Experimental, DFT dimeric modeling and AIM study of H-bond-mediated composite vibrational structure of Chelidonic acid

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ARTICLE INFO

Keywords:
Theoretical chemistry
Physical chemistry
Molecular physics

ABSTRACT

The composite vibrational structure near 3650-3200 and 3000-2400 cm⁻¹ in the observed IR absorption spectrum of Chelidonic acid has been explained in terms of intra- and inter-molecular –O–H···O H-bonding attributed to monomer and dimer species computed at B3LYP/6-311++G(d,p) level. Three of the six dimer species derived out of ten monomeric components have shown both intra- and inter-molecular H-bonding. Vibrational modes of the monomer and dimer species are satisfactorily identified with the observed IR and Raman bands including frequency shifts associated with the H-bondings. The H-bond interactions in the monomer and dimer species have been characterized in terms of electron density, ρ(ψ), its Laplacian, \( \nabla^2 \rho(\psi) \) and potential energy density at the O···H bond critical points (BCPs) based on the Atoms in Molecules (AIM) theory. The attractive (van der Waals, H-bonds) and repulsive steric clash (SC) interactions are explained using computed reduced density gradient values from the noncovalent interaction (NCI) method. The AIM analysis confirms the presence of the intra- and inter-molecular H-bondings in the monomer/dimer species. The natural bond orbital (NBO) analysis of the natural charges and stabilization energy of the H-bonds for the dimer species further points to the stronger inter-than intra-molecular H-bonding.

1. Introduction

The intra- and inter-molecular H-bonding in carboxylic acid (CBA) dimeric units are of unwavering interest and are commonly characterized by IR spectroscopic studies of –O–H stretching vibrations in the region 4000–400 cm⁻¹ [1-6]. The most common form of H-bonding is the dimerization between the two carboxylic groups often cyclically bound by a local center of inversion, resulting in a larger down-shift of the –O–H stretching frequency of the dimeric carboxylic acids (3000–2500 cm⁻¹) [1]. Diverse complexes such as these dimeric species governed by the structure and strength of the H-bonds have been largely the subject of intense experimental and theoretical studies with wider implications in multidisciplinary subjects [7, 8, 9, 10, 11]. In addition to their biological interest and anti-carcinogenic drug properties, the study of homo-/hetero-complexes of CBAs in gaseous, liquid, and solid states have provided insights into the nature of noncovalent interactions including –O–H···O=O=C interactions [12, 13, 14, 15]. In the recent past, studies on simple CBA systems, for example, the formic acid dimer species participating in strong to weak inter-molecular interactions have been reported [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15]. However, there have been apparently fewer similar investigations of the H-bond induced composite vibrational structure of the benzenedicarboxylic acids (BDAs) [16, 17, 18, 19, 20, 21]. Recently, Karabacak et al have assigned IR and Raman modes of the solid isophthalic acid on the basis of computed monomers and O···O bound dimer species [19]. Ab initio predictions of the effects of temperature and solvation on the dimerization of benzoic acid have been reported by Taylor et al [22]. They conclude that benzoic acids form strong H-bonds with each other in different complexes but a cyclic dimer among them is the most stable configuration. Martinsovich et al have reported modeling of the self-assembly of BDAs using Monte-Carlo and molecular dynamics simulations (MD) [23]. The structural studies by R. Alcala et al, J.L. Derissen and by M. He et al on isophthalic acid and 5-Fluoroisophthalic acid also supported the ordered cyclic structures stabilized by double O···H···O bonds between two carboxylic groups [24, 25, 26].

In the present work, we report extensive study of the structural, vibrational and electronic properties of the conformational and dimerization aspects of H-bonded species of Chelidonic acid (CA for short; it is also called 4-Oxo-4H-pyran-2,6-dicarboxylic acid, C₇H₄O₆, see Fig. 1). The CA is a pyran skeleton with dicarboxylic acid group and is a suitable intermediate in certain synthesis work but more importantly its pharmacological effects and therapeutic potential have been demonstrated.
[27, 28, 29]. From structural and spectroscopic view-points, the CA is an attractive candidate for the investigation of H-bonding in the formation of dimer species. This has been borne out by the observation of broad IR absorption bands near 3650–3200 cm⁻¹ with a series of bands in 3000–2400 cm⁻¹ (Fig. 2(a), see also Fig. S1, Supplementary Material). This vibrational structure extending from 3650 to 2400 cm⁻¹ including two IR and Raman bands near 1648 and 1723 cm⁻¹ is the apparent manifestation of intra- in monomer and both intra- and inter-molecular O—H⋅⋅⋅O bonding in the dimer species of CA (see Fig. 2). We have computed all the possible dimer species at B3LYP and BP86 methods combined with the 6-31G(d) and 6–311++G(d,p) basis sets, yielding six dimer species of which three are inter-molecularly H-bonded and three are mixed inter- and intra-molecularly H-bonded species. In the proposed dimer models, the two carboxylic motifs simultaneously act as H-bond donor and acceptor. The inter-H-bonds are strong since computed interaction energy per bond is 9 kcal/mol. As a consequence, the O—H and C=O stretching modes have shown large red-shifts in frequencies with broadening of the bands. We have shown that the simulated IR bands spectra derived from six dimer species of CA are in agreement with the measured spectrum in the 3700–400 cm⁻¹. Furthermore, we have characterized the inter- and intra-H-bonding in the dimer species as noncovalent interactions by the electron density topological analysis by employing the quantum theory of Atoms in Molecules (AIM) and non-covalent interaction (NCI) methods. The charge transfer in the monomer and dimer species due to the H-bonding interactions is explained using the natural bond orbital (NBO) analysis.

2. Methods

2.1. Experimental methods

The sample of Chelidonic acid (Sigma-Aldrich, part of Merck; assay, 98.0%; mp 265 °C) was used as received. The IR absorption spectrum of the sample was measured at room temperature using standard KBr pellet technique. The spectrum was measured at 2 cm⁻¹ resolution with 100 scans in the range 4000–400 cm⁻¹ on a Thermo-Fisher Nicolet 6700 FT-IR spectrometer equipped with a KBr beam splitter, a ETC EverGlo mid-IR radiation source, and a deuterated L-alanine doped triglycine sulfate (DLaTGS) detector. The Raman spectrum was measured from 3500–100 cm⁻¹ at a spectral resolution of 2 cm⁻¹ with a Thermo-Fisher NXR 6700 FT-Raman module spectrometer, equipped with a diode-pumped air cooled Nd:YVO₄ laser source (1064 nm excitation line) and a LN2 cooled high-performance Ge detector. The spectra were averaged over 500 scans. Both the spectrometers were purged with nitrogen to remove the interference due to the atmospheric CO₂ and moisture. The solid-phase near-IR (NIR) spectrum of Chelidonic acid was measured in the 4000–8000 cm⁻¹ region and for the sake of brevity, the analysis has been presented in the section S10 (see also Fig. S10a).

2.2. Computational methods

All the electronic structure calculations were performed using the Gaussian 09W, GaussView 5, Multiwfn, VMD and Chemcraft suite of programs [30, 31, 32, 33, 34, 35]. Molecular structure of CA is presented in Fig. 1. Initially, the conformational search was performed by a relaxed potential energy surface scan (PES) at B3LYP/6-31G(d) level by rotating the two –COOH groups from 0° to 350° with step of 10° (see Fig. S11). The initial PES scan at B3LYP/6-31G(d) level reduced the computational cost. However, this level for H-bonded structures is known to produce less accurate geometrical and energetic parameters when compared to the experimental values. Moreover, in addition to the inclusion of the electron correlation effects on geometry optimization as defined in the B3LYP method, the use of flexible basis set with polarization and diffuse functions on hydrogen atom orbitals is necessary for the accurate description of H-bond interactions. These basis set requirements are usually met by using the flexible and extended basis set 6–311++G(d,p). Therefore, in the present study, we used 6–311++G(d,p) basis set for the calculations. We found ten minima on the PES which were again optimized at the B3LYP/6–311++G(d,p) level. Moreover, the harmonic frequency analysis at the same level confirmed all the ten minima as true stationary points, yielding a total of ten monomers (Fig. 3). The observed nature and intensity of the IR and Raman stretching modes of –O—H and C=O groups near 3650–2400 cm⁻¹ and 1800–1600 cm⁻¹ region strongly suggest that the modes would arise in H-bonded dimer species from the monomers. As a next logical step, we constructed a total of six dimer species, Dᵢ (i = 1 to 6) that are shown in Fig. 4. The dimer species D₁, D₂ and D₃ are inter-molecularly bonded via –O—H⋅⋅⋅O=C and D₄, D₅ and D₆ are both intra- and inter-molecularly bonded, with the intra-molecular H-bond referring to –O—H⋅⋅⋅O(pyran ring). The optimized geometries of the most stable monomer and dimer species of CA with the numbering scheme are presented in Fig. 5. Calculations at BP86/6–31G(d) level were also performed, yielding slightly better frequency values than B3LYP/6–311++G(d,p) values. However, for the reasons already stated above and the B3LYP/6–311++G(d,p) level is known to predict fairly accurate results for AIM analysis, all the results obtained from this level alone will be discussed, though occasionally reference is made to BP86/6-31G(d) results. We computed the strength of the H-bonds as the energy difference between dimer and monomer components (ΔE_{int}, this energy is a measure of strength of the H-bond) and these resultant energies are corrected for the basis-set superposition-error (BSSE) using the counterpoise (CP) method of Boys and Bernardi [36]. The H-bond interactions in the dimer species have been characterized in terms of electron density, ρ(r), its Laplacian \nabla^2 \rho(r) and potential energy density at bond critical points (BCP) using the Multiwfn program based on the quantum theory of Atoms in Molecules (AIM) [32, 33] and reduced density gradient, \nabla \rho(r), by the non-covalent interaction (NCI) methods using the Multiwfn and VMD programs [37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48]. The nature of electronic charge delocalization accompanied by H-bond formation has been investigated by employing NBO analysis at the B3LYP/6–311++G(d,p) level [49].

3. Results and discussion

3.1. Vibrational and H-bonding analysis

The carboxylic acids show extensive inter-molecular H-bonding in the formation of dimer species and as a result, the IR frequency of the –O—H stretching mode shifts toward lower frequency region [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15]. Flett and others reported that, whereas the –O—H stretching frequency of monomer species lies near 3600 cm⁻¹, it gives rise to a broad absorption with many sub-bands near 2500–3000 cm⁻¹ due to dimeric species [50]. These assignments have been used as reference for the assignments of –O—H stretching mode and other modes of CA. The IR and Raman bands of CA are shown in Fig. 2 (see also Fig. S1, Supplementary Material). To satisfactorily account for the vibrational structure of CA apparently induced by intra- and inter-molecular H-bonding, we assume dimerization of its monomer components. Accordingly, as a first step, we computed ten possible monomer species.
(i.e. conformers), yielding, say, $M_1$, $M_2$, ..., $M_{10}$, that are shown in Fig. 3. The $M_1$, $M_2$, $M_3$ and $M_{10}$ species belong to $C_{2v}$ symmetry; $M_4$, $M_6$, $M_8$ and $M_9$ belong to $C_1$ symmetry. The $M_1$, $M_2$, $M_3$ do not show intra-molecular H-bonding, whereas, $M_4$ shows it (see Fig. S2). Except for the Boltzmann populations of $M_1$, $M_2$, $M_3$ and $M_4$, the populations of other monomer species are too small to be useful for discussion. Therefore, in the second step we computed ten dimer species all only from $M_1$, $M_2$, $M_3$ and $M_4$ species. Fig. 4 presents $D_1$, $D_2$, $D_3$, $D_4$, $D_5$ and $D_6$ dimer structures; the remaining four dimer species called $D_7$, $D_8$, $D_9$ and $D_{10}$ are identical and are separately presented in Fig. S3. The analysis of all the dimer species indicated that the computed geometrical, vibrational, AIM, NCI and NBO properties of the $D_7$–$D_{10}$ dimers are identical to those for the $D_1$–$D_6$ species. That is to say, $D_7$–$D_{10}$ dimers are not distinct and they map identically to the $D_1$–$D_6$ species. Therefore, only $D_1$–$D_6$ dimer species were chosen for the discussion. The $M_4$, $M_5$, $M_8$ and $M_9$ have twisted $\cdot\cdot\cdot$ bonding with the oxygen from the pyran ring (see Fig. S2). The $M_1$ is found to be the most stable and energies of other

Fig. 2. Experimental FT-IR (a) and simulated IR spectra for $D_4$ dimer (b) and $M_4$ monomer (c) species of Chelidonic acid. Experimental FT-Raman spectrum (d) is also shown.
monomers relative to \(M_1\)'s are shown in Table 1. The dimer energetics is collected in Table 2. The geometrical parameters of \(M_1\), \(M_4\) and \(D_4\) species are presented in Table 3. All the dimer species exhibit proton transfer reaction at the inter-molecular bonding site. Of the six dimer species, predicted IR bands of \(D_4\), \(D_5\) and \(D_6\) are identified with the observed \(-OH\) stretching bands because they have shown both \textit{intra-} and \textit{inter-}
inter-bonding. For the sake of brevity, only calculated and observed frequencies of the main bands of \(^{-}\text{C}=\text{O}\) and \(^{-}\text{C}=\text{C}\) groups are presented in Table 4 (see also Table S4) \([51, 52]\).

The geometrical criterion for the formation of an \(\cdots\text{O} \cdots\text{O}\) bond is the \(\text{O} \cdots\text{H}\) contact distance required to be less than the sum of van der Waals (vdW) radii of O and H, namely, 2.720 Å \([53]\). In Fig. 4, each dimer species has a double \(\cdots\text{O} \cdots\text{O}\) bonds involving two \(-\text{COOH}\) groups. In all the dimer species, the two \(\text{O} \cdots\text{H}\) bond angles are 177° (Table S5). Additionally, the \(D_4\) and \(D_5\) are stabilized by a single \(\cdots\text{intra}\)-bond and \(D_6\) is stabilized by two \(\cdots\text{intra}\)-bonds. The \(D_1\) is the most stable with the \(\Delta\text{E}_{\text{int}} = -17.77\) kcal/mol (Table 2). The two \(\text{O} \cdots\text{H}\) and \(\text{O} \cdots\text{O}\) contact distances are calculated at 1.674, 1.672 and 2.672, 2.670 Å respectively (Table S5). The \(D_2\) has \(\Delta\text{E}_{\text{int}} = -17.95\) kcal/mol. In this dimer the two \(\text{O} \cdots\text{O}\) bond lengths are nearly close, 2.670 and 2.669 Å. The \(D_3\) has \(\Delta\text{E}_{\text{int}} = -18.10\) kcal/mol. In \(D_4\) and \(D_5\), the \(\text{O}\cdots\text{H}\) distances being equal (2.671 Å). In \(D_4\) (\(\Delta\text{E}_{\text{int}} = -17.63\) kcal/mol) and \(D_5\) (\(\Delta\text{E}_{\text{int}} = -17.90\) kcal/mol), the O30–H31 group interacts with the pyran ring’s oxygen atom, O21, for which the contact distances, O21 \(\cdots\text{H}\), are calculated at 2.051 and 2.053 Å respectively (these are not shown in Table S5). The \(\text{O} \cdots\text{O}\) distances are computed at 2.669 and 2.670 Å. It may be noted that, although the relative energies of the six dimer species are not negligible, the differences in the \(\Delta\text{E}_{\text{int}}\) are rather very small and this may be attributed to the

![Fig. 5. Optimized structures of most stable monomer (a), and dimer (b) of Chelidonic acid.](image)

**Table 1**

| Monomers | Gibbs free energy, \(\Delta G\) (hartree) | Gibbs free energy, \(\Delta G\) (kcal/mol) | Relative Gibbs free energy, \(\Delta G\) (kcal/mol) |
|----------|------------------------------------------|------------------------------------------|------------------------------------------|
| \(M_1\)  | -720.638165                               | -452207.294607                            | 0.00                                      |
| \(M_2\)  | -720.637978                               | -452207.1772557                            | -0.12                                     |
| \(M_3\)  | -720.637411                               | -452206.82145791                           | -0.47                                     |
| \(M_4\)  | -720.636174                               | -452205.0142865                           | -1.25                                     |
| \(M_5\)  | -720.635810                               | -452203.9752975                           | -1.67                                     |
| \(M_6\)  | -720.632721                               | -452200.45851158                           | -6.84                                     |
| \(M_7\)  | -720.626495                               | -452199.97156420                           | -7.32                                     |
| \(M_8\)  | -720.625840                               | -452199.56054548                           | -7.73                                     |
| \(M_9\)  | -720.625313                               | -452199.22984797                           | -8.07                                     |
| \(M_{10}\)| -720.615112                              | -452192.8262356                            | -14.47                                    |
are corrected for basis set superposition error (BSSE). The geometrical parameters are calculated at B3LYP/6–311++G(d,p) level. For comparison of the geometrical parameters in the bonded and non-bonded case, M1 (free), M4 (intramolecularly bonded) and the dimer D4 (both intra- and inter-molecularly bonded) species were chosen [Ref 56].

Table 2

| Dimer | Monomer combinations | Gibbs free energy, △G (hartree) | ΔG (kcal/mol) |
|-------|----------------------|-------------------------------|--------------|
| D1    | M1 with M1           | -1.441.28157                  | -0.00         |
| D2    | M1 with M2           | -1.441.28073                  | -0.20         |
| D3    | M2 with M2           | -1.441.28078                  | -0.37         |
| D4    | M1 with M1           | -1.441.27855                  | -1.72         |
| D5    | M1 with M2           | -1.441.27826                  | -1.89         |
| D6    | M4 with M4           | -1.441.27538                  | -3.68         |

Table 3

| Parameter | Monomer | Dimer | △G Experimental |
|-----------|---------|-------|-----------------|

As shown in Fig. S1 (Supplementary Material), the absorptions in the 3650–2400 cm⁻¹ are characterized by a broad band structure with a series of closely-lying bands at 3629, 3601, 3557, 3468, 3418 cm⁻¹ and 2962, 2922, 2854, 2814, 2756, 2736 cm⁻¹ and 2597, 2564, 2489, 2474 cm⁻¹. We tentatively assign the bands near 3470–3410 cm⁻¹ to a free O–H stretching mode. The bands near 3470–3410 cm⁻¹ are assigned to both medium strong inter- and intra-molecularly bound O–H stretching modes and those near 2970–2470 cm⁻¹ to strong inter-molecularly bound O–H stretching modes. Two bands to medium strong bands at 3127 and 3055 cm⁻¹ are readily assigned to C–H stretching modes. Further, the strong bands near 1800–1600 cm⁻¹ in the IR and Raman spectra being characteristic bands of C–O stretching modes of –COOH groups are neither broad and red-shifted, indicating the participation of C–O groups in H-bonding. This is consistent with the assignments for formic acids and benzenedicarboxylic acids that show similar modified vibrational structure upon H-bonding [16, 19, 50].

The computed IR spectra of all the dimer species are presented in Table 4. The computed IR bands at 3629 and 3601 cm⁻¹ are assigned to the free O–H stretching vibrations. The corresponding predicted frequencies for the M1 are 3615 and 3614 cm⁻¹. In going from the monomers to dimers, except for the D4, D5 and D6, these two frequencies show no substantial shift. In D4, D5 and D6, the O30–H31 group is intramolecularly bonded to the pyran ring oxygen atom O21. This caused a small red-shift in the O–H stretching frequency predicted at 3601 cm⁻¹ for D4 and D5 and is tentatively correlated to a broad absorption at 3468 cm⁻¹, the difference in deviation being ~4%. It is also possible that in the solid phase of CA, the monomeric structures stabilized by intra-molecular H-bonding are not favored and therefore, in the absence of strong experimental evidence, we tentatively assign the bands observed near 3400 cm⁻¹ to both medium strong inter- and intra-molecularly bound O–H stretching modes. We have already noted the two band systems with sub-maxima at 2962, 2922, 2854, 2814, 2756, 2736 and 2597, 2564, 2489, 2474 cm⁻¹ in the 3000–2400 cm⁻¹ absorption region (see Fig. S1). We assume all of these bands to have originated from the strong inter-molecular H-bonding of the –O–H groups in the dimer species. The large red-shifts, 775 and
level will be evident in AIM analysis to be discussed later where another conformer component. For this premise by performing calculation at BP86/6-31G(d) level as well, far as agreement with the experimental values is concerned. However, we frequencies are calculated at B3LYP/6–31G(d) level. Each dimer species exhibits two –COOH groups of two different conformer components into an H-bonded dimer, the red-shifts of the carbonyl stretching frequencies are in agreement with the prediction. The symmetric and anti-symmetric carbonyl stretching frequencies for D3 are predicted at 1650 and 1697 cm$^{-1}$ respectively. The frequencies calculated at 1427, 1406, 1158, 1142 cm$^{-1}$ show contribution from –O–H in-plane bending mode. The mononeric band for M1 at 1130 cm$^{-1}$ show blue-shift in the dimer D3 and the frequency is computed at 1427 cm$^{-1}$. The corresponding IR band is observed at 1452 cm$^{-1}$ and the Raman band at 1444 cm$^{-1}$. The intra–molecularly bonded –O–H in-plane bending mode shows a small blue-shift and is predicted at 1162 cm$^{-1}$ for M6. The out-of-phase –O–H bending mode for M6 is calculated at 604 cm$^{-1}$ and is observed at 603 cm$^{-1}$ as an IR band. In D5, the two frequencies are calculated at 939 and 849 cm$^{-1}$; the band at 939 cm$^{-1}$ is observed at 969 cm$^{-1}$ in IR and at 965 cm$^{-1}$ in the Raman spectrum. To conclude, the characteristic blue-shifts in the frequencies of –O–H deformation vibrations are indicative of the –O–H group’s involvement in the dimerization. As for the modes of other groups, namely, –CH, –C=C and –CO below 1400 cm$^{-1}$, they are all satisfactorily assigned and for the sake of brevity, are summarized in Table 5 (also see Section S7).

### Table 4

| Experimental | M2 | M3 | D1 | D2 | D3 | D4 | D5 | D6 | Assignments |
|--------------|----|----|----|----|----|----|----|----|--------------|
| IR           | Raman |
| 2962         | –   | –   | 3100 | 3098 | 3101 | 3111 | 3111 | 3089 | O–H stretching (inter-bonded) |
| 2922         | –   | –   | 3009 | 3007 | 3010 | 2982 | 2982 | 2998 | O–H stretching (inter-bonded) |
| 3468         | –   | 3593 | –   | –   | –   | 3601 | 3601 | 3604 | O–H stretching (medium strong inter-and intra-bonded) |
| 3629         | 3615 | 3620 | 3614 | 3623 | 3624 | –   | 3623 | –   | O–H stretching (free) |
| 3651         | 3614 | –   | 3614 | 3614 | 3624 | 3614 | –   | –   | – |
| 1648         | 1646 | –   | 1702 | 1703 | 1703 | 1697 | 1698 | 1691 | O–C (carboxyl) stretching (inter-bonded) |
| 1723         | 1736 | –   | 1660 | 1661 | 1661 | 1650 | 1650 | 1643 | O–C (carboxyl) stretching (inter-bonded) |
| 1830         | 1738 | 1768 | 1737 | 1754 | 1755 | 1769 | 1769 | 1770 | O–C (carboxyl) stretching (free) |
| 1452         | 1444 | –   | 1423 | 1422 | 1421 | 1427 | 1426 | 1427 | O–H in-plane bending (inter-bonded) |
| 1423         | –   | –   | 1404 | 1404 | 1403 | 1406 | 1406 | 1410 | O–H in-plane bending (inter-bonded) |
| 1129         | 1134 | 1130 | 1127 | 1141 | 1141 | 1132 | 1142 | 1132 | O–H out-of-plane bending (inter-bonded) |
| 969          | 965  | –   | 920  | 921  | 920  | 939  | 939  | 932  | O–H out-of-plane bending (inter-bonded) |
| 603          | –   | 604 | 564 | 598 | 597 | 565 | 601 | 565 | O–H out-of-plane bending (free) |

The geometrical criterion satisfied by the dimer species derived from DFT calculations alone is not sufficient to characterize the –O–H –C=O bonding because computed H-bonded dimer populations for vapor phase do not adequately correspond to possible inter-molecular linkages in the solid phase of the sample of CA. The analysis of the topological properties of ρ(r) by Bader’s quantum theory of Atoms in Molecule (AIM) is an alternative tool to investigate inter–atomic interactions such as H-bonding [37, 38, 41]. The presence of bond critical point (BCP), where the gradient of electron density, \( \nabla \rho(r) \), vanishes between two interacting atoms, is a good measure for characterizing the H-bond [37, 38, 39, 40, 41, 42]. Experimentally, the crystal structure determinations by the low-temperature X-ray diffraction (XRD) measurements provide reasonably accurate values of the \( \rho(r) \) and \( \nabla^2 \rho(r) \) [44, 45, 48]. Recently, the inter– and intra–molecular interactions in crystalline Phthalic acid have been measured from the topology of the electron density distributions obtained from a low temperature (20 K) X-ray diffraction analysis and the values are in good agreement with theoretically-fit values [48]. In the present study, the geometries of the selected CA monomers and dimers showing BCP are presented in Fig. 7a–7d. The AIM analysis has provided BCP for each of the covalently bonded C–C, C–H, C=C, O=C and O–H groups. The existence of an intra–bonding between –O–H group and pyran ring oxygen in M6 is evidenced by a BCP between hydrogen and oxygen atom (see Fig. 7b). Each dimer species exhibits two –O–H –O–C inter-molecular H-bonds. The presence of these two bonds is confirmed by two BCPs between the interacting carboxylic groups (see Figs. 7c and 7d). Furthermore, for D6, a BCP for –O–H –O–C intra–molecular bonding has also been determined. The topological parameters calculated at the BCP values along the O–O–H contacts for the monomer and dimer species of CA are presented in Tables 6a and 6b (see also Table S8a – S8c). On comparing with the values of \( \rho(r) \) and \( \nabla^2 \rho(r) \) computed at the same B3LYP/6–311++G(d,p) level for the same H-bonding in 2-pyrollidine and pyrrrole-2-carboxylic acid, we find good agreement with the values computed for CA [57, 58]. However, as for the agreement with the XRD values of Phthalic acid,
it is not satisfactory with respect to the $\nabla^2 \rho(r)$ values because these are known to vary rapidly at bond curvatures depending on dimer species [39, 40, 41]. It is to be noted that the $\rho(r)$ values, 0.0446–0.0487 a.u. for the intermolecular H-bonds are evidently higher than the values, 0.0217–0.0219 a.u. for the intramolecular bonding ($\nu’$ and $\nu”$) are scaled by a suitable factor.

Noncovalent interactions (NCI) index developed by Johnson et al [43] investigates the van der Waals interactions (vdW), steric clashes (SC), and H-bonds in a molecule based on $\rho(r)$, and their reduced density gradient, $s(r)$, defined as,

$$s(r) = \frac{1}{2(3\pi)^{\frac{1}{2}}} \left( \frac{\nabla \rho(r)}{|\rho(r)|} \right)^2$$

An NCI plot of $s(r)$ versus $\rho(r)$ essentially identifies bonding or nonbonding situations by producing the change in $s(r)$ between the interacting units. Further, the value of $\rho(r)$ is a measure of the interaction...
D4 dimer frequencies (in cm$^{-1}$) for comparison of the bonded case, monomers $M_1$ (free), $M_4$ (intra-molecularly bonded) and the dimer $D_4$ (both intra- and inter-molecularly bonded) species were chosen. All the frequencies (in cm$^{-1}$) are scaled with the single scaling factor of 0.9688 [51,52].

| Observed frequencies | Computed frequencies | Assignments [Relative weight (%)] |
|----------------------|----------------------|-----------------------------------|
| Observed frequencies | Computed frequencies | Assignments [Relative weight (%)] |
| IR       | Raman | Monomer | Dimer | $M_1$ | $M_4$ | $D_4$ |
| 3629 w   | 3615  | 3620 | 3614 | OH stretch (free) [93] |
| 3601 w   | 3614  | -   | -   | OH stretch (free) [93] |
| 3468 s   | -     | -   | 3593 | 3601 | OH stretch (medium strong inter- and intra-bonded) [96] |
| 2962 ms  | -     | -   | -   | OH stretch (inter-bonded) [89] |
| 2922 ms  | -     | -   | -   | OH stretch (inter-bonded) [92] |
| 3172 s   | 3110  | 3101 | 3107, 3101 | CH stretch [97] |
| 3055 ms  | 3055  | 3101 | 3105, 3100 | CH stretch [98] |
| 1830 w   | -     | 1738 | 1768, 1769 | C=O (carboxyl) stretch (free) [93] |
| 1723 s   | 1736  | -   | -   | C=O (carboxyl) stretch (free) [94] |
| 1648 vs  | 1646  | -   | -   | C=O (oxo) stretch (free) [94] |
| 1603 sh  | 1592 s | 1604 | 1610, 1612, 1599 | CC stretch (ring) [79], CO (oxo) stretch [6] |
| 1579 vs  | 1547 s | 1571 | 1575, 1580, 1567 | CC stretch [78], CH deformation [12] |
| 1452 w   | 1444  | -   | -   | COH deformation (bonded) [76], OH out-of-plane bending [94] |
| 1423 ms  | -     | 1358 | 1352, 1358 | C=COOH stretch [9] |
| 1370 vv  | -     | -   | -   | CC stretch [60], COH deformation [15], CO (ring) stretch [8] |
| 1257 s   | 1269 ms | 1275 | 1280, 1280 | CH deformation (65), CC stretch [12], COH deformation [9], CO (ring) stretch [8] |
| 1241 s   | -     | 1181 | 1179, 1183, 1177 | CH deformation [83], CC stretch [13] |
| 1204 sh  | -     | 1153 | 1162, 1158 | COH deformation [82], C=COOH stretch [11] |
| 1129 s   | 1134 s | 1130 | 1127, 1142 | COH deformation [69], CC stretch (ring) + C=COOH [11], CO (ring) stretch [7] |
| -        | 1118 s | 1065 | 1077, 1091, 1075 | CH wag [69], CO stretch (carboxyl) [14], COC scissoring [14] |
| -        | 1054  | 1047 | 1060, 1048 | CH wag [53], CO stretch (ring + carboxyl) [24], CC stretch [13] |
| 969 s    | 965 ms | -   | -   | C=COOH stretch [93] |

Table 5 (continued)

| Observed frequencies | Computed frequencies | Assignments [Relative weight (%)] |
|----------------------|----------------------|-----------------------------------|
| IR                   | Raman               | Monomer | Dimer | $M_1$ | $M_4$ | $D_4$ |
| 921 s                | 931 w               | 927    | 930    | 931   | 928   | OH out-of-plane bending (inter-bonded) [87] |
| -                    | 906 ms              | 886    | 883    | 890   | 888   | CH wag (91) |
| 796 ms               | 796                 | 882    | 878    | 883   | 883   | CH out-of-plane bending [92] |
| -                    | 790                 | 871    | 866    | 880   | 878   | CCC sym stretch [70], COH deformation [13], C=COOH stretch [8] |
| 781 w                | 781                 | 866    | 863    | 870   | 865   | C=COOH stretch [72], ring deformation [16], CO stretch (carboxyl) [8] |
| 743 ms               | 748 sh              | 768    | 765    | 776   | 768   | C=COOH torsion [79], ring deformation [14] |
| -                    | 732 s               | 757    | 744    | 764   | 745   | C=COOH torsion [79], CH wag [12] |
| 694 s                | 682 w               | 687    | 686    | 688   | 685   | CCCO + COC torsion [63], CH wag [53] |
| -                    | 664                 | 677    | 672    | 691   | 694   | COCO (carboxyl) bend [69], CCC stretch [17], COC (ring) bend [6] |
| 603 w                | 622                 | 604    | 564    | 601   | 601   | C=COO (carboxyl) [70], CCC bend [24] |
| 535 w                | 550 sh              | 581    | 577    | 593   | 584   | OH out-of-plane bending [94] |
| -                    | 584                 | 547    | 539    | 539   | 539   | OH out-of-plane bending [93] |
| 486 vv               | 487 w               | 478    | 477    | 498   | 493   | C=COOH bend [66], COO (oxo) in-plane-bending [29] |
| -                    | 468                 | 436    | 436    | 451   | 450   | CCC bend [64], COC (ring) bend [17], C=COOH bend (oxo) [12] |
| 425                  | -                   | 434    | 435    | 441   | 434   | C=COOH (ring) [73], CCS (ring) rock [24] |
| 413                  | 387 s               | 420    | 427    | 459   | 432   | C=COH bending [93] |
| -                    | 365 ms              | 338    | 332    | 370   | 337   | CCC + COC (ring) bend [53], ring – COOH deformation [44] |
| -                    | 261 w               | 320    | 331    | 345   | 328   | COO (oxo) bend [50], C=COOH bend (oxo) [45] |
| -                    | 201 ms              | 205    | 208    | 239   | 227   | CCC + COCO (oxo) rock [61], C=COH rock [29] |
| -                    | 186 s               | 160    | 163    | 173   | 165   | CCCCO + CCCO (ring) torsion [82], CCCH torsion [14] |
| -                    | 150 ms              | 149    | 142    | 149   | 144   | CCCOC (ring) + COCD (oxo) torsion [90] |
| -                    | 128 ms              | 120    | 118    | 159   | 152   | C=COOH in-plane-bending [92] |
| -                    | 104                 | 109    | 101    | 125   | 112   | COO (oxo) torsion [51], ring – COOH torsion [45] |
| -                    | 48                  | 63     | 63     | 67    | 67    | Ring – COOH torsion [98] |
| -                    | 45                  | 52     | 50     | 42    | 42    | Ring – COOH torsion [94] |
strength. The attractive and repulsive interactions are discriminated by multiplying the $\rho(r)$ with the sign of second eigenvalue ($\lambda_2$) of the Hessian (a matrix of second-order partial derivatives of $\rho(r)$) \[43\]. The sign of $\lambda_2$ may either be negative or positive depending on the accumulation or depletion of the electron density between the two interacting atoms. The former situation corresponds to bonding (vdW and H-bonds) where $\lambda_2 < 0$, while the latter for nonbonding interactions (SC) with $\lambda_2 > 0$. We show in Fig. 8a–8e plots of the $\rho(r)$ against $\text{sign}(\lambda_2)\rho(r)$ for the monomers and dimers of CA. The plots display the features of the attractive and repulsive NCI in terms of two or more spikes in the low-density and low-gradient regions, while the weak vdW interactions are at near zero density values. Fig. 8f for $M_1$ shows low-density and low-gradient spikes lying around ±0.01 a.u, being indicative of weak vdW attractions. The spike for SC interactions has appeared at higher positive value. As discussed in the preceding Section 4.1, the $M_0$ geometry has one intra-molecular H-bond. In Fig. 8c, the low-gradient spike appeared at about $\text{sign}(\lambda_2)\rho(r) = -0.0219$ a.u is attributed to intra-molecular H-bond in $M_0$. The $\text{sign}(\lambda_2)\rho(r)$ of -0.0219 a.u for this bond as compared to the vdW interactions ($±0.01$ a.u) suggests that the intra-molecular H-bonding is relatively strong. The $\rho(r)$ versus $\text{sign}(\lambda_2)\rho(r)$ plots for the dimer species are shown in Fig. 8d (for $D_1$ without intra-bonding) and Fig. 8e (for $D_4$ with intra-bonding) respectively. In Fig. 8d, the low-gradient but high-density spike appeared at $\text{sign}(\lambda_2)\rho(r) = -0.0463$ a.u, indicating the presence of two strong intra-molecular H-bonds. For $D_4$, the spikes have appeared at $\text{sign}(\lambda_2)\rho(r) = -0.0219$ a.u for intra-bond, and -0.0447 and -0.0487 a.u for two inter-bonds. Furthermore, the two inter-molecular H-bonds of $D_4$ are discriminated as two separate spikes as compared to the one in $D_1$ due to the differences in the two O···H contact distances (0.033 Å and 0.002 Å respectively, Table S5). Owing to the large $\rho(r)$ values, the H-bonds due to inter-molecular association are stronger than intra-molecular association. This is consistent with the changes in the geometrical parameters and frequencies of the monomer and dimer species discussed in the preceding section 3.1 (see Table 4, Tables S4 and S5). Fig. 8b–8e also show the NCI iso-surface plots of the monomer and dimer species calculated at the B3LYP/6-311++G(d,p) level. The blue-green-red (BGR) color scheme is used in which the blue region represents strong attractive interactions (O–H···O bonds) and the green and red regions represent the weak van der Waals (and C–H···O bonds) and strong repulsive steric interactions respectively. The NCI iso-surface with a disc shaped volume (red) is characteristic of a strong repulsive steric interaction between the oxygen and carbon atoms of the pyran ring and oxygen of carboxylic groups. The iso-surface (green) between the pyran-ring oxygen and –OH of carboxyl group in the $M_0$ (Fig. 8c) and $D_4$ (Fig. 8e) species indicate the presence of the intra-molecular H-bond between the –OH and –CO groups. The blue NCI iso-surface between the two carboxylic groups in the $D_1$ and $D_4$ species is characteristic of the strong intra-molecular O–H···O bonding. The section S9 (see also Fig. S9a–S9f) presents the correlation of H-bond – OH group stretching frequencies of Chelidonic acid species with the $s^*\text{sign}(\lambda_2)\rho(r)$ and interaction energy.

3.3. Natural bond orbital (NBO) analysis

The nature of electronic charge delocalization accompanied by H-bond formation has been investigated by employing NBO analysis \[49\]. The
Topological parameters computed at the O26⋯H27 and O16⋯H17 bond critical points (BCPs) in the dimer species of Chelidonic acid. All the properties are computed at B3LYP/6-311++G(d,p) level. *Except interaction energy, E_{HB} (kcal/mol), all magnitudes are in a.u. The values of the E_{HB} listed in the above table are computed from potential energy density V(r), by using the expression E_{HB} = \frac{1}{2}(V(r)) [42].

| Species | O⋯H | \rho(r) | \nabla^2 \rho(r) | V(r) | Interaction Energy, E_{HB} | s\cdot\text{sign}(\lambda_u)\rho(r) |
|---------|-----|---------|----------------|-----|--------------------------|-------------------------------|
| D_1     | O26⋯H27 | 0.0463  | 0.1366 | -0.0435 | -13.65 | -0.0463 |
| D_1     | O16⋯H17 | 0.0465  | 0.1372 | -0.0439 | -13.76 | -0.0465 |
| D_2     | O26⋯H27 | 0.0464  | 0.1370 | -0.0437 | -13.70 | -0.0464 |
| D_2     | O16⋯H17 | 0.0466  | 0.1372 | -0.0439 | -13.78 | -0.0466 |
| D_3     | O26⋯H27 | 0.0463  | 0.1369 | -0.0436 | -13.69 | -0.0463 |
| D_3     | O16⋯H17 | 0.0463  | 0.1369 | -0.0436 | -13.69 | -0.0463 |
| D_4     | O26⋯H27 | 0.0447  | 0.1350 | -0.0416 | -13.05 | -0.0447 |
| D_4     | O16⋯H17 | 0.0487  | 0.1396 | -0.0467 | -14.64 | -0.0487 |
| D_5     | O26⋯H27 | 0.0446  | 0.1347 | -0.0415 | -13.01 | -0.0446 |
| D_5     | O16⋯H17 | 0.0487  | 0.1398 | -0.0467 | -14.65 | -0.0487 |
| D_6     | O26⋯H27 | 0.0466  | 0.1374 | -0.0440 | -13.81 | -0.0466 |
| D_6     | O16⋯H17 | 0.0466  | 0.1374 | -0.0440 | -13.81 | -0.0466 |

Fig. 8. Plots of the reduced density gradient, s, versus the electron density \rho(r), multiplied by the sign of second eigenvalue (\lambda_u) of the electron-density Hessian matrix, \text{sign}(\lambda_u)\rho(r) (left) and the corresponding isosurfaces with isovalue = 0.5 a.u (right) for Chelidonic acid structures. Isosurfaces are colored according to a BGR color scheme (Fig. 8a). Blue indicates strong attraction regime (intra-/-inter- H-bonding), green indicates weak interaction regime (such as \text{-C⋯H⋯O and van der Waals attraction), and red indicates strong repulsion regime (steric clashes). The 2D NCI plots are shown for M_1 (Fig. 8b) and M_2 (Fig. 8c) monomers and for D_1 (Fig. 8d) and D_4 (Fig. 8e) dimer structures. In each of the plots, the low-gradient spikes at about \text{sign}(\lambda_u)\rho(r) = \pm 0.01 a.u represents the weak van der Waals interactions. The spikes at about \text{sign}(\lambda_u)\rho(r) = -0.0219 a.u and \text{sign}(\lambda_u)\rho(r) = -0.0487 a.u represents the intra- and inter-molecular H-bonds respectively.
and hydroxyl groups are the consequences of the electronic charge to the bond lengths and red-shift in the stretching vibrations of the carbonyl monomers, in particular H-bond donor-acceptor behavior is con-
tact between the two species. As can be seen from Table 7a, on account of the association be-
lected atoms collected from natural population analysis are presented in Table 7b. All the dimers exhibit two inter-molecular donor-acceptor interactions or hyperconjugations de-
charge delocalization, in many cases, influences the conformational behavior, H-bond strengths and IR modes. The natural charges (NC) of the atoms and stabilization energy defined as the strength of the charge transfer between oxygen lone pair orbitals and –OH anti-bonding orbital have been computed to identify and confirm the single/double H-bond structures of CA. In all the D1, D2, D3, D4, D5 and D6 species, the lone pair orbitals of the carbonyl oxygen and anti-bonding orbital of the hydroxyl group have been identified as the donor and acceptor sites. The natural charges for some selected atoms collected from natural population analysis are presented in Table 7a. As can be seen from Table 7a, on account of the association between the two –COOH groups exchanging natural charges, their simulta-
Table 7a

| Atom | M2 | M4 | D1 | D2 | D3 | D4 | D5 | D6 |
|------|----|----|----|----|----|----|----|----|
| O16  | -0.6559 | -0.6705 | -0.6266 | -0.6271 | -0.6233 | -0.6273 | -0.6237 | -0.6431 |
| H17  | 0.4906 | 0.4956 | 0.5196 | 0.5173 | 0.52010 | 0.5171 | 0.5173 | 0.5173 |
| O18  | - | - | -0.6698 | -0.6696 | -0.6708 | -0.6610 | -0.6624 | -0.6593 |
| O26  | - | - | -0.6269 | -0.6229 | -0.6282 | -0.6477 | -0.6407 | -0.6407 |
| H27  | -0.5676 | -0.5563 | -0.6698 | -0.6687 | -0.6684 | -0.6679 | -0.6674 | -0.6591 |
| O1/O21 | -0.4496 | -0.4938 | -0.4465 | -0.4466 | -0.4413 | -0.4969 | -0.4979 | -0.4999 |
| H10/H131 | 0.4906 | 0.4964 | 0.4912 | 0.4911 | 0.4937 | 0.4943 | 0.4946 | 0.4938 |
| O9/O30 | -0.6559 | -0.6530 | -0.5668 | -0.6538 | -0.6777 | -0.6531 | -0.6526 | -0.6523 |

4. Conclusions

The –O–H⋯O H-bond mediated composite vibrational structure observed in the IR and Raman spectra (4000–100 cm$^{-1}$) of Chelidonic acid has been characterized by the structures, interaction energies and harmonic frequencies for the ten monomer and six dimer species computed at B3LYP/6-311++G(d,p) level. The AIM analysis has provided additional support to the H-bond characterization in terms of BCP values for both intra- and inter-molecular –O–H⋯O H-bonding. The existence of the both type of H-bonding has been demonstrated by BCPs for each of the O⋯H contacts. The electron density plots have provided insights into the nature of the H-bonds. The weak van der Waals and hydrogen bonding interactions exhibited low-gradient spikes at BCPs having different magnitudes of electron densities. The calculation of the natural charges and stabilization energy of the H-bonds for the dimer species by NBO analysis further points to the presence of the stronger inter-molecular H-bonding interactions than the intra-H-bonding. It has been noted that while the geometries and interaction energies are accurately predicted at B3LYP/6-311++G(d,p), the BP86/6-31G(d) level is shown to produce slightly more accurate frequencies. However, the benefits of the B3LYP/6-311++G(d,p) level outweighs when it produced better results for the AIM and NCI calculations. The proposed dimer model is to be treated as a basic unit in oligomers that may make up Chelidonic acid in its solid phase.

Declarations

Author contribution statement

Jagdish Tonannavar: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.
Shivanand S. Malaganvi: Performed the experiments; Wrote the paper.
Jayashree Yenagi: Analyzed and interpreted the data.

Funding statement

Shivanand S. Malaganvi was supported by the University Grants Commission (UGC), New-Delhi, for the award of Project Fellowship under Major Research Project (MRP) grant No. 41–874/2012 (SR).

Competing interest statement

The authors declare no conflict of interest.

Additional information

Supplementary content related to this article has been published online at https://doi.org/10.1016/j.heliyon.2019.e01586.

Acknowledgements

We thank the USIC, Karnataka University, Dharwad for FT-IR and FT-
Raman spectral measurements. We thank the Director of International and Inter-University Centre for Nanoscience and Nanotechnology, Mahatma Gandhi University, Kerala, for the solid-state near-IR spectral measurements.

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