medium behaves as a significantly more polar solvent. The analysis of the $\Delta H_0$ values obtained for DCE in PS and EB enabled confirmation of Eliel and Hofer's concept of the origin of the benzene effect; the effect is assigned to the relatively high anisotropy of the polarizability tensor of aromatic compounds. As a consequence, the electrostatic and dispersion interactions of a solute dipole with a neighbouring aromatic ring is crucial to their mutual orientation. Significantly non-linear (close to quadratic) dependencies $\ln(I_t/I_g)=f(T^{-1})$ were observed for DCE in toluene and EB in the range 180–370 K; the $\Delta H_0$ value increased from $-170$ cal mol$^{-1}$ at 358 K to 820 cal mol$^{-1}$ at 190 K for the toluene solution. These results are considered within the framework of the manifestations of the benzene effect. Significant changes in $\Delta S_0$ with the media have been found; they cover more than 2.0 cal mol$^{-1}$ K$^{-1}$ when going from the vapour phase to polar solvents. Satisfactory correlation between $\Delta H_0$ and $\Delta S_0$ (compensation effect) has been observed, the points corresponding to all the media, including methanol-$d_4$ and the aromatic solvents, being scattered along a straight line. The tangent of the slope $(\Delta\Delta S_0/\Delta\Delta H_0)=(1.4\pm 0.4)\times 10^{-3}$ K$^{-1}$ is close to those determined earlier for 1,2-bromofluoroethane, *trans*-1,2-dichlorocyclohexane and *o*-iodophenol.

---

[*] Corresponding author.

*SSDI* 0584-8539(95)01411-X

## 1. Introduction

The influence of medium on the thermodynamics parameters of conformational equilibria is well known. This problem is significant because, on one hand, the solvent (matrix) may serve as an instrument for monitoring physico-chemical processes with the participation of conformationally inhomogeneous compounds; on the other hand, the shift of the conformational equilibrium provides a test for demonstrating the applicability of various theoretical approaches to the description of intermolecular interactions [1–5]. Detailed reviews on this theme are given in [1,4,6,7]. All theoretical and semiempirical concepts are checked by comparison of calculations with experimental data, the latter being, as a rule, obtained for a small number of conformationally inhomogeneous compounds which serve as models. 1,2-Dichloroethane (DCE) is often used as the model in theoretical [1,3,6,8] and experimental [9] investigations. Therefore, the thermodynamic parameters of conformational equilibrium in DCE (enthalpy ($\Delta H_0$), free enthalpy ($\Delta G_0$) and entropy ($\Delta S_0$) differences between trans (t) and gauche (g) conformers) should be documented. However, an analysis of the published data shows a limited number of such values.

The vapour phase of DCE is the most extensively studied. Electron diffraction studies [10], a study of the temperature dependence of the dielectric constant [11], investigations of the temperature dependence of IR band intensities [11–14], photoelectron spectroscopy [15] and a study based on the calculations of the electrooptical parameters of DCE [16] have given $\Delta H_0$ values within the range $(1100 \pm 100)\,\mathrm{cal\,mol^{-1}}$. The enthalpy difference of conformers in the pure liquid was measured by investigating IR and Raman band intensities at different temperatures [13,14,17]. The deviation of the obtained value ($(0 \pm 50)\,\mathrm{cal\,mol^{-1}}$) from that for the vapour phase has been attributed to the strong effect of the medium [13,16,17]. There are also $\Delta H_0$ values for the solutions of DCE in *n*-hexane, *n*-heptane, carbon tetrachloride, carbon disulphide and methanol, obtained by investigating IR spectra and/or measuring the dielectric constant. These data were reviewed by Wada [17]. It should be noted that peak band intensities instead of integrated ones were used in all cited IR and Raman investigations of the pure liquid and solutions. The obtained values will be considered below.

The free enthalpy difference of the conformers ($\Delta G_0$) may be characterized by the ratio of the integrated intensities measured for the IR bands belonging to different conformers ($I_t/I_g$). In [18,19] the $\Delta G_0$ values were estimated by the corresponding peak intensity ratios, measured at room temperature for DCE in vapour and liquid states and in 13 different solvents. No attempts were made to estimate the entropy difference between trans and gauche conformers of DCE in the liquid state and in the solutions.

The aim of this work is to study the shifts of the enthalpy and entropy differences of the DCE conformers caused by different surroundings, using the same approach for 19 media. This approach is based on the measurements of the integrated IR band intensities of the conformers. There are five media for which the $\Delta H_0$ values have been determined via two different band pairs. We attempt to examine the deviations of the dependence $\ln(I_t/I_g) = f(T^{-1})$ from linearity caused by the temperature changes of the $\Delta H_0$ values. In addition to the vapour phase and liquid solvents, a glassy polystyrene (PS) matrix was used as one of the media. Particular attention has been given to the correlation between $\Delta S_0$ and $\Delta H_0$ values (compensation effect [20,21]). The conformational behaviour of DCE in aromatic media (including the PS matrix) gives an insight into the nature of the benzene effect in conformational analysis [1,6,17].

## 2. Experimental

DCE and non-deuterated solvents, listed in Table 1, were purified according to [22]. Deuterated methanol-$d_4$ was produced by IZOTOP (St. Petersburg) and used without further purification. Atactic PS, emulsion polymerized, viscosity-average molecular

Table 1
Spectroscopic and thermodynamic parameters of 1,2-dichloroethane in various media

| No. | Medium | $\varepsilon$ | Band pair [a] | $\ln(I_t/I_g)$ | $-RT\ln(I_t/I_g)$ [b] /cal mol$^{-1}$ | Temperature range/K | $\Delta H_0$ [c] /cal mol$^{-1}$ | $\Delta H_0$ [d] /cal mol$^{-1}$ | $R\ln(I_t/I_g)+(\Delta H_0/T)$ [b] /cal mol$^{-1}$ K$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | Vapour | 1.00 | *a* | 1.30 ± 0.15 | −770 ± 90 | 296 | – | −1100 ± 100 | −1.13 |
| 2 | *n*-Hexane | 1.89 | *a* | 1.00 ± 0.13 | −590 ± 75 | 187–200 | −730 ± 90 | −920 | −0.46 |
| 3 | *n*-Heptane | 1.92 | *a* | 0.96 ± 0.05 | −560 ± 25 | 195–296 | −710 ± 35 | −980 | −0.49 |
| 4 | $CCl_4$ | 2.23 | *a* | 0.87 ± 0.06 | −510 ± 35 | 256–343 | −760 ± 90 | −510 | −0.76 |
| | | | *b* | 0.56 ± 0.05 | | 256–343 | −720 ± 75 | | |
| 5 | Benzene | 2.28 | *a* | 0.13 ± 0.08 | −80 ± 45 | 280–337 | 90 ± 140 | | 0.56 |
| 6 | Toluene | 2.38 | *a* | 0.28 ± 0.05 | −160 ± 25 | 190–350 | −65 | | 0.33 |
| 7 | EB [e] | 2.41 | *a* | 0.30 ± 0.05 | −180 ± 25 | 180–368 | 280 | | 1.55 |
| 8 | EB + PS [f] | 2.46 | *a* | 0.23 ± 0.05 | −130 ± 25 | 180–296 | 440 ± 60 | | 1.94 |
| 9 | PS | 2.50 | *a* | 0.16 ± 0.05 | −90 ± 30 | 200–296 | −20 ± 40 | | 0.31 |
| 10 | $CS_2$ | 2.64 | *a* | 0.68 ± 0.08 | −400 ± 45 | 173–298 | −370 ± 50 | −360 | 0.11 |
| | | | *c* | 2.06 ± 0.10 [g] | | 296 | | | |
| 11 | DEE [h] | 4.34 | *c* | 1.68 ± 0.11 | −240 ± 90 [i] | 184–296 | 210 ± 90 | | 1.51 [i] |
| 12 | $CHBr_3$ | 4.39 | *a* | 0.51 ± 0.03 | −300 ± 20 | 282–371 | −150 ± 55 | | 0.70 |
| | | | *b* | 0.10 ± 0.02 | | 282–371 | −40 ± 45 | | |
| 13 | $CHCl_3$ | 4.70 | *b* | −0.07 ± 0.07 | −150 ± 80 [i] | 212–323 | −40 ± 65 | | 0.37 [i] |
| 14 | $CH_2Cl_2$ | 8.9 | *b* | −0.41 ± 0.07 | 50 ± 80 [i] | 184–296 | 130 ± 35 | | 0.27 [i] |
| 15 | Neat | 10.4 | *a* | −0.09 ± 0.04 | 50 ± 20 | 240–351 | 240 ± 35 | 0 ± 50 | 0.59 |
| | | | *b* | −0.32 ± 0.05 | | 240–351 | 220 ± 45 | | |
| 16 | Pyridine | 12.3 | *a* | −0.25 ± 0.07 | 150 ± 40 | 237–298 | 370 ± 80 | | 0.76 |
| 17 | Acetone | 20.7 | *c* | 0.76 ± 0.08 | 300 ± 70 [i] | 184–296 | 400 ± 70 | | 0.33 [i] |
| 18 | $CD_3OD$ | 32.4 | *a* | −0.26 ± 0.07 | 150 ± 40 | 184–292 | 55 ± 40 | 260 | −0.33 |
| | | | *b* | −0.62 ± 0.03 | | 184–292 | 80 ± 60 | | |
| 19 | $CH_3CN$ | 36.2 | *a* | −0.44 ± 0.15 | 260 ± 90 | 235–323 | | | 0.72 |
| | | | *c* | 0.74 ± 0.13 | | 235–323 | 470 ± 120 | | |

[a] The analytical band pairs are: (*a*) 1236, 1286 cm$^{-1}$; (*b*) 1453, 1435 cm$^{-1}$; (*c*) 710, 655 cm$^{-1}$. [b] $T = 296$ K. Only the magnitudes for the *a* band pair are shown. [c] This work. [d] Literature data [14,17] obtained from IR and Raman spectra (vapour, $CCl_4$, $CS_2$, pure liquid and methanol) and dielectric constant measurements (vapour, *n*-hexane and *n*-heptane). [e] Ethyl benzene. [f] Mixture (1:1) of ethyl benzene and polystyrene. [g] The temperature dependence has not been measured for this band pair. [h] Diethyl ether. [i] Values calculated for the *a*-band pair (see text).

weight $M_\eta = 1.1 \times 10^5$, was used as one of the media. The technique of preparation of the polymer solution of DCE is described in [23]. The volume fraction of DCE in all solutions was 0.025.

IR absorption spectra were measured with a SPECORD M-80 spectrometer combined with a computer. Spectra were recorded at the widths of slit function of 1.5 and 1.0 $cm^{-1}$, depending on the band widths of the DCE spectra. No slit correction was done since the minimal band widths under investigation exceeded 3.0 $cm^{-1}$ and only integrated intensities of the bands were determined.

The spectra of gas-phase DCE at room temperature were obtained using a standard cuvette with path length 10 cm. Low-temperature experiments were carried out with a single beam cryostat cooled by liquid nitrogen. The temperature was measured with a platinum resistor with an accuracy of ±1 K.

All the experiments were carried out in two stages. First, IR spectra of solutions were recorded at different temperatures. Then the same measurements were repeated for the pure solvent (matrix). Subtraction of the spectra was performed with the computer.

## 3. Results and discussion

### 3.1. *IR spectra of DCE and band resolution procedure*

Vibrational spectra of DCE were studied in detail in [16,24,25]. The following band pairs were found to be the most convenient, according to the transparency ranges of the solvents: 1236 (t), 1286 $cm^{-1}$ (g); 1453 (t), 1435 $cm^{-1}$ (g); 710 (t), 655 $cm^{-1}$ (g). We denote these three band pairs as *a*, *b* and *c* respectively.

IR spectra in the ranges 1370–1170, 1500–1360 and 740–620 $cm^{-1}$ were fitted by the sum of the components with the form of the multiplication of Lorentzian and Gaussian functions. The "Lorentzian" and "Gaussian" widths, band centres and maximal optical densities were the adjustable parameters. The experimental vibrational spectra can be satisfactorily described by the sum of such functions, as confirmed in [26,27]. The Davidon–Fletcher–Powell search algorithm [28] was used to minimize the residual sum-of-squares.

The IR spectra in the range of the *a*-band pair for DCE in pyridine and carbon disulphide are given in Fig. 1. For the majority of solvents this spectral range can be satisfactorily reproduced by five individual components. In addition to the 1236 (t) and 1286 $cm^{-1}$ (g) bands, the bands at 1330, 1315 and 1305 $cm^{-1}$ fall in this region. The band at 1315 $cm^{-1}$ is a fundamental of the gauche conformer [24], and the 1335 and 1305 $cm^{-1}$ bands are apparently the combination of 655 and 675 $cm^{-1}$ (g), and the overtone of 655 $cm^{-1}$ (g), respectively. At low temperatures the IR spectra reveal one more band near 1261 $cm^{-1}$ (Fig. 1(b)). We attribute this band to the combination of 1124 and 134 $cm^{-1}$ fundamentals of the trans conformer.

The IR spectral range 740–620 $cm^{-1}$ is satisfactorily reproduced by four components (Fig. 2). In addition to 710 (t) and 655 $cm^{-1}$ (g), the doublet at 684 and 675 $cm^{-1}$ falls in this range. One of the components belongs to the fundamental of the gauche conformer [24] and the other is probably the combination of the gauche fundamentals 412 and 272 $cm^{-1}$. A decrease in temperature causes sufficient intensity redistribution within this doublet, indicating strong interaction between its components. This shows that the peak intensity of this doublet is an unreliable measure of the content of the gauche conformer. Note that this doublet is used for this purpose in [18,19].

Fig. 3 shows the 1500–1380 $cm^{-1}$ range for pure DCE. Two components satisfactorily reproduce this range at temperatures lower than 270 K. At higher temperatures the simulated spectra do not fit the experimental ones so perfectly; they lack intensity in the spectral ranges near 1470, 1440 and 1415 $cm^{-1}$. This may be due to the manifestation of combination bands 770 + 710 (t), 1031 + 412 (g), and 2 × 710 $cm^{-1}$ (g). However, the deviations detected in the experiment may be partly explained by the presence of the "hot" bands on the low-frequency sides of the 1453 (t) and 1435 $\mathrm{cm}^{-1}$ (g) fundamentals as well. Nevertheless, any additional components which may appear at higher temperatures have been neglected, and the spectra have been fitted by only two components, independently of $T$. The closeness of the $\Delta H_0$ values obtained via the different band pairs (see below) confirms such an approximation.

### 3.2. Calculation of thermodynamic values

Accoridng to van't Hoff's equation and Beer's law, one may write:

$$\ln(I_t/I_g) = \ln(\alpha_t/\alpha_g) - \Delta H_0/RT + \Delta S_0/R \tag{1}$$

where $\alpha_t$ and $\alpha_g$ are the integral absorption coefficients of the analytical bands. The slope of the plot of $\ln(I_t/I_g)$ versus $T^{-1}$ enables one to determine $\Delta H_0$.

The function $\ln(I_t/I_g) = f(T^{-1})$ should not be linear if $\Delta H_0$ depends on the temperature. The possibility of such dependence was proposed by Abraham and

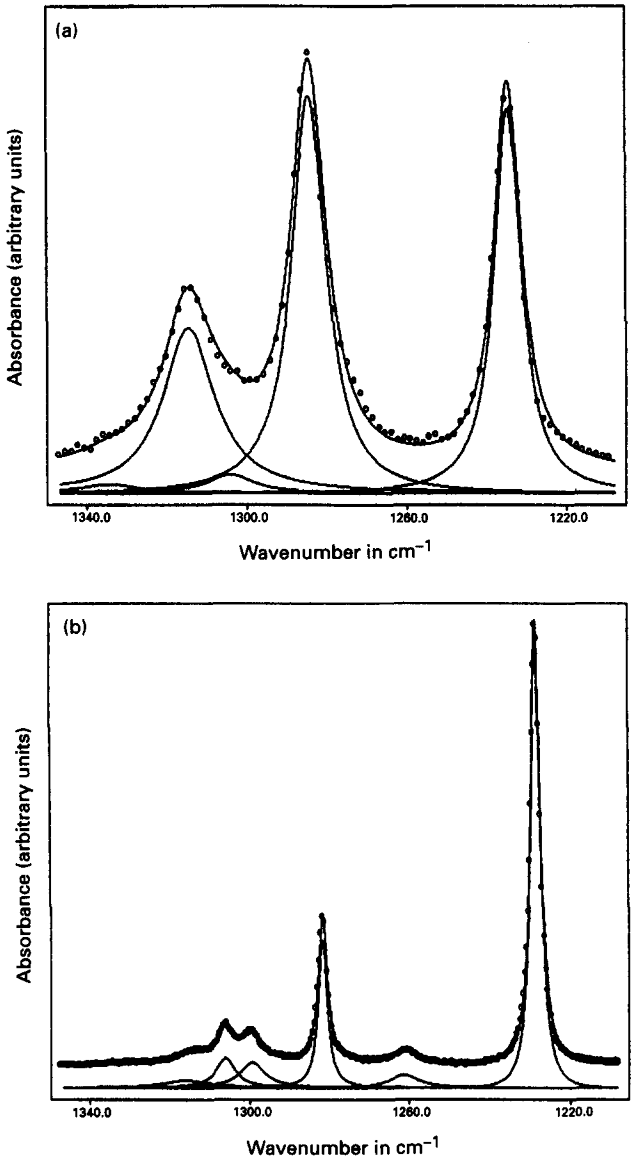

Fig. 1. IR spectra of 1,2-dichloroethane (2.5 vol%) in (a) pyridine at 298 K and (b) carbon disulphide at 173 K: (○) observed; (——) calculated.

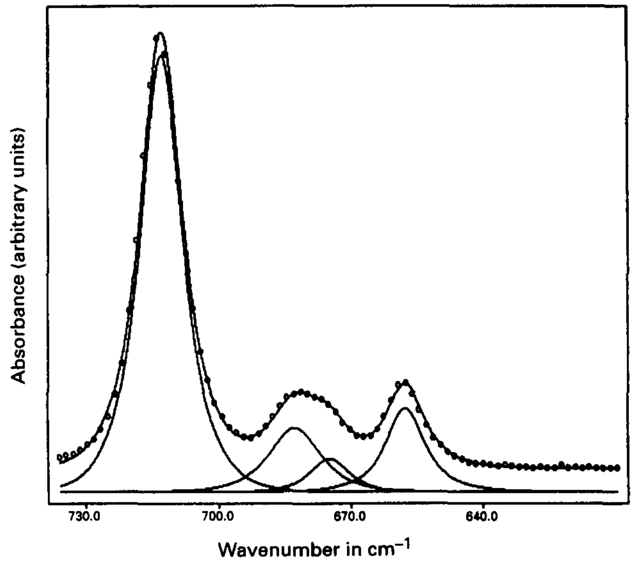

Fig. 2. IR spectra of 1,2-dichloroethane (2.5 vol%) in diethyl ether at 295 K: (○) observed; (——) calculated.

Bretschneider [1] on the basis of the reaction field model. It was also assumed that the "true" $\Delta H_0$ values ($\Delta H_0^{\text{true}}$) would not be equal to those observed experimentally ($\Delta H_0^{\text{obs}}$) if such a dependence exists [1]. However, as we have shown recently [20,21,29], in both cases $\Delta H_0^{\text{true}} = \Delta H_0^{\text{obs}}$. If $\Delta H_0^{\text{true}}$ depends on $T$, then $\Delta H_0^{\text{obs}}$ is equal to the $\Delta H_0^{\text{true}}$ value corresponding to the average temperature over the range under investigation.

We have attempted to find the deviations of the dependencies $\ln(I_t/I_g) = f(T^{-1})$ from linearity. Usually, the errors in the IR intensity measurements hide such deviations. Therefore, the dependence of $\Delta H_0$ on $T$ could be seen either when this dependence is very strong or when the accuracy of the intensity measurements is sufficient. In either case, a relatively large temperature range must be considered. On this basis we tried to find the dependence of $\Delta H_0$ on $T$ for neat DCE. On one hand, the intensity/noise ratio is increased by using the pure liquid instead of the dilute solution. On the other hand, it is for pure DCE that such dependence should be strongest [1]: the value of $-T(\mathrm{d}\Delta H_0/\mathrm{d}T)$ calculated according to the reaction field model falls in the range 440–530 cal mol$^{-1}$. IR

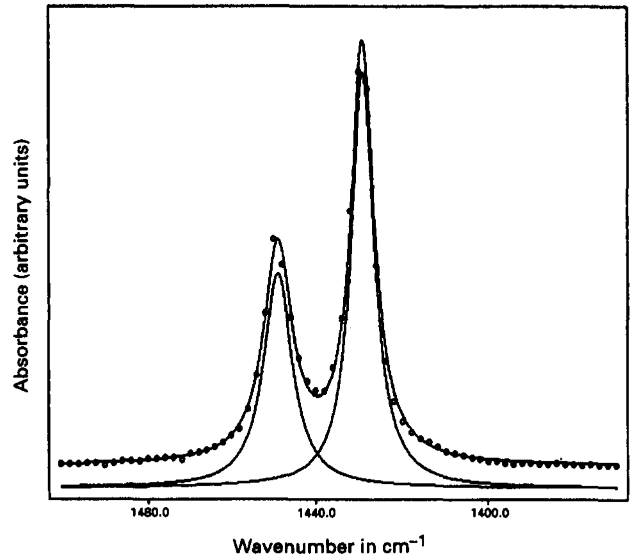

Fig. 3. IR spectra of neat 1,2-dichloroethane at 240 K: (○) observed; (——) calculated.

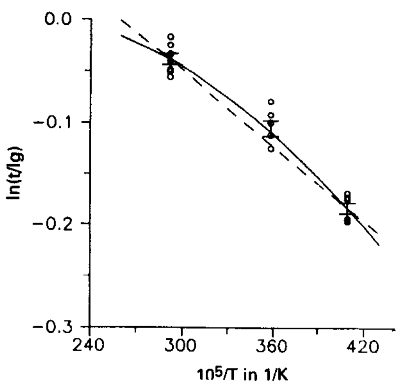

Fig. 4. The dependence of $\ln(I_t/I_g)$ upon $T^{-1}$ for the bands 1236 (t) and 1286 cm$^{-1}$ (g) of neat 1,2-dichloroethane. The experimental points (circles) are supplemented with error bars, reflecting the standard error of the mean. The dashed line and the continuous curve are explained in the text.

spectra in the 1370–1170 cm$^{-1}$ region were measured at three temperatures: 244, 279 and 342 K, six times at each $T$. The experimental $\ln(I_t/I_g)$ ratios for the $a$-band pair versus $T^{-1}$ are given in Fig. 4. The error bars correspond to the standard errors of the mean. We drew a straight line (dashed) and parabola (continuous curve) through the centres of the left and the right bars. The quadratic function was calculated assuming the linear dependence of $\Delta H_0$ on $T$ with the tangent corresponding to $-T(\mathrm{d}\Delta H_0/\mathrm{d}T) = 485$ cal mol$^{-1}$ at $T = 279$ K. It can be seen that there is no large difference between the descriptions of the experimental points by the straight line and the parabola, and more thorough measurements are needed to confirm the non-linearity (or linearity) of the plot. However, it seems reasonable to note that the quadratic function describes the experiment more satisfactorily than the linear one (Fig. 4). Thus, the results appeared to be close to those predicted by Abraham and Bretschneider [1].

The reaction field model [1] predicts the lack of dependence of $\Delta H_0$ on temperature for non-polar aromatic solutions. However, sufficiently non-linear dependencies of $\ln(I_t/I_g)$ upon $T^{-1}$ were found for the solutions of DCE in toluene and ethyl benzene (Fig. 5). Relatively wide temperature ranges, covering approximately 200 K, can be used to investigate these two solutions. Assuming again the linear dependence of $\Delta H_0$ on $T$, we fitted the experimental points using the quadratic functions

$$\ln(I_t/I_g) = -0.100(X - 3.21)^2 + 0.278 \qquad (2)$$

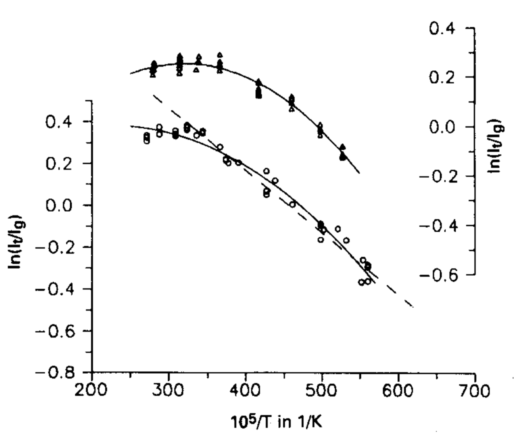

Fig. 5. The dependence of $\ln(I_t/I_g)$ upon $T^{-1}$ for the bands 1236 (t) and 1286 cm$^{-1}$ (g) of 1,2-dichloroethane dissolved in ethyl benzene (○, left Y-axis) and in toluene (△, right Y-axis). The continuous curves correspond to quadratic functions (2) and (3), the dahsed line describes the data for ethyl benzene solution in the 200–296 K range (see text).

for toluene and

$$\ln(I_t/I_g) = -0.064(X - 2.28)^2 + 0.382 \tag{3}$$

for ethyl benzene, where $X = 10^3 \times T^{-1}$. According to Eq. (2), the enthalpy difference of DCE in toluene changes sign at 312 K, the trans conformer being more stable at $T > 312$ K, and the gauche one at $T < 312$ K. It is interesting to compare $\Delta H_0$ values at the ends of the temperature range under investigation: $\Delta H_0(\mathrm{t-g}) = 820$ cal mol$^{-1}$ (190 K) and $-170$ cal mol$^{-1}$ (358 K). The $\Delta H_0$ values listed in the table correspond to 296 K. These results will be discussed below in more detail, in conjunction with those obtained for the other aromatic media.

Narrower temperature intervals and/or larger experimental errors for DCE in all the media, excluding pure liquid, toluene, and ethyl benzene, made it much more difficult to find the dependence of $\Delta H_0$ on $T$. Within the limits of experimental error, the plots of $\ln(I_t/I_g)$ versus $f(T^{-1})$ were found to be linear in the temperature ranges under investigation. Hence, listed $\Delta H_0$ values correspond to the average temperatures over the given ranges. The enthalpy differences were obtained for pure DCE and its carbon tetrachloride bromoform and methanol-$d_4$ solutions using two band pairs. The agreement between the corresponding magnitudes is satisfactory, and the averaged $\Delta H_0$ values are used for these four systems below.

The published $\Delta H_0$ values [14,17] are in rather poor agreement with ours (see Table 1), with the exception of the value for carbon disulphide. Possible errors in the data obtained by the dielectric constant measurements (for DCE in *n*-hexane and *n*-heptane) may be caused by the inaccurate estimation of the dipole moments of separate conformers, necessary for evaluation of $\Delta H_0$. The discrepancies between our data and those obtained by IR and Raman spectra (for DCE in carbon tetrachloride, methanol and the pure liquid) are probably due to the fact that peak band intensities were used in IR and Raman measurements [14,17] instead of integrated ones. As an example we calculated the enthalpy difference of the conformers for the pure liquid using the peak intensities of the bands 1453 and 1435 cm$^{-1}$. The result $\Delta H_0 = (-10 \pm 40)$ cal mol$^{-1}$ coincides with the literature data.

To obtain $\Delta S_0$ one must know the ratio of the integral absorption coefficients ($\alpha_t/\alpha_g$). There are several methods of determining this ratio [30–35]. It is proposed in [30] to take $\alpha_t$ and $\alpha_g$ from the relative molecules with "fixed" conformation. It is clear that such an approach cannot be applied to DCE. The methods [31–33] assume $\alpha_t$ and $\alpha_g$ to be independent either of the solvent or of the temperature. These assumptions are critically reviewed in [21,36]. Note that notwithstanding the fact that $\alpha_t$ and $\alpha_g$ depend significantly on $T$, the method [32] is widespread (see [37] and references cited in [21]).

The method [34] applies only to compounds for which the internal rotation barrier exceeds 7–8 kcal mol$^{-1}$. The approach to determine $\Delta S_0$ proposed recently by Raso and Garcia [35] is based on the assumption that there are linear dependencies of $\alpha_t$ and $\alpha_g$ upon $T$. Following this assumption one may determine the $\alpha_t/\alpha_g$ ratio from the equation:

$$I_g = b_0 + b_1 T - (\alpha_t/\alpha_g) I_t \tag{4}$$

where $b_0 = C_{\mathrm{tot}} l \alpha_g^0$, $b_1 = C_{\mathrm{tot}} l \alpha_g^1$, $C_{\mathrm{tot}}$ is the total concentration of the conformers, $l$ is the thickness of the absorbing layer and $\alpha_g = \alpha_g^0 + \alpha_g^1 T$. The $\alpha_t/\alpha_g$ ratio is calculated by fitting the multiple regression (4) [35,38,39]. Note that the limited accuracy in the measurements both of dependent ($I_g$) and of one of the independent ($I_t$) variables of this regression along with relatively small temperature changes in $I_t$ and $I_g$ lead to low reliability of the obtained $\Delta S_0$ values. For example, the entropy difference between cis and trans conformers of monochloroacetamide was found to be 3.8 cal mol$^{-1}$ K$^{-1}$ for its solution in acetonitrile and even 40.0 cal mol$^{-1}$ K$^{-1}$ for the solution of the same compound in dichloromethane [39]. The estimations of $\Delta S_0$ found in [35,38] are also too large.

As no method of determining the $\alpha_t/\alpha_g$ ratio can be applied to DCE, we have not determined the entropy differences, but only followed the tendency of the variation in $\Delta S_0$ with the solvent. The transformation of Eq. (1) gives

$$\Delta S_0 = R \ln(I_t/I_g) + \Delta H_0/T - R \ln(\alpha_t/\alpha_g) \tag{5}$$

The sum of the right-hand part of Eq. (5) with the accuracy, up to a degree the same for all solvents, is equal to the entropy difference of the conformers. It is tacitly assumed that $\alpha_t/\alpha_g$ does not depend on the solvent. To estimate the errors that may be the consequence of such an assumption one may compare the $I_t/I_g$ ratios obtained for different band pairs in the same solvent. The chosen analytical band pairs are assigned to different molecular vibrations, and therefore the dependence (if any) of $\alpha_t/\alpha_g$ on the solvent should be, in general, different for *a*, *b* and *c* band pairs. The differences $(\ln(I_t/I_g)_a - \ln(I_t/I_g)_b)$ observed for DCE in various solvents reflect such changes: $0.31 \pm 0.08$ (carbon tetrachloride); $0.40 \pm 0.03$ (bromoform); $0.21 \pm 0.06$ (neat); $0.37 \pm 0.10$ (methanol-$d_4$). One can see that the dependence of such a difference (if any) on the solvent is very weak. The average value $0.32 \pm 0.11$ was used to calculate the *a*-pair intensity ratios for the solutions in chloroform and dichloromethane, where it is impossible to measure $\ln(I_t/I_g)_a$ directly.

The analogous differences between *a* and *c* band pairs $(\ln(I_t/I_g)_a - \ln(I_t/I_g)_c)$ are $-1.37 \pm 0.13$ (carbon disulphide) and $-1.18 \pm 0.20$ (acetonitrile). The average value $-1.28 \pm 0.15$ was used to calculate the *a*-pair intensity ratios for the solutions of DCE in acetone and diethyl ether. Thus one may estimate the maximal error in the $\Delta S_0$ value caused by neglecting the possible solvent dependence of $\alpha_t/\alpha_g$: $\pm 0.3$ cal mol$^{-1}$ K$^{-1}$.

One can also follow the trend in the variation of $\Delta G_0$, since

$$-\Delta G_0 = RT(\ln(I_t/I_g) - \ln(\alpha_t/\alpha_g)) \tag{6}$$

The calculated values of $(R \ln(I_t/I_g) + \Delta H_0/T)$ and $RT \ln(I_t/I_g)$ are given in Table 1.

### 3.3. The correlations between $\Delta G_0$, $\Delta H_0$ and the dielectric constant

According to the reaction field model [1], there must be a correlation between $\Delta G_0$ and the Kirkwood function $K = (\varepsilon - 1)/(2\varepsilon + 1)$. The exceptions are the aromatic solvents and those which are self-associated by hydrogen bonds. As was shown by Samoshin and Zefirov [6], the correlation is improved when the parameter $\chi = (0.5 - K)^{1/2}$ is used as the independent variable instead of $K$. We obtained the correlation coefficients using both $K$ and $\chi$. The points corresponding to the aromatic solvents (Nos. 5-9) and methanol (No. 18) were not taken into account. The results are

$$RT \ln(I_t/I_g) = (2382 \pm 471)K - (969 \pm 163) \tag{7}$$

$r = 0.954 \qquad n = 13$

$$RT \ln(I_t/I_g) = -(2063 \pm 206)\chi + (604 \pm 88) \tag{8}$$

$r = -0.988 \qquad n = 13$

where $RT \ln(I_t/I_g)$ is in kcal mol$^{-1}$, $T = 296$ K; $r$ is the correlation coefficient and $n$ is the number of points.

Analogous correlations for $\Delta H_0$ were obtained

$$\Delta H_0 = (3739 \pm 548)K - (1351 \pm 190) \tag{9}$$

$r = 0.974 \qquad n = 13$

$$\Delta H_0 = -(3105 \pm 521)\chi + (1063 \pm 222) \tag{10}$$

$r = -0.966 \qquad n = 13$

The plots of $RT \ln(I_t/I_g)$ and $\Delta H_0$ against $\chi$ are given in Figs. 6 and 7. Good correlation coefficients confirm the reliability of the obtained data.

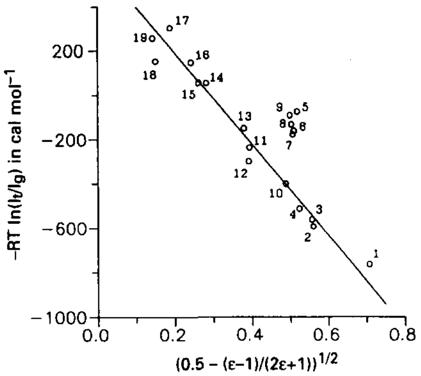

Fig. 6. The correlation between $RT \ln(I_t/I_g)$ and $\chi = (0.5-(\varepsilon-1)/(2\varepsilon+1))^{1/2}$. The point numbers correspond to those in Table 1.

### 3.4. Conformational equilibria in the aromatic media

There are considerable deviations of the points corresponding to methanol-$d_4$ and aromatic media from the straight line plots. The influence of hydrogen bond self-association of the solvent on conformational equilibria (as is the case for DCE in methanol-$d_4$) is discussed elsewhere [39,41]. In this section we will consider only the effects of aromatic media ("the benzene effect" [17]).

Several attempts to explain this effect are known. According to Oi and Coetzee [18], the benzene effect is mainly due to electrostatic interactions of solute molecules with benzene rings. It was proposed [18] that aromatic solvents are locally more polar than is expected from their macroscopic dielectric permittivities. This idea was developed by Eliel and Hofer [40] and more recently by Abraham and co-workers [41,42]. The effect was explained on the basis of the relatively high anisotropy of the polarizability tensor of the aromatic compounds; the polarizability is fully realized when the solute dipole is parallel to the plane of the nearby solvent molecules. However, it was assumed in [43,44] that the relatively high energy associated with cavity formation in aromatic solvents is responsible for the benzene effect. Thus, according to [43,44], the gauche conformer of DCE is better stabilized in benzene than in carbon disulphide due to its smaller volume in comparison with the trans conformer. Attempts to explain the benzene effect on the basis of hydrogen bonds formed by CH groups of solute molecules with $\pi$ systems of the benzene ring were also undertaken [18,40,45].

One of the ways to understand the nature of the benzene effect is to compare the $\Delta H_0$ values obtained for EB and PS. Since the molecule of EB is similar to the chain of PS and these media have similar dielectric constants (see Table 1), the same electrostatic

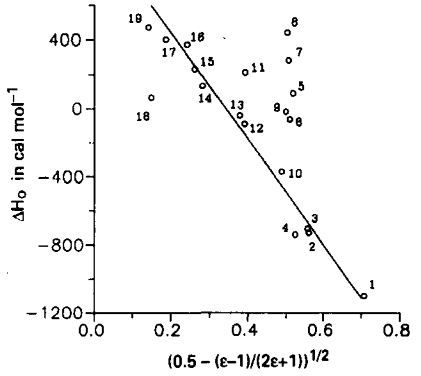

Fig. 7. The correlation between $\Delta H_0$ and $\chi$. The point numbers correspfond to those in Table 1.

contributions to $\Delta H_0$ values are expected. It is clear that the $\Delta H_0$ values to be compared must refer to the same temperature range. Because of this we used least squares to determine $\Delta H_0$ for DCE in EB in the range 200–296 K: $\Delta H_0 = 580 \pm 40$ cal mol$^{-1}$ (see dashed line in Fig. 5). Thus the difference between $\Delta H_0$ values obtained for DCE in EB and PS amounts to $\Delta\Delta H_0^{\mathrm{EB/PS}} = 600 \pm 80$ cal mol$^{-1}$. The enthalpy difference obtained for the mixture of EB and PS has a value intermediate between those for pure EB and PS (see Table 1). Analogous results were obtained earlier when studying conformational equilibria in methoxydichlorophosphine oxide [46] and *trans*-1,2-dichlorocyclohexane [47].

Three factors may contribute to the $\Delta\Delta H_0^{\mathrm{EB/PS}}$ value: (i) the cavity term, which is due to the changes in the molecular volume with conformation; (ii) the term due to specific interactions (i.e. hydrogen bonds formed by C–H groups of DCE with aromatic $\pi$ systems); (iii) the term due to non-specific (electrostatic and dispersion) interactions.

One can determine the sign of the cavity term. Although the mechanism of cavity formation in polymers is not yet understood, it should be noted that the cavity sizes are close to those of the solute molecules. The latter conclusion is based on the phenomenon of "freezing" the conformational transitions for conformationally inhomogeneous compounds dissolved in glass-forming polymers [21,23]. The density of PS (1.06 g cm$^{-1}$) is larger than that of EB (0.87 g cm$^{-1}$) and PS is a considerably more viscous medium in comparison with EB. Therefore, one may assume that the enthalpy associated with the cavity formation is larger for PS than for EB. It is well known that the gauche conformers have smaller volumes than the trans ones [48,49]. Thus the gauche conformer of DCE should be better stabilized in PS than in EB. However, this is in contrast to the experiment, and therefore the $\Delta\Delta H_0^{\mathrm{EB/PS}}$ value is not determined by the cavity term.

The enthalpies of hydrogen bonding of trans and gauche conformers of DCE with aromatic solvents are not known. However, they can be estimated on the basis of calorimetric and IR spectroscopic data obtained for cis and trans isomers of 1,2-dichloroethylene [50]. The difference between the enthalpies of specific interactions due to hydrogen bonding of cis and trans isomers with dimethyl sulphoxide does not exceed 350 cal mol$^{-1}$. Since aromatic compounds as proton acceptors are approximately six times weaker than dimethyl sulphoxide [51], the trans–gauche difference of specific interaction enthalpies should not exceed 60 cal mol$^{-1}$ for DCE in PS and EB. Furthermore, the contribution of specific interactions due to hydrogen bonding to $\Delta\Delta H_0^{\mathrm{EB/PS}}$ should be sufficiently smaller than 60 cal mol$^{-1}$, since the proton accepter abilities of PS and EB are expected to be similar. Note that the assignment of the benzene effect to hydrogen bonding is also criticized in [18,40,45].

Thus, the $\Delta\Delta H_0^{\mathrm{EB/PS}}$ value is determined mainly by the electrostatic and dispersion interactions. It seems to be difficult to separate these contributions.

The appearance of a solute molecule in a solvent results in the rearrangement of its surroundings; reorientation of the neighbouring molecules occurs to minimize the free enthalpy of the system. Needless to say, reorientation of the aromatic rings is essentially hindered in the glassy PS. Because of this, the different ability of the aromatic rings to undergo reorientation must be the main factor which is responsible for the better stabilization of the more polar gauche conformer in EB than in PS. According to the published data, benzene, toluene, EB and other alkyl-substituted aromatic compounds, notwithstanding their relatively low dielectric permittivity, have sufficient anisotropy of the polarizability tensor (in comparison with that of *n*-alkenes, carbon tetrachloride and carbon disulphide and other compounds with $\varepsilon \approx 2.5$) [52]. Thus the hindrance of reorientation of the aromatic rings in glassy PS results in their polarizability not being fully called into play. Therefore, the analysis of the contributions to the $\Delta\Delta H_0^{\mathrm{EB/PS}}$ value provides confirmation of Eliel and Hofer's assumptions [40] about the origin of the benzene effect.

As, on one hand, the orientation of the aromatic molecules in liquids is randomized by the temperature motion and, on the other hand, the interaction between the solute dipole and the neighbouring aromatic ring is crucial to their mutual orientation, then the

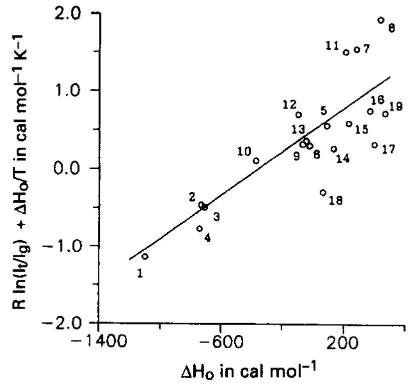

Fig. 8. The correlation between ($RT \ln(I_t/I_g) + \Delta H_0/T$) and $\Delta H_0$. The point numbers correspond to those in Table 1.

averaged interaction must increase when the solution is cooled. In other words, the local "polarity" of the liquid aromatic solvents must depend on the temperature, as is the case for the macroscopic dielectric permittivity of polar liquids. If one assumes, for an aromatic solvent, the linear dependence of the local dielectric permittivity function $(\varepsilon - 1)/(2\varepsilon + 1)$ on $T^{-1}$ (as is observed for polar liquids [53]) and the linear dependence of $\Delta H_0$ upon $(\varepsilon - 1)/(2\varepsilon + 1)$ (as is assumed in the reaction field model [1]), then the quadratic dependence of $\ln(I_t/I_g)$ upon $T^{-1}$ must be observed. This explains the experimental results given in Fig. 5. The deviations form the straight line were observed only for toluene and EB solutions, for which relatively wide temperature ranges were available. However, the same phenomenon is expected for other non-polar liquid aromatic solvents. Glassy PS does not exhibit such properties since the orientation of its aromatic rings is frozen. The slope of the dependence $\ln(I_t/I_g) = f(T^{-1})$ may be used as a measure of the local dielectric permittivity of an aromatic solvent. Thus, assuming that Eq. (2) is correct, one may conclude that the local dielectric permittivity of toluene at 360 K ($\Delta H_0 = -170$ cal mol$^{-1}$) is close to that of $CHBr_3$ ($\varepsilon = 4.39$, Table 1), whereas at $T = 190$ K ($\Delta H_0 = 820$ cal mol$^{-1}$) toluene is locally more polar than acetonitrile.

### 3.5. The correlation between $\Delta S_0$ and $\Delta H_0$

It was found in [29] that the enthalpy and entropy differences of the conformers shift in the same direction when going from one solvent to another. Such correlated variations are well known in physical chemistry (see references cited in [21]). They give rise to what is described as the compensation effect. The values characterizing $\Delta S_0$ ($R \ln(I_t/I_g) + \Delta H_0/T$) are plotted against $\Delta H_0$ values in Fig. 8. The following correlation is observed.

$$R \ln(I_t/I_g) + \Delta H_0/T = (1.4 \pm 0.4) \times 10^{-3} \Delta H_0 + (0.50 \pm 0.21) \qquad (11)$$

$$r = 0.855 \qquad n = 19$$

It is seen that the correlation coefficient is rather low. However, it should be noted that all the points (including those corresponding to the vapour phase, aromatic media and self-associated methanol-$d_4$) are scattered near the same straight line. The largest deviation from the line, observed for methanol-$d_4$, may be the result of self-association. The tangent of the slope ($\Delta\Delta S_0/\Delta\Delta H_0$) = $(1.4 \pm 0.4) \times 10^{-3}$ K$^{-1}$ is close to those for *o*-iodophenol ($(1.3 \pm 0.4) \times 10^{-3}$ K$^{-1}$ [21]), 1,2-bromofluoroethane ($(1.1 \pm 0.5) \times 10^{-3}$ K$^{-1}$ [54]) and *trans*-1,2-dichlorocyclohexane ($(1.4 \pm 0.5) \times 10^{-3}$ K$^{-1}$ [54], but is considerably smaller than that for methoxydichlorophosphine oxide ($(2.3 \pm 0.3) \times 10^{-3}$ K$^{-1}$ [21]).

In [20,29] an attempt to give a semiquantitative explanation of the compensation effect in the conformational analysis was made. According to these studies, the tangent $\Delta\Delta S_0/\Delta\Delta H_0$ may be estimated by the relation

$$\Delta\Delta S_0/\Delta\Delta H_0 \approx (mR)/(2\Delta H^{\neq}) \qquad (12)$$

where $\Delta H^{\neq}$ is the barrier to internal rotation and $m$ is the number of intramolecular coordinates taking part in conformational transitions. From the known values of $\Delta\Delta S_0/\Delta\Delta H_0$ and with $\Delta H^{\neq} = 5.15$ kcal mol$^{-1}$ [55], one may obtain $m \approx 7 \pm 2$. Thus, within the ramework of the model [20,29], not only is the torsional angle participating in the internal rotation in DCE, some other internal coordinates (apparently C–C bond length and CCCl and CCH angles) are also changing while conformational transition takes place.

Large changes in $\Delta S_0$ with the media are observed, covering more than 2.0 cal mol$^{-1}$ K$^{-1}$. This indicates that the assumption [1] about the same variation in $\Delta H_0$ and $\Delta G_0$ with the solvent is not correct. Thus, if $T = 300$ K then $\Delta\Delta G_0/\Delta\Delta H_0 \approx 0.58$.

## Acknowledgement

The authors acknowledge the Russian Foundation of Fundamental Research (Program N 93-03-5907) for support of this work.

## References

[1] R.J. Abraham and E. Bretschneider, in W.J. Orville-Thomas (Ed.), Internal Rotation in Molecules, Wiley, London, 1974.

[2] O. Sinanoglu, Int. J. Quantum Chem., 18 (1980) 381.

[3] B. Bigot, B.J. Costa-Cabral and J.L. Rivail, J. Chem. Phys., 83 (1985) 3083.

[4] B.Ya. Simkin and I.I. Sheikhet, Kvantovokhimicheskaya i Statisticheskaya Teoriya Rastvorov (Quantum and Statistical Theory of Solutions), Moscow, 1989 p. 196.

[5] T. Varnali, V. Aviyente, B. Terryn and M.F. Ruiz-Lopez, J. Mol. Struct. (Theochem), 280 (1993) 169.

[6] V.V. Samoshin and N.S. Zefirov, Zh. Vses. Khim. Ova., 29 (1984) 521.

[7] C. Reichardt, Solvent and Solvent Effects in Organic Chemistry, VCH, Weinheim, 1988.

[8] K.B. Wiberg and M.A. Murko, J. Phys. Chem., 91 (1987) 3616.

[9] Y.O. Aochi and W.J. Farmer, J. Colloid Interface Sci., 161 (1993) 106.

[10] K. Kveseth, Acta Chem. Scand., Ser. A, 32 (1978) 51.

[11] S. Mizushima, Y. Morino, I. Watanabe, T. Simanouti and S. Yamaguchi, J. Chem. Phys., 17 (1949) 591.

[12] H.J. Bernstein, J. Chem. Phys., 17 (1949) 248.

[13] K. Kuratani, T. Miyazawa and S. Mizushima, J. Chem. Phys., 21 (1953) 1411.

[14] Yu.A. Pentin, Ya.S. Bobovitch, D.B. Gurevitch and V.M. Tatevskii, Dokl. Akad. Nauk. SSSR, 89 (1953) 435.

[15] T.H. Gan, J.B. Peel and G.D. Willett, J. Chem. Soc., Faraday Trans., (1977) 965.

[16] K. Tanabe, Spectrochim. Acta. Part A, 28 (1972) 407.

[17] A. Wada, J. Chem. Phys., 22 (1954) 198, and references cited therein.

[18] N. Oi and J.F. Coetzee, J. Am. Chem. Soc., 91 (1969) 2478.

[19] M.F. El Bermani, A.J. Woodward and N. Jonathan, J. Am. Chem. Soc., 92 (1970) 6750.

[20] A.I. Fishman, A.A. Stolov and A.B. Remizov, Spectrochim. Acta. Part A, 46 (1990) 1037.

[21] A.I. Fishman, A.A. Stolov and A.B. Remizov, Spectrochim. Acta. Part A, 49 (1993) 1435.

[22] D.D. Perrin, W.L.F. Armarego and D.R. Perrin, Purification of Laboratory Chemicals, Pergamon Press, Oxford, 1980.

[23] A.A. Stolov, D.I. Kamalova, A.B. Remizov and O.E. Zgadzai, Polymer, 35 (1994) 2591.

[24] I. Nakagawa and S. Mizushima, J. Chem. Phys., 21 (1953) 2195.

[25] L.M. Sverdlov, M.A. Kovner and E.P. Krainov, Kolebatelnye Spekrty Mnogoatomnykh Molekul (Vibrational Spectra of Polyatomic Molecules), Moscow, 1970.

[26] A.S. Krauze, G.P. Mikhailov and I.S. Perelygin, Zh. Prikl. Spektrosk., 44 (1986) 431.

[27] I.S. Perelygin, A.S. Krauze and I.G. Itkulov, Khim. Fiz., 12 (1993) 404, and references cited therein.

[28] D.M. Himmelblau, Applied Nonlinear Programming, Mir, Moscow, 1975.

[29] A.B. Remizov, A.A. Stolov and A.I. Fishman, Zh. Fiz. Khim., 61 (1987) 2909.

[30] E.L. Eliel and R.J.L. Martin, J. Am. Chem. Soc., 90 (1968) 689.

[31] V.N. Nikitin and T.V. Yakovleva, Zh. Fiz. Khim., 28 (1954) 692.

[32] K.O. Hartman, G.L. Carlson, R.E. Witkowsky and W.G. Fateley, Spectrochim. Acta Part A, 24 (1968) 157.

[33] A.F. Vasilyev, Zh. Prikl. Spektrosk., 6 (1967) 467.

[34] A.I. Fishman, A.A. Stolov and A.B. Remizov, Spectrochim. Acta. Part A, 41 (1985) 505.

[35] M.A. Raso and M.V. Garcia, J. Mol. Struct., 239 (1990) 55.
[36] H. Braun and W. Luttke, J. Mol. Struct., 28 (1975) 391, 415.
[37] N. Kamiya, T. Sekigawa and S. Ikawa, J. Chem. Soc., Faraday Trans., 89 (1993) 489.
[38] M.I. Redondo and M.V. Garcia, J. Mol. Liq., 46 (1990) 75.
[39] E. Sanchez de la Blanca and M.V. Garcia, Spectrochim. Acta Part A, 50 (1994) 41.
[40] E.L. Eliel and O. Hofer, J. Am. Chem. Soc., 95 (1973) 8041.
[41] R.J. Abraham, E.J. Chambers and W.A. Thomas, J. Chem. Soc., Perkin Trans., 2 (1993) 1061.
[42] M.H. Abraham and R.J. Abraham, J. Chem. Soc. Perkin Trans., 2 (1975) 1677.
[43] L. Dumont, J. Moura Ramos, D. Zimmermann and J. Reisse, Tetrahedron Lett., (1974) 355.
[44] B.N. Solomonov, I.S. Antipin, V.V. Gorbatchuk and A.I. Konovalov, Zh. Obshch. Khim., 52 (1982) 696.
[45] J. Crossley and C.P. Smyth, J. Am. Chem. Soc., 91 (1969) 2478.
[46] D.I. Kamalova, A.B. Remizov, A.A. Stolov and A.I. Fishman, Zh. Fiz. Khim., 64 (1990) 898.
[47] A.A. Stolov and A.B. Remizov, Zh. Fiz. Khim., 69 (1995) 563.
[48] D.J. Gardiner, R.W. Jackson and B.P. Straughan, J. Chem. Soc., Chem. Commun., (1981) 159.
[49] M. Kato and Y. Taniguchi, J. Chem. Phys., 93 (1990) 4345.
[50] M.D. Broisover, A.A. Stolov, S.V. Izosimova, F.D. Baitalov, V.A. Breus and B.N. Solomonov, Zh. Fiz. Khim., 65 (1991) 545.
[51] M.D. Joesten and L.J. Schaad, Hydrogen Bonding, Marcel Dekker, New York, 1974.
[52] A.N. Verestchagin, Kharakteristiki Anizotropii Polyarizuemosti Molekul (Characteristics of Anisotropy of Molecular Polarizability), Nauka, Moscow, 1982.
[53] Ya.Yu. Akhadov, Dielektricheskie Svoistva Chistykh Zhidkostei (Dielectric Properties of Pure Liquids), Izdatelstvo Standartov, Moscow, 1972.
[54] A.A. Stolov, D.I. Kamalova, S.A. Smirnov, D.G. Gladikov and A.B. Remizov, Zh. Fiz. Khim., 67 (1993) 2388.
[55] G. Allen and S. Fewster, in W.J. Orville-Thomas (Ed.), Internal Rotation in Molecules, Wiley, London, 1974.