Very strong intramolecular hydrogen bonding of 1,2-dithenoylcyclopentadiene; DFT and spectroscopic studies

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HIGHLIGHTS

- Full tautomeric and conformational analyses have been done.
- Molecular structure comparisons show high electron delocalization.
- Short and almost linear hydrogen bond is confirmed.
- Very strong intramolecular hydrogen bond is also confirmed by experiment.

GRAPHICAL ABSTRACT
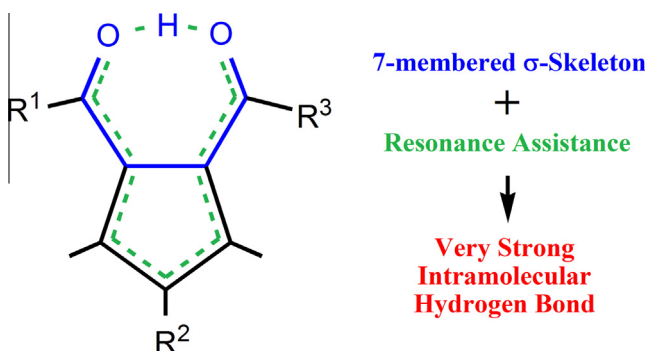
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ABSTRACT

Structure and intramolecular hydrogen bond (IHB) of 1,2-dithenoylcyclopentadiene (DTCP) have been investigated with quantum mechanical calculations using density functional theory at B3LYP level using some Pople-style basis sets augmented with polarized and diffuse functions. The full isomeric and conformational analyses have been done, and the relative stabilities for different chelated and non-chelated enol and different keto forms have been reported. The estimated IHB energy and the barrier height for proton transfer (19.34 and 0.31 kcal/mol, respectively), together with the value of 0.082 Å for the Q Gilli's symmetry coordinate and the σ-skeleton of the molecule (O···O distance of 1.463 Å), confirm a very strong, nearly symmetric, linear and short distance resonance assisted IHB (RAHB) in DTCP. The values of 18.29 ppm for the enolated proton chemical shift and 1128 cm^{-1} for out-of-plain bending of the OH bond, besides investigations on other IR and Raman bands associated with the IHB strength and electron delocalization in different segments of the molecule, confirm the results of the theoretical studies and a very strong RAHB in DTCP.

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Introduction

Over the years, the keto-enol tautomerism, the structure of the keto and enol forms, and the nature of the strong intramolecular O−H···O hydrogen bond (IHB) in the enol forms of a number of β-dicarbonyl compounds, and also their spectra properties have been the subject of many studies. These investigations have been performed using a large variety of different kinds of experimental and theoretical methods such as IR, Raman, MW and NMR spectroscopies, X-ray, electron and neutron diffraction measurements, and quantum-chemical calculations by use of different techniques and theories [1–3]. But to the best of our knowledge, the investigations have been done on the γ-dicarbonyl compounds with the

capability of forming IHB are very finite in literature. Among the published studies, maybe the majority, that are not so much, belong to a category of γ-dicarbonyls named 1,2-diacylcyclopentadiene (1,2-DACP). Though, the most studies on 1,2-DACPs have been attended to their synthesis and molecular structures. Maybe the difficulties of synthesis and working in the inert atmosphere and sensitivity of intermediate compounds to the moisture are the main reasons that studies on this category of the organic compounds are very few. Although they are almost one century years old, but the published papers are less than 100 which many of them are assigned to the synthesis methods [4–13]. 1,2-DACP compounds are also known as fulvene compounds because they can bidirectionally form equilibrium, as a result of enolization, with two different enol forms named 6-hydroxy-2-formylfulvenes (as illustrated in Fig. 1). The position of keto-enol equilibrium in 1,2-DACPs depends on the electronic nature and the influences of R1, R2 and R3 groups, temperature and media effects such as solvent property.

In the enol form of these compounds, like the enol forms of β-dicarbonyls, an IHB forms between the oxygen atom of carbonyl group and the proton of hydroxyl group. As a result of this IHB, and because of a long π-electronic conjugation between carbonyl and cyclopentadiene (CP) double bands, a 7-membered ring-like structure (see Fig. 1) is formed which is referred to as chelated or enolone ring (like 6-membered chelated ring in β-dicarbonyls). Since the chelated ring is heptagonal [14–18], the spatial orientations (distances and angles) for O and H—O segments of the molecule are more proper to form much stronger O···H—O hydrogen bond in 1,2-DACPs, in comparison to that of β-dicarbonyls. Also the longer resonance structure of delocalized π-electrons makes the resonance assisted intramolecular hydrogen band, RAHB [19–22], in this type of γ-dicarbonyls to be stronger than that of β-dicarbonyls. Gilli and Bertolasi named two simplest molecules of this category, 1,2-diformylcyclopentadiene and 1,2-diacetylcyclopentadiene, as ζ-dicarbonyl [1].

At the outset, the structure (I) in Fig. 1 was proposed as the structure of 1,2-diacyl-4-nitro-cyclopentadiene. But, for the first time, Hale talked about probability of an IHB, in 1916 [6]. NMR spectra of 1,2-diacetyl-4-nitrocyclopentadiene by Lloyd and co-workers [23,24] showed a fulvene structure (II) with strong IHB, which instead of a fast tautomeric equilibrium, a non-localized symmetric C2v form (III) can be suggested [24]. In 1964, the first IR investigation of this category of organic compound was performed by Hafner [15] on 6-hydroxy-fulvene-2-aldehyde. In 1972 and by use of MW spectroscopy method, Pickett studied the IHB structure in 6-hydroxy-2-formylfulvene (HFF or 1,2-diformylcyclopentadiene, DFCP) and reported a linear OHO bond in a symmetrical C2v molecular configuration [17], in consistent with the IR [15] and NMR [24] studies on this compound. Also proton diffraction study by Ferguson et al. (1975), indicated very short intramolecular OHO hydrogen bonds with a symmetrically delocalized

structure and the OHO angle of 177 and 172 degrees for 2,3-diacetyl- and 2,3-dibenzoyl-5-nitrocyclopentadiene, respectively [14]. They have also reported the O···O distances to be 2.446 (2) and 2.433(2) Å for the mentioned molecules, respectively, and a small amount of conjugation between the nitro-groups and CP rings. In 1978, Zahradnic and co-workers studied the UV spectra of the compounds with R1=R2=H, Me, and styrene [25]. They also used the semi-empirical ppp-SCF-MO method and achieved the same results as the UV experiment. They showed a strong IHB in the investigated molecules. Semi empirical calculations AM1, MNDO, MINDO/3 in 1990 [26] on IHB of 6-hydroxy-2-formyl-fulvene showed that hydrogen bonds in these compounds are symmetric.

X-ray and neutron diffraction data [16] showed the O···O distance for DFCP to be 2.513 and 2.550 Å, respectively. The OHO angle of 171.2 degrees and the OH band length of 1.343 and 1.214 are indicated by this neutron diffraction analysis which showed a little asymmetry in the hydrogen bond structure. In 1994, Millefiori and Alparone performed theoretical calculations on the molecular structure, polarizability and hyperpolarizability of DFCP, by use of electron correlated ab initio methods [27] and reported a C_s symmetry for IHB in this molecule and the values of 16.6 (calculated at MP3/6-31G(d,p)//MP2/6-31G(d,p)) and 66–78 kJ/mol for proton transfer barrier height and the IHB energy, respectively. Also, isotopic perturbation of equilibrium in the NMR analyses showed that the hydrogen bond of DFCP is asymmetric and that each species is a pair of rapidly interconverting tautomers [28,29].

It has been shown by ^{1}H NMR study on 1-formyl-2-acylcyclopentadien that the ethoxy group, in comparison to alkyl and aryl groups, decreases the IHB strength due to its electron-withdrawing effect [30]. Also, according to that study, it could be concluded that 1-formyl-2-acylcyclopentadien with alkyl group of high steric hindrance (tert-butyl) and aryl group with resonance effect (phenyl) form stronger IHB [30].

Recently, Tayyari et al. investigated the structure and IHB nature of 1,2-bis(dichloroacetyl) cyclopentadiene (DCACP) [31] and 1,2-bis (monochloroacetyl) cyclopentadiene (MCACP) [32], and compared the results with some β-dicarbonyls, such as malonaldehyde (MA), acetylacetone (AA), benzoylacetone (BA), nitromalonaldehyde (NO₂MA) and dibenzoylmethane (DBM). By using DFT calculations and vibrational observations, they showed that the IHBs of the studied 1,2-DACP compounds are stronger than selected β-dicarbonyls.

In the present work, 1,2-dithenoylcyclopentadiene (DTCP) is investigated with special attention to its IHB, in order to obtain detailed information on the conformational relative stabilities, geometrical parameters, and electron conjugation in its RAHB. It is also important to estimate the barrier height for proton transfer and the strength of the IHB, which is the main factor governing the conformational stability. The calculated geometrical parameters related to the IHB strength and also the calculated approximate IHB energy, E_HB, for the most stable conformer of DTCP are compared with those previously obtained for MCACP, DCACP, and some
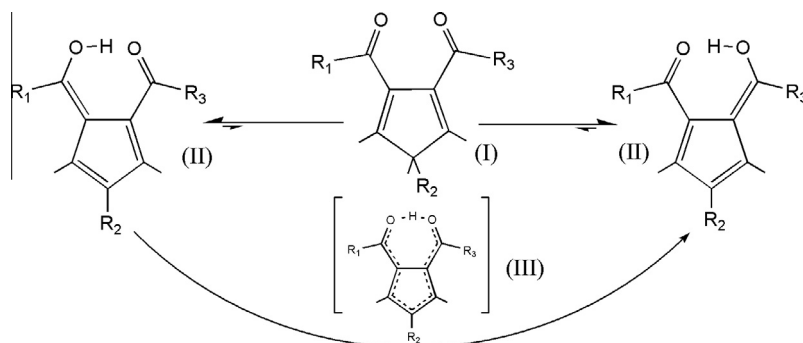

Fig. 1. Tautomerism and electron delocalization in 1,2-diacylcyclopentadienes.

β–dicarbonyls with the strongest IHB. In addition, the vibrational spectra (harmonic wave number and relative intensities for IR and Raman spectra) are predicted by means of theoretical calculations. Then, it is attempted to find and assign the observed bands associated with the electron delocalization and IHB strength of DTCP by considering the theoretical and experimental IR and Raman spectra of the compound and its deuterated analogue.

Experimental

Material

In order to synthesis DTCP compound, we adapted the procedure of Linn and Sharkey [7] for benzoylation of cyclopentadienyllithium. The procedure used is as followed: 0.3 mol Li was shaved in diethylether and poured in 3-neck flask equipped by a dropping funnel and a reflux apparatus, and 0.15 mol bromobenzene was added drop wise. Then 0.15 mol freshly distilled cyclopentadiene was added drop wise. Next 0.3 mol 2-thenoyl chloride in diethyl ether was added at 0 °C to the mixture, and allowed to reach the room temperature and stirred for another hour. The resulted mixture was neutralized by diluted acetic acid solution. The ether layer was separated and acid layer was extracted twice with diethyl ether and the whole ether solution was washed with water, and then dried by anhydrous sodium sulfate. The solvent was removed by suction, and red needle crystals were appeared which by recrystallization from CH_3Cl solution 4.4 gr (10% yields) pure compound was obtained.

Deuterated analogue of DTCP, D-DTCP, was prepared by dissolving the non-deuterated molecule in a mixture of dry CCl_4 and D_2O (5:1). After a few hours, the aqueous phase was removed in a nitrogen filled glove box and this approach was repeated three times. The latest organic phase was dried over anhydrous sodium sulfate and the solvent was removed in order to crystallize D-DTCP under vacuum.

Equipment

The mid-Infrared spectra were obtained in the range of 4000–500 cm^{-1} with spectral resolution of 2 cm^{-1} by coadding the results of 10 scans on a Bomem MB-154 Fourier Transform Spectrophotometer.

FT-Raman spectra from 3500 to 170 cm^{-1} were recorded using a 180° back-scattering geometry and a Bomem MB-154 Fourier Transform Raman spectrometer. It was equipped with a ZnSe beam splitter and a TE cooled InGaAs detector. Rayleigh filtering was afforded by a set of two holographic technology filters. Laser power at the samples was 300 mW. The spectra were collected with a resolution of 4 cm^{-1} by coadding the results of about 5000 scans.

All IR and Raman spectra were measured at room temperature. Solids for IR were examined as KBr discs and solution spectra were considered in CCl_4 solution.

^1H NMR spectra were recorded on a Varian Gemini 200 spectrophotometer at 200 Hz in $CDCl_3$. The chemical shifts were referenced to the signal of TMS at 20 °C.

Method of analysis

All quantum calculations were carried out with the GAUSSIAN 09W software package [33], applying the modern density functional theory, DFT method. The hybrid gradient-corrected (three-parameter nonlocal) exchange functional by Becke [34] with the gradient corrected (nonlocal) correlation functional of Lee, Yang and Parr [35] was selected. All possible enol and keto conformations of DTCP were fully optimized at the B3LYP level

using 6-31G(d,p) basis set. In addition, the geometry of all possible cis-enol conformers engaged in the intramolecular hydrogen bond, their corresponding trans-enol conformers, and the geometry of thiophene (for comparison) were also fully optimized using the 6-311G(d,p) and 6-311++G(d,p) basis sets, where the latter is a triple-zeta split valence basis set augmented with polarization and diffuse functions [36] on all atoms (504 basis functions and 802 primitive gaussians). Since the electron correlation methods have presented satisfactory results when investigating the weak interactions such as IHB, MP2 optimizations were also done on the enol forms to obtain their relative stabilities and their IHB interaction energies. Frequencies calculations were performed at the B3LYP level using 6-311G(d,p) basis set. The assignment of the calculated wavenumbers is aided by the animation option of GaussView 5.0 graphical interface [37] for Gaussian programs, which gives a visual presentation of the shape of the vibrational modes. In order to estimate the barrier height for proton transfer in the most stable enol forms, the enolated proton was placed in the midway of oxygen atoms of the chelated ring (H-centered forms, HC, in Fig. 2, as the transition states, TS). The only restriction for the calculations of the H-centered species is the equality of O(1)—H(10) and O(2)—H(10) bond distances; all other geometrical parameters are relaxed for full optimization. The atom numbering scheme of the system is also shown in Fig. 2.

Results and discussion

Conformational stability

From the theoretical point of view, in addition to the three H-centered conformations (which are supposed as the transition states for proton transfer), 74 different keto and enol conformers can be drawn for DTCP, which some of them are shown in Figs. 2–4. Half of all 32 enol forms are cis-enol (in which the O—H and C5=C6 bonds are in the cis arrangement, and designated as *I*), and the second half are trans-enol conformations (designated as *II*). Among 16 cis-enol forms, there are only 4 chelated enol (*CE*) forms, i.e. the CE1(I), CE2(I), CE3(I), and CE4(I) conformers in Fig. 2, which have the 7-membered chelated ring of the IHB. Remainder 12 cis-enol forms, in addition to the 16 trans-enol forms, are non-chelated enol (*NE*) conformers (Fig. 3). Also there are 42 keto forms which are classified as K_a, K_b and K_c. The H10 (the enolated H atom in the enol forms) is adjoined to the C6, C7 and C8 to form K_a, K_b and K_c keto forms, respectively (Fig. 4). The atom numbering scheme of the system, and the H-centered conformations are also shown in Fig. 2.

For comparison, the relative energies of all enol and some keto tautomers of DTCP calculated at the B3LYP/6-31G(d,p) level of theory are given in Figs. 2–4. These relative energies clearly suggest that the chelated cis-enol conformers are so stable that the presence of other conformers in significant amounts in the sample is unlikely. Such high relative stability can be attributed to the strong IHB that is also assisted by resonance, RAHB, which is absent in the keto and non-chelated enol conformers. The relative stability of the keto forms, about 15–18 kcal/mol, is the next in line. The most unstable forms are those non-chelated enol (including 16 transenol and 12 cis-enol) conformers, due to the diverse steric hindrances. Their relative stabilities vary from 17.8 to 24.5 kcal/mol, with respect to the most stable chelated form, CE4(I).

The calculated relative stabilities of the four most stable chelated cis-enol forms, their corresponding trans-enol conformers, and H-centered structures are listed in Table 1. B3LYP calculations using different basis sets show that the conformer CE4(I) is at least about 1.0 kcal/mol more stable than other chelated conformations. Also MP2 method has been used to confirm this stability and showed that CE4(I) enol form is the most stable conformer in this method, too.
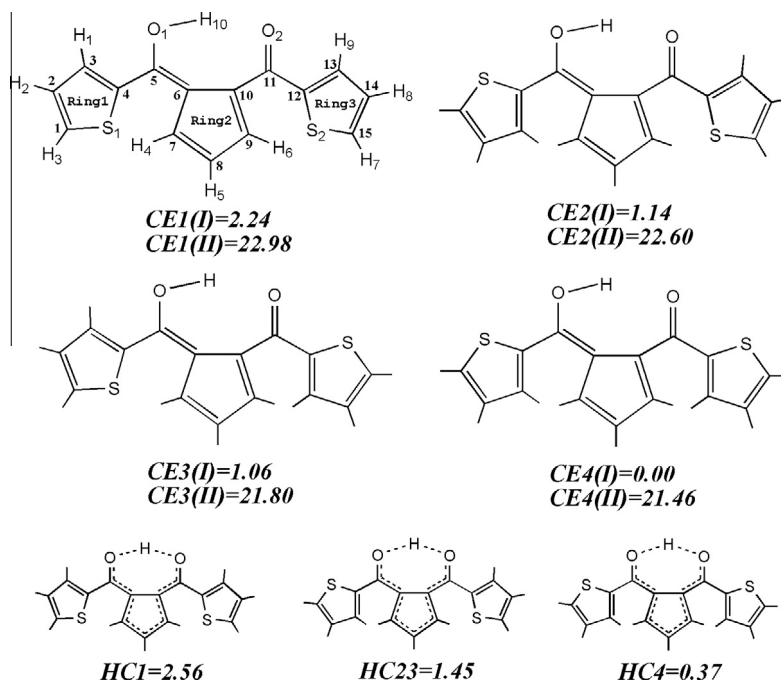
Fig. 2. Chelated enol (cis and trans) and H-centered forms of DTCP, and their relative stabilities (in kcal/mol) at B3LYP/6-31G(d,p) level, and the atom numbering scheme of the molecule.

This is predicted from all levels of calculation that the conformations CE4 and CE1 are the most stable and the most unstable chelated forms, respectively. This result can be rationalized by electrostatic attractions between partial positive charge of the sulfur atoms of the thienyl rings (due to the contribution of its lone pair electrons to the ring electron resonance) and the lone-pair electrons of the oxygen atoms. In the CE4 conformer, there are two interactions of this kind, and so, this form is the most stable. Also, in the conformer CE3 this electrostatic attraction becomes more significant than CE2 conformer, since in CE3 the sulfur atom of the ring 3 is near to the carbonyl group in which the lone pair of the oxygen atom is in the thienyl ring plane (see Fig. 2). Hence, the stability trend of chelated cis-enol forms is as follows: CE1 < CE2 < CE3 < CE4.

Molecular structure

The fully optimized structural parameters of the four chelated cis-enol forms of DTCP calculated at B3LYP with three basis sets are summarized in Table 2. For comparison, the optimized geometry of non-substituted thiophene and fulvene molecules calculated at B3LYP/6-311++G(d,p) level along with thiophene experimental results [38,39] are also given in this table. According to our literature surveys there is no report on the experimental structure of DTCP compound, which the calculated results could be compared with. After comparing the calculated geometrical parameters of the thienyl groups in DTCP and those of the free thiophene heterocyclic molecule in Table 2, the following points could be concluded.

Both C═C bonds of each thienyl group in DTCP are longer, whereas the C—C single bond length is shorter than the corresponding bond lengths in thiophene. These results suggest an increase of π-electron delocalization into the enolone ring of DTCP.

Thiophene, a heterocyclic molecule with C_{2v} symmetry, has aromatic character. The shorter S(1)—C(1) and S(1)—C(4) bonds and the longer S(2)—C(12) and S(2)—C(15) bond lengths in the thienyl rings of DTCP compared with the corresponding bonds of thiophene, indicate an asymmetric structure for the thienyl groups.

This is caused by the well-oriented conjugations between the thienyl rings and the enol ring.

Because the dihedral angles between the CP ring and the thienyl rings, due to their steric hindrance, are in the range of 21–34°, for all optimized geometries of CE conformers of DTCP in different level of calculations, the strong conjugation of π-electron system between these rings are less probable. This is confirmed by C4—C5 and C11—C12 bond lengths of DTCP, which are very close to the length of single bonds, indicating low π-electron delocalization of the thienyl rings with the CP and chelated rings. Also, higher bond order and the shorter bond length of 1.450 Å for C4—C5 bond in thenoyltrifluoroacetone, TTFA, (a β-dicarbonyl with a co-planar thienyl ring in a β position [40]) compared to that of DTCP, is in agreement with the less conjugation in the latter. By investigating all double and single bond lengths in thienyl rings of DTCP and TTFA, which are shorter and longer, respectively, in DTCP compared to those of TTFA, the less delocalization in this segment of DTCP is again confirmed.

Although the π-electron delocalization between the thienyl and chelated rings in DTCP is not as much as TTFA, but it is more probable in the side of the C—O single bond than the side of C═O double bond of DTCP. This is concluded by comparing the bond lengths of C4—C5 and C11—C12, which is meaningfully shorter for the former, showing more double bond character in the C—O side.

Data in Table 2 also show that the C═C and C–C bonds of the CP ring of DTCP are respectively longer and shorter than those of fulvene ring. These indicate more electron delocalization in the CP ring of DTCP, compared to non-substituted fulvene molecule. Also a comparison between these bond lengths with their corresponding bonds in DCACP [31] and MCACP [32] shows more electron delocalization in this segment of DTCP molecule. Because of this more electron delocalization between CP and chelated rings, the C(5)═C(6) bond length in DTCP (1.401 Å) is longer than corresponding bond in fulvene (1.341 Å), MCACP (1.387 Å) and DCACP (1.396 Å).

The enolone ring in different conformers of DTCP has a dihedral angle of range 16–19° with the CP ring. This is because of deviation
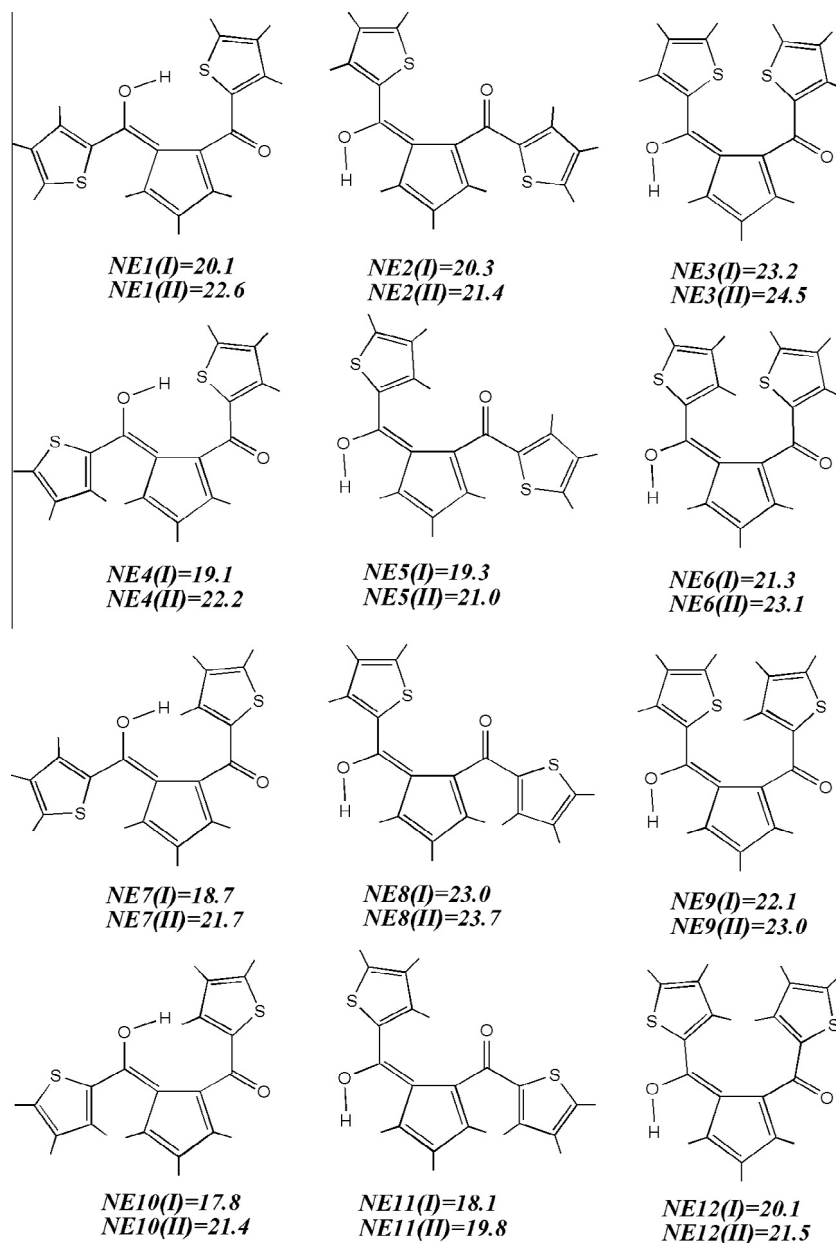
Fig. 3. Non-chelated enol (cis and trans) conformers of DTCP, and their relative stabilities (in kcal/mol) compared to the most stable enol form, at B3LYP/6-31G(d,p) level.

from planarity in enolone ring. In fact the C=O bond of this ring has two choices of plane for being co-planar with, in order to reduce energy by π-electron delocalization. These choices are thienyl and CP planes, which themselves have a dihedral angle of range 21–34° with each other, as mentioned before. Therefore the C=O bond has a restraint to arrange somewhere between these two plains. This constraint is well confirmed when the trans-enol conformers are investigated. In these forms, there is no enolone ring, and according to the optimized geometries of all trans-enol forms of DTCP, the C=O and C—O bonds lay in the thienyl and CP planes, respectively, without restraint.

It has been shown in the enol forms of β-dicarbonyl compounds that the Gilli's symmetry coordinates, q_1 ($d_{C-C}-d_{C=C}$), q_2 ($d_{C-O}-d_{C=O}$), and Q ($q_1 + q_2$) [41], offer a criterion for the bond equalization in their chelated ring due to their resonance assisted hydrogen bonding (RAHB). The values of $q_1 = 0.15$ and $q_2 = 0.17$ for the standard bond distances in the absence of π delocalization [42] lead to $Q = 0.32$ for the completely π-localized enol forms,

while $Q = 0.0$ corresponds to the fully π-delocalized structures [19,41]. These Gilli's parameters for the most stable enol form of DTCP, in comparison with MCACP, DCACP and some β-dicarbonyl compounds are represented in Table 3. In the case of 1,2-DACPs, we used two ways to obtained q_1 parameter; first the value obtained from difference of two C(10)—C(11) and C(5)=C(6) bonds, second the averaged values obtained from differences between C(6)—C(7), C(8)—C(9) and C(10)—C(11) single bonds and C(5)=C(6), C(7)=C(8) and C(9)=C(10) double bonds (see footnote of Table 3). The values obtained from the second way could be used as a criterion for bond equalization in the enolone ring by π-electron delocalization through the CP ring. The relatively very low values of q_1 and q_2 indicate high delocalization for the π-electrons of the system in DTCP molecule. For comparison, the Q parameters obtained from related bond lengths of DTCP, dibenzoylmethane (DBM) [43], benzoylacetone (BA) [44], TTFA [40], α-cyanoacetylacetone (CNAA) [45], 2,2,6,6-tetramethyl-3,5-heptanedione (TMHD) [46], and acetylacetone (AA) [47] are
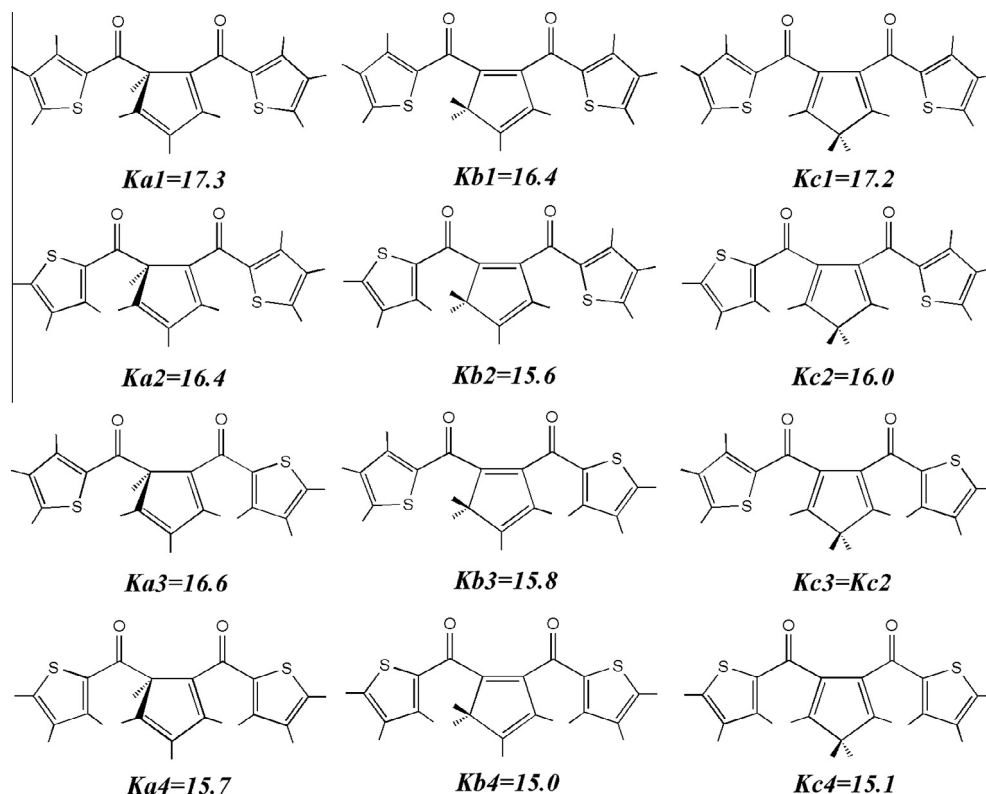
Fig. 4. Selected conformations for different kinds of keto tautomers of DTCP, and their relative stabilities (in kcal/mol) at B3LYP/6-31G(d,p) level, compared to the most stable enol form.

Table 1
Calculated relative energies of the chelated cis-enol (I) conformations of DTCP and their corresponding open (II), and also H-centered (HC) structures (in kcal/mol)[a].

Conformer	B3LYP			MP2
	6-31G(d,p)	6-311G(d,p)	6-311++G(d,p)	6-31G(d,p)
CE1(I)	2.24	2.25	2.00	2.45
CE2(I)	1.14	1.16	1.00	1.24
CE3(I)	1.06	1.04	0.95	1.15
CE4(I)	0.00[b]	0.00[c]	0.00[d]	0.00[e]
HC11	2.56	2.77	2.56	-
HC23	1.45	1.67	1.55	-
HC44	0.37	0.61	0.61	-
CE1(II)	22.98	21.63	20.54	16.76
CE2(II)	22.60	21.40	20.24	15.93
CE3(II)	21.80	20.44	19.60	15.52
CE4(II)	21.46	20.24	19.34	14.79

[a] The relative energies of the open structures were employed to evaluate the IHB energies.
[b] The absolute value is −1524.4209828 Hartrees.
[c] The absolute value is −1524.6356464 Hartrees.
[d] The absolute value is −1524.6487452 Hartrees.
[e] The absolute value is −1518.5443201 Hartrees.

0.082, 0.133, 0.140, 0.142, 0.144, 0.147 and 0.150, respectively, all calculated at B3LYP/6-311++G(d,p) level of theory. This trend clearly indicates three points as followed; First, the resonance conjugation of phenyl, thienyl, CP and cyano groups assist the delocalization of π-electrons in the chelated ring of IHB. Secondly, the IHB strengths, which do not follow the mentioned trend of Q values, should depend on some other parameters (such as σ-skeleton) besides the resonance assisting of functional groups in IHB. Third, the delocalization in 7-membered chelated ring of DTCP γ-dicarbonyl compound is very much more assisted compared to that in 6-membered chelated ring of β-dicarbonyl molecules. Comparison between the Gilli's symmetry coordinates of DTCP with those of

MCACP and DCACP shows more π-electrons resonance conjugation in the enolone and CP rings of DTCP, which could be attributed to the reinforcement of the thienyl rings. This is the reason for shorter and longer lengths of single and double bonds, respectively, in the CP ring of DTCP, compared to those in MCACP and DCACP.

Intramolecular hydrogen bonding

In order to investigate the IHB strength of DTCP, the calculated IHB energy, E_{HB}, estimated by energy difference between the cis-enol (I) and the trans-enol (II) conformations, is compared with E_{HB} of MCACP and DCACP, and also with some β-dicarbonyls with the strongest IHBs in Table 4. According to the data in this table, the estimated E_{HB} in all CE forms of DTCP is even higher than that in the β-dicarbonyls with the strongest IHB which have been reported previously in the literature (TMHD, DBM, and CNAA). Also in comparison with other 1,2-DACPs (MCACP and DCACP), Table 4 shows that DTCP have stronger IHB. DFT calculated harmonic frequencies for different OH and OD stretching and bending vibrational motions are also collected in Table 4. The stronger IHB of DTCP is well confirmed by comparison between its given vibrational properties with those of the selected β-dicarbonyls and 1,2-DACPs (lower the values for stretching and higher the values for bending frequencies, stronger the IHB).

The calculated barrier height for proton transfer is also good criterion to be investigated for IHB strength. Table 3 also shows the barrier heights for proton transfers in the most stable chelated conformer of DTCP in comparison with some other 1,2-DACPs and β-dicarbonyls. The barrier height energies, E_{BH}, for four chelated conformers of DTCP, calculated as their energy differences with their corresponding HC forms at B3LYP/6-31G(d,p), are in the range of 0.31–0.39 kcal/mol. The corresponding barrier heights for AA, and HFAA are 1.71 and 2.45 kcal/mol, [48] respectively. Also, the lowest

Table 2
Fully optimized structural parameters[a] of cis-enol chelated forms of DTCP, also those of thiophene (beside its experiment) and cyclopentadiene ring in fulvene, DCACP and MCACP.

Bond Lengths	DTCP												Fulvene[b]	DCACP[c]	MCACP[b]	Thiophene[d]	
	B3LYP/6-31G(d,p)				B3LYP/6-311G(d,p)				B3LYP/6-311++G(d,p)				B3LYP/6-311++G(d,p)				Exp.
	CE1	CE2	CE3	CE4	CE1	CE2	CE3	CE4	CE1	CE2	CE3	CE4					
S(1)—C(1)	1.727	1.726	1.727	1.725	1.725	1.723	1.724	1.723	1.724	1.723	1.724	1.723				1.733	1.714
C(1)—C(2)	1.371	1.372	1.371	1.372	1.369	1.369	1.369	1.369	1.370	1.370	1.370	1.370				1.366	1.370
C(2)—C(3)	1.418	1.419	1.418	1.419	1.415	1.417	1.415	1.417	1.416	1.417	1.416	1.417				1.428	1.432
C(3)—C(4)	1.381	1.381	1.381	1.381	1.378	1.378	1.378	1.378	1.379	1.379	1.379	1.379				1.366	1.370
S(1)—C(4)	1.752	1.752	1.752	1.752	1.749	1.750	1.750	1.750	1.750	1.750	1.750	1.750				1.733	1.714
C(4)—C(5)	1.466	1.461	1.466	1.461	1.465	1.460	1.464	1.459	1.464	1.460	1.464	1.459					
C(5)—C(6)	1.406	1.405	1.406	1.405	1.402	1.401	1.402	1.401	1.402	1.401	1.402	1.401	1.341	1.386	1.387		
C(6)—C(7)	1.430	1.430	1.431	1.430	1.431	1.431	1.431	1.431	1.431	1.431	1.432	1.432	1.474	1.437	1.434		
C(7)—C(8)	1.387	1.387	1.387	1.387	1.383	1.383	1.383	1.383	1.384	1.384	1.384	1.384	1.351	1.379	1.382		
C(8)—C(9)	1.411	1.412	1.411	1.412	1.411	1.412	1.412	1.413	1.412	1.413	1.412	1.414	1.475	1.416	1.416		
C(9)—C(10)	1.405	1.405	1.404	1.404	1.401	1.401	1.400	1.400	1.401	1.401	1.401	1.401	1.351	1.396	1.397		
C(10)—C(11)	1.437	1.438	1.438	1.438	1.439	1.439	1.440	1.440	1.439	1.439	1.439	1.439					
C(11)—C(12)	1.478	1.478	1.472	1.471	1.479	1.478	1.472	1.472	1.478	1.477	1.472	1.472					
C(12)—C(13)	1.379	1.379	1.380	1.380	1.376	1.376	1.377	1.378	1.377	1.377	1.378	1.378				1.366	1.370
C(13)—C(14)	1.418	1.418	1.420	1.420	1.416	1.416	1.418	1.418	1.417	1.417	1.419	1.418				1.428	1.432
C(14)—C(15)	1.371	1.371	1.372	1.372	1.369	1.369	1.369	1.369	1.370	1.370	1.370	1.370				1.366	1.370
C(15)—S(2)	1.727	1.727	1.726	1.726	1.725	1.725	1.723	1.723	1.725	1.725	1.723	1.723				1.733	1.714
S(2)—C(12)	1.753	1.753	1.751	1.751	1.750	1.750	1.748	1.748	1.750	1.750	1.748	1.748				1.733	1.714
O(1)—C(5)	1.307	1.307	1.307	1.307	1.306	1.307	1.307	1.307	1.308	1.308	1.308	1.309					
O(2)—C(11)	1.266	1.266	1.267	1.267	1.258	1.258	1.258	1.258	1.260	1.259	1.260	1.260					
O(1)···O(2)	2.434	2.436	2.440	2.442	2.450	2.452	2.457	2.461	2.452	2.456	2.458	2.463					
O(1)—H(10)	1.063	1.063	1.060	1.060	1.047	1.046	1.044	1.043	1.047	1.046	1.045	1.043					
O(2)···H(10)	1.379	1.383	1.388	1.392	1.413	1.418	1.422	1.428	1.414	1.421	1.422	1.430					
C(3)—H(1)	1.082	1.082	1.082	1.082	1.081	1.080	1.080	1.080	1.081	1.080	1.081	1.080				1.082	1.081
C(2)—H(2)	1.084	1.084	1.084	1.084	1.082	1.082	1.082	1.082	1.082	1.082	1.082	1.082				1.082	1.081
C(1)—H(3)	1.081	1.082	1.082	1.082	1.079	1.080	1.079	1.080	1.080	1.080	1.080	1.080				1.079	1.078
C(7)—H(4)	1.080	1.080	1.080	1.080	1.078	1.078	1.078	1.079	1.078	1.079	1.078	1.079	1.081	1.080	1.079		
C(13)—H(9)	1.083	1.083	1.082	1.082	1.081	1.081	1.080	1.080	1.081	1.081	1.081	1.080				1.082	1.081
Bond angles																	
C(1),S(1),C(4)	91.6	91.4	91.6	91.4	91.5	91.3	91.5	91.3	91.6	91.4	91.6	91.4				91.5	92.2
C(3),C(4),S(1)	110.2	110.6	110.2	110.6	110.3	110.6	110.3	110.6	110.3	110.6	110.3	110.6				111.5	111.5
S(1),C(4),C(5)	125.4	118.9	125.4	118.9	125.2	119.0	125.2	119.1	125.0	119.3	125.0	119.3				120.0	119.9
S(1),C(1),C(2)	112.1	112.3	112.1	112.3	112.1	112.3	112.1	112.3	112.1	112.3	112.1	112.3				111.5	111.5
C(1),C(2),C(3)	112.5	112.5	112.5	112.5	112.5	112.5	112.5	112.5	112.5	112.5	112.5	112.5				112.7	112.5
C(2),C(3),C(4)	113.6	113.2	113.6	113.2	113.5	113.2	113.6	113.2	113.5	113.2	113.5	113.2				112.7	112.5
C(3),C(4),C(5)	124.1	130.3	124.1	130.3	124.3	130.2	124.3	130.1	124.4	130.0	124.4	130.0					
C(4),C(5),C(6)	124.9	123.2	125.0	123.2	124.8	123.1	124.9	123.1	124.9	123.1	124.9	123.1					
H(1),C(3),C(4)	121.7	122.8	121.7	122.8	121.8	122.8	121.8	122.8	121.9	122.8	121.9	122.8				123.3	123.3
H(9),C(13),C(12)	121.4	121.4	122.9	122.9	121.4	121.4	122.9	122.9	121.7	121.6	122.9	122.9				123.3	123.3
C(5),O(1),H(10)	110.8	110.5	111.1	110.8	110.8	110.5	111.0	110.8	110.9	110.6	111.2	110.9					
O(1),H(10),O(2)	170.5	169.9	170.3	169.7	170.1	169.5	170.0	169.2	170.2	169.5	170.1	169.4					
Dihedral angles																	
∠C3,C4,C5,C6	−157.2	31.5	−157.4	31.2	−155.2	33.3	−155.7	33.0	−154.6	34.2	−155.2	33.7					
∠C10,C11,C12,C13	158.5	158.9	−29.4	−28.8	157.4	157.4	−30.7	−30.1	156.3	156.7	−31.6	−31.2					
∠C9,C10,C11,O2	164.2	163.8	162.8	162.3	163.0	162.6	161.7	161.1	162.6	162.2	161.7	161.3					

[a] Bond lengths are in Å, and bond angles are in degrees.
[b] Data from [32].
[c] Data from [31].
[d] Calculated results from [40], and the X-ray experimental data from [38,39].

Table 3
Gilli's symmetry coordinates, IHB and barrier height energies for DTCP, in comparison with some 1,2-DACPs and β-dicarbonyls[a].

Parameter	DTCP[b]	DCACP[b]	MCACP[b]	DBM[c]	BA[c]	TTFA[d]	CNAA[e]	TMHD[f]	AA[c]
q_1	0.033(0.038)	0.040(0.042)	0.044(0.044)	0.061	0.066	0.065	0.074	0.070	0.070
q_2	0.049	0.052	0.054	0.072	0.074	0.076	0.070	0.077	0.080
Q	0.082	0.092	0.098	0.133	0.140	0.142	0.144	0.147	0.150
E_{HB}	19.34	16.60	18.39	16.15	16.07	13.57	16.26	17.90	15.87
E_{BH}	0.31	1.46	–	1.61	–	1.89	1.33	1.28	1.71

[a] Symmetry coordinates (in Å) and IHB energies, E_{HB}, at B3LYP/6-311++G(d,p); E_{BH} at B3LYP/6-31G(d,p); energies are given in kcal/mol.
[b] For 1,2-DACPs, the values for q_1 were obtained from $q_1 = \frac{1}{3}\sum_{i=6,8,10}\{d[C(i) - C(i+1)] - d[C(i-1) = C(i)]\}$ equation, while the values in parentheses are the difference of two C(10)—C(11) and C(5)=C(6) bonds.
[c] Data from [43].
[d] Data from [40].
[e] Data from [45].
[f] Data from [46].

Table 4
Calculated non-scaled spectroscopic parameters[a] (in cm^{-1}) related to the IHB strength, and IHB energies (E_{HB} in kcal/mol) for all chelated tautomers of DTCP, in comparison with some 1,2-DACPs and β-dicarbonyls.

Parameter	DTCP				DCACP[b]	MCACP[c]	CNAA[d]	DBM[e]	TMHD[f]
	CE1	CE2	CE3	CE4					
νOH	2321	2305	2282	2268	2229	2459	2760	2914	3006
νOD	1779	1772	1760	1754	1753	1865	1996	2136	2201
δOH	1649	1655	1654	1656	1627	1658	1699	1639	1636
γOH	1143	1143	1145	1143	1088	1138	1060	1002	989
γOD	828	828	831	836	795	829	796	714	699
E_{HB}[g]	20.74	21.46	20.75	21.46	17.97	20.53	–	–	–
E_{HB}[h]	19.38	20.23	19.40	20.24	16.48	19.93	–	–	–
E_{HB}[i]	18.54	19.24	18.65	19.34	16.60	18.39	16.26	16.15	17.9
E_{HB}[j]	14.31	14.70	14.38	14.79	–	–	–	–	–

[a] ν, Stretching; δ, in-plain bending; γ, out-of-plain bending; all calculated at B3LYP/6-311G(d,p), otherwise mentioned.
[b] Non-scaled spectroscopic parameters obtained from scaled values calculated at B3LYP/6-31G(d,p) [31].
[c] Non-scaled spectroscopic parameters obtained from scaled values calculated at B3LYP/6-311++G(d,p) [32].
[d] spectroscopic parameters for OH calculated at B3LYP/6-31G(d,p), and for OD calculated at B3LYP/D95** [45].
[e] Data from [43].
[f] Data from [46].
[g] Calculated at B3LYP/6-31G(d,p).
[h] Calculated at B3LYP/6-311G(d,p).
[i] Calculated at B3LYP/6-311++G(d,p).
[j] Calculated at MP2/6-31G(d,p).

E_{BH} for proton transfer in the stable conformations of TTFA and TMHD are 1.89 [40] and 1.28 kcal/mol [46], respectively. For CNAA and DBM, which have the strongest IHBs that have been reported for β-dicarbonyls, the proton transfer barrier heights were calculated in this work at the mentioned level of theory and the values of 1.33 and 1.61 kcal/mol are obtained, respectively. Thus, the barriers for proton transfer in all DTCP conformers are significantly much lower than those in all mentioned β-dicarbonyls. These results also confirm that the IHB strength in DTCP conformers is stronger even than those in the β-dicarbonyls with the strongest reported IHBs. Besides, the estimated barrier for DTCP compound is much lower than the corresponding value reported for MCACP (1.46 kcal/mol) by Tayyari et al. [32]. The very low barrier height for proton transfer in DTCP approves a very strong IHB in this compound.

In order to confirm that the IHB of DTCP is stronger than the strongest IHB of β-dicarbonyls, and also stronger than MCACP and DCACP, the geometrical parameters related to the IHB strength for DTCP, DCACP, MCACP, as well as those of selected β-dicarbonyls with the strongest IHB, are collected in Table 5. The O···O distances of the given β-dicarbonyls lie between 2.496 and 2.508 Å, while for DCACP and MCACP, these are shorter and more proper to form stronger IHB. The steric hindrance of the thienyl groups and σ-skeleton of the chelated ring in DTCP, make the O···O distance in this molecule even shorter than that in DCACP and MCACP γ-dicarbonyl compounds. Also, O···H distances and O—H bond

Table 5
Calculated enolone structural parameters for the most stable chelated cis-enol forms of DTCP, and some 1,2-DACPs and β-dicarbonyls[a].

Parameter	DTCP	DCACP[b]	MCACP[c]	CNAA[d]	DBM[e]	TMHD[f]
dO···O	2.463	2.472	2.489	2.496	2.502	2.508
dO···H	1430	1.442	1.462	1.570	1.574	1.583
dO—H	1.043	1.039	1.035	1.012	1.010	1.008
∠OHO	169.4	170.2	170.7	149.6	150.4	150.3

[a] d in Å, ∠ in degrees, all calculated at B3LYP/6-311++G(d,p).
[b] Data from [31].
[c] Data from [32].
[d] Data from [45].
[e] Data from [43].
[f] Data from [46].

lengths in Table 5 confirm that DTCP has the strongest IHB. Therefore, in addition to the more RAHB, it is concluded that the σ-skeleton of DTCP molecule is responsible for its very strong IHB.

Experimental investigations

In order to experimentally investigate the IHB strength, and also the electron delocalization in the chelated, thiophene, and CP rings, the vibrational studies have been performed on DTCP compound. The special attention has been paid to the stretching modes of OH, C=C and C=O bonds, as well as the in-plane and out-of-plain

bending mode of OH bond. The collected IR spectrum of DTCP in the solid state in the range of 3150–500 cm^{-1} is given in Fig. 5. Also, Fig. 6 compares the IR spectra of DTCP and its deuterated analogue in CCl$_4$ solutions in the range of 1650–1000 cm^{-1}. In order to assign the observed bands to their attributed vibrational motions, the IR spectra of DTCP have been compared with the measured IR spectrum of its deuterated analogue, and also with the DFT calculated vibrational spectra for the most stable enol forms of DTCP and its deuterated analogue. Also, the Raman spectrum of this compound in the solid phase has been employed to increase the assignment accuracy.

Two strong bonds are observed in the region of 1570–1610 cm^{-1} in the IR spectrum of MCACP, which were assigned to the stretching vibration of the C=O and C=C bonds of the chelated ring, strongly coupled with in-plane bending mode of the OH bond, δOH [32]. The same bands are observed in the same region in the IR spectrum of DCACP compound [31]. But, in the case of DTCP molecule, these bands shift to the region of 1540–1600 cm^{-1} (we attributed the strong band at 1518 cm^{-1} to the motion 14 of the thienyl rings, in accordance to the characterization of the thiophene vibrational modes in our previous work on TTFA [3], coupled with δOH). This shows more single character for C=O and C=C bonds, which is caused by more electron delocalization in the chelated ring of DTCP in comparison with MCACP and DCACP compounds. Also, more electron delocalization in the chelated ring of DTCP compared to β-dicarbonyl compounds is confirmed, since the mentioned bands for β-dicarbonyls are observed around or above 1600 cm^{-1} region.

According to our assignment, asymmetric stretching of C7=C8 and C9=C10 bonds of the CP ring is observed at 1459 cm^{-1} of

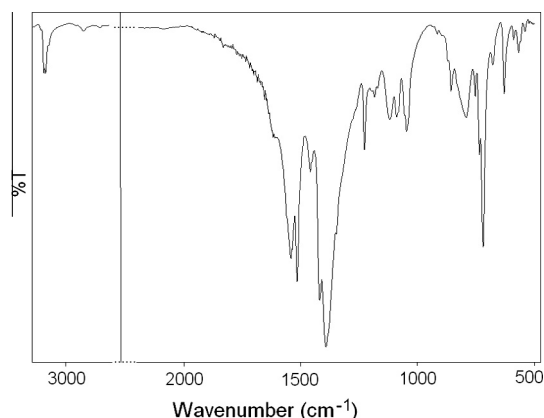**Fig. 5.** The solid phase IR spectrum of DTCP, in the region of 3150–500 cm^{-1}.

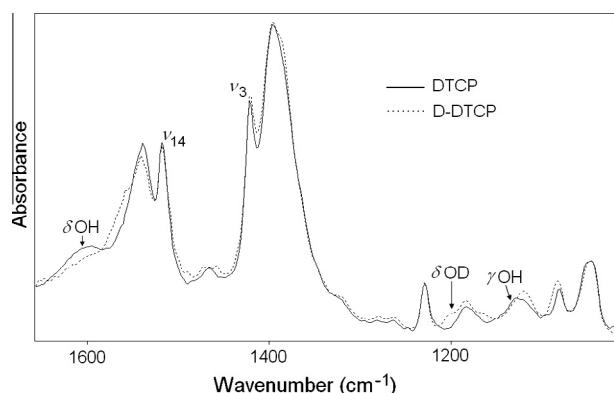**Fig. 6.** Comparison between IR spectra of DTCP and its deuterated analogue in CCl$_4$ solutions, in the region of 1650–1000 cm^{-1}.

the IR spectrum of DTCP in the solid phase. The corresponding bands in the solid phase spectra of DCACP and MCACP are observed at 1484 and 1504 cm^{-1}, respectively [31,32]. This downward shift in DTCP spectrum, which is confirmed by Raman spectra, is attributed to the more electron delocalization in the CP ring of this compound compared to DCACP and MCACP compounds.

The most intense Raman band of DTCP at 1422 cm^{-1} is assigned to the ν_sC=C of the thienyl rings. This band, which is ν_3 mode of the thienyl rings according to the thiophene vibrational modes' characterization in our work on TTFA [3], is observed also as the most intense band at 1410 cm^{-1} of the Raman spectrum of TTFA molecule [3]. The less electron delocalization in the thienyl rings of DTCP compared to that of TTFA molecule, which was also obtained by geometrical comparisons in the molecular structure section, is well confirmed by the upward shift for ν_sC=C band of the thienyl rings in DTCP, which is in agreement with the DFT calculated spectra. The corresponding IR bands appear at 1418 and 1414 cm^{-1}, for DTCP and TTFA, respectively.

According to the results of the theoretical studies in the previous section, because of the electron delocalization and σ-skeleton of the molecule (short O⋯O distance and near linear O–H⋯O bond), the IHB in DTCP molecule is almost symmetric and very strong. In addition, according to the results of ^{1}H NMR study on DTCP in CDCl$_3$, which the spectra is given in Fig. 7, the value of 18.29 ppm for chemical shift of the enolated proton confirms a very strong IHB in this compound. In such system, a very broad band for νOH is expected to be observed in a comparatively very low frequency region (about 1000–2000 cm^{-1}) [49], which is overlapped by other bands in this region [49,50] and losses its real shape. Therefore recognition of this band is very difficult for such system with linear, low barrier, nearly symmetric and very strong IHB. Moreover, according to the DFT calculations, the νOH and νC=O vibrations of DTCP are strongly coupled with each other. This causes difficulty also in determination of the νC=O band place. However, very low frequency for C=O stretching in DTCP molecule confirms its very strong IHB.

In addition to the OH stretching mode, out-of-plain bending motion of the OH bond, γOH, which is often pure and appears as a broad band, could be a good criterion for evaluation of the IHB strength in the systems with chelated rings. As illustrated in Fig. 6, based on our assignment the γOH band is observed at 1128 cm^{-1} in the IR spectrum of DTCP compound, which disappears upon deuteration. The corresponding bands for DCACP and MCACP compounds are observed at 1074 and 1105 cm^{-1}, respectively [31,32]. This confirms stronger IHB in DTCP compared to DCACP and MCACP compounds.

Although δOH is not as pure as νOH and γOH bands, but this might be also as a criterion for IHB strength in the chelated systems. Because this vibration is often coupled to some other modes (such as νC=C and νC–C), and therefore its position is sensitive to the neighboring substitutions, more carefulness should be taken into account when using this motion as criterion for IHB strength. The IR spectrum of DTCP shows a near strong band at 1596 cm^{-1} that disappears by deuteration. Based on this behavior, and according to the DFT calculations, we attribute this band to in-plane bending vibration of the OH bond, which is strongly coupled to νC5=C6 motion. This band disappears upon deuteration and a new band for δOD is observed at 1200 cm^{-1} (see Fig. 6). This band shift (about 400 cm^{-1}) is also in agreement with the theoretical calculations. For DCACP and MCACP molecules, the corresponding band frequencies of δOH/δOD motions (which are coupled to νC=C and νC=O motion) have been reported at 1613/1157 and 1610/1163 cm^{-1}, respectively [31,32].

Table 6 compares the observed spectroscopic properties for DTCP with those of some ζ- and β-dicarbonyls, with very strong IHB, in order to perform a comparison between the influences of
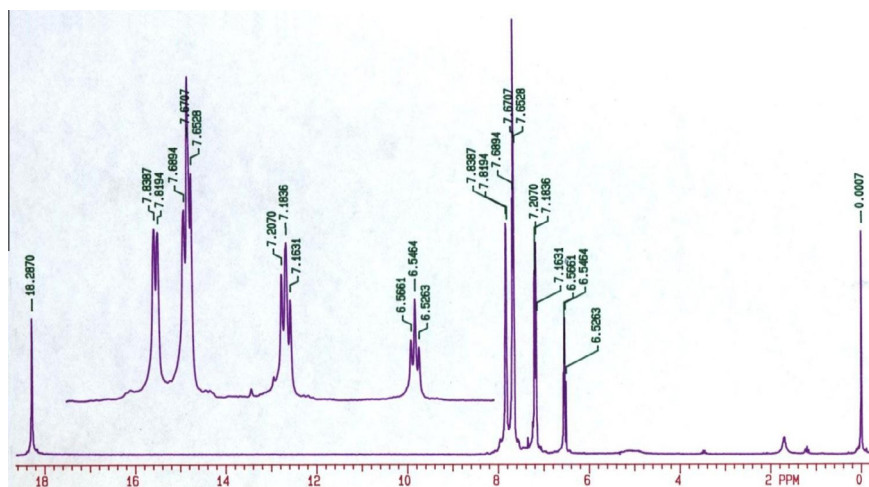
Fig. 7. ^{1}H NMR spectra of DTCP, in CDCl$_3$ solution at 20 °C.

Table 6
Empirical spectroscopic parameters related to the IHB strength of DTCP, and some 1,2-DACPs and β-dicarbonyls[a].

Parameter	DTCP	DCACP[b]	MCACP[c]	CNAA[d]	DBM[e]	TMHD[f]
δ OH(ppm)	18.29	17.34	17.30	16.9	16.8	16.27
ν OH(cm^{-1})	–	1718	1690	2633	2620	2634
ν OD(cm^{-1})	–	–	–	1970	1950	1957
δ OH(cm^{-1})	1596	1613	1610	1547	1572	1584
δ OD(cm^{-1})	1200	1157	1163	–	1080	1060
γ OH(cm^{-1})	1128	1074	1105	993	965	964
γ OD(cm^{-1})	–	756	–	744	720	673

[a] δOH, in ppm is enolated proton chemical shift in ^{1}H NMR study; ν, δ, and γ, in cm^{-1}, are stretching, in-plain, and out-of-plane bending vibrational frequencies in IR study.
[b] Data from [31].
[c] Data from [32].
[d] Data from [45].
[e] Data from [43].
[f] Data from [46].

the resonance amount, and also the σ-skeleton of the molecular structure, on the strength of IHB of the chelated systems. According to the data of this table, 7-membered chelated rings form stronger IHB, even in comparison with 6-membered chelated rings with the strongest IHB. Between all compared compounds, DTCP has the strongest IHB, in accordance with the theoretical results. We attribute this to the more proper σ-skeleton of DTCP and also more electron delocalization in this molecule.

Conclusion

DTCP ζ-dicarbonyl, which is a 1,2-DACP compound, forms a very strong IHB in its enol form. According to the DFT calculations at B3LYP/6-311++G(d,P) level, it is almost linear IHB is a very short hydrogen bond with the O···O distance of 1.463 Å, and the evaluated energy of its IHB is 19.34 kcal/mol. The strength of this IHB is well attributed to the RAHB and also to the σ-skeleton of the molecule. This IHB is even stronger then that in selected β-dicarbonyls (TMHD, DBM, and CNAA) with the strongest IHB in their category. This is also stronger than the IHBs of DCACP and MCACP compounds of ζ-dicarbonyl kind. The chemical shift of 18.29 ppm for the enolated proton confirms the theoretical results, showing low barrier, nearly symmetric and very strong IHB. Investigating the observed bands related to the electron delocalization and IHB strength in the IR and Raman spectra of DTCP, and comparing

the results with those of the selected ζ- and β-dicarbonyls, confirm the strongest RAHB in DTCP compound.

References

[1] G. Gilli, V. Bertolasi, The chemistry of enols, in: Z. Rappoport (Ed.), Wiley, New York, 1990.
[2] J. Emsley, Struct. Bond. 57 (1984) 147.
[3] A-R. Nekoei, S.F. Tayyari, M. Vakili, S. Holakoei, A.H. Hamidian, R.E. Sammelson, J. Mol. Struct. 932 (2009) 112. and references there in.
[4] W.J. Hale, J. Am. Chem. Soc. 34 (1912) 1580.
[5] W.J. Hale, L. Thorp, J. Am. Chem. Soc. 35 (1913) 68.
[6] W.J. Hale, J. Am. Chem. Soc. 38 (1916) 2535.
[7] W.J. Linn, W.H. Sharkey, J. Am. Chem. Soc. 79 (1957) 4970.
[8] W.F. Little, R.C. Koestler, J. Org. Chem. 26 (1961) 3245.
[9] R. Riemschneider, M. Kruger, Monatsh. Chem. 90 (1959) 573.
[10] K. Hafner, K.H. Vopel, G. Ploss, C. Konig, Liebigs Ann. Chem. 661 (1963) 52.
[11] K. Hafner, G. Schulz, K. Wagner, Liebigs Ann. Chem. 678 (1964) 39.
[12] T. I Godovikova, S.P. Golova, S.V. Dozmorov, D. Lloyd, S. Novikov, L.I. Khmelnitskii, Russ. Chem. Bull. 21 (1972) 2313.
[13] K. Hartke, A. Kohl, T. Kampchen, Chem. Ber. 116 (1983) 2653.
[14] G. Fergusen, W.C. Marsh, R.J. Restivo, D. Lloyd, J. Chem. Soc. Perkin Trans. 2 (1975) 998.
[15] K. Hafner, H.A.E. Kramer, H. Musso, G. Ploss, G. Schulz, Chem. Ber. 97 (1964) 2066.
[16] H. Fuess, H.J. Lindner, Chem. Ber. 108 (1975) 3069.
[17] H.M. Pickett, J. Am. Chem. Soc. 95 (1973) 1770.
[18] R.S. Brown, A. Tse, T. Nakashima, R.C. Haddon, J. Am. Chem. Soc. 101 (1979) 3157.
[19] G. Gilli, F. Bellucci, V. Ferretti, V. Bertolasi, J. Am. Chem. Soc. 111 (1989) 1023.
[20] V. Bertolasi, P. Gilli, V. Ferretti, G. Gilli, Acta Crystallogr. Sect. B 51 (1995) 1004.
[21] V. Bertolasi, P. Gilli, V. Ferretti, G. Gilli, J. Chem. Soc. Perkin Trans. 2 (1997) 945.
[22] G. Gilli, P. Gilli, J. Mol. Struct. 552 (2000) 1.
[23] A.N. Campbell-Crawford, A.M. Gorringe, D. Lloyd, Chem. Ind. (London) (1966) 1961.
[24] D. Lloyd, N.W. Preston, J. Chem. Soc. C (1969) 2464.
[25] P. Zahradnic, S. Toma, M. Pariciova, Collect. Czech. Chem. Commun. 43 (1978) 938.
[26] M. Eckert-Maksic, Z.B. Maksic, D. Margetić, Croat. Chem. Acta 62 (1989) 645.
[27] S. Millefiori, A. Alparone, J. Chem. Soc. Faraday Trans. 90 (1994) 2873.
[28] C.L. Perrin, B.K. Ohta, Bioorg. Chem. 30 (2002) 3.
[29] C.L. Perrin, B.K. Ohta, J. Mol. Struct. 644 (2003) 1.
[30] M.T. Blankenbuehler, J.P. Selegue, J. Organometallic Chem. 642 (2002) 268.
[31] S.F. Tayyari, S. Laleh, M. Zahedi-Tabrizi, M. Vakili, J. Mol. Struct. 1036 (2013) 151.
[32] S.F. Tayyari, S. Laleh, M. Zahedi-Tabrizi, M. Vakili, J. Mol. Struct. 1038 (2013) 177.
[33] Gaussian 09, Revision A.02, M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery, Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S.

Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian Inc, Wallingford CT, 2009.9W.

[34] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.

[35] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B37 (1988) 785.

[36] T. Clark, J. Chandrasekhar, G.W. Spitznagel, P.V.R. Schleyer, J. Comp. Chem. 4 (1983) 294.

[37] GaussView 5.0.8, Gaussian Inc., Garnegie Office, Park, Pittsburgh, PA 15106, USA.

[38] J.S. Kwiatkowski, J. Leszczynski, I. Teca, J. Mol. Struct. 436–437 (1997) 451.

[39] B. Bak, D. Christensen, L. Hansen-Nygaard, J. Rastrup-Andersen, J. Mol. Spectrosc. 7 (1961) 58.

[40] S.F. Tayyari, A.R. Nekoei, M. Vakili, Y.A. Wang, J. Theor. Comp. Chem. 5 (2006) 647.

[41] V. Bertolasi, P. Gilli, V. Ferretti, G. Gilli, J. Am. Chem. Soc. 113 (1991) 4917.

[42] F.H. Allen, O. Kennard, D.G. Watson, L. Brammer, A.G. Orpen, R. Taylor, J. Chem. Soc. Perkin Trans. 2 (1987) S1.

[43] S.F. Tayyari, H. Rahemi, A.R. Nekoei, M. Zahedi-Tabrizi, Y.A. Wang, Acta, Part A 66 (2007) 394.

[44] S.F. Tayyari, J.S. Emampour, M. Vakili, A.R. Nekoei, H. Eshghi, S. Salemi, M. Hassanpour, J. Mol. Struct. 794 (2006) 204.

[45] S.F. Tayyari, H. Reissi, F. Milani-Nejad, I.S. Butler, Vib. Spectrosc. 26 (2001) 187.

[46] M. Vakili, S.F. Tayyari, A.R. Nekoei, H. Miremad, S. Salemi, R.E. Sammelson, J. Mol. Struct. 970 (2010) 160.

[47] S.F. Tayyari, F. Milani-Nejad, Spectrochim. Acta, Part A 56 (2000) 2679.

[48] S.F. Tayyari, F. Milani-Nejad, H. Rahemi, Spectrochim. Acta, Part A 58 (2002) 1669.

[49] M. Rajabi, M. Sc. Thesis, Ferdowsi University of Mashhad, Mashhad, Iran, 1994.

[50] K. Szczepaniak, W.B. Person, D. Hadzi, J. Phys. Chem. A 109 (2005) 6710.