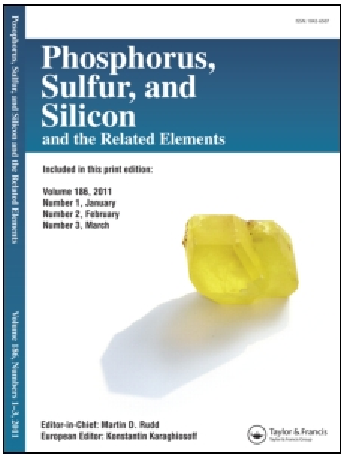

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THE STUDY OF 2-CHLORO-5,5-DIMETHYL-2-OXO-1,3,2-DIOXAPHOSPHORINANE IN SOLUTIONS BY MOLECULAR DYNAMICS METHODS USING IR AND RAMAN SPECTROSCOPY

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THE STUDY OF 2-CHLORO-5,5-DIMETHYL-2-OXO-1,3,2-DIOXAPHOSPHORINANE IN SOLUTIONS BY MOLECULAR DYNAMICS METHODS USING IR AND RAMAN SPECTROSCOPY

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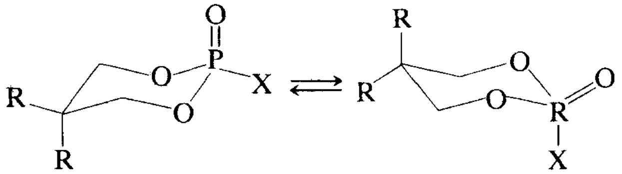
2-Chloro-5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinane has been studied in CCl_4, $CHCl_3$ and CD_3CN solutions by IR and Raman line shape analysis. Equilibrium process of dimerization and ring conversion in CCl_4 solutions have been considered. On the contrary to the commonly expected dominance of the conformer with the equatorial oriented P=O bond for 2-halo-2-oxo-1,3,2-dioxaphosphorinanes, it was found that for the 2-chloro derivative both conformers are nearly equally distributed. It has been shown that the interactions induced absorption is an important mechanism of relaxation in the studied compound and this mechanism gives significant contribution to the total IR band broadening, while the interaction induced light scattering is negligible. The obtained results show that the molecular dynamics method can be useful in studying cyclic compounds in solutions.

Key words: IR spectroscopy and Raman spectroscopy of 2-chloro-5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinane in solutions; Vibrational line shape analysis of molecular motions in 2-chloro-5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinane.

INTRODUCTION

Structure and stereochemical as well as spectroscopic studies of 2-substituted 2-oxo-1,3,2-dioxaphosphorinanes and their derivatives have received considerable attention in the last two decades and the results have been collected by Maryanoff *et al.*[1]

The ring conformation of 2-X-5,5-R,R-2-oxo-1,3,2-dioxaphosphorinanes **1** in solutions has been studied by NMR[2–10] and IR[2–5,11–16] spectroscopic methods, dipole moment measurements[2,3,17–22] and theoretical considerations.[23,24]



(1)

1a **1b**

$\mathbf{2} = \mathbf{1}$ (X = Cl, R = Me)

The conformational behaviour of the X substituent in molecules **1** is determined by the competition between numerous factors. The most important are dipole–

dipole and higher multipole interactions as well as anomeric, steric and solvent effects.

Spectroscopic measurements in solution[2–22] suggest that structures **1** in which X = halogen, alkoxy or aryloxy have the chair form **1b** as preferred conformation, while those with X = alkyl or amino are expected to have the axial P═O position. These results are supported by X-ray crystallographic data[24–29] and they are in agreement with the theoretical consideration of anomeric[24,30] and solvent effects.[31]

Spectroscopic methods may be a valuable tool for conformational equilibrium studies, if the phosphorus stereochemical assignments have been correctly made. The IR experiments suggest that the IR phosphoryl stretching criterion is more ambiguous than it was commonly supposed.[3,4] The results obtained by IR and NMR techniques for systems with conformationally reduced mobility (4,6-dimethyl derivatives of 2-oxo-1,3,2-dioxaphosphorinanes) can be misleading[3] in deducing the conformation of molecules of type 1. Thus, we can conclude that the conventional IR and NMR criteria can be applied with caution and new approach to IR spectroscopy in determination of the ring conformations would be useful.

X-ray analysis of solid 2-chloro-5,5dimethyl-2-oxo-1,3,2-dioxaphosphorinane **2** has shown[29] the conformer **2b**. Spectroscopic measurements have suggested that the same conformer **2b** is preferred in solutions.[10,16]

The purpose of this paper is an application of molecular dynamics method based on IR and Raman line shape analysis for studying conformational equilibrium of **2** in solutions containing solvents of different polarities. This method could eliminate some of the ambiguities in determination of conformers distribution of non-rigid molecules **1**.

RESULTS AND DISCUSSION

The IR transmission spectra of P═O stretching mode of **2** in carbon tetrachloride, chloroform and ($^2H_3$)acetonitrile show (Figure 1) that the shape of the P═O profiles strongly depends on the solvent. The broad band of the P═O mode in the CCl_4 solution consists clearly of at least two strong bands at 1322 and 1333 cm^{-1} and a weak peak at 1307 cm^{-1} in the band wing, which is observed even at the concentration as low as 0.005 mol/l. On the contrary only one band at about 1310 cm^{-1} has been observed in the $CHCl_3$ and CD_3CN solutions. Taking into account its broadeness, however, it is quite possible that this band in $CHCl_3$ and CD_3CN consists of two closely spaced bands.

For many 2-X-2-oxo-1,3,2-dioxaphosphorinanes the bands at about 1310 cm^{-1} and 1260–1280 cm^{-1} have been assigned[3,4,12] to phosphoryl stretching of the **1b** and **1a** conformers, respectively. In the examined solutions of compound **2** we have not observed any peaks in the 1300–1200 cm^{-1} region at concentration below 0.1 mol/l, but at higher concentration a very weak peak has appeared at 1285 cm^{-1} in all solvents used. In all of the examined solutions the well known weak band at about 1376 cm^{-1} of the CH_3 symmetric deformation has been noticed.

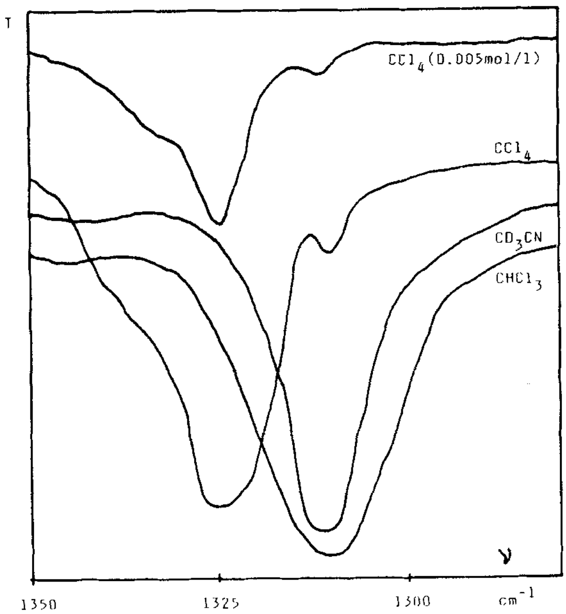


FIGURE 1 IR spectra of the P═O stretching mode of **2** in carbon tetrachloride, acetonitrile and chloroform at concentrations 0.0125 mol/l and 0.005 mol/l (cuvette KBr 503 μm).

EQUILIBRIUM OF 2 IN CCl_4 SOLUTION

The P═O bands at several concentrations of **2** in CCl_4 solutions were fitted with three Lorentzians (Table I). Two strong bands I and II at 1333 and 1322 cm^{-1}, respectively, may be discussed as the equilibrium of **2a** and **2b** conformers or as the equilibrium of the free conformer **2b** and its dimer complex formed by intermolecular interactions. The latter assignment should be taken into account for molecules like **2** containing the highly polar phosphoryl bond in a non-polar solvent such as CCl_4.

The temperature dependence of the P═O band contour in CCl_4 (Figure 2) shows that the integral absorption of the band at lower frequency decreases with the increase of temperature. We, therefore, assign this band to the complex while the free band appears at higher frequency. We have considered a selfassocaition process:

$$2\,\mathbf{2b} = (\mathbf{2b})_2 \tag{2}$$

The equilibrium constant of this dimerization reaction can be written as:

$$K^{II} = \frac{1 - x_I}{2cx_I^2} \tag{3}$$

where x_I is the monomer fraction of total concentration ($c = c_{monomer} + 2c_{dimer}$). Assuming the same values of molar extinction coefficients of the monomer **2b** and

TABLE I

The values of fitting parameters by three Lorentzians, integral absorptions B and molecular extinction coefficients ε for separated bands of the P=O band of 2-chloro-5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinane in carbon tetrachloride at room temperature[a]

Parameter	Conc. mmol/l	Band I	Band II	Band III
maximum peak position cm^{-1}	5.0 ÷ 25.0	1333.1 ± 0.2	1322.0 ± 0.5	1307.4 ± 0.3
maximum absorbance intensity	25.0	0.332	0.934	0.040
	25.0	0.261	0.916	0.156
	20.0	0.290	0.845	0.039
	15.0	0.315	0.734	0.011
	12.5	0.220	0.529	0.053
	5.0	0.080	0.201	0.001
band width cm^{-1}	25.0	16.15	10.03	4.19
	25.0	15.94	9.11	3.96
	20.0	17.00	9.10	3.87
	15.0	16.60	7.94	4.00
	12.5	14.84	9.41	4.96
	5.0	14.06	6.44	3.99
base line	25.0		−0.066	
	25.0		−0.076	
	20.0		−0.069	
	15.0		−0.050	
	12.5		−0.038	
	5.0		0.001	
integral absorption B cm^{-1}	25.0	19.39	33.90	0.61
	25.0	15.06	30.18	0.71
	20.0	17.84	27.82	0.54
	15.0	18.91	21.08	0.16
	12.5	11.83	18.02	0.30
	5.0	4.06	4.67	0.01
molar extinction coefficients ε $1\ \text{mol}^{-1}\,\text{cm}^{-2}$	5.0 ÷ 25.0	$(4.32 \pm 0.73) \cdot 10^4$		386 ± 220

[a] Statistical errors of average values are given. Errors of concentration and thickness cuvettes are omitted.

of a mer in $(\mathbf{2b})_2$, values of the x_{I} can be approximated from the integral absorptions B_{I} and B_{II} of the I and II bands, respectively (Table I):

$$x_{\text{I}} = \frac{B_{\text{I}}}{B_{\text{I}} + B_{\text{II}}} \tag{4}$$

Values of the dimerization constant K^{I} for different concentrations and temperatures are listed in Table II.

The enthalpy ΔH° of the reaction (2) calculated from van't Hoff's equation is equal to $-30.9 + 8.6$ kJ and the K^{I} value at 25°C equals $88.3 + 18.5$ l/mol. Values of ΔG°_{25} and ΔS°_{25} for the reaction (2) have been calculated as $-11.1 + 0.5$ kJ and $-66.5 + 29.1$ J/K, respectively. Thus, the two **2b** molecules in a dimer would be

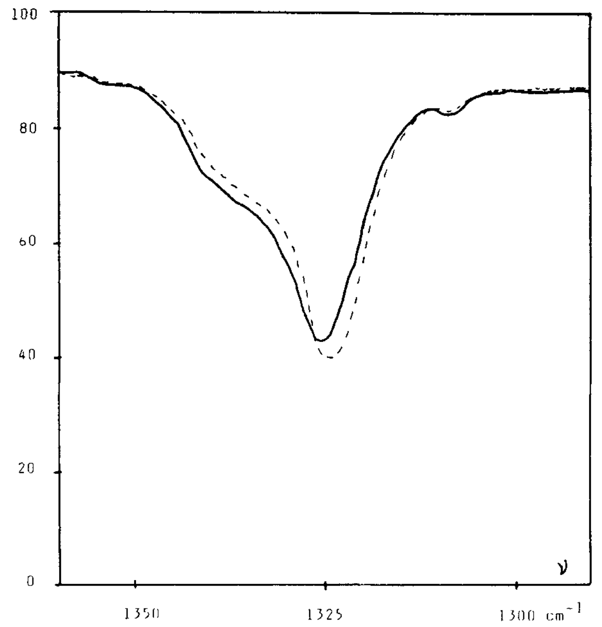


FIGURE 2 The temperature dependence of the P=O band of **2** in carbon tetrachloride at concentration of 0.025 mol/l (—— temp 52.3°C ---- temp 30.1°C).

thermodynamically "strong". The ΔS°_{25} value may be reasonable for the dimerization reaction. The K^I and ΔH° values are, however, unacceptable large for the non-specific dipole–dipole interactions. Similar values of the constants and enthalpies were observed by Laskorin *et al.*[32] for H-bonded dimers of amidophosphates in CCl_4 solutions. Moreover, it would not be easy to explain why the width at half height of band II of the dimer is narrower than band I of the monomer.

TABLE II

The values of equilibrium constants K^I and K^{II}

Conc. mmol/l	Temp. °C	$x_I = \frac{B_I}{B_I + B_{II}}$	$K^I = \frac{1 - x_I}{2cx_I^2}$	$K^{II} = \frac{1 - x_I}{x_I}$
5.0	23 ÷ 25	0.465	247	1.15
12.5	(room)	0.396	153.8	1.52
15.0		0.473	78.6	1.12
20.0		0.391	99.8	1.56
25.0		0.333	120.3	2.00
25.0		0.364	96.1	1.75
29.3		0.343	95.0	1.91
25.0	30.1	0.409	70.5	1.44
25.0	31.2	0.415	68.1	1.41
25.0	43.0	0.478	45.8	1.10
25.0	52.3	0.548	30.1	0.83
	25.0	(0.375)[a]	(88.3)[a]	(1.67)[a]

[a] Extrapolated from van't Hoff's plots to 25°C.

The strong double P=O band of compound **2** (I and II bands in Table I) can thus be attributed to the presence of two conformational isomers **2a** and **2b**. Majoral *et al.*,[16] however, reported only one P=O band of **2** in benzene at 1321 cm^{-1} and two bands in carbon disulfide at 1322 and 1296 cm^{-1}. The band at higher frequency in CS_2 was assigned to the conformer **2b**. On the basis of correlation between Taft's constants of substituents and phosphoryl frequencies the authors proposed that the axial P=O conformers of compounds of type 1 should exist at about 26 cm^{-1} lower frequencies than the equatorial ones, but their correlations were drastically bad for the compound **2**.

The very weak band at 1285 cm^{-1} which we observe at higher concentrations of **2** in CCl_4 might be regarded as the confirmation of Majoral's expectation. The solvent shift of this band in $CHCl_3$ is very small unlike to the shift of the band at 1322 cm^{-1}. Therefore, the assignment of the band at 1285 cm^{-1} to $\nu_{P=O}$ is uncertain. In addition White *et al.*[4] have pointed out that the band at 1285 cm^{-1} may not be due to P=O stretching mode because some weak band appears in spectra of corresponding phosphites. Therefore, we have left out this very weak peak from the further considerations.

For compounds like **1**, which exhibit two considerably separated bands (about 26 cm^{-1}), Kainosho *et al.*[12] have assigned a band at higher frequency to the equatorial P=O bond. It can be seen, however, in Table I that the band at lower frequency has greater intensity. Taking into account that in the solid state only the conformer **2b** exists[29] and that the dipole moment of this conformer is greater than that of the axial one, we have assigned the band II at lower frequency to the conformer **2b**. Assuming that the molar extinction coefficients of both conformers are the same, we have calculated the equilibrium constant K^{II} from the equation:

$$K^{II} = \frac{1 - x_I}{x_I} \tag{5}$$

Here x_I is the mole fraction of the conformer **2a** and its values, calculated from Equation (4), were given in Table II, which also contains the K^{II} values for different concentrations and temperatures. The increase of K^{II} values with the increase of the concentration may be caused by solute–solute interactions.

From van't Hoff's equation the enthalpy $\Delta H°$ of the reaction (1) has been evaluated as equal to -20.2 ± 6.7 kJ/mol. Values of ΔG°_{25} and ΔS°_{25} values are equal to -1.3 ± 0.4 kJ/mol and -63.6 ± 23.2 J/mol K, respectively. The negative large value of the enthropy would mean that the arrangement of solvent molecules around the conformer **1b** in the CCl_4 solution is much higher than that of the conformer **1a**. It enabled us to write the equilibrium reaction (1) as follows:

$$\mathbf{2a} + \text{solvent} = \mathbf{2b} \tag{6}$$

It seems to be reasonable because the equatorial P=O form with large dipole moment may be better solvated than the axial one.

Our K^{II} values disagree with the results obtained by CNDO/2,[23] ab initio[24] and spectroscopic methods[10,16] because the data in Table II show that both conformers in CCl_4 would exist with a slight preference of the **2b** form at room temperature. This results disagree with commonly accepted (but not necessarily realistic) opinion that the dominant forms of 2-halo-2-oxo-1,3,2-dioxaphosphorinane in solutions are conformers **1b**.

TABLE III

The values of fitting parameters by one Lorentzian, integral absorptions B and molar extinction coefficients ε calculated for the P═O band of 2-chloro-5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinane in chloroform and acetonitrile at room temperature[a]

Parameter	Conc. mmol/l	$CHCl_3$	CD_3CN
maximum peak position cm^{-1}	5.0 ÷ 25.0	1311.8 ± 0.6	1313.0 ± 0.8
maximum absorbance intensity	25.0	0.961	1.141
	12.5	0.489	0.528
	5.0	0.192	0.272
band width cm^{-1}	25.0	16.68	9.05
	12.5	16.53	9.60
	5.0	19.01	9.29
base line	25.0	−0.099	0.020
	12.5	−0.057	−0.007
	5.0	−0.007	0.012
integral absorption β cm^{-1}	25.0	58.01	37.35
	12.5	29.27	18.34
	5.0	13.20	9.14
molar extinction coefficients ε $l\ mol^{-1}\ cm^{-2}$	5.0 ÷ 25.0	$(4.84 \pm 0.89) \cdot 10^4$	$(3.17 \pm 0.98) \cdot 10^4$

[a] Statistical errors of average values are given. Errors of concentration and thickness cuvettes are omitted.

The P═O bands in $CHCl_3$ and CD_3CN are broad and we cannot reject the possibility that they represent the overlapping of closely separated two bands like bands I and II in CCl_4. The comparison, however, of the results from fitting by one (Table III) or two bands seems to prefer one Lorentzian band. It would mean that the equilibrium in $CHCl_3$ and CD_3CN are shifted towards the equatorial P═O form, because these solvents are more polar than CCl_4.

INTERACTION INDUCED ABSORPTION

Figures 3 and 4 show the IR P═O dipole correlation functions calculated from the bands I and II in CCl_4 and the band in CD_3CN. As it can be seen the functions of the band II in CCl_4 (Figure 3) decay with the same rates within the experimental error as the functions of the P═O band in acetonitrile (Figure 4) which corresponds to the equatorial conformer. These results confirm the assignment of the band II to the conformer **2b** as it has been made above in the conformational equilibrium analysis. Thus, band I can be attributed to the conformer **2a**.

In Figure 5 we present the concentration dependence of the IR P═O correlation times τ_c calculated as the integrals of the dipole correlation functions for both bands in CCl_4. The values of the correlation time $\tau_{c(II)}$ for the band II

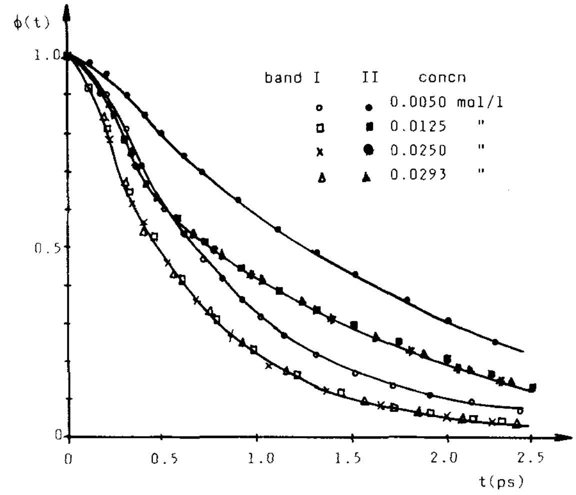


FIGURE 3 IR P=O dipole correlation functions of bands I (1333 cm^{-1}) and II (1322 cm^{-1}) of **2** as a function of concentration in carbon tetrachloride.

are significantly larger than those of the $\tau_{c(\text{I})}$ for the band I and both correlation times increase with dilution. The IR correlation time τ_c in CD_3CN, resulting from Figure 4, also decreases with the increase of concentration. This trend is also shown in Figure 6 in which the concentration dependence of the full width at half height $\Delta_{1/2}$ of the IR absorption band in CD_3CN is given. The concentration dependences of the τ_c and IR absorption $\Delta_{1/2}$ values may be caused by intermolecular interactions mainly through dipole–dipole interactions. It is, however, worth emphasizing that the decays of the IR dipole correlation functions are much slower at the lowest studied concentration (0.005 mol/l), where intermolecular interactions can be regarded as negligible. Making a

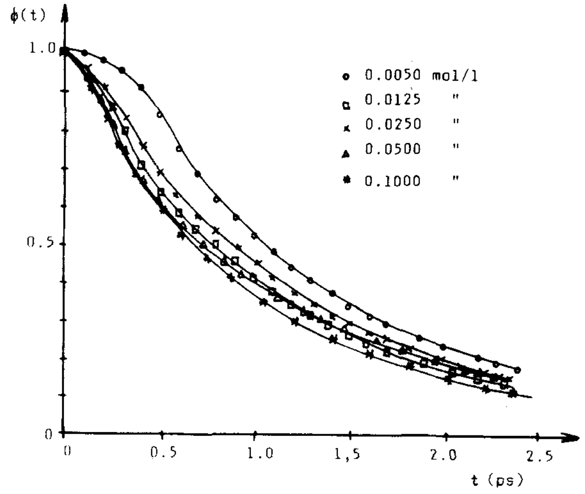


FIGURE 4 IR P=O dipole correlation function of **2** as a function of concentration in acetonitrile.

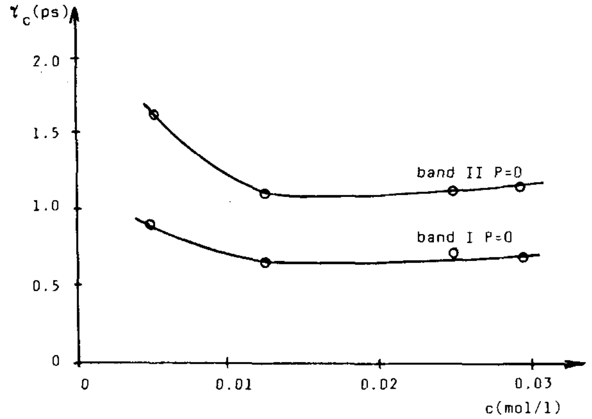


FIGURE 5 IR correlation times as a function of concentration of **2** in carbon tetrachloride.

comparision between the functions in Figures 3 and 4 we can see that intermolecular interactions are weaker in CD_3CN than in CCl_4 what supports the importance of electrostatic interactions.

As mentioned above the IR $\Delta_{1/2}$ values increase with the increase of the concentration. It is surprising because the opposite effect would be expected for reorientational relaxation. Indeed, in diluted solutions reorientational processes should become faster. The contributions from single particle reorientations may be estimated from the band widths of the isotropic and anisotropic Raman bands. For compound **2** the Raman band widths are practically the same (Figure 6) indicating once again the neglecting role played by single particle reorientational correlations. It seems that the most reasonable explanation of the differences in the Raman and IR band widths may be interaction induced effects and their various efficiencies for Raman and IR band. Interaction induced light scattering or interaction induced absorption are caused by the fact that polarizability α or dipole moment μ of a pair of molecules at a distance r is not equal to the sum of the polarizabilities or dipole moments of the isolated molecules, respectively.[33]

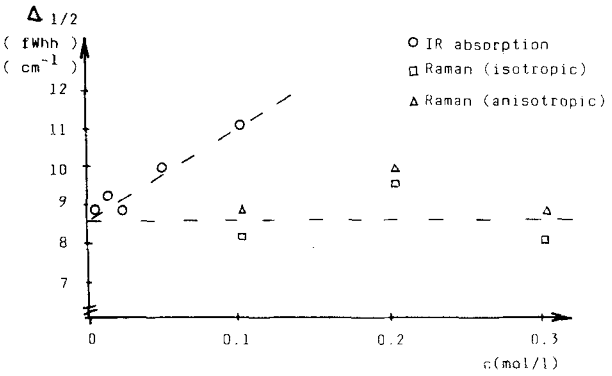


FIGURE 6 The IR and Raman P═O band width of **2** in acetonitrile as a function of concentration ($\Delta_{1/2}$ were calculated using the formula $\Delta^{t}_{1/2} = \Delta^{a}_{1/2}\,(1 - 2s/\Delta^{a}_{1/2})^{1/2}$. The all symbols in this equation have been explained elsewhere[38]).

Using the expressions for the electric fields multipole expansion,[34] it can be found that the additional $\Delta\mu$ and $\Delta\alpha$ induced by interactions are given in the dipole-induced dipole (DID) approximation by

$$\Delta\mu_\alpha = \alpha_{\alpha\beta} T^{(2)}_{\beta\gamma} \mu_\gamma \tag{7}$$

$$(\Delta\alpha)_{\alpha\beta} = \alpha_{\alpha\beta} T^{(2)}_{\beta\gamma} \alpha_{\gamma\sigma} \tag{8}$$

We have shown[35] that the interaction induced light scattering can be negligible as the relaxation mechanism for P═O stretching mode while interaction induced absorption may be an important factor of the IR band broadening. It can explain why the IR band is broader than isotropic Raman band. The contribution of the DID mechanism can be estimated from the difference between Raman and IR band widths. For compound **2** the DID effect is large, because its contribution is about 25% of the total band broadening. The strong dipole-induced dipole interactions suggested by molecular dynamics results are consistent with the conformational equilibrium data obtained in this paper. As we have shown, the equilibrium constant K^{II} remarkably depends on the solute–solute interactions.

EXPERIMENTAL

Materials. 2-Chloro-5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinane **2** was prepared according to Stec and Zwierzak procedure.[36] The product was purified by passage through silica gel column using chlorform-acetone (3:1) mixture as the eluent followed by recrystalization (60% yield) from benzene-hexane (1:2).

Chloroform (Merck) and carbon tetrachloride (POCh, Poland) for spectroscopy and ($^2H_3$) acetonitrile (ORiPJ, Poland) were dried by standard procedures.

Spectroscopic measurements and numerical analysis. The IR transmission bands were recorded with a Perkin–Elmer model 580 double-beam spectrometer with a slit width of 2 cm^{-1} and scanning speed of 10 cm^{-1}/min. The cuvettes of KBr (503 and 228 μm) have been used. Raman spectra were recorded with a Coderg model PHO spectrometer and Spectra Physics 164 argon-ion laser operating at 488 nm. The slit width was 4 cm^{-1}. The scan speed was 10 cm^{-1}/min with a time constant 1.6 s.

The signal-to-noise ratio for the IR and Raman spectra achieved at these resolutions was about 40 even in the worst cases at small concentrations. The contour analysis have been made to separate overlapped bands. The digitized spectra were fitted with one or three Lorentzians using a Marquardt least square fit procedure.[37]

The vibrational correlation functions and IR dipole correlation functions were calculated as a Fourier transformation of the normalized intensities in the way described previously.[38,39]

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