Dielectric Relaxation in Substituted Benzaldehydes

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The measurements of the relative permittivity at frequencies of 1 MHz and 9.274 GHz and of the refractive index at sodium D-line have been carried out at 30 °C for *o*-chlorobenzaldehyde (A), *m*-chlorobenzaldehyde (B), *p*-chlorobenzaldehyde (C), *o*-nitrobenzaldehyde (D), *m*-nitrobenzaldehyde (E), and *p*-nitrobenzaldehyde (F), in dilute solutions of benzene, cyclohexane, carbon tetrachloride, *p*-dioxane and Nujol. The dielectric relaxation times for the overall rotation and the electric dipole moments for these molecules have been calculated. These results have been used to calculate the dipole moment for the internal rotations, possibly of the CHO-group, in the molecule. The results are analyzed in terms of the solute-solvent interactions for these molecules. The bonding between the hydrogen atom of the aldehyde group and the oxygen atom of the dioxane molecule seems to be fairly weak. The comparative behavior of the chlorobenzaldehydes and the nitrobenzaldehydes has also been discussed.

In the past decade, attempts have been made to detect intramolecular rotations of the polar group in the organic molecules by using the dielectric dispersion techniques.[1,2] Several interesting results have been obtained especially when one of the hydrogen atoms of the benzene ring is replaced by any of the groups namely, $-OH$, $-OCH_3$, $-NH_2$, $-CH_2Cl$. In some cases, the results have led to the quantitative interpretations about the mechanisms of the intramolecular rotations. Measurements have been made on a particular molecule over several decades of frequency. The results have been analyzed using either the Cole-Cole[3] plot or the Scaife's polarizability[4] plot in terms of the molecular relaxation time, τ_1, the intramolecular relaxation time, τ_2, and their respective contributions to the observed dielectric dispersion.

Recently,[5,6] an attempt has been made to analyze the data in terms of two arbitrary dielectric relaxation times defined by the equations given below:

$$\tau(1) = \frac{a''}{w(a'-a_\infty)} \tag{1}$$

$$\tau(2) = \frac{a_0-a'}{wa''} \tag{2}$$

where w is the pulsatance, a_0, a', a'', a_∞ are defined in linear range by the equations,

$$\left.\begin{aligned} \varepsilon &= \varepsilon_1 + a_0 w_2, \\ \varepsilon' &= \varepsilon_1' + a' w_2, \\ \varepsilon'' &= a'' w_2, \\ \varepsilon_\infty &= \varepsilon_{1\infty} + a_\infty w_2. \end{aligned}\right\} \tag{3}$$

Subscript 1 refers to the pure solvent, 2 to the solute and the subscript ∞ refers to the values of the relative permittivity at infinite frequency. w_2 is the weight fraction of the solute. The analysis reported in the paper[6] has shown that $\tau(1)$ is dependent on τ_1,τ_2 and on the relative contribution of τ_2 to the observed dielectric loss, C_2. It has also been shown that for certain cases, $\tau(2)$ leads to τ_1. It has also been proved[7] that $\tau(1)$ is approximately equal to the dielectric relaxation time, $\tau_{G.K.}$, determined using the Gopala Krishna method.[8] It follows, therefore, that $\tau_{G.K.}$ depends on τ_1,τ_2 and C_2. As a consequence the value of $\tau_{G.K.}$ provides only with an indication of the presence of the intramolecular rotations in the molecule. The presence of these rotations is concluded only when $\tau(2)$ and $\tau_{G.K.}$ differ significantly from each other.

The following parameters, however, are introduced to quantify these rotations. First we calculate $\tau(2)$ using Eq. (2) and then we calculate a_∞ from Eq. (1) on the assumption that $\tau(1)$ is equal to $\tau(2)$. Then the parameter a_∞ would correspond to those rotations of the molecule to which the value of $\tau(2)$ corresponds. For simplification, this parameter is designated as $a_{\infty 2}$. Now the parameter governing the slope of a_∞ *versus* concentration curve is differentiated from $a_{\infty 2}$ and is designated as $a_{\infty 1}$. The difference between $a_{\infty 2}$ and $a_{\infty 1}$ is suggested to provide us with the magnitude of the residual dipole moment taking part in the internal rotations of the molecule.

To our knowledge, no systematic work on the measurements of the substituted benzaldehydes is available in literature. However, the values of $\tau_{G.K.}$ are reported[9] for some of the molecules in *p*-xylene solution. In this paper, we report the results of the measurements on the *o*-, *m*- and *p*-chlorobenzaldehydes and of the nitrobenzaldehydes in the dilute solutions of benzene, cyclohexane, carbon tetrachloride, *p*-dioxane and Nujol at the temperature of 30 °C. These measurements are of relevance because the results can help in advancing the understanding of the dielectric relaxation mechanism of the methoxy compounds which are being studied in Professor Walker's laboratory.[10] A methoxy or an aldehyde group when attached to the benzene ring should have similar dielectric relaxation mechanisms. The paper also deals with examining the possibility of detecting the solute-solvent interactions of the aldehydes with the solvent molecules. This is important particularly when the carbonyl groups are known to have interactions with the π-orbital electrons of the benzene molecule.

Materials and the Dielectric Measurements

The name and the specifications of the materials, as given by the manufactures, are given in parentheses of the particular sample.

1. *o*-chlorobenzaldehyde (Fluka A.G., purum).
2. *m*-chlorobenzaldehyde (Koch Light, pure grade).
3. *p*-chlorobenzaldehyde (Koch Light, pure grade).
4. *o*-nitrobenzaldehyde (Koch Light, puriss).

5. *m*-nitrobenzaldehyde (B.D.H., L. R.).
6. *p*-nitrobenzaldehyde (Koch Light, pure grade).

The materials mentioned above, with the exception of the *m*-nitrobenzaldehyde, were used without further purification. *m*-Nitrobenzaldehyde was crystallised in methanol and was thereafter vacuum-dried to remove traces of the solvent. The materials with serial number 3—6 were checked for their melting points. The refractive indices for the materials 1 and 2 were measured. For the cases studied, the agreement between the measured value and its literature value was good.

The solvents namely benzene, cyclohexane, carbon tetrachloride, *p*-dioxane and Nujol were of the same purity specifications as already given.[11] These solvents were treated similarly for further purification. The measurements of the relative permittivity at the frequency of 9.274 GHz and of the refractive index at wavelength of the sodium D-line were made in the same way as already described.[11,12] The relative permittivity measurements at frequency of 1 MHz were taken using the dielectrometer based on the principle of heterodyne beat method.[13] This piece of equipment was assembled to the same specifications as already reported in the paper by one of the authors (JKV). The Rohde and Schwarz[14] two terminal dielectric cell (Type KMF BN 5721) was used. The capacitance between the inner and the outer electrode is measured to be 37.09 pF. Both the terminals of the dielectric cell are properly screened from each other.

Results

The values of a_0, a', a'', of the so called slopes, defined by Eq. (3), are given in Table. a_D is defined as given below:

$$n_D^2 = n_{1D}^2 + a_D w_2.$$

These slopes have been determined by fitting the appropriate data of the appropriate equation using the multiple regression program on the IBM 360/44 digital computer. The standard errors of estimate, as obtained, are given with their coefficients. An examination, of the coefficients and of their standard deviations, indicates that the errors in a_0, a', a'' and a_D are of the order of 2%, 3%, 4% and 5%, respectively. Bearing in mind that the total number of observations in each case is only 7 and also taking into account the errors involved in the measurement of a particular parameter, one leads to the conclusion that Eq. (3) are valid within the experimental range of the solute concentration in dilute solutions. The range of the solute concentration by weight is approximately 7% of the solvent in each case.

The experimental data is analyzed by determining $\tau(2)$. Hereinafter this parameter would be denoted as the dielectric relaxation time for the overall rotations,

Table 1. Values of a_0 (slope of ε *versus* concentration curve) a' (slope of ε' *versus* concentration curve), a'' (slope of ε'' *versus* concentration curve) and a_D (slope of n_D^2 *versus* concentration curve)

Medium	a_0	a'	a''	a_D
	o-Chlorobenzaldehyde			
Benzene	7.306±0.160	4.508±0.083	2.451±0.075	0.142±0.006
Cyclohexane	5.858±0.082	3.888±0.124	1.876±0.059	0.243±0.003
Carbon tetrachloride	12.466±0.169	6.374±0.125	4.889±0.098	0.449±0.009
p-Dioxane	8.768±0.161	3.564±0.072	3.380±0.092	0.346±0.007
Nujol	5.763±0.160	2.448±0.063	1.810±0.060	0.169±0.073
	m-Chlorobenzaldehyde			
Benzene	5.638±0.130	3.448±0.049	2.118±0.068	0.158±0.001
Cyclohexane	4.820±0.002	3.096±0.040	1.670±0.050	0.220±0.059
Carbon tetrachloride	10.640±0.212	4.414±0.168	3.200±0.141	0.393±0.013
p-Dioxane	6.504±0.192	2.564±0.043	2.240±0.010	0.352±0.006
Nujol	5.265±0.003	1.435±0.040	1.03 ±0.045	0.155±0.003
	p-Chlorobenzaldehyde			
Benzene	3.522±0.057	1.920±0.05	0.913±0.029	0.164±0.001
p-Dioxane	3.937±0.038	1.890±0.06	1.430±0.040	0.361±0.007
	o-Nitrobenzaldehyde			
Benzene	14.320±0.195	7.100±0.180	5.200±0.120	0.200±0.010
Cyclohexane	10.080±0.200	6.676±0.200	3.789±0.072	0.231±0.012
Carbon tetrachloride	22.599±0.184	10.258±0.132	9.137±0.178	0.451±0.012
p-Dioxane	17.151±0.144	4.895±0.150	5.350±0.150	0.348±0.008
	m-Nitrobenzaldehyde			
Benzene	8.944±0.146	4.030±0.060	3.268±0.065	0.174±0.006
Carbon tetrachloride	15.802±0.176	6.211±0.123	5.622±0.139	0.461±0.011
p-Dioxane	10.615±0.175	3.071±0.037	3.441±0.063	0.394±0.007
	p-Nitrobenzaldehyde			
Benzene	4.559±0.003	2.281±0.102	1.206±0.055	0.174±0.006
p-Dioxane	5.771±0.003	2.065±0.032	1.811±0.051	0.393±0.005

τ. For reasons given in the introduction, this value of τ is plugged into Eq. (1) to calculate a_{∞_2}. Equation (1) is written as

$$a_{\infty_2} = a' - \frac{a''}{w\tau} \tag{4}$$

Under these conditions, the physical significance of a_{∞_2} is that it is the slope of the relative permittivity when plotted against concentration. The relative permittivity values are measured at frequency such that the electric dipole taking part in the molecular rotations ceases to follow the alternations of the field. In other words, for frequencies higher than this limit, only the dipole moment for the internal rotations can contribute to the dielectric loss in the liquid.

Now the magnitude of the dipole moment involved in the internal rotations is calculated as follows.

The parameter a_0 in the modified Higasi's equation[15] is replaced by the parameter a_{∞_2}, determined as outlined above. Higasi's equation for the dipole moment of the internal rotations is written as:

$$\mu_{\text{int.rot.}} = B\sqrt{(a_{\infty_2} - a_{\infty_1})}\,, \tag{5}$$

where

$$B = \frac{1}{2(\varepsilon_1 + 2)}\sqrt{\frac{27kTM_2}{\pi N_A d_1}}$$

and ε_1 is the relative permittivity of the solvent, k is the Boltzmann constant, T is the absolute temperature of the material, N_A is the Avogadro's number and d_1 is the density of the solvent.

The parameter a_{∞_1} is calculated from the parameter a_D by the equation

$$a_{\infty_1} = a_D + \Delta a_D$$

whereas Δa_D is calculated using the following equation suggested by Higasi *et al.*[16]

$$\frac{\Delta P_E}{P_E} = \frac{3a_D}{(\bar{n}_{2D}^2 + 2)(\bar{n}_{2D}^2 - 1)}$$

on putting

$$\frac{\Delta P_E}{P_E} = 0.05$$

where

$$\bar{n}_{2D}^2 = n_{1D}^2 + a_D$$

The subscript 1 refers to the solvent and 2 refers to the solute.

The electric dipole moment of these molecules in the dilute solutions of the non-polar solvents is calculated using the modified Higasi's equation[15] given below:

$$\mu = B\sqrt{(a_0 - a_{\infty_1})} \tag{6}$$

where the constant B is the same as in Eq. (5).

Discussion

The experimental dipole moment for *p*-chlorobenzaldehyde as shown in Table 2 agrees well with its literature value. There does not seem to be any literature value available for *o*-chloro- and *m*-chlorobenzaldehydes based on measuring the static relative permittivity in solutions. There seems to be a constant difference of 0.2 D in the moments for *o*- and *m*-nitrobenzaldehydes when compared to their literature values, a point worth noting. An experimental error of this magnitude seems to be unlikely.

The dielectric relaxation times for *o*-nitrobenzaldehyde and *p*-nitrobenzaldehyde in *p*-xylene and for *o*-chlrobenzaldehyde in *p*-dioxane have been determined by Mehrotra and Saxena[9] at a temperature of 22 °C, using the Gopala Krishna (G.K.) method.[8] The method adopted over here is different, for reasons already stated. The viscosity of *p*-xylene when compared to benzene is within 1%. A comparison of the τ values in the two solvents determined by the same method is therefore of interest. By using the G.K. method, our data yields the $\tau_{\text{G.K.}}$ values for *o*-nitrobenzaldehyde and for *p*-nitrobenzaldehyde in benzene solution as 14.1 ps and 10.8 ps respectively. On the basis of the standard errors of estimates in the parameters a_0, a', a'', and a_D, given in Table 1, the standard error in the estimate of the τ values is 10%. The agreement in the τ values is reasonably good when a temperature difference of 8 °C and a change in the nature of the solvent is considered. The τ value for *o*-chlorobenzaldehyde is 19.2 ps/30 °C when compared to its literature value of 16.6 ps/22 °C. Obviously, there is no explanation for the disagreement. The authors have not quoted the accuracy in their determination of the τ value.

The remarks made in the previous section lead us to the conclusion that the τ values given in Table 2 correspond either to those for the overall rotation or to that of the longest relaxation time of the molecule. The results also indicate that these molecules have a higher frequency dipolar absorption. This is evidenced by a large difference between the a_{∞_2} and the a_{∞_1} values, given in Table 2. The difference between the a_{∞_2} and a_{∞_1} values has also been thought of in terms of the dipole moment for the internal rotations ($\mu_{\text{int.rot}}$) of these molecules. From the structural considerations of these molecules alone, one would not expect any moment for the internal rotations for the chlorobenzene or the nitrobenzene molecules. This is because rotations of the chloro or the nitro group along their respective bonds to the carbon atom of the molecules do not give rise to a change in the direction of the dipole moment. But the situation is, however, different when the –CHO group is attached to the benzene ring. The dipole makes an angle of 55° with the C–C bond. The rotations of the –CHO group along the C–C bond of these molecules as shown

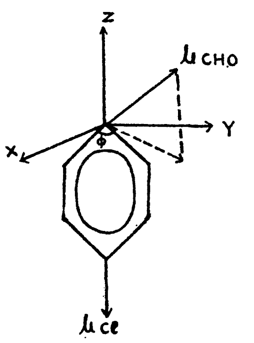

Fig. 1. *p*-Chlorobenzaldehyde.

TABLE 2. CALCULATED VALUES OF THE DIELECTRIC RELAXATION TIME FOR OVERALL ROTATION, THE ELECTRIC DIPOLE MOMENT AND THE DIPOLE MOMENT FOR INTERNAL ROTATIONS

Medium	$\tau(=\tau_{(2)})\times 10^{12}$ s		Dipole moments μ (D)		a_{∞_2}	a_{∞_1}	$(a_{\infty_2}-a_{\infty_1})$	$\mu_{\text{int.rot.}}$ (D)
	Expt. value	Lit. value	Experiment	Literature				
			o-Chlorobenzaldehyde					
Benzene	18.5	—	3.09	—	2.09	0.342	1.748	1.55
Cyclohexane	16.7	—	3.02	—	1.73	0.427	1.303	1.51
Carbon tetrachloride	21.5	—	3.04	—	2.47	0.687	1.783	1.17
p-Dioxane	26.4	16.6[9,a]	3.14	—	1.37	0.543	0.827	0.99
Nujol	33.8	—	2.83	—	1.54	0.358	1.182	1.30
			m-Chlorobenzaldehyde					
Benzene	18.0	—	2.69	—	1.41	0.360	1.050	1.20
Cyclohexane	17.8	—	2.73	—	1.48	0.402	1.078	1.35
Carbon tetrachloride	33.4	—	2.78	—	2.76	0.620	2.140	1.29
p-Dioxane	30.2	—	2.67	—	1.29	0.550	0.740	0.94
Nujol	63.9	—	2.59	—	1.15	0.349	0.804	1.06
			p-Chlorobenzaldehyde					
Benzene	30.2	—	2.08	2.05[19]	1.40	0.369	1.031	1.19
p-Dioxane	24.6	—	2.01	—	0.89	0.561	0.329	0.63
			o-Nitrobenzaldehyde					
Benzene	23.8	14.9[9,a]	4.44	4.26[20],	3.36	0.412	2.943	2.04
Cyclohexane	17.7	—	4.32	4.30[17]	2.95	0.391	2.559	2.20
Carbon tetrachloride	23.2	—	4.26	—	3.49	0.721	2.769	1.52
p-Dioxane	39.5	—	4.62	4.35[20]	2.52	0.545	1.975	1.60
			m-Nitrobenzaldehyde					
Benzene	25.8	—	3.55	3.32[20]	1.86	0.381	1.479	1.60
Carbon tetrachloride	29.3	—	3.54	—	2.92	0.701	1.919	1.36
p-Dioxane	37.6	—	3.59	3.39[20]	1.50	0.596	0.904	1.08
			p-Nitrobenzaldehyde					
Benzene	32.4	12.3[9,a]	2.43	2.40[21] 2.43[19], 2.47[20]	1.643	0.381	1.262	1.34
p-Dioxane	35.2	—	2.53	2.65[20]	1.176	0.599	0.577	0.85

a) These literature values are for τ in *p*-xylene solvent and are calculated using the Gopala Krishna method.

in Fig. 1, can be depicted by resolving the dipole moment, in three components along the Cartesian axes. The problem is illustrated by considering the case of *p*-chlorobenzaldehyde as shown in Fig. 1.

Let θ be the angle between the μ_{CHO} and the C–C bond and ϕ be the angle that the projection of μ_{CHO} on the X–Y plane, makes with the x-axis.

$$\mu_x = \mu_{\text{CHO}} \sin\theta \cos\phi$$

$$\mu_y = \mu_{\text{CHO}} \sin\theta \sin\phi$$

$$\mu_z = \mu_{\text{CHO}} \cos\theta - \mu_{\text{C-Cl}}$$

On the basis of free rotations of the groups, the total dipole moment and the dipole moment for internal rotations in these molecules can, therefore, be written as

$$\mu = (\mu_{\text{CHO}}{}^2 + \mu_{\text{C-Cl}}{}^2 - 2\mu_{\text{CHO}}\cdot\mu_{\text{C-Cl}}\cdot\cos\theta)^{1/2}$$

$$\mu_{\text{int.rot.}} = \mu_{\text{CHO}} \sin\theta$$

The determined values of $\mu_{\text{int. rot.}}$ are nearly consistent with the model. However, the difference is that the angle θ comes out to be of the order of 45 °C. There are several approximations made in calculating the resultant dipole moment of the molecule. One of them is that an addition of another group to the benzaldehyde molecule leads to a change in the angle which the dipole of the –CHO group makes with the C–C bond. Secondly, the magnitude of the group moment of the –CHO group changes with an addition of another polar group to the molecule due to the phenomenon of mesomerism. It may be desirable to mention here that the dipole moment studies of the nitrobenzaldehydes[17] reveal that the dipole of the –CHO group makes an angle of 36.5° with the C–C bond.

The dependence of the magnitude of $\mu_{\text{int. rot}}$ on the solvent can be interpreted in terms of its interactions with the –CHO group. A lower value possibly indicates hindrances to free rotations of the –CHO group. One notices that the values of the $\mu_{\text{int. rot.}}$ in cyclohexane, particularly for *o*-chlorobenzaldehyde and *o*-nitrobenzaldehyde, are higher when compared to other solvents. Therefore there is a possibility of the interaction of the remaining solvents with the benzaldehyde group. These observations are extended further by considering a plot of log τ *versus* log η, shown in Fig. 2, for these molecules. Firstly, one

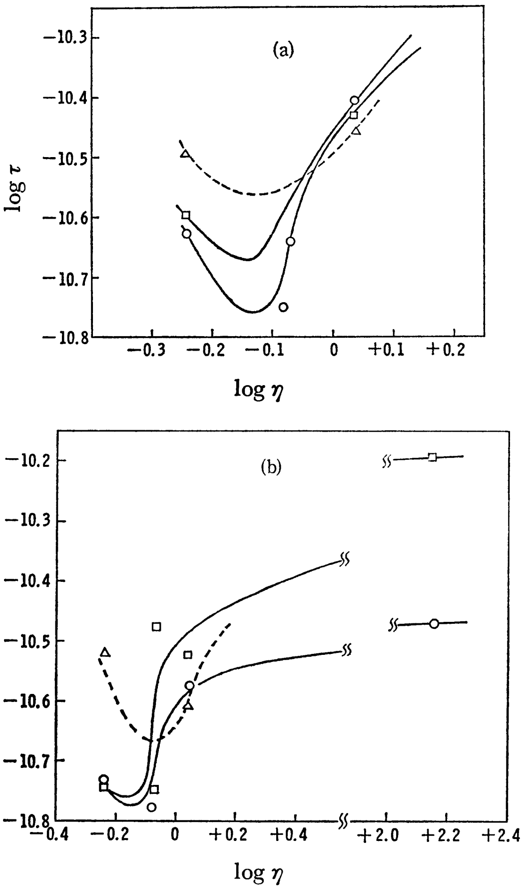

Fig. 2. Plot of log τ *vs.* log η.
(a) ○: *o*-Nitrobenzaldehyde, □: *m*-nitrobenzaldehyde, △: *p*-nitrobenzaldehyde.
(b) ○: *o*-Chlorobenzaldehyde, □: *m*-chlorobenzaldehyde, △: *p*-chlorobenzaldehyde.

notices that the τ values for the molecules increase from the *o*- to *p*-substituents through the *m*-position for both the chlorobenzaldehydes and nitrobenzaldehydes. Secondly, the τ values for the isomers of the nitrobenzaldehyde are larger than the corresponding isomer of the chlorobenzaldehyde. This trend is repeated by nearly all the solvents. The first observation is in line with our ealier studies[11)] on the chloroanilines, and is thought of arising due to the shape of the molecule. Possibly, this indicates that the greater the departure from the spherical shape, the longer is the dielectric relaxation time for the molecule. In the case of the *p*-substituent the molecule is elongated in comparison with the *o*- and *m*-substituents and therefore the dielectric relaxation time appears to increase in the following order, *o*-, *m*-, and *p*-substituent. The second observation can be explained on the basis of the molecular volumes. The molecular volume for the nitrobenzaldehydes is approximately 20% higher than the value for the chlorobenzaldehydes.

One of the interesting features of these studies is that the dielectric relaxation time in benzene, τ_B, for the molecules under study seems to be larger than anticipated because of the low viscosity of benzene when compared with the values in other solvents. It is suggested that these molecules could be undergoing an interaction with the benzene molecules. The effect seems to be independent of the isomer and appears to be a result of the aldehyde group only. There is a possibility of transfer of π-electrons from the benzene ring to the C=O bond resulting to the formation of a complex. This could account for the increase in the dielectric relaxation time of the molecules in benzene and in a decrease of the dipole moment for the internal rotations of the –CHO group. Similarly, the dielectric relaxation times in carbon tetrachloride for the three molecules A, B and D, are larger by about 30% of the τ values of these molecules in cyclohexane. The viscosity of carbon tetrachloride over cyclohexane is only 3% greater. The anomalous behavior of the carbon tetrachloride follows a general trend exhibited by a number of molecules. This is thought of being due to the 'sticky' nature of the carbon tetrachloride which arises possibly from the fairly large short range forces between the molecules of the solute and of the carbon tetrachloride. The effect is further evidenced by comparatively small magnitude of the dipole moment for internal rotations of the –CHO group in carbon tetrachloride. The dielectric relaxation times in *p*-dioxane when compared to those in other solvents are expected on the basis of its viscosity alone. There is no great difference in the total dipole moment values of the molecules in dioxane and in benzene. These observations are in contrast to those already reported on anilines.[13,18)] One would have normally expected a hydrogen bonding between the hydrogen atom of the –CHO group and the oxygen atom of the dioxane molecule. The findings suggest that such a bonding, if at all there, is fairly weak. Possibly, the oxygen atom of the –CHO group does not allow formation of the intermolecular bond. It is suggested that a qualitative experimental study of these system should be made in order to verify these predictions.

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