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# Conformation and vibrational spectra and assignment of 2-thenoyltrifluoroacetone 

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## A R T I C L E I N F O

## Article history:

Received 13 April 2009
Received in revised form 22 May 2009
Accepted 26 May 2009
Available online 3 June 2009

## Keywords:

2-Thenoyltrifluoroacetone
$\beta$-Diketone
Conformational analysis
Solvent effect
Vibrational assignment


#### Abstract

The conformational stabilities of different tautomers of 2-thenoyltrifluoroacetone (4,4,4-trifluoro-1-(2-thienyl)butane-1,3-dione, TTFA) in several solutions have been investigated at the B3LYP level using 6$311++G^{* *}$ basis set. The self-consistent Onsager reaction field model was used to study the solvent effects. It was determined that the energy differences of the most stable conformers (stabilized by the hydrogen bridge), which are negligible in the gas phase, increase in the solvent media. The harmonic vibrational frequencies were calculated at the B3LYP level using 6-31G* and 6-311G* basis sets. A complete vibrational assignment has been clearly provided for the experimental IR and Raman spectra of TTFA and its deuterated analogue, which shows coexisting of four conformations in the sample. This vibrational spectroscopy analyses confirms more content of the " $A$ " forms in the solution than the " $B$ " forms, although the reverse is true in the solid state, in agreement with the theoretical DFT calculations and the experimental X-ray results.


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## 1. Introduction

By understanding the keto-enol tautomerism, it is straightforward to show that a $\beta$-diketone can transform bidirectionally into two cis-enol forms as illustrated in Fig. 1. In these cis-enol forms, because of the spatial shape of the molecule, it is possible for the hydrogen atom of the hydroxyl group to lie in a suitable orientation and distance for encountering an intramolecular hydrogen bond (IHB). The strong IHB stabilizes the cis-enol form of the $\beta$ diketone [1-4]. The hydroxyl, carbonyl, and alkene functional groups involved in the enol forms contain six atoms that can contribute in a $\pi$-electronic resonance conjugation to induce a ring like structure, which is referred to as a chelated ring. The remarkable aim here is to crosscheck the effects of different $\alpha$ or $\beta$-substitutions on the stability and IHB strength of each of the mentioned conformers. Malonaldehyde, MA, and acetylacetone, AA, are the simplest $\beta$-dicarbonyls ( $\beta$-dialdehyde and $\beta$-diketone, respectively) and several experimental and theoretical studies have proven their asymmetrical structures due to the strong IHB in their most stable conformers, the chelated cis-enol forms [4-11].

Vibrational spectra of numerous molecules of this category have been extensively investigated, where the existence of a strong

[^0]intramolecular hydrogen bond has been established in the chelated cis-enol tautomers [9-29].

Any factor which affects the electronic properties of the chelated ring will change the intramolecular hydrogen bond strength and the tautomerization equilibrium. Whenever $\mathrm{R}_{1}$ and $\mathrm{R}_{3}$ substitutions are electronically different, one of the two cis-enol forms is more stable. This fact has been established by theoretical and experimental studies such as quantum-mechanical calculations, IR, Raman, microwave, and NMR spectroscopies, X-ray, electron, and neutron diffraction measurements of $A A$ and its derivatives [10-16,30-37].

Additional studies have shown that the IHB strength increases when a bulky group is posited in $\alpha$ position [38-42]. Several experimental studies suggest that the substitution of electron-withdrawing groups, such as trifluoromethyl $\left(-\mathrm{CF}_{3}\right)$, in $\beta$ position, weakens the IHB, while the electron supplying groups such as phenyl $\left(-\mathrm{C}_{6} \mathrm{H}_{5}\right)$ make IHB stronger [16,34,43-45].

Many $\beta$-dicarbonyl compounds exist exclusively in an enol structure in the solid state $[18,46-49] . \mathrm{C}_{4} \mathrm{H}_{3} \mathrm{~S}-\mathrm{COCH}_{2} \mathrm{CO}-\mathrm{CF}_{3}$, 4,4,4-trifluoro-1-(2-thienyl)butane-1,3-dione, known as 2-thenoyltrifluoroacetone (TTFA), is also in the enol form in the solid state as indicated by X-ray diffraction data. The unit cell consists of two molecules, which have slightly different geometrical structures [50]. According to the X-ray results, the enolization is favored near to the electron-withdrawing $-\mathrm{CF}_{3}$ group, i.e. B 2 conformer. TTFA has two $\beta$-substituted groups with different


Fig. 1. The keto-enol tautomerism leads to two different chelated enol forms for asymmetric $\beta$-dicarbonyls.
electron-withdrawing, steric, and resonance effects; hence in our previous work [24] the effects of these substitutions on stability and intramolecular hydrogen bond strength and also on the structure of molecule have been investigated. There, it was shown that among 40 possible conformers of TTFA only four cis-enol chelated conformers are engaged in the IHB system. Between these conformers (A1, A2, B1, and B2), MP2 calculations showed that the B 2 conformer in which the hydroxyl group is in the $-\mathrm{CF}_{3}$ side is significantly more stable than others (see Fig. 2), which is in line with the X-ray diffraction results.

The present paper is a continuance of our aforementioned work. Since the vibrational spectroscopy is a highly sensitive technique to experimentally examine the hydrogen bonding and interaction with solvents, therefore we used this data as the empirical witness. Since the stable conformers in solution may differ from gaseous and solid states, the theoretical prediction could be very helpful for a clear spectral assignment. This paper predicts the conformational stabilities in solution and the vibrational characteristics (such as harmonic fundamental band wavenumbers and corresponding intensities of IR and Raman spectra) of TTFA by means of density functional theory (DFT) level. The calculated harmonic force constants of TTFA were used for predicting the Raman and IR spectra of deuterated analogue, $\mathrm{D}_{2}$-TTFA. The calculated vibrational frequencies for the predicted most stable conformers in different media are compared with those observed experimentally. To our knowledge, no vibrational spectroscopic data has been reported for TTFA. In this report, we present a clear vibrational assignment of TTFA by considering the IR and Raman spectra of its deuterated analogue and theoretical calculations.

## 2. Experimental

TTFA was purchased from Aldrich chemical company with the purity of $99 \%$ in the solid form and was purified by sublimation.



Fig. 2. Possible chelated cis-enol tautomers of TTFA and their relative stability at MP2/6-31G**.
$\mathrm{D}_{2}$-TTFA was prepared by dissolving the non-deuterated molecule in a mixture of dry $\mathrm{CCl}_{4}$ and $\mathrm{D}_{2} \mathrm{O}(5: 1)$. After a few hours, the aqueous phase was removed in a nitrogen filled glove box and this approach was repeated three times. The final organic phase was dried over $\mathrm{P}_{2} \mathrm{O}_{5}$ and then the solvent was removed under vacuum in order to crystallize $\mathrm{D}_{2}$-TTFA.

The mid-Infrared spectra were obtained in the range of 4000$500 \mathrm{~cm}^{-1}$ with spectral resolution of $2 \mathrm{~cm}^{-1}$ by averaging the results of 20 scans on a Bomem MB-154 Fourier Transform Spectrophotometer.

The far-Infrared spectra in the $500-50 \mathrm{~cm}^{-1}$ region were collected employing a Thermo Nicolet NEXUS 870 FT-IR spectrometer equipped with a DTGS/polyethylene detector and a solid substrate beam splitter. The spectra were collected with a resolution of $4 \mathrm{~cm}^{-1}$ by averaging the results of about 60 scans.

All FT-Raman spectra from 3500 to $170 \mathrm{~cm}^{-1}$ were recorded using a $180^{\circ}$ 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 $4 \mathrm{~cm}^{-1}$ by coadding the results of about 1000 scans.

All spectra were measured at room temperature. The solid samples for IR were examined as KBr discs and solution spectra were considered in $\mathrm{CCl}_{4}, \mathrm{CS}_{2}$, and $\mathrm{CH}_{3} \mathrm{CN}$ solutions.

## 3. Method of analysis

All quantum calculations were carried out with the GAUSSIAN 03 software package [51], applying the modern density functional theory, DFT method. The hybrid gradient-corrected (three-parameter nonlocal) exchange functional by Becke [52] with the gradient corrected (nonlocal) correlation functional of Lee et al. [53] was selected.

In our previous study on TTFA [24], all the possible enol and keto conformations of molecule have been fully optimized and the results were discussed. In this work, the self-consistent Onsager reaction field model [54-55] was used to study the solvent effects on the four most stable chelated cis-enol tautomers of TTFA. In this approach, a solute molecule with a certain dipole moment is placed in a spherical cavity in a polarizable continuum, representing the solvent, with a dielectric constant $(\varepsilon)$. The cavity sizes were calculated from molecular volumes. Specific solute-solvent effects are not taken into account at this level of calculation and the obtained solvation energies correspond to the electrostatic contributions, which, however, play a dominant role in tautomerization reactions [56]. These solvent calculations were performed at the B3LYP level of DFT theory using the $6-311++G * *$ basis set, which is a triple-zeta split valence set augmented with polarization and diffused functions [57] on all atoms (351 basis functions, and 563 primitive Gaussians).

The calculations of vibrational frequencies and IR intensities for the A1, A2, B1 and B2 conformers and their deuterated species were achieved at the B3LYP/6-311G** level. The Raman intensities were calculated at the B3LYP/6-31G** level. The assignment of the
calculated wavenumbers is aided by the animation option of GaussView 3.0 graphical interface [58] for Gaussian programs, which gives a visual presentation of the shape of the vibrational modes.

Vibrational normal modes of thiophene were also calculated at the B3LYP/6-311G** level of theory. The notations for 2-thienyl group vibrations are according to these theoretical normal modes of thiophene, which are illustrated by Molekel 4.3 program [59,60].

Lorentzian functions have been utilized for deconvolution of all IR and Raman spectra using Genplot package [61].

## 4. Results and discussions

### 4.1. Solvent influences

Theoretical calculation at the B3LYP level using a variety of basis sets have shown [24] that all chelated A and B conformers of TTFA have nearly the same stabilities in the gaseous phase (so that the highest energy difference between them except for B1, even at the B3LYP/6-311G** with the most different results, is less than $0.44 \mathrm{kcal} / \mathrm{mol}$ ). However, these results are not reliable in solution states with the solvent of different polarities because the four chelated conformations have relatively different dipole moments and a solvent can enhance the energy differences between them.

In order to study the solvent influences on stability and structure of the molecule, several calculations on the chelated forms have been done in various solvents. As previously mentioned, to achieve this aim, the Onsager method [54-55] was applied with $6-311++G * *$ basis set at the B3LYP level of theory. Initially, the recommended cavity radius for the SCRF calculation of each possible chelated conformation ( $a_{0}=4.62,4.38,4.60$, and $4.54 \AA$ for A1, A2, B1, and B2, respectively) was obtained from single point VOLUME calculations. Then fully optimizations were performed for the SCRF calculations in carbon tetrachloride ( $\mathrm{CCl}_{4}$ ), 1,2-dichloroethane ( $\mathrm{Cl}_{2} \mathrm{Eth}$ ), acetonitrile $\left(\mathrm{CH}_{3} \mathrm{CN}\right)$, and dimethylsulfoxide (DMSO) as the solvents with different polarities, characterized by their dielectric permittivity constant ( $\varepsilon=2.228,10.36,36.64$, and 46.7 , respectively). The results of relative stability energies for chelated cis-enol forms in solution, in comparison with the most unstable form in the gaseous state, B1, along with their calculated dipole moments in the gas and solution phases are summarized in Table 1. Predictably, the greater the dipole moment a conformation has, the greater the stability it can obtain in a more polar solvent. Fig. 3 shows that the energy differences of the chelated forms, which are negligible in their gaseous states, become quite noticeable as the medium polarity increases. This causes the contents of the B conformers to be underestimated compare to the A conformers in the solution. For instant, the relative energies of A1, B2, and B1 chelated forms with respect to A 2 in $\mathrm{CH}_{3} \mathrm{CN}$ and DMSO are about 1.3, 2.5 , and $3.3 \mathrm{kcal} / \mathrm{mol}$, respectively.

### 4.2. Vibrational analysis

The assignments of the experimental frequencies are based on the observed band frequencies and intensity changes in the Raman


Fig. 3. The solvent influence on the relative stability of TTFA chelated forms, in comparison with the gaseous state of B1 conformer, as a function of $\varepsilon$, predicted at B3LYP/6-311++G**.
and infrared spectra of the deuterated species, confirmed by establishing one to one correlation between the observed and the theoretically calculated frequencies. The calculated harmonic vibrational band frequencies and their approximate assignments for the enol forms of TTFA and their corresponding deuterated analogous, $\mathrm{D}_{2}$-TTFA, along with the observed infrared and Raman frequencies are listed in Tables 2 and 3, respectively. The IR spectra of TTFA and $D_{2}$-TTFA in the OH/OD stretching region are compared in Fig. 4. The IR and Raman spectra of TTFA and $\mathrm{D}_{2}$-TTFA in the region below $1700 \mathrm{~cm}^{-1}$ are compared in Figs. 5 and 6, respectively. The IR spectra of TTFA in the solid state and in the $\mathrm{CCl}_{4}$ solution are compared in Fig. 7. The deconvoluted IR spectrum of TTFA in the $1350-830 \mathrm{~cm}^{-1}$ region is presented in Fig. 8. Lorentzian functions have been utilized for deconvolution of the IR and Raman spectra. The notations for thienyl group vibrations are according to the characterization of vibrational normal modes of thiophene, which are illustrated in Fig. 9. The calculated frequencies are slightly higher than the observed values for the majority of the normal modes. In addition to the error of the theoretical method used, the difference between the computed and experiment frequencies may be due to many different factors that are usually not even considered in the theory, such as anharmonicity, Fermi resonance, solvent effects, etc.

### 4.2.1. CH stretching modes

The only CH bonds in the molecule are those of thienyl ring and that of the $\alpha$-position in the chelated (enol) ring. In contrast with the latter, the formers are not affected by deuteration of the molecule. The deconvoluted Raman spectrum of TTFA indicates six bands at $3117,3112,3108,3101,3095$, and $3084 \mathrm{~cm}^{-1}$. It will be shown that the existence of these bands could be well attributed to the presence of the four most stable tautomers of TTFA (A1, A2, B1, and B2) in comparable amounts in the sample. As shown in Tables 2 and 3, this is well supported with the presence of other

Table 1
The relative stability energies for chelated cis-enol conformers of TTFA in comparison with the gaseous B1 (in kcal/mol), and their dipole moment (Debye) in several solvent at B3LYP/6-311++G** level of theory.

|  | Relative energy |  |  |  |  | Dipole moment |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Gas | $\mathrm{CCl}_{4}$ | $\mathrm{Cl}_{2}$ Eth | $\mathrm{CH}_{3} \mathrm{CN}$ | DMSO | Gas | $\mathrm{CCl}_{4}$ | $\mathrm{Cl}_{2}$ Eth | $\mathrm{CH}_{3} \mathrm{CN}$ | DMSO |
| A1 | -0.706 | -2.165 | -4.150 | -4.775 | -4.834 | 6.043 | 7.290 | 9.078 | 9.661 | 9.702 |
| A2 | -0.767 | -2.513 | -5.142 | -6.040 | -6.127 | 6.024 | 7.527 | 10.009 | 10.815 | 10.876 |
| B1 | 0.000 | -0.991 | -2.312 | -2.717 | -2.755 | 4.983 | 5.951 | 7.270 | 7.685 | 7.722 |
| B2 | -0.653 | -1.707 | -3.151 | -3.559 | -3.600 | 5.050 | 6.040 | 7.437 | 7.852 | 7.883 |

Table 2
Fundamental band assignment of TTFA (frequencies in $\mathrm{cm}^{-1}$ ). ${ }^{\text {a }}$

| Theoretical |  |  |  |  |  |  |  |  |  |  |  | Experimental |  |  |  | Assignment |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| A1 |  |  | A2 |  |  | B1 |  |  | B2 |  |  | IR |  | Raman |  |  |
| Freq | $I_{\text {IR }}$ | $A_{\text {R }}$ | Freq | $I_{\text {IR }}$ | $A_{\text {R }}$ | Freq | $I_{\text {IR }}$ | $A_{\text {R }}$ | Freq | $I_{\text {IR }}$ | $A_{\text {R }}$ | $\mathrm{CCl}_{4}$ | Solid | $\mathrm{CCl}_{4}$ | Solid |  |
|  |  |  | 3255 | 2 | 36 |  |  |  | 3253 | 1 | 39 | 3121(3) | 3118(12) | 3117(6) | 3117(10) | $v \mathrm{CH}_{\alpha}$ |
| 3246 | 1 | 204 | 3244 | 1 | 214 | 3244 | 0 | 207 | 3242 | 1 | 209 | 3114(4) | 3112(6) | 3112(5) | 3114(5) | 1 |
| 3241 | 5 | 33 |  |  |  | 3237 | 1 | 34 |  |  |  | 3109(3) | 3109(10) | 3108(10) | 3110(12) | $v \mathrm{CH}_{\alpha}$ |
| 3231 | 1 | 91 |  |  |  | 3228 | 1 | 88 |  |  |  | 3103(1) | 3102(5) | 3101(3) | 3100(5) | 2 |
|  |  |  | 3220 | 1 | 102 |  |  |  | 3219 | 2 | 102 | 3096(3) | 3094(9) | 3095(4) | 3094(7) | 2 |
| 3211 | 4 | 145 | 3207 | 4 | 82 | 3209 | 3 | 136 | 3206 | 5 | 87 | 3084(3) | 3085(7) | 3084(3) | 3085(5) | 13 |
| 3070 | 306 | 7 | 3028 | 327 | 6 | 3062 | 336 | 100 | 3080 | 340 | 115 | 2850(2) | n.c. | - | - | $\nu \mathrm{OH}$ |
|  |  |  |  |  |  | 1688 | 503 | 57 | 1685 | 537 | 59 | 1651(25) | 1657(47) | 1657(4) | 1656(8) | $v_{\mathrm{a}} \mathrm{O}=\mathrm{C}-\mathrm{C}=\mathrm{C}+\delta \mathrm{OH}$ |
| 1669 | 128 | 39 |  |  |  |  |  |  |  |  |  | 1636(18) | 1639(40) | 1639(7) | 1638(7) | $v_{\mathrm{a}} \mathrm{C}=\mathrm{C}-\mathrm{C}=\mathrm{O}+\delta \mathrm{OH}$ |
|  |  |  | 1662 | 170 | 135 |  |  |  |  |  |  | 1623(11) | 1624(35) | 1625(11) | 1621(9) | $v_{\mathrm{a}} \mathrm{C}=\mathrm{C}-\mathrm{C}=\mathrm{O}+\delta \mathrm{OH}$ |
| 1641 | 802 | 360 | 1637 | 734 | 211 |  |  |  |  |  |  | 1601(36) | 1600(35) | 1594(25) | 1595(14) | $v_{\mathrm{s}} \mathrm{C}=\mathrm{C}-\mathrm{C}=\mathrm{O}+\delta \mathrm{OH}+v \mathrm{C}$-thio |
|  |  |  |  |  |  | 1631 | 46 | 181 |  |  |  | 1583(29) | 1583(45) | 1584(20) | 1578(26) | $v_{s} \mathrm{O}=\mathrm{C}-\mathrm{C}=\mathrm{C}+\delta \mathrm{OH}+v \mathrm{C}-\mathrm{CF}_{3}$ |
|  |  |  |  |  |  |  |  |  | 1631 | 58 | 247 | 1583(29) | 1583(45) | 1584(20) | 1578(26) | $v_{s} \mathrm{O}=\mathrm{C}-\mathrm{C}=\mathrm{C}+\delta \mathrm{OH}+14+\nu \mathrm{C}-\mathrm{CF}_{3}$ |
|  |  |  | 1567 | 28 | 120 |  |  |  |  |  |  | 1522(7) | 1523(25) | 1524(13) | 1525(9) | $14+\nu \mathrm{C}-\mathrm{O}+\delta \mathrm{OH}$ |
|  |  |  |  |  |  | 1562 | 96 | 45 |  |  |  | 1519(4) | 1520(29) | 1520(15) | 1519(11) | $14+\delta \mathrm{OH}+\delta \mathrm{CH}_{\alpha}$ |
|  |  |  |  |  |  |  |  |  | 1563 | 36 | 10 | 1519(4) | 1520(29) | 1520(15) | 1519(11) | $14+v_{\mathrm{s}}(\mathrm{C}=\mathrm{O}, \mathrm{C}-\mathrm{O})+v \mathrm{C}-\mathrm{C}+\delta \mathrm{CH}_{\alpha}$ |
| 1552 | 30 | 59 |  |  |  |  |  |  |  |  |  | 1508(1) | 1505(12) | 1504(5) | 1510(5) | $14+v_{\mathrm{a}} \mathrm{C}=\mathrm{C}-\mathrm{C}+\delta \mathrm{OH}+\delta \mathrm{CH}_{\alpha}$ |
| 1489 | 134 | 2 |  |  |  |  |  |  |  |  |  | 1456(3) | 1457(10) | 1455(4) | 1456(5) | $v \mathrm{aO}-\mathrm{C}=\mathrm{C}-\mathrm{C}+\delta \mathrm{OH}+\delta \mathrm{CH}_{\alpha}+v \mathrm{C}-\mathrm{CF}_{3}+3$ |
|  |  |  | 1484 | 204 | 6 |  |  |  |  |  |  | 1448(6) | 1447(22) | 1445(8) | 1448(9) | $v \mathrm{aO}-\mathrm{C}=\mathrm{C}-\mathrm{C}+\delta \mathrm{OH}+\delta \mathrm{CH}_{\alpha}+\nu \mathrm{C}-\mathrm{CF}_{3}$ |
|  |  |  |  |  |  | 1479 | 18 | 27 | 1476 | 43 | 37 | 1437(3) | 1436(8) | 1437(14) | 1440(13) | $v \mathrm{aC}-\mathrm{C}=\mathrm{C}-\mathrm{O}+\delta \mathrm{OH}+\delta \mathrm{CH}_{\alpha}+3$ |
| 1459 | 146 | 648 | 1456 | 80 | 732 |  |  |  |  |  |  | 1414(21) | 1418(35) | 1412(100) | 1410(87) | $3+v \mathrm{C}-\mathrm{O}$ |
|  |  |  |  |  |  | 1448 | 155 | 327 | 1448 | 147 | 282 | 1412(28) | 1407(55) | 1410(85) | 1406(100) | $3+v_{\mathrm{a}}(\mathrm{C}=\mathrm{O}, \mathrm{C}-\mathrm{O})+\delta \mathrm{CH}_{\alpha}$ |
|  |  |  | 1419 | 30 | 12 |  |  |  |  |  |  | 1389(3) | 1388(7) | 1392(8) | 1387(9) | $v_{\mathrm{s}} \mathrm{O}-\mathrm{C}=\mathrm{C}-\mathrm{C}+4+v \mathrm{C}=\mathrm{O}+\delta \mathrm{OH}$ |
|  |  |  |  |  |  | 1408 | 127 | 61 |  |  |  | 1370(4) | 1372(10) | 1370(8) | 1374(8) | $v_{s} \mathrm{C}-\mathrm{C}=\mathrm{C}-\mathrm{O}+\delta \mathrm{OH}+v \mathrm{C}=\mathrm{O}$ |
| 1402 | 73 | 15 |  |  |  |  |  |  |  |  |  | 1361(6) | 1365(15) | 1362(13) | 1361(15) | $v \mathrm{SO}-\mathrm{C}=\mathrm{C}-\mathrm{C}+4+v \mathrm{C}=\mathrm{O}+\delta \mathrm{OH}$ |
|  |  |  |  |  |  |  |  |  | 1401 | 70 | 298 | 1361(6) | 1369(10) | 1362(13) | 1361(15) | $v_{s} \mathrm{C}-\mathrm{C}=\mathrm{C}-\mathrm{O}+\delta \mathrm{OH}+\nu \mathrm{C}=\mathrm{O}$ |
|  |  |  |  |  |  |  |  |  | 1385 | 37 | 11 | 1356(13) | 1361(36) | 1357(17) | 1358(24) | 4 |
| 1381 | 105 | 174 |  |  |  | 1378 | 147 | 286 |  |  |  | 1353(16) | 1358(43) | 1353(20) | 1354(34) | $4+8 \mathrm{OH}$ |
|  |  |  | 1363 | 81 | 43 |  |  |  |  |  |  | 1317(26) | 1315(63) | 1317(11) | 1318(15) | $4+v a(C-O, C=O)+\delta O H$ |
| 1315 | 364 | 164 | 1316 | 401 | 234 |  |  |  |  |  |  | 1283(30) | 1289(50) | 1287(19) | 1285(40) | $\delta \mathrm{OH}+v \mathrm{C}-\mathrm{CF}_{3}+v \mathrm{C}=\mathrm{C}+v \mathrm{C}$-thio +15 |
|  |  |  |  |  |  |  |  |  | 1313 | 840 | 75 | 1279(41) | 1256(51) | 1276(28) | 1259(21) | $\delta \mathrm{OH}+v \mathrm{C}=\mathrm{C}+v \mathrm{C}-\mathrm{CF}_{3}+v \mathrm{C}$-thio +15 |
|  |  |  |  |  |  | 1305 | 770 | 22 |  |  |  | 1274(49) | 1254(56) | 1271(23) | 1254(22) | $\delta \mathrm{OH}+v \mathrm{C}-\mathrm{CF}_{3}+v \mathrm{C}=\mathrm{C}+v \mathrm{C}$-thio +15 |
| 1265 | 85 | 14 | 1270 | 60 | 7 | 1266 | 42 | 5 | 1268 | 48 | 4 | 1252(28) | 1261(61) | 1251(18) | 1261(23) | $15+\delta \mathrm{CH}_{\alpha}+v \mathrm{C}$-thio $+v \mathrm{C}-\mathrm{CF}_{3}$ |
|  |  |  |  |  |  |  |  |  | 1249 | 75 | 15 | 1244(11) | 1240(30) | 1243(19) | 1239(14) | $15+v \mathrm{C}-\mathrm{CF}_{3}+\delta \mathrm{CH}_{\alpha}+v \mathrm{C}_{4}-\mathrm{S}$ |
|  |  |  | 1238 | 185 | 15 |  |  |  |  |  |  | 1231(21) | 1233(35) | 1229(10) | 1234(13) | $15+v \mathrm{C}-\mathrm{CF}_{3}+\delta \mathrm{CH}_{\alpha}+\delta \mathrm{OH}+v \mathrm{C}_{4}-\mathrm{S}$ |
| 1234 | 12 | 2 |  |  |  |  |  |  |  |  |  | 1231(21) | 1233(35) | 1229(10) | 1234(13) | $15+v \mathrm{C}-\mathrm{CF}_{3}+\delta \mathrm{CH}_{\alpha}+v \mathrm{C}_{4}-\mathrm{S}$ |
|  |  |  |  |  |  | 1215 | 10 | 3 |  |  |  | 1222(8) | 1219(49) | - | 1214(8) | $15+v \mathrm{C}_{4}-\mathrm{S}+\delta \mathrm{CH}_{\alpha}+v \mathrm{C}-\mathrm{CF}_{3}$ |
|  |  |  |  |  |  | 1194 | 354 | 3 | 1192 | 339 | 3 | 1205(71) | 1200(94) | - | 1195(10) | $v \mathrm{CFF}_{3}$ |
| 1189 | 276 | 1 | 1188 | 263 | 2 |  |  |  |  |  |  | 1199(69) | 1188(85) | - | 1191(15) | $v \mathrm{aCF}_{3}$ |
| 1170 | 284 | 3 | 1169 | 280 | 3 |  |  |  |  |  |  | 1165(100) | 1155(80) | - | 1163(10) | $v \mathrm{aCF}_{3}$ |
|  |  |  |  |  |  | 1171 | 296 | 4 | 1171 | 296 | 4 | 1162(44) | 1144(100) | - | 1163(10) | $v \mathrm{aCF}_{3}$ |
|  |  |  |  |  |  | 1135 | 88 | 2 | 1132 | 87 | 1 | 1110(71) | 1110(75) | 1112(5) | 1113(8) | $\delta \mathrm{CH}_{\alpha}+v_{\mathrm{s}} \mathrm{CF}_{3}+\nu \mathrm{C}-\mathrm{O}+6$ |
| 1131 | 238 | 8 | 1131 | 222 | 12 |  |  |  |  |  |  | 1110(71) | 1110(75) | 1112(5) | 1113(8) | $\delta \mathrm{CH}_{\alpha}+v_{\mathrm{s}} \mathrm{CF}_{3}+\nu \mathrm{C}-\mathrm{C}+6$ |
| 1110 | 16 | 25 | 1110 | 1 | 42 |  |  |  |  |  |  | 1084(9) | 1095(42) | 1082(39) | 1093(32) | 5 |
|  |  |  |  |  |  | 1108 | 6 | 12 | 1109 | 7 | 18 | 1084(9) | 1084(31) | 1082(39) | 1082(25) | 5 |
|  |  |  | 1087 | 23 | 16 |  |  |  |  |  |  | 1065(14) | 1066(62) | 1070(4) | 1072(8) | 6 |
| 1083 | 14 | 17 |  |  |  |  |  |  | 1085 | 39 | 6 | 1063(10) | 10654(58) | 1063(13) | 1064(15) | 6 |
|  |  |  |  |  |  | 1075 | 59 | 2 |  |  |  | 1059(3) | 1051(35) | 1058(7) | 1054(4) | $6+v \mathrm{C}-\mathrm{C}$ |
| 1049 | 80 | 1 |  |  |  |  |  |  |  |  |  | 1032(12) | 1028(19) | - | - | $v_{5} \mathrm{C}=\mathrm{C}-\mathrm{C}+v \mathrm{C}-\mathrm{O}+6+v \mathrm{C}_{4}-\mathrm{S}+\delta_{5} \mathrm{CF}_{3}$ |
|  |  |  |  |  |  | 1045 | 7 | 2 |  |  |  | 1028(2) | 1023(15) | - | - | $v_{5} \mathrm{C}=\mathrm{C}-\mathrm{C}+5+v \mathrm{C}_{4}-\mathrm{S}+\delta_{5} \mathrm{CF}_{3}$ |
|  |  |  | 1035 | 26 | 2 |  |  |  |  |  |  | 1020(2) | 1016(10) | - | - | $v_{s} \mathrm{C}=\mathrm{C}-\mathrm{C}+v \mathrm{C}-\mathrm{O}+5+v \mathrm{C}_{4}-\mathrm{S}+\delta_{5} \mathrm{CF}_{3}$ |
|  |  |  |  |  |  |  |  |  | 1008 | 13 | 3 | 996(3) | 997(21) | - | 1000(4) | $v_{\mathrm{s}} \mathrm{C}=\mathrm{C}-\mathrm{C}+5+v \mathrm{C}_{4}-\mathrm{S}+\delta_{5} \mathrm{CF}_{3}$ |
|  |  |  | 957 | 78 | 1 |  |  |  |  |  |  | 889(4,br) | 890(22,br) | - |  | $\gamma \mathrm{OH}$ |
|  |  |  |  |  |  | 945 | 3 | 2 |  |  |  | 877(6,br) | 880(16,br) | - | - | $9+\gamma \mathrm{OH}$ |
|  |  |  |  |  |  | 941 | 72 | 1 |  |  |  | 877(6,br) | 880(16,br) | - | - | $\gamma \mathrm{OH}+9$ |
| 941 | 53 | 1 |  |  |  |  |  |  | 933 | 71 | 1 | 877(6,br) | 880(16,br) | - | - | $\gamma \mathrm{OH}$ |
| 937 | 26 | 4 |  |  |  |  |  |  |  |  |  | - | 924(14) | - | 924(6) | $9+\gamma \mathrm{OH}$ |
| 928 | 41 | 15 | 932 | 31 | 25 |  |  |  |  |  |  | 906(6) | 903(27) | 906(14) | 905(29) | $\delta$ CCC + 17 |
|  |  |  | 927 | 0 | 3 |  |  |  | 926 | 4 | 7 | - | 918(11) | - | 916(7) | 9 |
|  |  |  |  |  |  | 919 | 18 | 12 | 922 | 8 | 13 | 911(1) | 910(8) | 908(10) | 912(10) | $\delta$ CCC +17 |
| 872 | 2 | 1 |  |  |  | 878 | 1 | 1 |  |  |  | 852(3) | 850(22) | 849(4) | 851(5) | 19 |
|  |  |  | 870 | 19 | 6 |  |  |  | 870 | 15 | 9 | 862(13) | 861(39) | 864(7) | 863(17) | $7+17$ |
| 865 | 23 | 4 |  |  |  | 866 | 25 | 6 |  |  |  | 860(14) | 859(30) | 862(11) | 860(28) | $7+17$ |
|  |  |  | 855 | 4 | 2 |  |  |  | 857 | 2 | 1 | 842(3) | 844(14) | 835(5) | 843(4) | 19 |
|  |  |  |  |  |  | 832 | 61 | 1 | 832 | 57 | 2 | 802(14)** | 811(38) | 804(3)+ | 809(6) | $\gamma \mathrm{CH}_{\alpha}+19$ |
| 818 | 58 | 1 | 817 | 59 | 1 |  |  |  |  |  |  | 792(12) | 802(55) | 804(3)+ | 809(6) | $\gamma \mathrm{CH}_{\alpha}+19$ |
|  |  |  |  |  |  | 794 | 11 | 2 |  |  |  | 787(6) ${ }_{\text {* }}$ | 789(20) | 785(8)+ | 787(5) | $\delta_{5} \mathrm{CF}_{3}+\Delta+18+\nu \mathrm{C}-\mathrm{CF}_{3}$ |
| 780 | 9 | 3 |  |  |  |  |  |  | 781 | 23 | 2 | 774(3)** | 776(17) | 778(5)+ | 779(7) | $\delta_{5} \mathrm{CF}_{3}+\Delta+18+\nu \mathrm{C}-\mathrm{CF}_{3}$ |
|  |  |  | 769 | 9 | 3 |  |  |  |  |  |  | 771(3)* | 773(11) | 774(3)+ | 773(18) | $\delta_{5} \mathrm{CF}_{3}+\Delta+18+\nu \mathrm{C}-\mathrm{CF}_{3}$ |
| 762 | 2 | 0 | 762 | 12 | 1 |  |  |  |  |  |  | - | - | - | - | $\gamma \mathrm{CH}_{\alpha}+\Gamma$ |
| 752 | 5 | 8 |  |  |  | $752$ | 4 | 9 |  |  |  | 755(1)** | 750(40) | 757(8)+ | 754(10) | 18 |
|  |  |  |  |  |  | 751 | 0 | 0 |  |  |  | 755(1)* | 750(40) | 757(8)+ | 754(10) | $\gamma \mathrm{CH}_{\alpha}+\Gamma+20$ |

Table 2 (continued)

| Theoretical |  |  |  |  |  |  |  |  |  |  |  | Experimental |  |  |  | Assignment |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| A1 |  |  | A2 |  |  | B1 |  |  | B2 |  |  | IR |  | Raman |  |  |
| Freq | $I_{\text {IR }}$ | $A_{\text {R }}$ | Freq | $I_{\text {IR }}$ | $A_{\text {R }}$ | Freq | $I_{\text {IR }}$ | $A_{\text {R }}$ | Freq | $I_{\text {IR }}$ | $A_{\text {R }}$ | $\mathrm{CCl}_{4}$ | Solid | $\mathrm{CCl}_{4}$ | Solid |  |
| Freq |  |  |  |  |  |  |  |  | 749 | 7 | 0 | 752(3)** | 746(58) | 751(16)+ | 750(25) | $18+\gamma \mathrm{CH}_{\alpha}+\Gamma+\delta_{\mathrm{s}} \mathrm{CF}_{3}$ |
|  |  |  |  |  |  |  |  |  | 749 | 8 | 10 | 752(3)** | 746(58) | 751(16)+ | 750(25) | $\gamma \mathrm{CH}_{\alpha}+\Gamma+18$ |
|  |  |  | 749 | 11 | 12 |  |  |  |  |  |  | 752(3)* | 746(58) | 751(16)+ | 750(25) | $18+\delta_{s} \mathrm{CF}_{3}$ |
|  |  |  |  |  |  |  |  |  | 731 | 65 | 2 | 726(8) ${ }^{\text {* }}$ | 732(64) | 728(4)+ | 731(4) | $20+\gamma \mathrm{CH}_{\alpha}$ |
| 727 | 72 | 3 | 725 | 59 | 1 | 728 | 72 | 3 |  |  |  | 719(66)* | 726(39) | 719(7) | 723(5) | $20++\gamma \mathrm{CH}_{\alpha}$ |
| 707 | 3 | 1 | 707 | 0 | 1 | 712 | 0 | 0 | 714 | 0 | 1 | 710(1) | 706(17) | 707(6) | 709(7) | $\Gamma+10$ |
| 704 | 38 | 10 |  |  |  |  |  |  |  |  |  | 695(3) | 694(8) | 696(8) | 692(9) | $8+\delta_{s} \mathrm{CF}_{3}+\Delta$ |
|  |  |  | 688 | 39 | 19 | 690 | 22 | 8 |  |  |  | 681(4) | 681(36) | 680(25) | 681(56) | $8+\delta_{5} \mathrm{CF}_{3}+\Delta$ |
|  |  |  |  |  |  |  |  |  | 682 | 13 | 30 | 672(2) | 671(15) | 673(12) | 673(21) | $8+\Delta+\delta_{5} \mathrm{CF}_{3}$ |
|  |  |  |  |  |  |  |  |  | 649 | 63 | 5 | 641(14) | 640(43) | 640(12) | 641(17) | $8+\delta_{s} \mathrm{CF}_{3}+\Delta$ |
|  |  |  | 644 | 40 | 10 |  |  |  |  |  |  | 634(1) | 632(14) | 636(9) | 637(14) | $8+\Delta+\delta_{5} \mathrm{CF}_{3}$ |
| 615 | 33 | 10 |  |  |  | 615 | 40 | 5 |  |  |  | 607(10) | 608(8) | 606(11) | 607(7) | $8+\Delta+\delta_{5} \mathrm{CF}_{3}$ |
|  |  |  |  |  |  | 580 | 10 | 1 | 579 | 11 | 1 | 580(11) | 584(22) | 586(5) | 584(8) | $\delta_{\mathrm{a}} \mathrm{CF}_{3}+\Delta$ |
| 574 | 19 | 1 | 573 | 19 | 2 |  |  |  |  |  |  | 578(8) | 578(10) | 579(6) | 575(6) | $\delta_{\mathrm{a}} \mathrm{CF}_{3}+\Delta$ |
|  |  |  |  |  |  | 571 | 1 | 0 | 571 | 1 | 0 | 563(1) | 563(9) | 562(6) | 563(9) | 11 |
| 569 | 1 | 0 | 568 | 1 | 0 |  |  |  |  |  |  | 558(1) | 558(12) | 555(5) | 559(7) | 11 |
| 514 | 2 | 1 | 514 | 2 | 1 | 515 | 1 | 1 |  | 1 | 2 | 518(1) | 517(7) | 518(7) | 515(9) | $\delta_{\mathrm{a}} \mathrm{CF}_{3}+\Gamma$ |
|  |  |  |  |  |  |  |  |  | $480$ | 3 | 9 | 470(1) | 471(11) | 471(10)** | 471(34) | $\Delta+\delta \mathrm{C} \text {-thio }$ |
|  |  |  | 465 | 4 | 2 |  |  |  |  |  |  | 461(3) | 458(18) | 457(10)* | 457(14) | $\Delta+21$ |
|  |  |  | 464 | 4 | 1 |  |  |  |  |  |  | 461(3) | 458(18) | 457(10)** | 457(14) | $21+4$ |
|  |  |  |  |  |  | 461 | 3 | 2 | 464 | 3 | 1 | 461(3) | 458(18) | 457(10)* | 457(14) | 21 |
| 462 | 3 | 1 |  |  |  |  |  |  |  |  |  | 461(3) | 458(18) | 457(10)** | 457(14) | $21+\Gamma$ |
|  |  |  |  |  |  | 458 | 9 | 13 |  |  |  | 461(3) | 458(18) | 457(10)* | 457(14) | $\Delta+\delta \mathrm{C}$-thio |
| 445 | 0 | 2 |  |  |  |  |  |  |  |  |  | 434(2) | 434(3) | 433(10)** | 430(9) | $\delta \mathrm{C}-$ thio $+\delta_{\mathrm{a}} \mathrm{CF}_{3}$ |
| 443 | 0 | 0 | 442 | 0 | 1 |  |  |  |  |  |  | 434(2) | 434(3) | 433(10)** | $430(9)$ | $\delta_{\mathrm{a}} \mathrm{CF}_{3}+\delta \mathrm{C}-\mathrm{CF}_{3}+\Delta$ |
|  |  |  |  |  |  | $437$ | $2$ | $0$ | 434 | 2 | 1 | 434(2) | 434(3) | 433(10) | 430(9) | $\delta_{\mathrm{a}} \mathrm{CF}_{3}+\delta \mathrm{C}-\mathrm{CF}_{3}+\Delta$ |
|  |  |  |  |  |  | 360 | 1 | 1 |  |  |  |  |  |  |  | $\Delta$ |
| 353 | 3 | 1 | 355 | 3 | 1 |  |  |  |  |  |  | 354(1) | 355(2) | 345(8) | 346(10) | $\Delta$ |
|  |  |  |  |  |  |  |  |  | 346 | 0 | 2 | 348(1) | 348(4) | 339(7) | 340(9) | $\Delta$ |
| 325 | 3 | 1 |  |  |  |  |  |  |  |  |  | 304(3) | 305(7) | 304(11) | 303(27) | $v \mathrm{O} \cdots \mathrm{O}+\rho \mathrm{CF}_{3}$ |
|  |  |  | 316 | 4 | 1 | 312 | 4 | 4 | 313 | 9 | 3 | 294(1) | 293(4) | 299(13) | 297(25) | $\nu \mathrm{O} \cdots \mathrm{O}+\rho \mathrm{CF}_{3}$ |
|  |  |  |  |  |  | 302 | 0 | 0 | 304 | 0 | 1 | - | - | - | - | $\pi \mathrm{CF}_{3}+\Gamma$ |
| 285 | 0 | 0 | 285 | 1 | 0 |  |  |  |  |  |  | - | - | - | - | $\pi \mathrm{CF}_{3}+\Gamma$ |
| 243 | 2 | 6 |  |  |  | 243 | 1 | 1 |  |  |  | 241(1) | 234(6) | 239(20) | 239(27) | $\Delta$ |
|  |  |  | 232 | 1 | 7 |  |  |  | 234 | 2 | 1 | 234(3) | 229(4) | 232(26) | 235(25) | $\Delta$ |
| 220 | 1 | 3 | 221 | 1 | 3 |  |  |  |  |  |  | 218(2) | 225(2) | 225(26) | 222(23) | $\pi$ thio $+\Gamma$ |
|  |  |  |  |  |  | 197 | 0 | 4 | 201 | 0 | 4 | 206(2) | 208(4) | 208(38) | 210(39) | $\pi$ thio $+\Gamma$ |
| 196 | 1 | 2 | 191 | 2 | 1 | 197 | 3 | 1 | 191 | 3 | 1 | 195(3) | 197(6) | n.m. | 198(34) | $\rho \text { thio }+\delta \mathrm{C}-\mathrm{CF}_{3}$ |
|  |  |  |  |  |  | 129 | 3 | 1 | 131 | 3 | 1 | 138(3) | 139(15) | n.m. | - | $\gamma \mathrm{C}-\mathrm{CF}_{3}+\Gamma$ |
| 109 | 1 | 1 | 110 | 1 | 1 |  |  |  |  |  |  | n.c. | 108(3) | n.m. | 101 | $\gamma \mathrm{C}-\mathrm{CF}_{3}+\Gamma$ |
| 97 | 0 | 1 | 94 | 0 | 1 |  |  |  |  |  |  | n.c. | 73(13) | n.m. | 71 | $\Gamma$ |
|  |  |  |  |  |  | 88 | 0 | 0 | 84 | 0 | 0 | n.c. | n.c. | n.m. | - | $\Gamma$ |
| 83 | 0 | 0 | 87 | 0 | 0 | 81 | 0 | 0 | 84 | 0 | 1 | n.c. | n.c. | n.m. | - | $\delta \mathrm{C}_{\alpha}-\mathrm{C}$-thio $+\Delta$ |
| 36 | 1 | 6 | 35 | 0 | 4 | 39 | 1 | 6 | 41 | 0 | 4 | n.m. | n.m. | n.m. | 37 | $\tau$ thio |
| 24 | 0 | 1 | 22 | 0 | 2 | 20 | 0 | 1 | 18 | 0 | 2 | n.m. | n.m. | n.m. | n.m. | $\tau \mathrm{CF}_{3}$ |

${ }^{\text {a }}$ Freq, vibrational wavenumber (calculated at the B3LYP/6-311G** level); $I_{\text {IR }}$, IR intensities in $\mathrm{kM} / \mathrm{mol}$ (calculated at the B3LYP/6-311G*** level); $A_{R}$, Raman activities in $A^{* *} 4 /$ AMU (calculated at the B3LYP/6-31G** level); experimental intensities are given in parenthesis; vbr, very broad; $v$, stretching; $\delta$, in-plane bending; $\gamma$, out-of-plane bending; $\rho$, in-plane rocking; $\pi$, out-of-plane rocking; $\Delta$, in-plane ring deformation; $\Gamma$, out-of-plane ring deformation; $\tau$, torsion; n.c., not certain; n.m., not measured; thio, thienyl group; *, in $\mathrm{CS}_{2}$ solution; +, in $\mathrm{CH}_{3} \mathrm{CN}$ solution.
bands corresponding to these tautomers in the entire region of both Raman and IR spectra of TTFA. Upon deuteration, the bands at 3117 and $3108 \mathrm{~cm}^{-1}$ disappear and a relatively weak band appears at $2322 \mathrm{~cm}^{-1}$. Therefore we assigned these two bands to the $\mathrm{CH}_{\alpha}$ stretching and the four other bands to the CH stretching modes of the thienyl group.

### 4.2.2. OH stretching mode

The position and the shape of the $\mathrm{O}-\mathrm{H}$ stretching band are closely related to the shape of the potential energy function governing the motion of the proton. The enol form of $\beta$-diketones exhibits an extremely broad band in the $3500-2200 \mathrm{~cm}^{-1}$ region of the IR spectrum, which upon deuteration of the enolic proton, appears as a new narrower but still broad band in the $2200-1800 \mathrm{~cm}^{-1}$ region [16-20]. Because of the broadness and mixing with several combinations and overtones, and overall lose of their real spectral shapes, it is difficult to determine the center of these $v \mathrm{OH}$ and $v \mathrm{OD}$ bands (see Fig. 4). But deconvolutions of the infrared spectrum of TTFA solutions in $\mathrm{CCl}_{4}$ and $\mathrm{CS}_{2}$ in the $3000-2400 \mathrm{~cm}^{-1}$ region dis-
play a broad band centered at $2850 \mathrm{~cm}^{-1}$ with a half width at half maximum (HWHM) of about $300 \mathrm{~cm}^{-1}$, which is assigned to the OH stretching frequency. Deconvolution of the broad band in the $2300-1800 \mathrm{~cm}^{-1}$ region in the IR spectrum of $D_{2}$-TTFA in the $\mathrm{CCl}_{4}$ solution indicates a relatively narrower band centered at about $2080 \mathrm{~cm}^{-1}$ with a HWHM of about $200 \mathrm{~cm}^{-1}$. These frequencies are considerably higher than those observed for $A A / D_{2}-A A$, $2750 / 2020 \mathrm{~cm}^{-1}$ [16], but lower than those of TFAA/D $\mathrm{D}_{2}$-TFAA (1,1,1-trifluoroacetylacetone), $2900 / 2120 \mathrm{~cm}^{-1}$ [16]. This indicates a weaker IHB and a stronger IHB for TTFA in comparison with those of AA and TFAA, respectively [24]. These results are in agreement with the ${ }^{1} \mathrm{H}$ NMR of these compounds, which reports the proton chemical shifts for AA, TTFA, and TFAA as 15.4, 14.9, and 14.2 ppm (all in $\mathrm{CCl}_{4}$ solution), respectively [34].

### 4.2.3. $1700-1000 \mathrm{~cm}^{-1}$ region

Beside the $\mathrm{C}-\mathrm{C}$ stretching and $\mathrm{C}-\mathrm{H}$ bending modes of the thienyl ring and $\mathrm{CF}_{3}$ stretching modes, five bands are expected to be observed in this region related to the vibrations of the chelated

Table 3
Fundamental band assignment of $\mathrm{D}_{2}$-TTFA (frequencies in $\mathrm{cm}^{-1}$ ).

| Theoretical |  |  |  |  |  |  |  |  |  |  |  | Experimental |  |  |  | Assignment |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| A1 |  |  | A2 |  |  | B1 |  |  | B2 |  |  | IR |  | Raman |  |  |
| Freq | $I_{\text {IR }}$ | $A_{\text {R }}$ | Freq | $I_{\text {IR }}$ | $A_{\text {R }}$ | Freq | $I_{\text {IR }}$ | $A_{\text {R }}$ | Freq | $I_{\text {IR }}$ | $A_{\text {R }}$ | $\mathrm{CCl}_{4}$ | Solid | $\mathrm{CCl}_{4}$ | Solid |  |
| 3246 | 1 | 209 | 3244 | 1 | 216 | 3244 | 0 | 211 | 3242 | 1 | 212 | 3114(2) | 3113(18) | 3112(11) | 3116(15) | 1 |
| 3231 | 1 | 92 |  |  |  | 3228 | 1 | 90 |  |  |  | 3103(1) | 3104(12) | 3104(6) | 3100(9) | 2 |
|  |  |  | 3221 | 2 | 108 |  |  |  | 3219 | 2 | 109 | 3096(1) | 3094(13) | 3096(5) | 3094(12) | 2 |
| 3211 | 4 | 145 | 3208 | 4 | 83 | 3209 | 4 | 136 | 3206 | 5 | 87 | 3084(1) | 3086(12) | 3084(4) | 3085(8) | 13 |
|  |  |  | 2405 | 2 | 11 |  |  |  | 2404 | 3 | 11 | 2314(2) | 2318(9) | 2322(2) | 2318(3) | $v \mathrm{CD}$ |
| 2396 | 5 | 11 |  |  |  | 2393 | 2 | 11 |  |  |  | 2314 | 2318 | 2322 | 2318 | $\nu$ CD |
| 2247 | 247 | 5 | 2218 | 263 | 5 | 2237 | 215 | 24 | 2249 | 214 | 29 | 2080(2) | 2090(4) | - | - | $\nu$ OD |
|  |  |  |  |  |  | 1664 | 432 | 17 | 1661 | 505 | 17 | 1634(38) | 1637(61) | 1635(7) | 1635(7) | $v_{\mathrm{a}} \mathrm{O}=\mathrm{C}-\mathrm{C}=\mathrm{C}$ |
| 1659 | 133 | 19 |  |  |  |  |  |  |  |  |  | 1626(40) | 1629(50) | 1627(8) | 1628(6) | $v_{\mathrm{a}} \mathrm{C}=\mathrm{C}-\mathrm{C}=\mathrm{O}$ |
|  |  |  | 1651 | 161 | 37 |  |  |  |  |  |  | 1621(34) | 1623(62) | 1617(10) | 1618(7) | $v_{\mathrm{a}} \mathrm{C}=\mathrm{C}-\mathrm{C}=0$ |
|  |  |  |  |  |  | 1579 | 84 | 199 | 1581 | 39 | 428 | 1563(20) | 1560(40) | 1561(29) | 1555(30) | $v_{\mathrm{s}} \mathrm{O}=\mathrm{C}-\mathrm{C}=\mathrm{C}+14+v \mathrm{C}-\mathrm{CF}_{3}+\delta \mathrm{OD}$ |
| 1574 | 526 | 471 | 1574 | 303 | 369 |  |  |  |  |  |  | 1539(47) | 1534(42) | 1537(51) | 1534(37) | $v_{\mathrm{s}} \mathrm{C}=\mathrm{C}-\mathrm{C}=\mathrm{O}+14+v \mathrm{C}$-thio |
|  |  |  |  |  |  | 1558 | 84 | 253 | 1559 | 46 | 68 | 1520(23) | 1522(36) | 1519(25) | 1522(23) | $14+v_{s}(\mathrm{C}=\mathrm{O}, \mathrm{C}-\mathrm{O})+v_{\mathrm{a}} \mathrm{C}-\mathrm{C}=\mathrm{C}+v \mathrm{C}-\mathrm{CF}_{3}$ |
|  |  |  | 1530 | 761 | 178 |  |  |  |  |  |  | 1498(21) | 1500(20) | 1494(11) | 1500(11) | $v_{\mathrm{a}} \mathrm{C}=\mathrm{C}-\mathrm{C}+v \mathrm{C}-\mathrm{O}+\delta \mathrm{OD}+14$ |
| 1526 | 599 | 107 |  |  |  |  |  |  |  |  |  | 1490(19) | 1491(21) | 1487(10) | 1486(8) | $v_{\mathrm{a}} \mathrm{C}=\mathrm{C}-\mathrm{C}+v \mathrm{C}-\mathrm{O}+\delta \mathrm{OD}+14$ |
| 1462 | 93 | 700 |  |  |  |  |  |  |  |  |  | 1419(28) | 1428(39) | 1420(38) | 1422(30) | $3+v \mathrm{C}$-thio $+v \mathrm{C}-\mathrm{O}$ |
|  |  |  | 1457 | 65 | 743 |  |  |  |  |  |  | 1411(31) | 1419(48) | 1417(100) | 1416(100) | $3+v \mathrm{C}-$ thio $+v \mathrm{C}-0$ |
|  |  |  |  |  |  | 1457 | 109 | 367 | 1456 | 119 | 385 | 1411(31) | 1419(48) | 1417(100) | 1416(100) | $3+v \mathrm{C}-\mathrm{O}+v \mathrm{C}-$ thio |
|  |  |  |  |  |  | 1429 | 35 | 29 | 1428 | 58 | 22 | 1407(26) | 1407(47) | 1410(64) | 1409(50) | $v_{\mathrm{a}} \mathrm{C}-\mathrm{C}=\mathrm{C}-\mathrm{O}+v \mathrm{C}=\mathrm{O}+3+v \mathrm{C}-\mathrm{CF}_{3}$ |
|  |  |  | 1420 | 46 | 2 |  |  |  |  |  |  | 1398(16) | 1398(41) | 1399(17) | 1396(19) | $4+v_{a}(C-O, C=0)$ |
| 1412 | 57 | 22 |  |  |  |  |  |  |  |  |  | 1390(12) | 1389(29) | 1387(10) | 1383(12) | $v_{\mathrm{a}} \mathrm{O}-\mathrm{C}=\mathrm{C}-\mathrm{C}$ |
| 1394 | 16 | 82 | 1394 | 45 | 116 |  |  |  |  |  |  | 1363(15) | 1366(20) | 1362(9) | 1359(11) | $4+v_{\mathrm{a}} \mathrm{O}-\mathrm{C}=\mathrm{C}-\mathrm{C}+v \mathrm{C}-\mathrm{CF}_{3}+v \mathrm{C}$-thio $+\delta \mathrm{OD}$ |
|  |  |  |  |  |  | 1387 | 273 | 47 |  |  |  | 1356(23) | 1357(45) | 1354(14) | 1354(20) | $4+v C-0$ |
|  |  |  |  |  |  |  |  |  | 1384 | 50 | 19 | 1356(23) | 1357(45) | 1354(14) | 1354(20) | 4 |
|  |  |  | 1353 | 21 | 4 |  |  |  |  |  |  | 1332(17) | 1333(44) | - | - | $4+v_{s} \mathrm{O}-\mathrm{C}=\mathrm{C}-\mathrm{C}+\nu \mathrm{C}-\mathrm{CF}_{3}$ |
| 1351 | 55 | 1 |  |  |  |  |  |  |  |  |  | 1332(17) | 1333(44) | - | - | $4+v \mathrm{C}-\mathrm{CF}_{3}+v_{\mathrm{s}} \mathrm{C}=\mathrm{C}-\mathrm{C}$ |
|  |  |  |  |  |  |  |  |  | 1332 | 625 | 4 | 1313(41) | 1314(62) | 1312(7) | 1315(6) | $v \mathrm{C}-\mathrm{C}+\nu \mathrm{C}-\mathrm{CF}_{3}+\nu \mathrm{C}$-thio |
|  |  |  |  |  |  | 1314 | 527 | 17 |  |  |  | 1281(29) | 1289(55) | 1278(13) | 1282(8) | $v \mathrm{C}-\mathrm{C}+\nu \mathrm{C}-\mathrm{CF}_{3}+\nu \mathrm{C}$-thio |
|  |  |  |  |  |  |  |  |  | 1258 | 1 | 7 | 1253(25) | 1261(49) | 1252(8) |  | 15 |
|  |  |  | 1253 | 5 | 4 |  |  |  |  |  |  | - | - | 1244(8) | 1244(7) | $15+v \mathrm{C}-\mathrm{O}$ |
| 1252 | 60 | 7 |  |  |  |  |  |  |  |  |  | 1232(24) | 1239(42) | 1232(6) | 1238(6) | $15+v_{s} \mathrm{CF}_{3}$ |
|  |  |  |  |  |  | 1245 | 83 | 7 |  |  |  | 1217(32) | 1225(67) | 1220(4) | - | $15+v \mathrm{C}-\mathrm{CF}_{3}$ |
| 1203 | 393 | 5 | 1221 | 528 | 10 |  |  |  |  |  |  | 1113(29) | 1112(62) | 1111(5) | - | $v_{\mathrm{s}} \mathrm{CF}_{3}+v \mathrm{C}_{4}-\mathrm{S}+v_{\mathrm{a}} \mathrm{C}=\mathrm{C}-\mathrm{C}+\delta \mathrm{OD}+\delta \mathrm{CD}$ |
|  |  |  |  |  |  | 1202 | 93 | 8 | 1217 | 254 | 2 | 1113(29) | 1112(62) | 1111(5) | - | $v_{\text {s }} \mathrm{CF}_{3}+v \mathrm{C}_{4}-\mathrm{S}+v \mathrm{C}-\mathrm{O}+\delta \mathrm{CD}$ |
|  |  |  |  |  |  | 1195 | 266 | 0 |  |  |  | 1191(49) | 1188(94) | 1187(4) | 1193(5) | $v_{2} \mathrm{CF}_{3}+v \mathrm{C}_{4}-\mathrm{S}$ |
|  |  |  |  |  |  |  |  |  | 1194 | 238 | 1 | 1191(49) | 1188(94) | 1187(4) | 1193(5) | $v_{\mathrm{a}} \mathrm{CF}_{3}$ |
| 1188 | 223 | 9 | 1188 | 256 | 1 |  |  |  |  |  |  | 1203(100) | 1200(100) | 1198(4) | 1206(5) | $v_{\mathrm{a}} \mathrm{CF}_{3}$ |
|  |  |  |  |  |  | 1171 | 288 | 4 | 1171 | 289 | 4 | 1164(89) | 1155(87) | 1167(3) | 1164(5) | $v_{\mathrm{a}} \mathrm{CF}_{3}$ |
| 1169 | 287 | 12 | 1169 | 284 | 3 |  |  |  |  |  |  | 1157(55) | 1143(99) | 1159(4) | 1151(4) | $v_{2} \mathrm{CF}_{3}$ |
| 1127 | 41 | 14 |  |  |  |  |  |  |  |  |  | 1091(8) | 1092(38) | 1083(20) | 1095(13) | $5+\delta \mathrm{OD}$ |
|  |  |  | 1120 | 31 | 7 | 1124 | 94 | 44 | 1123 | 111 | 44 | 1091(8) | 1085(28) | 1083(20) | 1084(23) | $5+\delta \mathrm{OD}$ |
| 1103 | 9 | 30 | 1101 | 4 | 40 | 1102 | 33 | 30 | 1104 | 38 | 44 | 1075(7) | 1072(20) | 1075(16) | 1075(20) | $16+\delta O D$ |
|  |  |  |  |  |  |  |  |  | 1079 | 127 | 34 | 1051(14) | 1055(37) | 1049(14) | 1053(29) | $\delta O D+6$ |
|  |  |  | 1075 | 65 | 67 |  |  |  |  |  |  | 1045(19) | 1050(41) | 1042(19) | 1047(25) | $\delta O D+6$ |
| 1068 | 30 | 45 |  |  |  |  |  |  |  |  |  | 1040(17) | 1042(36) | 1038(14) | 1039(10) | $\delta O D+6$ |
|  |  |  |  |  |  | 1064 | 148 | 16 |  |  |  | 1040(17) | 1042(36) | 1038(14) | 1039(10) | $\delta O D+6+v_{s} \mathrm{C}=\mathrm{C}-\mathrm{C}$ |
| 1046 | 125 | 1 |  |  |  |  |  |  |  |  |  | 1032(15) | 1028(25) | - | - | $6+v_{s} \mathrm{C}=\mathrm{C}-\mathrm{C}+\nu \mathrm{C}_{4}-\mathrm{S}+\delta_{5} \mathrm{CF}_{3}+v \mathrm{C}-\mathrm{O}$ |
|  |  |  |  |  |  | 1042 | 24 | 0 |  |  |  | 1024(11) | 1025(24) | - | - | $5+v_{5} \mathrm{C}=\mathrm{C}-\mathrm{C}+\nu \mathrm{C}_{4}-\mathrm{S}+\delta_{5} \mathrm{CF}_{3}+v \mathrm{C}-\mathrm{O}$ |
|  |  |  | 1039 | 76 | 0 |  |  |  |  |  |  | 1018(8) | 1015(22) | - | - | $v_{\mathrm{s}} \mathrm{C}=\mathrm{C}-\mathrm{C}+5+\nu \mathrm{C}_{4}-\mathrm{S}+\delta_{5} \mathrm{CF}_{3}+\nu \mathrm{C}-\mathrm{O}$ |
|  |  |  |  |  |  |  |  |  | 1016 | 22 | 1 | 996(7) | 993(26) | - | 998(6) | $v_{5} \mathrm{C}=\mathrm{C}-\mathrm{C}+5+v \mathrm{C}_{4}-\mathrm{S}+\delta_{5} \mathrm{CF}_{3}+v \mathrm{C}-\mathrm{O}$ |
|  |  |  |  |  |  | 945 | 1 | 2 |  |  |  | - | 935(3) | 935(2) | 933(2) | 9 |
| 938 | 0 | 3 |  |  |  |  |  |  |  |  |  | - | 923(4) | 921(2) | 924(2) | 9 |
|  |  |  | 927 | 0 | 3 |  |  |  | 926 | 0 | 2 | - | 918(5) | 921(2) | 919(2) | 9 |
| 897 | 24 | 13 |  |  |  |  |  |  |  |  |  | 891(3) | 889(14) | 893(6) | 890 (7) | $\delta \mathrm{CD}+4$ |
|  |  |  |  |  |  | 896 | 9 | 0 |  |  |  | 891(3) | 889(14) | 893(6) | 890 (7) | $\delta \mathrm{CD}+17$ |
| 889 | 20 | 2 | 894 | 24 | 25 |  |  |  |  |  |  | 881(5) | 870(16) | 873(6) | 873(18) | $\delta$ CCC $+17+\delta$ D |
|  |  |  |  |  |  |  |  |  | 883 | 1 | 8 | 891(3) | 889(14) | 893(6) | 890(7) | $\delta \mathrm{CD}+17$ |
|  |  |  | 882 | 14 | 8 |  |  |  |  |  |  | 891(3) | 889(14) | 893(6) | 890 (7) | $\delta \mathrm{CD}+17+4$ |
|  |  |  |  |  |  | 872 | 4 | 2 | 870 | 12 | 8 | 855(10) | 861(22) | 853(7) | 855(9) | $\delta$ CCC $+17+\delta$ OD |
|  |  |  | 863 | 21 | 1 |  |  |  |  |  |  | 844(6) | 850(30) | 842(9) | 841(13) | $7+17+\delta$ CD |
| 863 | 31 | 4 |  |  |  |  |  |  |  |  |  | 844(6) | 850(30) | 842(9) | 841(13) | $7+17+4$ |
|  |  |  |  |  |  | 858 | 40 | 10 |  |  |  | 844(6) | 850(30) | 842(9) | 841(13) | $7+\delta C C C+\delta O D$ |
| 872 | 2 | 1 | 856 | 1 | 2 | 878 | 1 | 1 | 858 | 0 | 1 | 839(3) | 842(17) | 835(7) | 843(11) | 19 |
|  |  |  |  |  |  |  |  |  | 856 | 26 | 5 | 839(3) | 842(17) | 835(7) | 843(11) | $7+\delta \mathrm{CD}+\delta \mathrm{OD}$ |
| 804 | 56 | 1 | 803 | 53 | 0 | 801 | 61 | 1 | 800 | 51 | 1 | sol. | 807(27) | sol. | 814(4) | $\Gamma+19$ |
|  |  |  |  |  |  | 784 | 6 | 2 |  |  |  | sol. | 800(15) | sol. | 800(12) | $\Delta+v \mathrm{C}-\mathrm{CF}_{3}+\delta_{5} \mathrm{CF}_{3}$ |
|  |  |  |  |  |  |  |  |  | 778 | 16 | 2 | sol. | 775(34) | sol. | 773 (11) | $18+\Delta+\nu \mathrm{C}-\mathrm{CF}_{3}+\delta_{5} \mathrm{CF}_{3}$ |
| 763 | 12 | 3 |  |  |  |  |  |  |  |  |  | sol. | 769(23) | sol. | 766(5) | $17+\Delta+\nu \mathrm{C}-\mathrm{CF}_{3}+\delta_{5} \mathrm{CF}_{3}$ |
|  |  |  | 760 | 5 | 4 |  |  |  |  |  |  | sol. | 769(23) | sol. | 766(5) | $18+\Delta+\nu \mathrm{C}-\mathrm{CF}_{3}+\delta_{5} \mathrm{CF}_{3}$ |
| 751 | 4 | 8 |  |  |  | 752 | 4 | 9 |  |  |  | sol. | 746(63) | sol. | 750(22) | 18 |
|  |  |  | 748 | 11 | 11 |  |  |  | 749 | 6 | 10 | sol. | 746(63) | sol. | 750(22) | $18+\delta_{s} \mathrm{CF}_{3}$ |

Table 3 (continued)

| Theoretical |  |  |  |  |  |  |  |  |  |  |  | Experimental |  |  |  | Assignment |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| A1 |  |  | A2 |  |  | B1 |  |  | B2 |  |  | IR |  | Raman |  |  |
| Freq | $I_{\text {IR }}$ | $A_{\text {R }}$ | Freq | $I_{\text {IR }}$ | $A_{\mathrm{R}}$ | Freq | $I_{\text {IR }}$ | $A_{\mathrm{R}}$ | Freq | $I_{\text {IR }}$ | $A_{\text {R }}$ | $\mathrm{CCl}_{4}$ | Solid | $\mathrm{CCl}_{4}$ | Solid |  |
|  |  |  |  |  |  |  |  |  | 732 | 74 | 2 | sol. | 731(83) | sol. | 729(4) | 20 |
| 727 | 73 | 3 | 729 | 84 | 2 | 729 | 56 | 3 |  |  |  | 721(45) | 725(57) | 721(9) | 723(2) | 20 |
| 715 | 0 | 1 | 714 | 0 | 0 | 715 | 7 | 0 | 718 | 1 | 1 |  | 706(19) | 707(8) | 706(5) | $\Gamma+10$ |
| 700 | 34 | 12 |  |  |  |  |  |  |  |  |  | 696(4) | - | 696(6) | 691(5) | $\delta_{5} \mathrm{CF}_{3}+8+\Delta$ |
|  |  |  | 687 | 36 | 19 |  |  |  |  |  |  | 680(6) | 677(31) | 677(19) | 680(27) | $8+\delta_{5} \mathrm{CF}_{3}+\Delta$ |
|  |  |  | 686 | 16 | 1 |  |  |  |  |  |  | 629(7) | 631(41) | 627(6) | 631(8) | $\gamma \mathrm{OD}+\gamma \mathrm{CD}$ |
|  |  |  |  |  |  | 680 | 18 | 9 | 677 | 10 | 30 | 675(4) | 667(14) | 670(13) | 675(40) | $8+\Delta+\delta_{5} \mathrm{CF}_{3}$ |
| 675 | 18 | 1 |  |  |  | 677 | 19 | 1 | 672 | 20 | 1 | 629(7) | 631(41) | 627(6) | 631(8) | $\gamma \mathrm{OD}+\gamma \mathrm{CD}$ |
|  |  |  |  |  |  |  |  |  | 641 | 63 | 3 | 638(9) | 639(40) | 638(7) | 637(8) | $8+\delta_{5} \mathrm{CF}_{3}+\Delta$ |
|  |  |  | 635 | 40 | 9 |  |  |  |  |  |  | 635(9) | 636(45) | 634(6) | 637(8) | $8+\delta_{5} \mathrm{CF}_{3}+\Delta$ |
|  |  |  |  |  |  | 614 | 42 | 5 |  |  |  | 606(7) | 609(17) | 606(9) | 606(4) | $8+\delta_{5} \mathrm{CF}_{3}+\Delta$ |
| 612 | 33 | 10 |  |  |  |  |  |  |  |  |  | 606(7) | 609(17) | 606(9) | 606(4) | $8+\Delta+\delta_{5} \mathrm{CF}_{3}$ |
|  |  |  |  |  |  | 593 | 14 | 1 |  |  |  | 573(10) | 571(42) | 572(7) | 569(5) | $\gamma \mathrm{CD}+\gamma \mathrm{OD}+11$ |
|  |  |  |  |  |  |  |  |  | 588 | 16 | 0 | 573(10) | 571(42) | 572(7) | 569(5) | $\gamma \mathrm{CD}$ |
| 587 | 12 | 0 | 585 | 14 | 0 |  |  |  |  |  |  | 573(10) | 571(42) | 572(7) | 569(5) | $\gamma \mathrm{CD}+11$ |
|  |  |  |  |  |  | 578 | 10 | 1 | 577 | 10 | 1 | 580(10) | 583(34) | 583(4) | 582(5) | $\delta_{\mathrm{a}} \mathrm{CF}_{3}+\Delta$ |
|  |  |  |  |  |  |  |  |  | 571 | 1 | 0 | 563(4) | 565(29) | 562(5) | 562(7) | 11 |
| 570 | 20 | 2 | 569 | 19 | 2 |  |  |  |  |  |  | 577(11) | 578(40) | 577(7) | 576(5) | $\delta_{\mathrm{a}} \mathrm{CF}_{3}+\Delta$ |
| 564 | 9 | 0 | 564 | 0 | 0 | 567 | 6 | 0 |  |  |  | 558(3) | 558(33) | 555(4) | 559(5) | $11+\gamma \mathrm{CD}$ |
| 513 | 1 | 1 | 512 | 1 | 1 | 512 | 0 | 1 | 512 | 0 | 1 | 511(2) | 513(8) | 513(8) | 511(6) | $\delta_{\mathrm{a}} \mathrm{CF}_{3}+\Gamma$ |
|  |  |  |  |  |  |  |  |  | 474 | 3 | 9 | n.m. | 466(9) | sol. | 467(27) | $\Delta+\delta \mathrm{C}$-thio |
| 461 | 4 | 1 | 463 | 6 | 2 | 460 | 3 | 2 | 463 | 4 | 1 | n.m. | 455(25) | sol. | 455(9) | 21 |
|  |  |  | 456 | 3 | 1 | 451 | 9 | 12 |  |  |  | n.m. | 455(25) | sol. | 455(9) | $\Delta+\delta \mathrm{C}$-thio |
| 439 | 0 | 1 | 438 | 0 | 1 |  |  |  |  |  |  | n.m. | - | sol. |  | $\Delta+\delta_{\mathrm{a}} \mathrm{CF}_{3}+\delta \mathrm{C}-\mathrm{CF}_{3}$ |
| 436 | 1 | 2 |  |  |  |  |  |  |  |  |  | n.m. | - | sol. |  | $\Delta+\delta \mathrm{C}$-thio |
|  |  |  |  |  |  | 431 | 2 | 0 | 427 | 1 | 1 | n.m. | 430(5) | sol. | 437(5) | $\Delta+\delta_{\mathrm{a}} \mathrm{CF}_{3}+\delta \mathrm{C}-\mathrm{CF}_{3}$ |
|  |  |  | 352 | 3 | 1 | 357 | 1 | 1 |  |  |  | n.m. | 345(2) | sol. | 339(8) | $\Delta$ |
| 347 | 4 | 2 |  |  |  |  |  |  | 342 | 1 | 1 | n.m. | 336(3) | sol. | 335(6) | $\Delta$ |
| 320 | 3 | 0 |  |  |  |  |  |  |  |  |  | n.m. | 297(11) | sol. | 298(26) | $\nu \mathrm{O} \cdots \mathrm{O}+\rho \mathrm{CF}_{3}$ |
|  |  |  | 307 | 4 | 1 | 303 | 4 | 4 | 303 | 9 | 4 | n.m. | 290(9) | sol. | 289(13) | $\nu \mathrm{O} \cdots \mathrm{O}+\rho \mathrm{CF}_{3}$ |
|  |  |  |  |  |  | 299 | 0 | 0 | 300 | 0 | 1 | n.m. | - | sol. | - | $\pi \mathrm{CF}_{3}+\Gamma$ |
| 282 | 0 | 0 | 283 | 1 | 0 |  |  |  |  |  |  | n.m. | - | sol. | - | $\pi \mathrm{CF}_{3}+\Gamma$ |
| 241 | 3 | 6 |  |  |  | 240 | 1 | 1 |  |  |  | n.m. | - | sol. | 235(18) | $\Delta$ |
|  |  |  | 230 | 1 | 7 |  |  |  | 232 | 3 | 1 | n.m. | n.m. | sol. | 231(14) | $\Delta$ |
| 218 | 1 | 3 | 219 | 1 | 3 |  |  |  |  |  |  | n.m. | n.m. | sol. | 220(15) | $\pi$ thio $+\Gamma$ |
|  |  |  |  |  |  | 196 | 0 | 4 | 199 | 0 | 4 | n.m. |  | sol. | 207(24) | $\pi$ thio $+\Gamma$ |
| 194 | 1 | 2 | 190 | 2 | 1 | 195 | 3 | 1 | 190 | 3 | 1 | n.m. | n.m. | sol. | 191(24) | $\rho$ thio $+\delta \mathrm{C}-\mathrm{CF}_{3}$ |
|  |  |  |  |  |  | 126 | 3 | 1 | 128 | 3 | 0 | n.m. | n.m. | n.m. | n.m. | $\gamma \mathrm{C}-\mathrm{CF}_{3}+\Gamma$ |
| 107 | 1 | 1 | 109 | 1 | 1 |  |  |  |  |  |  | n.m. | n.m. | n.m. | n.m. | $\gamma \mathrm{C}-\mathrm{CF}_{3}+\Gamma$ |
| 94 | 0 | 1 | 92 | 0 | 2 | 86 | 0 | 0 | 82 | 0 | 1 | n.m. | n.m. | n.m. | n.m. | $\Gamma$ |
| 83 | 0 | 0 | 86 | 0 | 0 | 81 | 0 | 0 | 84 | 0 | 0 | n.m. | n.m. | n.m. | n.m. | $\delta C_{\alpha}-\mathrm{C}$-thio $+\Delta$ |
| 36 | 1 | 6 | 35 | 0 | 4 | 39 | 1 | 6 | 41 | 0 | 4 | n.m. | n.m. | n.m. | n.m. | $\tau$ thio |
| 24 | 0 | 1 | 22 | 0 | 2 | 20 | 0 | 1 | 18 | 0 | 2 | n.m. | n.m. | n.m. | n.m. | $\tau \mathrm{CF}_{3}$ |

${ }^{\text {a }}$ See footnotes of Table 2.


Fig. 4. The IR spectra of TTFA (-) and D2-TTFA ( $\cdots$ ) in the OH/OD stretching region.
enol ring, which arise from the $\mathrm{C}-\mathrm{O}, \mathrm{C}=\mathrm{O}, \mathrm{C}-\mathrm{C}$, and $\mathrm{C}=\mathrm{C}$ stretching and the $\mathrm{O}-\mathrm{H}$ in-plane bending motions. In the $\mathrm{C}=\mathrm{O}$ and $\mathrm{C}=\mathrm{C}$ stretching region, with the exception of TFAA and HFAA
(1,1,1,5,5,5-hexafluoroacetylacetone), only one single band has apparently been observed in the IR spectra of the enol form of $\beta$ diketones [18-23]. By deconvolution of the IR spectra of AA and its deuterated analogue, $\mathrm{D}_{6} \mathrm{AA}$, it was shown that another strong and broad band, corresponding to the very strong and relatively broad Raman band, lies under this band at the lower frequency side [12]. In the case of AA, these bands appear at 1642 and $1624 \mathrm{~cm}^{-1}$ in the gas phase and are shifted downward in the condensed phases [12]. Considering the vibrational behavior of other $\beta$-diketones, and with respect to the IR and Raman studies for thiophene by Pasterny [62], and also according to the calculated normal mode's frequencies of TTFA, we expect to observe three bands in the $1650-1500 \mathrm{~cm}^{-1}$ region due to the asymmetric and symmetric $\mathrm{C}=\mathrm{C}-\mathrm{C}=\mathrm{O}$ stretching and $v 14$ (see Fig. 9) of the thienyl group. The deconvoluted IR and Raman spectra of TTFA in this region indicate existence of eight bands in this region with considerable intensities in either the Raman or IR spectra. As previously explained, the existence of these additional bands can be attributed to all four stable conformations of TTFA being present in comparable amounts in the sample. Considering the calculated results, the first three bands of the mentioned eight observed bands in the double bond region, which occur at 1651,1636 , and $1623 \mathrm{~cm}^{-1}$, are attributed to the


Fig. 5. The IR spectra of TTFA (-) and D2-TTFA ( $\ldots$ ) in $\mathrm{CCl}_{4}$ solution.


Fig. 6. The Raman spectra of TTFA (-) and D2-TTFA (...) in solid states.
$v_{\mathrm{a}} \mathrm{C}=\mathrm{C}-\mathrm{C}=\mathrm{O}$ coupled to the OH bending movement in B 1 and B 2 , in A1, and in A2 conformations, respectively. Upon deuteration, these IR strong bands move downward to 1634, 1626, and $1621 \mathrm{~cm}^{-1}$, which are in agreement with the calculated results and support the assignment. The next two bands at 1601 and $1583 \mathrm{~cm}^{-1}$ with strong IR and Raman intensities, are assigned to the symmetric $\mathrm{C}=\mathrm{C}-\mathrm{C}=\mathrm{O}$ stretching strongly coupled to the OH in-plane bending for A and B tautomers, respectively. Upon deuteration these bands shift downward to 1539 and $1563 \mathrm{~cm}^{-1}$ and become strongly perturbed by the thienyl $v 14$ vibrational mode.

These five assigned bands are of special interest because in all IR and Raman spectra collected in the solid state, the intensities of the bands related to the B2 conformer dominate those of the other conformers. Contrarily, in the solutions, the intensities of bands for the A conformers are stronger than those of the B conformers (see Fig. 7). This means that in the solid state the major content of the sample is in the B2 form and in the solution states the A forms have more significant amounts. This result is in good agreement with the experimental X-ray results [50] in the solid state and the theoretical calculations in solution.


Fig. 7. The IR spectra of TTFA in $\mathrm{CCl}_{4}(-)$ and TTFA in solid state ( - ).


Fig. 8. The deconvoluted IR spectrum of TTFA in $\mathrm{CCl}_{4}$ solution.

The last bands of this group are at 1522,1519 , and $1508 \mathrm{~cm}^{-1}$, which are assigned to the $v 14$ of the thienyl group in the different conformers. According to the calculations, upon deuteration this vibration is strongly coupled to $v_{\mathrm{s}} \mathrm{C}=\mathrm{C}-\mathrm{C}=\mathrm{O}$ and shifts toward higher frequencies.

According to the calculations and the experimental Raman spectrum of thiophene [62], the strongest Raman band at about $1410 \mathrm{~cm}^{-1}$, which upon deconvolution indicates two bands at 1412 and $1410 \mathrm{~cm}^{-1}$, is assigned to the symmetric $\mathrm{C}=\mathrm{C}-\mathrm{C}=\mathrm{C}$ stretching of the thienyl group, $v 3$, in the different conformers.

Three relatively weak and broad bands are observed at 1456, 1448 , and $1437 \mathrm{~cm}^{-1}$. The first two bands are assigned to the asymmetric $\mathrm{C}-\mathrm{C}=\mathrm{C}-\mathrm{O}$ stretching, coupled to $\delta \mathrm{OH}$, for A1 and A 2 conformers, respectively, and the latter is the corresponding band for the B1 and B2 conformers. Upon deuteration, these bands shift about $50 \mathrm{~cm}^{-1}$ towards lower frequencies which is in agreement with the theoretical results.

The relatively strong bands at 1356 and $1353 \mathrm{~cm}^{-1}$ are assigned to the $v 4$ vibrational mode of the thienyl ring.

Deconvolution shows other relatively strong bands at 1283, 1279 , and $1274 \mathrm{~cm}^{-1}$, which are attributed to the OH in-plane


$746 \mathrm{~cm}^{-1}$

$916 \mathrm{~cm}^{-1}$

$1276 \mathrm{~cm}^{-1}$

$3196 \mathrm{~cm}^{-1}$

$834 \mathrm{~cm}^{-1}$

$1053 \mathrm{~cm}^{-1}$

$1395 \mathrm{~cm}^{-1}$

$3210 \mathrm{~cm}^{-1}$

$877 \mathrm{~cm}^{-1}$

$1106 \mathrm{~cm}^{-1}$

$1447 \mathrm{~cm}^{-1}$

$1558 \mathrm{~cm}^{-1}$


Fig. 9. Characterization of the ring vibrational modes of thiophene molecule, obtained at B3LYP/6-311G** level of calculation.
bending modes of the A1 and A2 conformers, B2 conformer, and B1 conformer, respectively. This vibrational mode is strongly coupled to some other motions like $\mathrm{C}=\mathrm{C}, \mathrm{C}$-thio, and $\mathrm{C}-\mathrm{CF}_{3}$ stretching movements and $v 15$ of the thienyl group. The coupling with the $C=C$ stretching explains the strength of the bands in the Raman spectrum. Upon deuteration these bands disappear and three relatively strong bands appear at 1051,1045 , and $1040 \mathrm{~cm}^{-1}$ for $D_{2^{-}}$ TTFA, which is attributed to the OD in-plane bending coupled to the $v 6$ of the thienyl group. The corresponding bands in $A A / D_{2^{-}}$ $A A$ appear at $1298 / 1081 \mathrm{~cm}^{-1}$. The considerably lower frequency of this mode in $D_{2}$-TTFA compared to that in $D_{2}-A A$ is partly due to its coupling to $v 6$ mode of the thienyl group and partly due to a weaker hydrogen bond in TTFA compared to that in AA.

Four relatively strong IR bands are observed at 1252, 1244, 1231 , and $1222 \mathrm{~cm}^{-1}$. The first is assigned to $v 15$ for all four conformations coupled strongly to the C-thio stretching. The 1244 and $1222 \mathrm{~cm}^{-1}$ bands are assigned to $v 15$ coupled mainly to C4-S stretching for B2 and B1, respectively. The band at $1231 \mathrm{~cm}^{-1}$ is the corresponding band for the A conformers. Upon deuteration these bands become less mixed and lose their Raman intensities, without any significant frequency shift, which is in good agreement with the calculated results.

The deconvoluted IR spectrum of TTFA shows four very strong bands at $1205,1199,1165$, and $1162 \mathrm{~cm}^{-1}$. According to the calculated results, these bands arise from pure asymmetric $\mathrm{CF}_{3}$ stretch-
ing of the molecule. The symmetric $\mathrm{CF}_{3}$ stretching frequency, which is strongly coupled to the $\delta \mathrm{CH}_{\alpha}$, is observed at $1110 \mathrm{~cm}^{-1}$. The corresponding $\mathrm{CF}_{3}$ stretching bands in the IR spectrum of TFAA are observed at 1200,1162 , and $1109 \mathrm{~cm}^{-1}$ [21], which are very close to those observed in the IR spectrum of TTFA.

The $\mathrm{CH}_{\alpha}$ in-plane bending, which is strongly coupled to the $v_{\mathrm{s}} \mathrm{CF}_{3}$ and $v 6$ of the thienyl ring, is observed at $1110 \mathrm{~cm}^{-1}$. Upon deuteration this band moves downward to $891 \mathrm{~cm}^{-1}$ for $\delta \mathrm{CD}$.

The $1084,1065,1063$, and $1059 \mathrm{~cm}^{-1}$ bands, which are medium intense in both IR and Raman spectra and sensitive to deuteration, are assigned to $v 5$ and $v 6$ of the thienyl group. Upon deuteration, these two nearly pure motions become strongly coupled to $\delta O D$.

The medium and relatively weak bands at 1032, 1028, 1020, and $996 \mathrm{~cm}^{-1}$ are assigned to the symmetric stretching of $\mathrm{C}=\mathrm{C}_{\alpha}-\mathrm{C}$ segment that is coupled to the stretching of $\mathrm{C} 4-\mathrm{S}$ in thienyl ring and symmetric deformation of $\mathrm{CF}_{3}$, for $\mathrm{A} 1, \mathrm{~B} 1, \mathrm{~A} 2$, and B 2 conformers, respectively. The character and frequency of these motions are not affected by deuteration. This result is also consistent with the theoretical calculations and can be used as additional evidence for the existence of all four conformations in both solid and solution states.

### 4.2.4. Below $1000 \mathrm{~cm}^{-1}$ region

Two bands at 911 and $906 \mathrm{~cm}^{-1}$, which show medium intensities in both the IR and Raman spectra, are attributed to the
$\delta \mathrm{C}-\mathrm{C}_{\alpha}-\mathrm{C}$ coupled to the $v 17$ of thienyl ring. As a result of deuteration, these bands disappear and two new bands are observed at 881 and $855 \mathrm{~cm}^{-1}$, which is consistent with the theoretical calculations.

The relatively weak and broad bands at 889 and $877 \mathrm{~cm}^{-1}$ in the IR spectrum of TTFA are assigned to the OH out-of-plane bending mode. For the deuterated analogue, $\mathrm{D}_{2}$-TTFA, these bands disappear and a new band appears at about $629 \mathrm{~cm}^{-1}$, which is assigned to $\delta O D$ coupled to $\delta \mathrm{CD}$. The corresponding band in the IR spectrum of AA/D2-AA appears at $957 / 707 \mathrm{~cm}^{-1}$ [12], which suggests that the intramolecular hydrogen bond in $A A$ is considerably stronger than that in TTFA.

The relatively strong IR bands at 802 and $792 \mathrm{~cm}^{-1}$ are assigned to the out-of-plane bending mode of $\mathrm{CH}_{\alpha}$ coupled to $v 19$ of the thienyl group. Upon deuteration these bands disappear and a new band appears at $573 \mathrm{~cm}^{-1}$.

According to the calculated results, the 304 and $294 \mathrm{~cm}^{-1}$ bands are attributed to the $0 \cdots O$ stretching mode. In AA, the $0 \cdots O$ stretching appears at $366 \mathrm{~cm}^{-1}$, which also supports a much stronger hydrogen bond in AA than in TTFA.

## 5. Conclusion

Among 40 possible conformers of TTFA, only four conformers have the chelated IHB. The stability calculations in different solutions confirm that the energy differences of these four conformers, which are negligible in the gas phases, increase in polar solvents. This is in such a way that the A forms become clearly more stable than the $B$ forms and new trend of stabilities in solution phase is $\mathrm{A} 2>\mathrm{A} 1>\mathrm{B} 2>\mathrm{B} 1$.

The theoretical frequency calculations for different conformers and the results of the experimental IR and Raman studies suggest that all four chelated forms coexist in the solid and solution states. However, in agreement with the theoretical stability calculations and X-ray experimental investigation, the vibrational spectroscopy analysis specify a more ratio of A forms in the solution phases, and a more ratio of $B$ forms in the solid state in the sample.

A complete vibrational assignment of the TTFA is presented. The FTIR spectrum of the molecule shows a very broad absorption band in the 3000-2400 $\mathrm{cm}^{-1}$ region centered at about $2850 \mathrm{~cm}^{-1}$, which is attributed to $v \mathrm{OH}$. By comparison of this frequency and $v \mathrm{OD}$ (about $2080 \mathrm{~cm}^{-1}$ ) of TTFA with those of AA and TFAA, it is concluded that the IHB strength trend for these molecules is AA > TTFA $>$ TFAA. This is confirmed by the further comparison of some other vibrational frequencies.

## References

[1] A.H. Lowrey, C. George, P. D'Antonio, J. Karle, J. Am. Chem. Soc. 93 (1971) 6399.
[2] R.S. Brown, A. Tse, A.T. Nakashima, R.C. Haddon, J. Am. Chem. Soc. 101 (1979) 3157.
[3] J. Emsley, Structure and Bonding, vol. 57, Springer, Berlin, 1984.
[4] R. Boese, M.Y. Antipin, D. Blaser, K.A. Lyssenko, J. Phys. Chem. B 102 (1998) 8654.
[5] K. Iijima, A. Onhogi, D. Shibata, J. Mol. Struct. 156 (1987) 111.
[6] A. Camerman, D. Mastropaolo, N. Camerman, J. Am. Chem. Soc. 105 (1983) 1584.
[7] M.A. Rios, J. Rodriguez, J. Mol. Struct. (Theochem) 204 (1990) 137.
[8] F. Hibbert, J. Emsley, Hydrogen Bonding and Chemical Reactivity, Advances in Physical Chemistry, vol. 26, Academic Press, London, 1990, p. 255.
[9] S.F. Tayyari, F. Milani-Nejad, Spectrochim. Acta A 54 (1998) 255.
[10] S.F. Tayyari, Th. Zeegers-Huyskens, J.L. Wood, Spectrochim. Acta A 35 (1979) 1289.
[11] S.F. Tayyari, M. Zahedi, F. Tayyari, F. Milani-Nejad, J. Mol. Struct. (Theochem) 637 (2003) 171.
[12] S.F. Tayyari, F. Milani-Nejad, Spectrochim. Acta A 56 (2000) 2679.
[13] T. Chiavassa, P. Verlaque, L. Pizalla, P. Roubin, Spectrochim. Acta A 50 (1994) 343.
[14] T. Chiavassa, P. Roubin, L. Pizzala, P. Verlaque, A. Allouche, F. Marinelli, J. Phys. Chem. 96 (1992) 10659.
[15] H. Ogoshi, K. Nakamoto, J. Chem. Phys. 45 (1966) 3113.
[16] S.F. Tayyari, T. Zeegers-Huyskens, J.L. Wood, Spectrochim. Acta A 35 (1979) 1265.
[17] M. Zahedi, S.F. Tayyari, F. Tayyari, M. Behforouz, Spectrochim. Acta A 60 (2004) 111.
[18] S.F. Tayyari, S. Salemi, M. Zahedi Tabrizi, M. Behforouz, J. Mol. Struct. 694 (2004) 91.
[19] S.F. Tayyari, F. Milani-Nejad, H. Rahemi, Spectrochim. Acta A 58 (2002) 1669.
[20] S.F. Tayyari, Z. Moosavi-Tekyeh, M. Zahedi-Tabrizi, H. Eshghi, J.S. Emampour, H. Rahemi, M. Hassanpour, J. Mol. Struct. 782 (2006) 191.
[21] M. Zahedi-Tabrizi, F. Tayyari, Z. Moosavi-Tekyeh, A. Jalali, S.F. Tayyari, Spectrochim. Acta A 65 (2006) 387.
[22] S.F. Tayyari, M. Vakili, A.R. Nekoei, H. Rahemi, Y.A. Wang, Spectrochim. Acta A 66 (2007) 626.
[23] S.F. Tayyari, J.S. Emampour, M. Vakili, A.R. Nekoei, H. Eshghi, S. Salemi, M. Hassanpour, J. Mol. Struct. 794 (2006) 204.
[24] S.F. Tayyari, A.R. Nekoei, M. Vakili, Y.A. Wang, J. Theor. Comp. Chem. 5 (2006) 647.
[25] S.F. Tayyari, H. Rahemi, A.R. Nekoei, M. Zahedi-Tabrizi, Y.A. Wang, Spectrochim Acta A 66 (2007) 394.
[26] S.F. Tayyari, A.R. Nekoei, H. Rahemi, J. Mol. Struct. 882 (2008) 153.
[27] S.F. Tayyari, Z. Moosavi-Tekyeh, M. Soltanpour, A.R. Berenji, R.E. Sammelson, J. Mol. Struct. 892 (2008) 32.
[28] R.E. Sammelson, A. Najafi, M. Azizkhani, F. Lorestani, S.F. Tayyari, J. Mol. Struct. 889 (2008) 165.
[29] S.F. Tayyari, M. Zahedi-Tabrizi, R. Afzali, S. Laleh, H.A. Mirshahi, Y.A. Wang, J. Mol. Struct. 873 (2008) 79.
[30] V. Bertolasi, P. Gilli, V. Ferretti, G. Gilli, J. Am. Chem. Soc. 113 (1991) 4917.
[31] M. Bassetti, G. Cerichelli, B. Floris, Tetrahedron 44 (1988) 2997.
[32] M. Bassetti, G. Cerichelli, B. Floris, Gazz. Chim. Ital. 116 (1986) 579.
[33] J. Tollec, in: Z. Rappoport (Ed.), The Chemistry of the Enols, Wiley, New York, 1990, p. 366.
[34] R.L. Lintvedt, H.F. Holtzclaw Jr., J. Am. Chem. Soc. 88 (1966) 2713.
[35] A.L. Andreassen, D. Zebelman, S.H. Bauer, J. Am. Chem. Soc. 93 (1971) 1148.
[36] K. Iijima, Y. Tanaka, S. Onuma, J. Mol. Struct. 268 (1992) 315.
[37] J. Emsley, Struct. Bonding 57 (1984) 147.
[38] J. Emsley, L.Y.Y. Ma, S.C. Nyburg, A.W. Parkins, J. Mol. Struct. 240 (1990) 59.
[39] J. Emsley, L.Y.Y. Ma, P.A. Bates, M. Motevalli, M.B. Hursthouse, J. Chem. Soc., Perkin Trans. 2 (1989) 527.
[40] J. Emsley, L.Y.Y. Ma, P.A. Bates, M. Motevalli, M.B. Hursthouse, J. Mol. Struct. 216 (1990) 143.
[41] J. Emsley, N.J. Freeman, P.A. Bates, M.B. Hursthouse, J. Chem. Soc., Perkin Trans. I (1988) 297.
[42] G. Buemi, F. Zuccarello, Electr. J. Theor. Chem. 2 (1997) 302.
[43] Z. Yoshida, H. Ogoshi, T. Tokumitsu, Tetrahedron 26 (1970) 5691.
[44] D.J. Sardella, D.H. Heinert, B.L. Shapiro, J. Org. Chem. 34 (1969) 2817.
[45] A. Reiser, in: D. Hadzi, H.W. Thompson (Eds.), Hydrogen Bonding, Pergamon Press, Oxford, 1959, p. 447.
[46] D. Semingsen, Acta Chem. Scand. B 28 (1974) 169.
[47] P. Piaggio, M. Rui, G. Dellepiane, J. Mol. Struct. 75 (1981) 171.
[48] G. Lundgren, B. Aurivililus, Acta Chem. Scan. 18 (1964) 1642.
[49] W.S. Sheldrick, W. Trowitzsch, Z. Naturforsch B 38 (1983) 220.
[50] R.D.G. Jones, Acta Crystallogr. B 32 (1976) 1224.
[51] Gaussian 03, Revision B.05, M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian, Inc., Pittsburgh, PA, 2003.
[52] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.
[53] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.
[54] L. Onsager, J. Am. Chem. Soc. 58 (1936) 1486.
[55] M.W. Wong, M.J. Frisch, K.B. Wiberg, J. Amer. Chem. Soc. 113 (1991) 4776.
[56] V. Barone, C. Adamo, J. Phys. Chem. 99 (1995) 15062.
[57] T. Clark, J. Chandrasekhar, G.W. Spitznagel, P.V.R. Schleyer, J. Comp. Chem. 4 (1983) 294.
[58] GaussView 3.0, Gaussian Inc., Pittsburgh, PA, 2003.
[59] P. Flükiger, H.P. Lüthi, S. Portmann, J. Weber, MOLEKEL 4.3, Swiss Center for Scientific Computing, Manno (Switzerland) 2000-2002.
[60] S. Portmann, H.P. Lüthi, MOLEKEL: Chimia 54 (2000) 766.
[61] Genplot Package Computer Service, Cornel University, Utica, New York, 1990.
[62] K. Pasterny, R. Wrzalik, T. Kupka, G. Pasterna, J. Mol. Struct. 614 (2002) 297.


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