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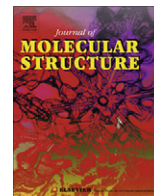


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Intra- and intermolecular H-bond mediated tautomerization and dimerization of 3-methyl-1,2-cyclopentanedione: Infrared spectroscopy in argon matrix and CCl₄ solution

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ABSTRACT

Mid-infrared spectra of 3-methyl-1,2-cyclopentanedione (3-MeCPD) have been recorded by isolating the molecule in a cold argon matrix (8 K) and also in CCl₄ solution at room temperature. The spectral features reveal that in both media, the molecule exists exclusively in an enol tautomeric form, which is stabilized by an intramolecular O—H...O hydrogen bond. NBO analysis shows that the preferred conformer is further stabilized because of hyperconjugation interaction between the methyl and vinyl group of the enol tautomer. In CCl₄ solution, the molecule undergoes extensive self association and generates a doubly hydrogen bonded centrosymmetric dimer. The dimerization constant (K_d) is estimated to have a value of $\sim 9 \text{ L mol}^{-1}$ at room temperature (25 °C) and the thermodynamic parameters, ΔH° , ΔS° and ΔG° , of dimerization are estimated by measuring K_d at several temperatures within the range 22–60 °C. The same dimer is also produced when the matrix is annealed at a higher temperature. In addition, a non-centrosymmetric singly hydrogen bonded dimer is also identified in the argon matrix. A comparison between the spectral features of the two dimers indicates that the dimerization effect on doubly H-bonded case is influenced by cooperative interaction between the two H-bonds.

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1. Introduction

3-Methyl-1,2-cyclopentanedione (3-MeCPD) is a natural product found in the coffee extract and responsible for coffee aroma [1]. It is a potential antioxidant and scavenges the activity of some reactive oxygen and nitrogen species such as nitric oxide (NO), superoxide radical ($\cdot\text{O}_2^-$) and their byproduct peroxyxynitrite (ONOO^-) [2]. 3-MeCPD also plays a central role in anti-inflammatory and anti-aging process of living organism [3]. It modulates the signalling pathway and target genes of the redox sensitive transcription factor, nuclear factor Kappa (NF- κ B), which plays an important role in inflammation and aging process by inducing pro-inflammatory genes [3]. In spite of being such a biologically significant system, very little attention has been paid to it for studying its structure in the ground state, and its aggregation behaviour under different physical conditions. We report here for the first time the infrared spectra of the molecule in a cold inert gas matrix and in CCl₄ solution, and also its dimerization behaviour in both media. In this regard, it is noteworthy that complexation in low temperature inert matrix can be studied in a very controlled

manner and in recent years numerous studies have been performed on different types of hydrogen bonded (HB) complexes in inert matrix [4–10].

Two six member analogues of the molecule, 3-methyl-1,2-cyclohexanedione (3-MeCHD) and 1,2-cyclohexanedione (CHD) have been studied recently by our group using vibrational spectroscopic methods [11,12]. It has been shown that both molecules exist almost exclusively in monoenol tautomeric forms in an inert gas matrix environment, and in each case the tautomeric form is stabilized by an intramolecular O—H...O H-bond between the adjacent keto and enol groups. Furthermore, in the case of 3-MeCHD, it has been found that of the two possible enol tautomers, the one where the methyl group is attached with the vinyl carbon and adjacent to the enolic group is preferred most. In addition to the intramolecular O—H...O hydrogen bonding, this tautomer is stabilized further by a weak C—H...O H-bond between the enolic oxygen and one of the methyl C—H groups. In the present five membered ring system, the angular orientation and spacial separation among the three groups (C=O, O—H and CH₃) are different compared to those of the previous systems, and in consequence – the intramolecular O—H...O H-bonding is relatively weaker. We show below that such weakening of the intramolecular H-bonding has profound effect on its affinity to form intermolecular association complexes.

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2. Materials and methods

2.1. Experimental

3-MeCPD was procured from Aldrich and purified further by vacuum sublimation. The FTIR spectra were recorded using a Bruker IFS66S Fourier transform infrared spectrometer equipped with a deuterated triglycine sulphate (DTGS) detector and a KBr beam splitter. The spectral resolution of the spectrometer throughout the measurements was 1 cm^{-1} . The spectrometer compartment was continuously purged with dry N_2 to remove water vapour and CO_2 . For matrix isolation studies, a pre-mixed gas consisting of 3-MeCPD vapour and ultrahigh pure Argon (Ar) was condensed onto a thin KBr window cooled at $\sim 8\text{ K}$ temperature by a closed cycle helium refrigerator (Advanced Research Systems, Inc., Model No.: DE202). To prepare the H-bonded dimers, the matrix was annealed at temperatures up to 25 K , and after annealing, the matrix was cooled down to 8 K for recording an FTIR spectrum.

A home-made solution cell consisting of a pair of KBr windows and a Teflon spacer of 1 mm thickness was used for measurements of the IR spectra of CCl_4 solutions. The spectra at different temperatures of the sample solutions were recorded using a home-made temperature-variation cell made with a pair of CaF_2 windows, and the path length of the cell is 1.5 mm .

2.2. Theoretical calculation

The geometries of all possible tautomers of 3-MeCPD and their hydrogen bonded dimers were optimized by B3LYP theoretical method using 6-311++G(d,p) basis set. The same theoretical method was used to calculate the gas-phase infrared spectra of all the molecular species at harmonic approximation, and also to calculate the thermodynamic quantities, ΔH° and ΔS° for complex formation at 298 K . The transition frequencies for the vibrational fundamentals of the two enol tautomers of 3-MeCPD were also calculated by anharmonic method at DFT/B3LYP/6-311++G(d,p) level, and the results presented below indicate that the predictions obtained by this method display excellent agreement with the observed frequencies. Natural bond orbital (NBO) analysis was performed to calculate the natural charges at the donor–acceptor sites and hyperconjugation interaction energies from the second order perturbation analysis of the Fock matrix. All calculations reported here were carried out using Gaussian 03 program package [13]. For calculation of the binding energies of the dimers, basis set superposition errors (BSSE) were corrected using counterpoise method of Boys and Bernardi [14]. A commercial software package OPUS 6.5 was used to perform spectral normalizations and for estimation of the vibrational band areas.

3. Results and discussion

3.1. Theoretical predictions for tautomeric preferences

In Fig. 1 we have presented the geometric shapes and relative energies corresponding to the optimized structures of the diketo and two intramolecularly hydrogen bonded enol tautomers of 3-MeCPD. Of the latter two, the one where the methyl group is adjacent to the enolic group and attached with a sp^2 hybridized carbon, labelled Enol-1 (structure b), is favoured most and energetically it is preferred over the diketo (a) and Enol-2 (c) tautomers by ~ 36.8 and $\sim 20.1\text{ kJ/mol}$, respectively. The factor that is primarily responsible for preferential stability of Enol-1 (b) over Enol-2 (c) is the hyperconjugation of the methyl C–H bonds with the vinyl group. NBO analysis has been performed for both Enol-1 and Enol-2 tautomers, and the second order perturbation analysis have been given

as [Supplementary material](#). It has been observed that in the case of Enol-1, the two out-of-plane C–H bonds have strong interactions (11.1 kJ/mol) with the vinyl C=C bond but the in-plane C–H bond does not interact. In Enol-2 such an interaction is absent because of larger separation of the methyl group from the C=C bond. In Enol-1, due to this interaction, the bond lengths of the two out-of-plane C–H bonds are elongated to 1.096 Å compared to the in-plane C–H bond (1.090 Å). In Enol-2 and diketo tautomers, the three C–H bond lengths of the methyl group are nearly the same (1.092 and 1.093 Å). All the methyl C–H bond lengths for the three tautomers are depicted in Fig. 1. A comparison of the geometric parameters of the Enol-1 tautomer with those of the most preferred tautomer of the six membered analogue, 3-MeCHD, reveals that the ring size profoundly affects the attributes of the intramolecular O–H...O H-bond. For example, the HB length of the present system is predicted significantly longer (2.318 Å) compared to that of the six membered analogue (2.042 Å) [11]. This difference implies that the H-bond in the present system is weaker, and it is consistent with the measured values of the ν_{OH} frequencies of the two systems. According to theory, the value of ν_{OH} of 3-MeCPD is predicted $\sim 50\text{ cm}^{-1}$ lower compared to that of 3-MeCHD. We show below that this difference in intramolecular HB strengths of the two molecules has dramatic effect on their tendencies to form hydrogen bonded dimers in CCl_4 solution at room temperature as well as in argon matrix. Under steady state, the singly hydrogen bonded dimer (SHBD) is likely to be a transient species. However, we show below that the rigid environment of the argon matrix allows trapping of the SHBD in addition to the more stable doubly hydrogen bonded dimeric (DHBD) species. In Fig. 1, we have shown the optimized structures of two probable dimers of the Enol-1 tautomer; centrosymmetric doubly hydrogen bonded species which we label as DHBD and a singly hydrogen bonded one which has been labelled as SHBD. Some of the relevant optimized geometric parameters of the two dimers are presented in Table 1. These data indicate that in DHBD two O–H...O intermolecular HBs gain additional stabilization via cooperative effect between the two. Thus, the said HB length in DHBD is 1.798 Å , whereas in SHBD it is 1.823 Å . In such situation, the binding energy of DHBD is expected to be more than double as compared to that of SHBD. However, the SHBD shows somewhat extra stabilization. While the binding energy of DHBD is 41.0 kJ/mol , that of SHBD is 27.6 kJ/mol . The optimized structure of SHBD presented in Fig. 1 indicates that there is an additional source of stabilization of this species in the form of C–H...O interaction between the carbonyl oxygen on one moiety and the ring C–H on the other, where the C–H...O distance is 2.35 Å . The cooperative effect is more vividly manifested in the spectral features as discussed below.

3.2. IR spectrum of 3-MeCPD in Ar matrix

In Fig. 2 (part a) we have shown the FTIR spectrum of 3-MeCPD isolated in Ar matrix at 8 K . To aid in assigning the vibrational bands in this spectrum, the theoretical infrared spectrum of the most stable Enol-1 tautomer, calculated by DFT method with B3LYP functional and 6-311++G(d,p) basis set, is presented in lower panel. Here the predicted vibrational frequencies are scaled by a factor 0.98. The intense band at 3507 cm^{-1} in the top panel has been assigned to O–H stretching fundamental (ν_{OH}) of the Enol-1 tautomer, and the obvious red shift of this vibrational frequency compared to the typical ν_{OH} values of free alcoholic groups indicates the existence of intramolecular hydrogen bond between the keto and enol groups. It is worth mentioning that the observed ν_{OH} frequency of the present system is 47 cm^{-1} higher compared to that of the six membered analogue, 3-MeCHD ($\nu_{\text{OH}} = 3460\text{ cm}^{-1}$) [11], and this difference implies that the intramolecular hydrogen bonding in the present five membered ring system is relatively

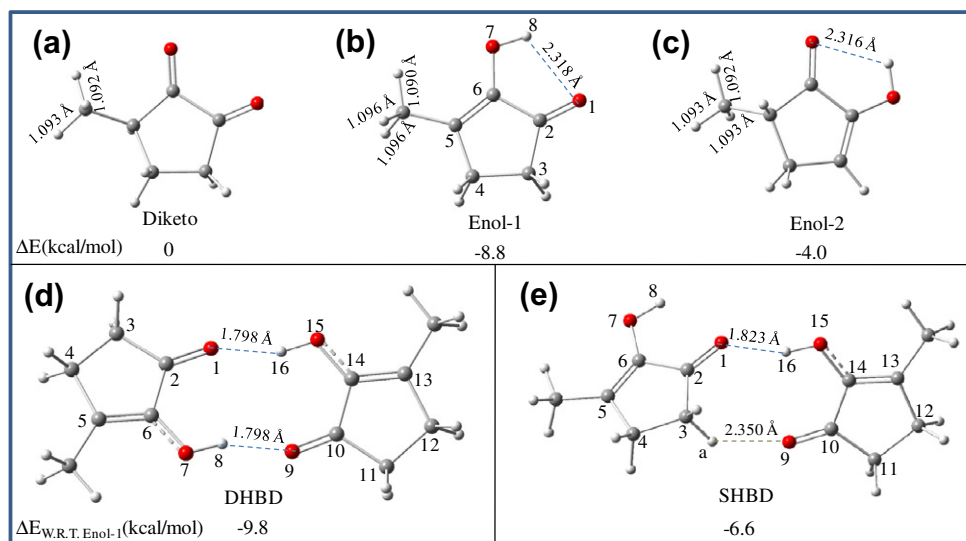


Fig. 1. Optimized structures and relative energies of the diketo (a) and two monoenol tautomers (b and c) of 3-MeCPD and doubly and singly hydrogen bonded dimers of tautomer b (d and e) calculated at B3LYP/6-311++G(d,p) level of theory.

Table 1

Some important geometrical parameters of Enol-1 tautomer of 3-MeCPD and its doubly and singly hydrogen bonded dimers calculated by B3LYP/6-311++G(d,p) level of theory.

Optimized geometrical parameters	Monomer (Enol-1)	DHBD	SHBD
O ₁ –C ₂ (Å)	1.219	1.224	1.227
C ₂ –C ₆ (Å)	1.467	1.467	1.461
C ₆ –O ₇ (Å)	1.351	1.341	1.352
O ₇ –H ₈ (Å)	0.97	0.979	0.97
C ₅ –C ₆ (Å)	1.347	1.354	1.348
O ₉ –C ₁₀ (Å)	–	1.224	1.219
C ₁₀ –C ₁₄ (Å)	–	1.467	1.472
C ₁₄ –O ₁₅ (Å)	–	1.341	1.343
O ₁₅ –H ₁₆ (Å)	–	0.979	0.981
O ₁ –H ₁₆ (Å)	–	1.798	1.823
H ₈ –O ₉ (Å)	–	1.798	–
O ₉ –H _a (Å)	–	–	2.358
O ₁ –C ₂ –C ₆ (°)	123.7	126.2	122.7
C ₂ –C ₆ –O ₇ (°)	120	124	120.5
C ₆ –O ₇ –H ₈ (°)	106.5	112.6	106.6
O ₉ –C ₁₀ –C ₁₄ (°)	–	126.3	125.8
C ₁₄ –O ₁₅ –H ₁₆ (°)	–	112.6	112.5
C ₁₀ –C ₁₄ –O ₁₅ (°)	–	124.1	123.7
O ₁ –C ₂ –C ₆ –O ₇ (°)	0	–0.4	–0.15
C ₂ –C ₆ –O ₇ –H ₈ (°)	0	–5.1	0.5
O ₉ –C ₁₀ –C ₁₄ –O ₁₅ (°)	–	–0.4	0
C ₁₀ –C ₁₄ –O ₁₅ –H ₁₆ (°)	–	–5.1	–8.94

weaker. The predicted harmonic frequency for the mode is 3635 cm^{-1} (scaled by 0.98), and the large deviation from the measured value, in spite of use of a scale factor, is an indication of significant anharmonicity of the mode. It is obvious that a single scaling factor cannot take into account of the mode dependent anharmonicity. More accurate predictions for the vibrational modes are obtained from anharmonic calculation at B3LYP/6-311++G(d,p) level, and the corresponding ν_{OH} frequency is 3515 cm^{-1} . A comparison between the harmonic and anharmonic frequencies for the IR-active vibrational fundamentals is presented in Table 2.

In the spectral region of carbonyl stretching fundamental ($\nu_{\text{C=O}}$), two intense bands are observed, at 1684 and 1731 cm^{-1} , and the same feature is also displayed in the predicted spectrum. Calculation of potential energy distributions reveals that these

two modes correspond to in-phase and out-of-phase combinations of C=O and C=C stretching, mixed partly with enolic OH bending. It is noteworthy that for the Enol-2 tautomer, calculation also predicts two modes of similar vibrational frequencies. However, the calculated intensity ratio (6:1) does not match with observation, and we infer that both the bands originate from Enol-1 tautomer only. Furthermore, each band shows a weak shoulder in the lower frequency edge, and we assign them (see below) to hydrogen bonded dimers. In the fingerprint region of the spectrum, the agreement between the observed and calculated features is satisfactory, and the detailed assignments of the vibrational bands in the spectrum are provided in Table 2. The calculated normal mode harmonic frequencies for the Enol-2 and diketo tautomers and their assignments are given in Supplementary material.

3.3. Infrared spectroscopy of the dimer

3.3.1. Dimerization in Ar matrix

In a well-dispersed argon matrix, dimerization of the doped molecules is initiated only when the matrix is annealed and the molecules are allowed to diffuse close to each other through the non-rigid matrix. In the present study, the Ar matrix was annealed at 17 K and 23 K , and before recording the spectra, the matrices were cooled down to 8 K . In Fig. 3, we have displayed the two annealed spectra along with the one before annealing. It is seen that upon annealing, the intensities of the two $\nu_{\text{C=O}}$ monomer bands at 1731 and 1684 cm^{-1} are diminished with appearance of several new bands at lower frequencies, and we assign these lower frequency bands to H-bonded dimers of 3-MeCPD.

It has been mentioned before that in addition to the most stable doubly hydrogen bonded dimer (DHBD), the rigid environment of the matrix can also trap singly hydrogen bonded dimeric species (SHBD). Therefore, in order to interpret the new spectral features developed in Fig. 3 upon annealing, we have presented in the lower two panels the predicted IR fundamentals corresponding to $\nu_{\text{C=O}}$ and ν_{OH} transitions of the two dimers. For the C_2 symmetric DHBD, calculation predicts two IR active $\nu_{\text{C=O}}/\nu_{\text{C=C}}$ normal modes at 1711 and 1662 cm^{-1} of relative intensities 100 and 49, respectively. On the basis of the correspondences between the band structures in the upper and lower panel of Fig. 3, we assign the 1714 and 1663 cm^{-1} bands of the measured spectra to the two $\nu_{\text{C=O}}$ funda-

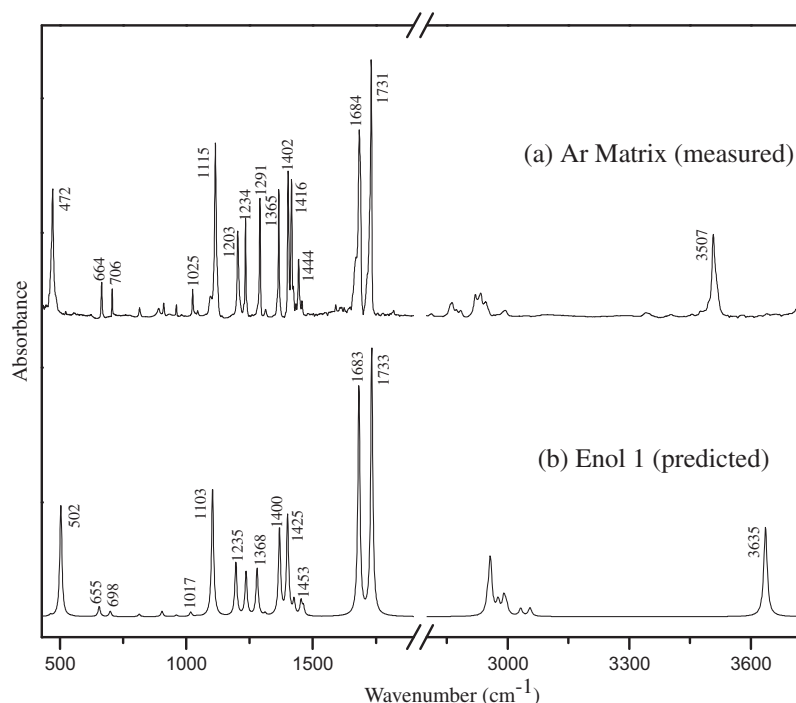


Fig. 2. The FTIR spectrum of 3-MeCPD in Ar matrix (a) and calculated spectrum of Enol-1 tautomer (b) at B3LYP/6-311++G(d,p) level.

Table 2

Assignments of the vibrational bands in the matrix isolation FTIR spectrum of 3-MeCPD.

Experimental frequency in Ar matrix (cm^{-1})	Calculated frequency B3LYP/6-311++G**		Assignment
	Harmonic (scale factor .98)	Anharmonic	
3507	3635	3515	$\nu_{\text{O-H}}$
2993	3054	2966	$\nu_{\text{C-H}}$ (methyl)
2945	2949	2938	$\nu_{\text{C-H}}^{\text{asym.}}$
2933	3031	2936	$\nu_{\text{C-H}}^{\text{sym.}}$
2920	2995	2923	$\nu_{\text{C-H}}^{\text{asym.}}$ (methyl)
2884	2956	2901	$\nu_{\text{C-H}}^{\text{sym.}}$ (methyl)
2862	2975	2879	$\nu_{\text{C-H}}^{\text{C-H}}$
1731	1733	1733	$(\nu_{\text{C=O}} + \nu_{\text{C=C}})_{\text{IP}} + \delta_{\text{O-H}}$
1684	1683	1679	$(\nu_{\text{C=O}} + \nu_{\text{C=C}})_{\text{IP}} + \delta_{\text{O-H}}$
1457	1463	1458	$\delta_{\text{C-H}}$ (scissoring)
1444	1453	1446	$\delta_{\text{C-H}}$ (methyl)
1416	1425	1412	$\delta_{\text{C-H}}$ (scissoring)
1402	1400	1386	$\delta_{\text{O-H}}^{\text{IP}} + \delta_{\text{C-H}}$ (methyl)
1365	1368	1356	$\delta_{\text{O-H}}^{\text{IP}} + \delta_{\text{C-H}}$ (methyl)
1291	1279	1302	$\delta_{\text{O-H}}^{\text{IP}} + \delta_{\text{C-H}}$ (wagging)
1234	1235	1228	$\delta_{\text{C-H}}$ (wagging)
1203	1196	1195	$\nu_{\text{C=O}} + \delta_{\text{C}^3/4-\text{H}}$ (wagging)
1115	1103	1094	$\nu_{\text{C}^2-\text{C}^3} + \nu_{\text{C}^6-\text{O}} + \delta_{\text{C}^4-\text{H}}$
1044	1040	1038	$\delta_{\text{C}^3/4-\text{H}}$ (rocking)+ $\delta_{\text{C-H}}$ (methyl)
1025	1017	1042	$\delta_{\text{O-H}} + \delta_{\text{C-H}}$ (methyl)
960	960	965	$\delta_{\text{C}^3/4-\text{H}}$ (rocking)+ $\delta_{\text{C-H}}$ (methyl)
909	903	900	$\delta_{\text{C-H}}$ (methyl)
815	813	815	$\nu_{\text{C}^4-\text{C}^5}$ (rocking)
706	698	702	Ring breathing
664	655	658	Ring deformation
472	502	523	$\delta_{\text{O-H}}^{\text{OP}}$

ν = stretching, δ = bending.

mentals of the molecule in DHBD and 1723 and 1668 cm^{-1} bands to the same two transitions in SHBD. The predicted normal mode frequencies for the SHBD are 1721 and 1667 cm^{-1} . To exclude the possibility that the bands assigned to SHBD are not due to site splitting of DHBD or monomer, we have performed the measurement also in N_2 matrix. The site splitting pattern in N_2 and Ar matrices are expected to be different but the genuine vibrational bands should appear in the same pattern, and usually show only small shifts, which depend upon the nature of the vibrational mode. The $\nu_{\text{C=O}}$ region of the spectrum recorded in a nitrogen matrix is shown in the inset-2 of Fig. 3. It is seen that except of a small spectral shift, the general features of the spectra in both matrices are identical. For example, the 1714 (assigned to DHBD) and 1723 cm^{-1} (assigned to SHBD) bands of the argon matrix spectrum for one of the $\nu_{\text{C=O}}$ modes reappear at 1715 and 1724 cm^{-1} , respectively, in the nitrogen matrix. For the other $\nu_{\text{C=O}}$ mode, the DHBD and SHBD bands appear more prominently in nitrogen matrix without any spectral shifts. Furthermore, upon annealing, there is a possibility that the SHBD forms higher order clusters which is not possible in case of DHBD. Of course, there are a few weaker bands near 1690 and 1640 cm^{-1} which develop upon annealing, and those could be due to higher order clusters.

In the ν_{OH} region, the monomer peak appears at 3507 cm^{-1} and after annealing a broad band develops with the maxima at 3300 cm^{-1} along with a sharp hump at 3339 cm^{-1} . We assign the latter feature to the ν_{OH} band of the SHBD, and the broad feature to ν_{OH} of DHBD. This assignment has been corroborated by noting that in CCl_4 solution at room temperature, the sharp feature assigned to SHBD disappears (see below). Here much larger broadening and shift of the ν_{OH} band of DHBD is a manifestation of cooperative interactions between the H-bonds. It is worth mentioning that such spectral broadening is a common trait of doubly hydrogen bonded dimers involving OH/NH groups, and has been observed before in the IR spectra of the dimers of Benzoic acid [15], acetic acid [16,17], 7-Azaindole [18], etc. Theoretical studies have revealed that both homogeneous and inhomogeneous factors contribute to the broadening [17,18].

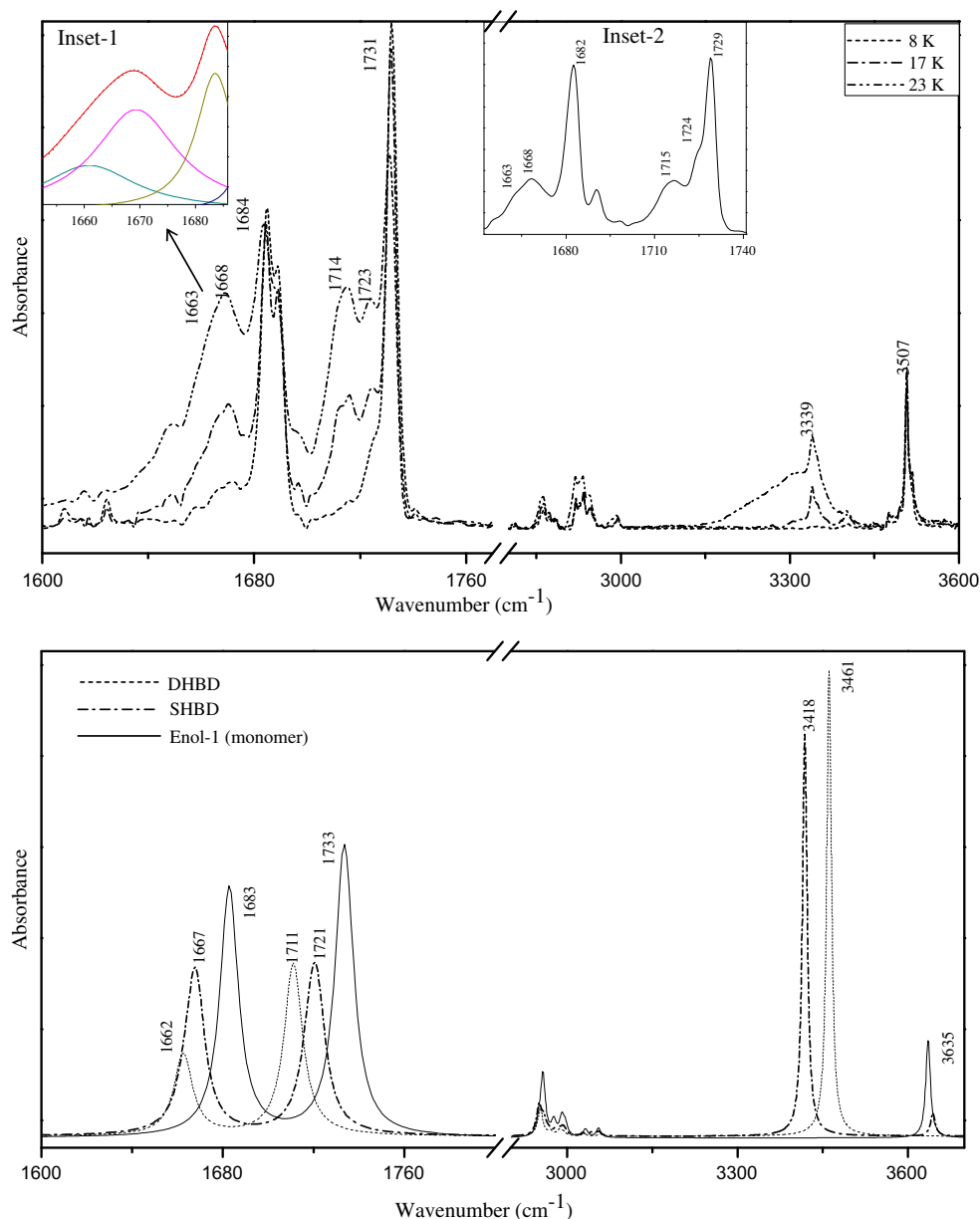


Fig. 3. Matrix isolation FTIR spectra of 3-MeCPD in Ar matrix (upper panel) at 8 K temperature and annealed spectra at 17 K and 23 K along with the theoretically predicted infrared spectra (lower panel) of Enol-1, SHBD and DHBD at B3LYP/6-311++G(d,p) level. Inset-1 shows the curve fitting of the band near 1670 cm⁻¹ and inset-2 shows the FTIR spectrum of 3-MeCPD in N₂ matrix in $\nu_{\text{C=O}}/\nu_{\text{C=C}}$ region.

3.3.2. Dimerization of 3-MeCPD in CCl₄ solution

We have recorded the FTIR spectra of 3-MeCPD for several sample concentrations within the range of 0.01–0.03 M in CCl₄ solution, and the segments of the $\nu_{\text{C=O}}$, $\nu_{\text{C-H}}$ and $\nu_{\text{O-H}}$ regions of those spectra are shown in Fig. 4. The spectra are presented after normalization with respect to $\nu_{\text{C-H}}$ fundamentals, because these bands are almost insensitive to dimerization of the molecules. In CCl₄, two $\nu_{\text{C=O}}$ vibrational fundamentals of the monomer appear at 1675 and 1721 cm⁻¹, i.e., with respect to Ar matrix, both the bands show ~10 cm⁻¹ red shift. With increase in sample concentration, the intensity of both the monomer bands diminishes with development of two new bands at lower frequencies whose band maxima appear at 1663 and 1708 cm⁻¹. We assign these two new bands to doubly H-bonded dimer of 3-MeCPD (Fig. 1d). Here, both $\nu_{\text{C=O}}$ bands undergo ~13 cm⁻¹ red shifting upon dimerization, and this agrees quite well with the predicted red shift (20 cm⁻¹) by electronic structure calculation at B3LYP/6-311++G(d,p) level. The

inset presented in the frame of Fig. 4 shows that the changes in relative intensities of the monomer and dimer $\nu_{\text{C=O}}$ bands for varying the sample concentration results to a distinct isosbestic point, and this indicates that only two species, monomer and dimer, are in equilibrium in the CCl₄ solution.

The changes of the spectral features of the ν_{OH} band of the molecule upon dimerization in CCl₄ solution are nearly similar to what has been observed in argon matrix. With increase in sample concentration, the monomer band at 3504 cm⁻¹ is gradually diminished with appearance of a broad dimer feature in range of 3450–3200 cm⁻¹ with maximum at 3345 cm⁻¹. Here the most striking feature is that the sharp peak in the matrix spectrum, assigned to ν_{OH} of SHBD does not show up, because this species in solution is a transient one. To confirm that the broad peak is originating from only DHBD and not from any higher order clusters, we have normalized three spectra for three different concentration with respect to the broad peak and it is seen that their is no con-

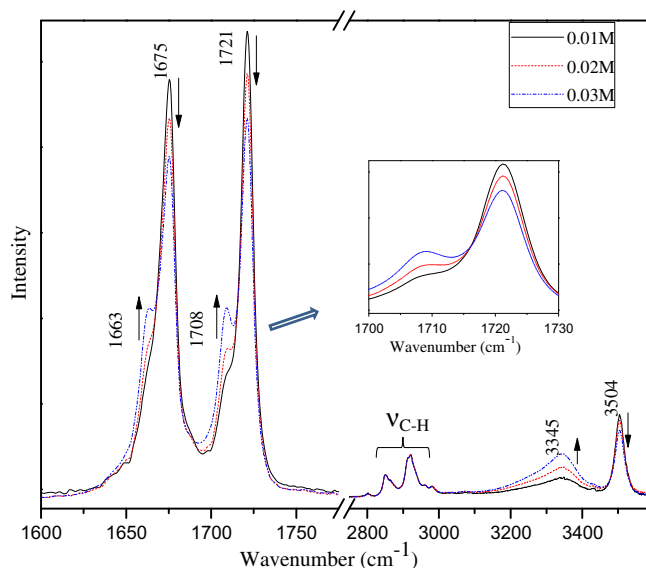


Fig. 4. Normalized spectra recorded for three different concentration of 3-MeCPD in CCl_4 solution. The normalization has been performed with respect to ν_{CH} fundamentals.

centration dependent asymmetry. If the higher order clusters are produced with increasing concentration, the broad feature would have appeared asymmetric at red and blue edges. Thus, we conclude that only DHBD is produced in CCl_4 solution. It is worth mentioning that the six membered analogue of this compound does not undergo dimerization in CCl_4 solution at room temperature and one of the possible reasons is due to presence of much stronger intramolecular hydrogen bonding between the keto and enol groups.

3.3.2.1. Determination of dimerization constant (K_d). The dimerization constant (K_d) has been estimated following the approaches described in Refs. [19,20]. In the first approach, only the change in intensity of the ν_{OH} band of the monomer with sample concentration is monitored, and in the second approach, the intensity changes of both monomer and dimer ν_{OH} bands are taken into consideration. Basic aspects of the two approaches are briefly described in [Supplementary material](#). From the first approach, estimated value of K_d is 9.4 L mol^{-1} and that from the second is 8.4 L mol^{-1} . Thus, the estimated values of K_d by the two approaches are nearly same.

3.3.2.2. Temperature variation study and determination of the thermodynamic parameters. The FTIR spectra in CCl_4 solutions for the two said sample concentrations have been recorded at seven different temperatures, 22, 30, 35, 40, 45, 50 and 60°C , using a home-built temperature-variation cell, and the spectral changes are depicted in [Fig. 5](#). At each temperature, K_d has been estimated following the second approach mentioned above, and the results are presented in [Table 3](#).

The thermodynamic parameters, ΔH° and ΔS° , for the dimerization process have been worked out using the van't Hoff equation

$$\ln K_d = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

The van't Hoff plot, $\ln K_d$ vs $1/T$, is shown in the inset of [Fig. 5](#), and the estimated values of the two thermodynamic parameters are presented in [Table 4](#). The values for these parameters predicted by electronic structure calculation are also presented in [Table 4](#) for comparison. The deviations between experimental and theoretical values, as we see in our study, are comparable with the deviations determined for dimerization of lactams by Adler et al. [19].

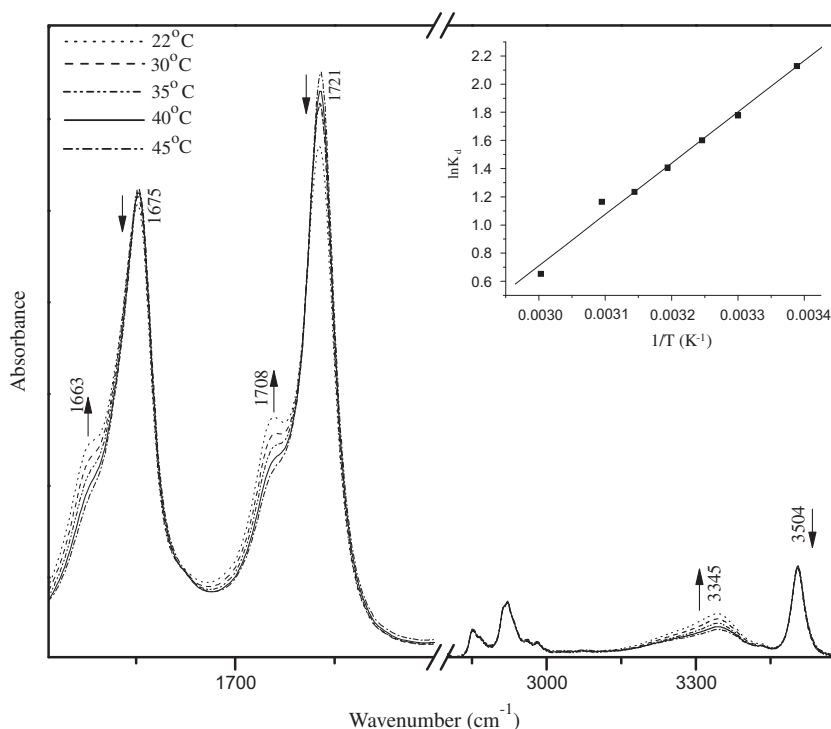


Fig. 5. Spectral evolution with temperature variation for 0.03 M 3-MeCPD in CCl_4 . The inset represents Van't Hoff plot showing the temperature dependence of equilibrium constant.

Table 3

Estimated dimerization constants of 3-MeCPD at different temperatures. At each temperature the dimerization constant has been calculated following the approach as in Ref. [20].

Temperature (°C)	Dimerization constant (K_d) in L mol^{-1}
22	8.4
30	5.9
35	4.9
40	4.1
45	3.4
50	3.2
60	1.9

Table 4

Estimated thermodynamic parameters of dimerization from van't Hoff plot and the theoretical values at 298 K.

	Experimental	Theoretical (298 K)
ΔH° (kJ mol^{-1})	−30.3	−36.1
ΔS° ($\text{JK}^{-1}\text{mol}^{-1}$)	−84.9	−108.8
ΔG° (kJ mol^{-1})	−4.9	−3.7

4. Summary

Here, we have reported for the first time the mid-infrared spectra of 3-methyl-1,2-cyclopentanedione in a cold argon matrix and also in CCl_4 solution at room temperature. The spectral features reveal that in both media, the molecules exist exclusively in a monoenol tautomeric form, which is stabilized by an intramolecular H-bond as well as hyperconjugation involving the methyl group. Electronic structure calculation reveals that the intramolecular H-bonding in the five membered ring system is much weaker compared to that of its six member analogue, 3-methyl-1,2-cyclohexanedione. We have shown that this difference profoundly influences the dimerization efficiency of the two molecules through intermolecular H-bonding. While the present system undergoes efficient dimerization in CCl_4 solution as well as in solid argon matrix, no dimerization under similar condition was detected for the six membered species by FTIR spectroscopy. Measuring the changes of the relative intensities of monomer and dimer ν_{OH} bands for several sample concentrations in CCl_4 solution, the dimerization constant was estimated to be $\sim 9 \text{ L mol}^{-1}$. The thermodynamic parameters, ΔH° , ΔS° and ΔG° have also been estimated by measuring K_d at a series of temperatures, and the estimated values show nice agreement with those calculated by theoretical methods at B3LYP/6-311++G(d,p) level. Furthermore, the spectra also reveal trapping of a singly hydrogen bonded dimeric species in argon matrix, and the measured spectral shifts

of the $\nu_{\text{C=O}}$ bands of the two dimers display very good agreement with those predicted by electronic structure calculation.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.molstruc.2011.03.002](https://doi.org/10.1016/j.molstruc.2011.03.002).

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