

1,1,1-Trichloro-3-(1-phenethylamino-ethylidene)-pentane-2,4-dione—synthesis, spectroscopic, theoretical and structural elucidation

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ABSTRACT: 1,1,1-Trichloro-3-(1-phenethylamino-ethylidene)-pentane-2,4-dione is spectroscopically and structurally elucidated by means of linear-polarized IR spectroscopy (IR-LD) of oriented solids as a colloidal suspension in nematic liquid crystal. Structural information and IR-spectroscopic assignment are supported by quantum chemical calculations at MP2 and B3LYP level of theory and 6-311++G** basis set. The geometry is characterized with an intramolecular hydrogen bond of NH···O=C with length of 2.526 Å and a NHO angle of 140.5(1)°. The NH—C(CH₃)C=C—C=O(CH₃) fragment is nearly flat with a maximal deviation of total planarity of 10.4°. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: 1,1,1-Trichloro-3-(1-phenethylamino-ethylidene)-pentane-2,4-dione; IR-LD spectroscopy; solid-state; colloidal suspension in nematic liquid crystal; quantum chemical calculations; ¹H-NMR

INTRODUCTION

Enaminones, as defined by Greenhill¹ are compounds that combine the ambient electrophilicity of enones with the ambient nucleophilicity of enamines. For this reason their chemical reactivities are very diverse and they have found numerous synthetic applications.^{2–4} The potential biological activity motivates structural and spectroscopic studies of these derivatives. Structural and theoretical studies on enaminones have been published previously,^{5–7} but to the best of our knowledge linear dichroic infrared (IR-LD) spectroscopy has been used only on one object, 3-ethylamino-2-(4-nitro-benzoyl)-but-2-enoic acid phenylamide,⁷ which belongs to this interesting class of organic compounds. In this paper we describe the application of the solid-state LD-IR technique for structural investigation of 1,1,1-trichloro-3-(1-phenethylamino-ethylidene)-pentane-2,4-dione (Scheme 1) – an enaminone with interesting structural features. This compound was synthesized as a part of synthetic methodology project⁸ according to Scheme 2. The compound studied is an example of resonance assisted hydrogen bonding, which is a synergistic interplay between π -delocalization and hydrogen bond strengthening originally introduced

by Gilli and co-authors⁵ to explain the abnormally strong intramolecular NH···O=C bonds formed in β -enaminones and related compounds. This type of intramolecular H-bond and the possible rotamers and tautomers make the title compound an interesting object for LD-IR studies.

EXPERIMENTAL

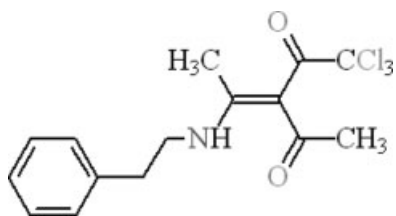
Synthesis

4-Phenethylamino-pent-3-en-2-one (2). Acetylacetone (0.300 g, 3 mmol) was added to a solution of 2-phenylethyl amine (0.364 g, 3 mmol) in DCM (10 ml). Then Na₂SO₄ (1 g) was added and the mixture was stirred overnight at 25 °C. After that, the sodium sulfate was filtered off and the solvent was removed by distillation. **2** was isolated as 0.597 g of yellow oil (98%).

¹H-NMR δ (ppm) = 1.83 (s, 3H), 2.01 (s, 3H), 2.85 (t, 2H, J = 7.0 Hz), 3.43–3.51 (m, 2H), 5.01 (s, 1H), 7.25–7.61 (m, 5H) and 10.85 (Br, 1H).

1,1,1-Trichloro-3-(1-phenethylamino-ethylidene)-pentane-2,4-dione (3). To a cooled (0–5 °C) and stirred solution of the enaminone **2** (0.203 g, 1 mmol) and Et₃N (0.14 ml, 1 mmol) in CH₂Cl₂ (5 ml) was slowly added trichloroacetyl chloride (1 mmol). The reaction mixture was allowed to reach room temperature and the

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Scheme 1. Chemical diagram of 1,1,1-Trichloro-3-(1-phenethylamino-ethylidene)-pentane-2,4-dione

stirring continued overnight. The mixture was then washed with water (200 ml), dried (Na_2SO_4) and the solvent was removed on a rotavap. Column chromatography on neutral alumina in Et_2O : petroleum gave **3** as yellow crystals (0.279 g, 80%, m.p. 70–71 °C).

$^1\text{H-NMR}$ δ (ppm) = 1.88 (s, 3H), 2.22 (s, 3H), 2.95 (t, 2H, $J = 6.8$ Hz), 3.56–3.70 (m, 2H), 7.25–7.50 (m, 5H) and 12.03 (Br, 1H).

Materials and methods

4000–400 cm^{-1} solid-state IR spectra were recorded on a Bruker 113 v FT-IR spectrometer (resolution 2 cm^{-1} , 250 scans) equipped with a Specac wire-grid polarizer. Oriented solid samples were obtained by the new method^{9,10} applied in linear-polarized IR spectroscopy, i.e. a colloidal suspension in a nematic liquid crystal of the 4'-cyano-4'-alkylbicyclohexyl type (ZLI 1695, Merck). The validation of the method, based on a colloidal suspension in nematic liquid crystal for accuracy, precision and the influence of the liquid crystal medium on peak positions and integral absorbances of the guest molecule bands have been presented.¹¹ Optimization of experimental conditions and an experimental design for quantitative evaluation of the impact of four input factors has been presented.^{11,12} The number of scans, the rubbing-out of KBr-pellets, the amount of studied compounds included in the liquid crystal medium and the ratios of Lorentzian to Gaussian peak functions in the curve fitting procedure on the spectroscopic signal at five different frequencies have been studied.^{11,12} The nature and balance of the forces in the nematic liquid crystal suspension system, the mathematical model for their clearance, morphology of the suspended particles and the influence of the space system types on the degree of orientation, i.e., ordering parameter have been shown¹³ using 5 liquid crystals and 15 compounds. Applicability of the last approach for

experimental IR-spectroscopic band assignment and especially for obtaining of structural information has been demonstrated in series of organic systems and metal complexes,¹⁴ Cu(II) complexes,¹⁵ polymorphs,¹⁶ codeine derivatives,¹⁷ peptides their Au(III) complexes, hydrochlorides and hydrogensquarates.^{18,19} IR-LD spectroscopy and the interpretation of the linear-polarized IR spectra by so-called reducing-difference procedure^{20–23} are described.^{10–23}

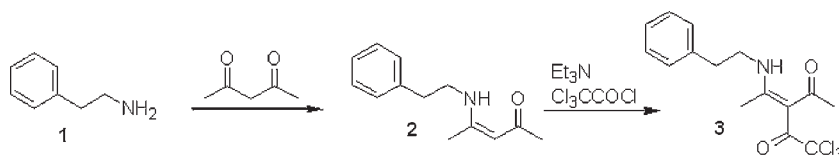
$^1\text{H-NMR}$ measurements, referred to TMS, were made at 298 K with a Bruker DRX-250 spectrometer using 5 mm tubes and CDCl_3 as solvent.

Quantum chemical calculations were performed with GAUSSIAN 98 program package.²⁴ The visualization is achieved by ChemCraft program.²⁵ The theoretical approximation approach has been described.⁹ The geometry of the studied compound was optimized at two levels of theory: second-order Moller–Pleset perturbation theory (MP2) and density functional theory (DFT) using 6-311++G** basis set. DFT method employed is B3LYP, which combines Becke's three-parameter non-local exchange functional with the correlation function of Lee, Yang and Parr. Molecular geometries of the studied species were fully optimized by the force gradient method using Bernys' algorithm. For every structure the stationary points found on the molecule potential energy hyper surface were characterized using standard analytical harmonic vibrational analysis. The absence of imaginary frequencies, as well as of negative eigenvalues of the second-derivative matrix, confirmed that the stationary points correspond to minima of the potential energy hyper surfaces. The calculated vibrational frequencies and infrared intensities were checked for agreement with the experimental data. The DFT method provides more accurate vibrational data, as the calculated standard deviations are 10 cm^{-1} (B3LYP) and 13 cm^{-1} (MP2), respectively. For this reason the B3LYP/6-311++G** data are presented, where for better correspondence between the experimental and theoretical values, a modification of the results using the empirical scaling factor 0.9614 is done.

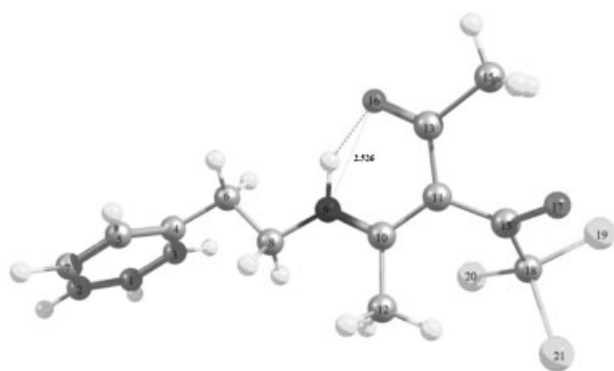
RESULTS AND DISCUSSION

Theoretical data

Molecular structures. According to the quantum chemical calculation only one potential energy hyper



Scheme 2. Reaction scheme



Scheme 3.

surface minimum of the studied compound is obtained (Scheme 3). When energy is corrected by zero point vibration energy contribution the form shows an E_{rel} of 1.0 kJ mol^{-1} . The predicted geometry shows an intramolecular hydrogen bond of $\text{NH} \cdots \text{O}=\text{C}$ type (Scheme 3) with bond length of 2.526 \AA and a NHO angle of $140.5(1)^\circ$. The computed geometry parameters, i.e., bond lengths and angles are collected in Table 1. The $\text{NH}-\text{C}(\text{CH}_3)\text{C}=\text{C}-\text{C}=\text{O}(\text{CH}_3)$ fragment is nearly flat with a maximal deviation of total planarity of 10.4° , thus proposing a co-linear orientation of the out-of-plane (o.p.) transition moments in the frame of the fragment. However, the direction of the aromatic o.p. transition moments are near to perpendicular oriented due to the corresponding space disposition of both moieties of 100.3° . Total dipole moment of 6.078 Debye is calculated and the distribution of the group charges is presented in Scheme 4.

Vibrational analysis. The theoretical IR spectrum of the studied compound in gas phase is presented in Fig. 1. Table 2 contains the IR-characteristic bands and their assignment. Comparison between the calculated spectrum and the experimental one (Fig. 1, Table 2) in solid state is made. The predicted IR spectrum is characterized with the highest absorption maximum at 3021 cm^{-1} assigned to **20a** stretching in-plane (i.p.) mode of aromatic system. The bands in $3100\text{--}2950 \text{ cm}^{-1}$ correspond to other i.p. maxima of aromatic fragments, and the asymmetric and symmetric stretching peaks of CH_3 and CH_2 groups are obtained in $2950\text{--}2800 \text{ cm}^{-1}$ region. The $1700\text{--}1400 \text{ cm}^{-1}$ region shows the highest frequency and intensive peaks at 1699 and 1627 cm^{-1} belonging to $\nu_{\text{C}=\text{O}}$ peaks of $\text{C}=\text{O}(\text{Cl}_3)$ and $\text{C}=\text{O}(\text{CH}_3)$ groups. Both maxima are with mixed character with participation of δ_{NH} motion (Scheme 5A and B). Other maxima are assigned as i.p. transition moments of benzene ring with A_1 and B_2 symmetry class, which are noted as **8a**, **8b**, **19a**, **19b** in Wilson's nomenclature^{26,27} as well as to stretching mode of the double $\text{C}=\text{C}$ bond ($\nu_{\text{C}=\text{C}}$) (Table 2). B_1 -out-of-plane (o.p.) peaks of *m*-substituted benzene ring are obtained at 725 cm^{-1} (**11- γ_{CH}**) and 698 cm^{-1} (**4- γ_{Ar}**). These maxima are uninfluenced from

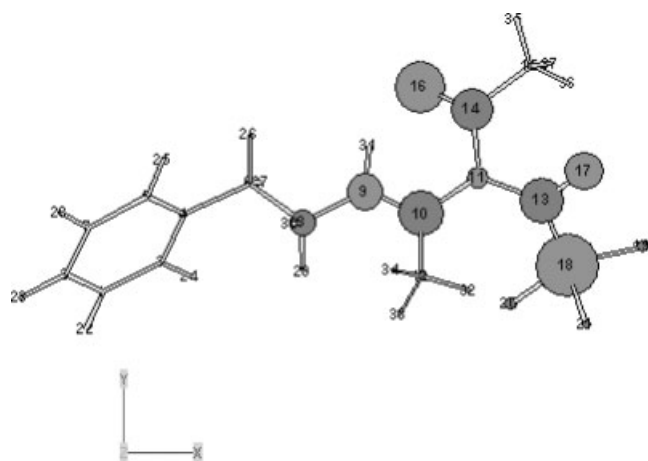
Table 1. Calculated (MP2/6-311++G**) geometry parameters as bond lengths (\AA) and angles ($^\circ$) of compound studied using atom numbering of Scheme 3

Name definition	Values	Name definition	Values
R(1,2)	1.397	A(2,1,3)	120.1 (8)
R(1,3)	1.396	A(1,2,7)	119.7 (1)
R(2,7)	1.397	A(1,3,4)	120.6 (2)
R(3,4)	1.401	A(3,4,5)	118.8 (8)
R(4,5)	1.401	A(3,4,6)	120.5 (7)
R(4,6)	1.518	A(5,4,6)	120.5 (4)
R(5,7)	1.396	A(4,5,7)	120.6 (0)
R(6,8)	1.547	A(4,6,8)	109.9 (5)
R(8,9)	1.475	A(2,7,5)	120.0 (9)
R(9,10)	1.333	A(6,8,9)	109.5(3)
R(10,11)	1.417	A(8,9,10)	125.7 (8)
R(10,12)	1.512	A(9,10,11)	120.2 (6)
R(11,13)	1.451	A(9,10,12)	116.9 (3)
R(11,14)	1.465	A(10,11,12)	122.4 (6)
R(13,17)	1.234	A(10,11,13)	123.2 (1)
R(13,18)	1.590	A(10,11,14)	118.9 (5)
R(14,15)	1.520	A(13,11,14)	117.6 (7)
R(14,16)	1.268	A(11,13,17)	126.7 (3)
R(18,19)	1.869	A(11,13,18)	118.7 (1)
R(18,20)	1.866	A(17,13,18)	113.9 (5)
R(18,21)	1.879	A(11,14,15)	119.7 (4)
—	—	A(11,14,16)	121.9 (3)
—	—	A(15,14,16)	118.3 (2)
—	—	A(13,18,19)	107.0 (9)
—	—	A(13,18,20)	116.8 (5)
—	—	A(13,18,21)	109.2 (8)
—	—	A(19,18,20)	106.9 (4)
—	—	A(19,18,21)	107.1 (6)
—	—	A(20,18,21)	109.0 (8)
Dihedral angles ($^\circ$)			
D(3,1,2,7)	0.2	D(12,10,11,14)	162.1
D(2,1,3,4)	0.1	D(10,11,13,17)	135.4
D(1,2,7,5)	0.2	D(10,11,13,18)	54.1
D(1,3,4,5)	0.0	D(14,11,13,17)	39.7
D(1,3,4,6)	177.4	D(14,11,13,18)	130.6
D(3,4,5,7)	0.0	D(10,11,14,15)	170.9
D(6,4,5,7)	177.4	D(10,11,14,16)	10.0
D(3,4,6,8)	88.7	D(13,11,14,15)	4.5
D(5,4,6,8)	88.6	D(13,11,14,16)	174.4
D(4,5,7,2)	0.1	D(11,13,18,19)	123.0
D(4,6,8,9)	179.9	D(11,13,18,20)	3.2
D(6,8,9,10)	176.2	D(11,13,18,21)	121.1
D(8,9,10,11)	172.3	D(17,13,18,19)	48.5
D(8,9,10,12)	0.6	D(17,13,18,20)	168.3
D(9,10,11,13)	174.4	D(17,13,18,21)	67.2
D(9,10,11,14)	10.4	—	—
D(12,10,11,13)	13.0	—	—

the intermolecular interactions. The obtained differences between theoretically and experimentally obtained values of 2 cm^{-1} indicate a good theoretical approximation of the presented approach.

Experimental conventional and linear-polarized IR data

The experimental IR-spectroscopic pattern is characterized with a strong overlapping, and the adequate



Scheme 4. Calculated group charges

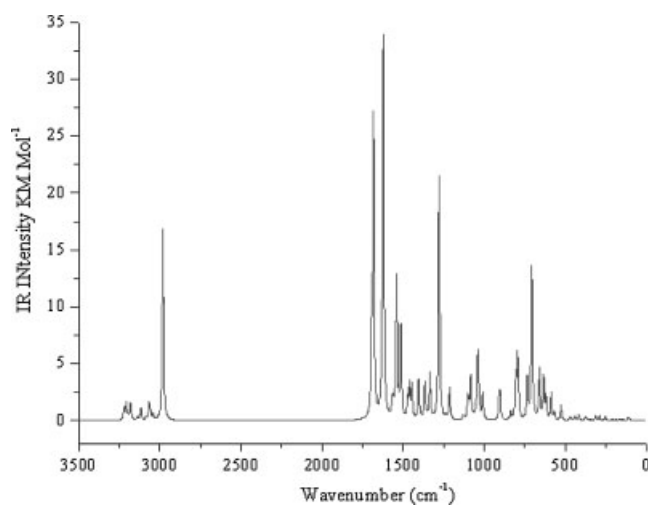
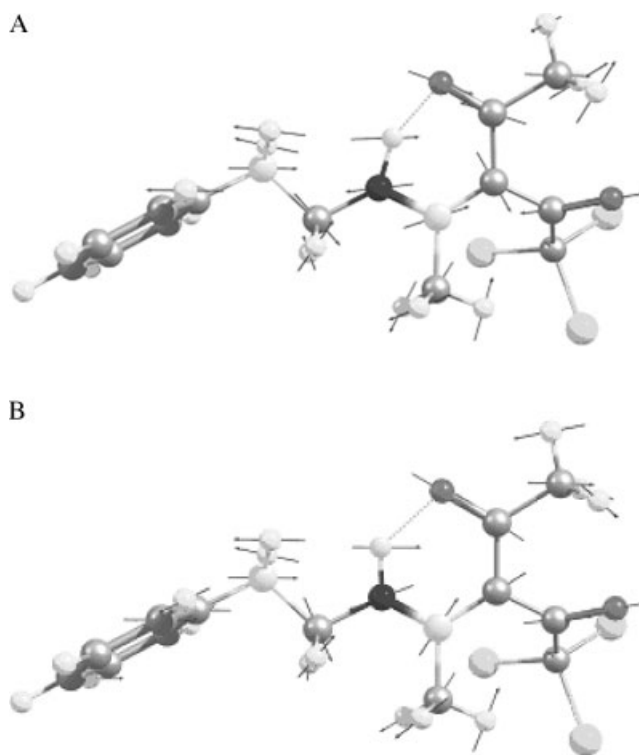


Figure 1. Theoretical IR spectrum of 1,1,1-Trichloro-3-(1-phenethylamino-ethylidene)-pentane-2,4-dione

interpretation of the IR-spectroscopic bands is achieved by preliminary procedures of deconvolution and curve fitting. The experimental confirmation of IR-characteristic band assignment (Table 2) is achieved by means of linear-polarized IR spectra and the application of



Scheme 5. Visualization of selected transition moment directions in 1,1,1-Trichloro-3-(1-phenethylamino-ethylidene)-pentane-2,4-dione

reducing-difference procedure for their interpretation. For the assignment of modes of both phenyl fragments is used the Wilson's notation.^{26,27} The difference IR-LD spectrum (Fig. 2) of the compound showed good orientation of the crystalline sample in the liquid crystal medium and resulted in adequate conclusions using the criteria marked.^{11,12} All the obtained data of *mono*-substituted phenyl fragment correlated well with data for other compounds containing the discussed fragments.²⁷ The 3500–3100 cm⁻¹ IR-spectroscopic region is characterized with a broad absorption band at 3413 cm⁻¹ belonging to ν_{NH} , affected by moderate interactions. The theoretical value of 3466 cm⁻¹ is also low frequency

Table 2. Theoretical (B3LYP/6-311++G**) and experimental solid-state IR-spectroscopic data of 1,1,1-Trichloro-3-(1-phenethylamino-ethylidene)-pentane-2,4-dione

Assignment	ν (cm ⁻¹)		Assignment	ν (cm ⁻¹)	
	Theoretical	Experimental		Theoretical	Experimental
ν_{NH}	3466	3413	3 (B ₂)	1255	1254
$\nu_{\text{C=O}}(\text{CCl}_3)$	1699	1695	1 (A ₁)	1000	1000
$\nu_{\text{C=O}}(\text{CH}_3)$	1627	1600	$\gamma_{\text{C=O}}(\text{Cl}_3)$	811	823
8a (A ₁)	1613	1610	$\gamma_{\text{C=O}}(\text{CH}_3)$	666	671
8b (B ₂)	1600	1598	γ_{NH}	660	698
$\nu_{\text{C=C}}$	1590	1583	11 (B ₁)	725	727
19a (A ₁)	1509	1507	4 (B ₁)	698	700
19b (B ₂)	1444	1447	—	—	—

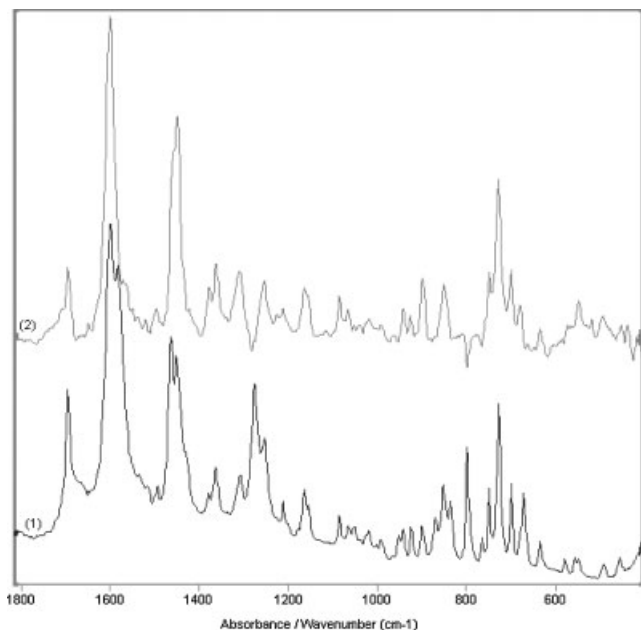


Figure 2. Non-polarized IR (1) and difference (2) IR-LD spectrum of 1,1,1-Trichloro-3-(1-phenethylamino-ethylidene)-pentane-2,4-dione

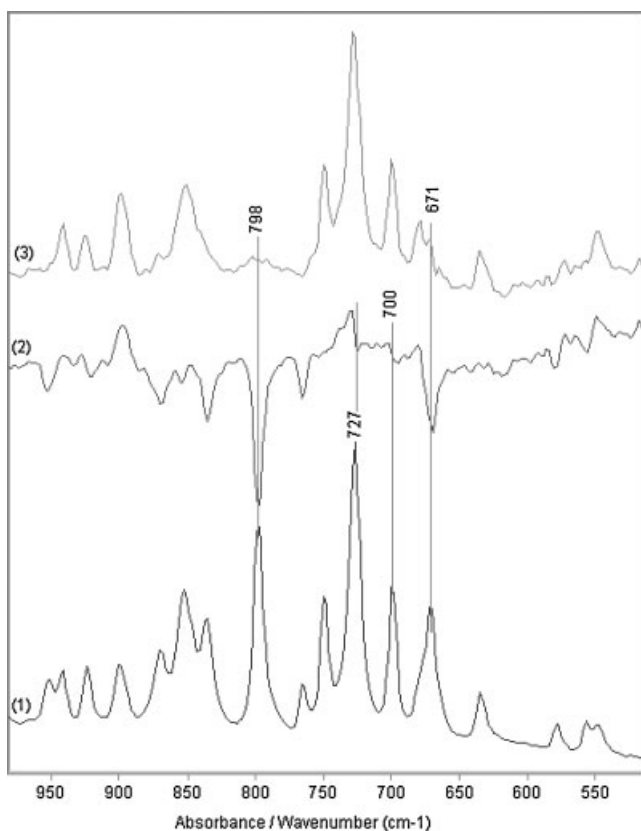


Figure 3. Non-polarized IR spectrum labelled as (1) and reduced IR-LD spectra after elimination of the peaks at 727 and 798 cm^{-1} , labelled as (2) and (3)

shifted due to the intramolecular interaction. In contrast to typical enolic form like in curcumine, where the $\text{OH}\cdots\text{O}$ bond is extremely short with bond length of 2.440 Å²⁸ and no ν_{OH} IR band presents in the IR spectrum in solid state,²⁹ here a moderate $\text{NH}\cdots\text{O}=\text{C}$ bond affects the peak position similarly to β -enaminones described by Gilli and co-authors.⁵ The presence of only one ν_{NH} band suggests the stabilization of only one form, i.e. with $\text{N}-\text{H}\cdots\text{O}$ hydrogen bond.

The application of reducing-difference procedure to polarized IR-LD spectra resulted in: (i) elimination of the bands at 727 and 700 cm^{-1} (Fig. 3(2)) belonging to **11**- γ_{CH} and **4**- γ_{Ar} o.p. modes (B_1) of *m*-substituted benzene in same dichroic ratio, confirming their shown origin. However the intensive peak at 798 cm^{-1} is negative oriented. (ii) Its elimination (Fig. 3(3)) resulted in a disappearance of the peak at 671 cm^{-1} , suggesting an origin from γ_{NH} and $\gamma_{\text{C}=\text{O}(\text{CH}_3)}$ motion. This result is in accordance with the theoretically predicted geometry in Scheme 3. (iii) The reduction of the highest frequency peaks in 1700–1500 cm^{-1} region in different dichroic ratio also supported the proposed structure of the studied compound.

CONCLUSION

The experimental polarized IR data have shown that heteronuclear resonance assisted intramolecular hydrogen bonding is preferred rather than intermolecular interactions in solid state. It is shown that in contrast to typical enolic form like in curcumine, where the $\text{OH}\cdots\text{O}$ bond is extremely short with bond length of 2.440 Å²⁸ and no ν_{OH} IR band presents in the IR spectrum in solid state,²⁹ here a moderate $\text{NH}\cdots\text{O}=\text{C}$ bond affects the peak position similarly to β -enaminones. The presence of only one ν_{NH} band suggests the stabilization of only one form, i.e. with $\text{N}-\text{H}\cdots\text{O}$ hydrogen bond. The conclusions drawn are corroborated by extended DFT and *ab initio* MP2 quantum chemical calculations at B3LYP and MP2 levels of theory and 6-31++G** basis set.

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