Spectroscopic and quantum chemical investigation of enol-enol tautomerism of 2-acetyltetronic acid

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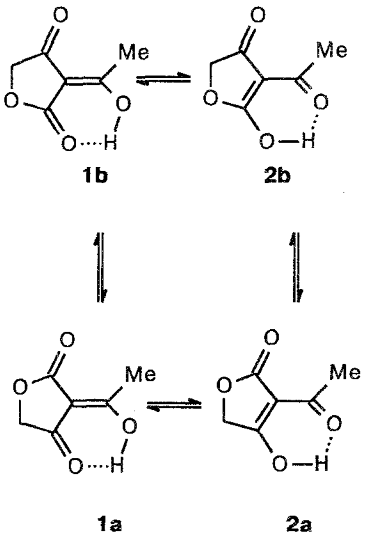
Vibratonal spectra of 2-acetyltetronic acid (ATA) (3-acetyloxolane-2,4-dione) were investigated in different aggregate states. *Ab initio* quantum chemical calculations (3-21G basis set) of 2-formyltetronic acid as analogue of ATA and semi empirical calculation of ATA were carried out. The tautomeric forms of ATA can be arranged in the following series with respect to thermodynamic stability (in decresing order): **1a**, **1b**, **2a**, **2b**.

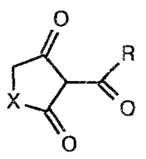
Key words: tautomerim of β,β'-triketones, 2-acetyltetronic acid, vibrational spectra, quantum-chemical calculation, intramolecular hydrogen bond.

β,β'-Triketones are known to be widely used as synthones for the preparation of various biologically active compounds.[1] A β,β'-tricarbonyl moiety is an important constituent of many natural and synthetic biologically active compounds.[2] For example, derivatives of 3-acetyltetronic acid (ATA) (3-acetyloxolane-2,4-dione, **A**) and 3-acetyltetramic acid (3-acetylazolidine-2,4-dione, **B**) constitute a large group of biostimulators[3] that are of great importance in medicine.

Owing to the ability of the β,β'-tricarbonyl group to enolize with the formation of a six-membered chelate cycle stabilized by reasonably strong intramolecular hydrogen bond (6.6 kcal mol^{-1} in 2-acetylcyclopentane-1,3-dione (ACPD, **C**)[4]), these compounds exist in four isomeric forms **1a**—**2b** distinguished by an *exo*- or *endo*-position of the C=C bond in the five-membered ring and mutual orientation of chelate ring and heteroatom.[3,5] Pure β,β'-triketone forms **A**—**C** seem not to be formed under ordinary conditions.



1b **2b** **1a** **2a**



A: X = O
B: X = NH
C: X = CH$_2$
R: Me, H

In the literature there is no consensus on the isomeric composition of these compounds under different conditions and, consequently, the relative thermodynamic stability of the four enol forms. According to the NMR spectroscopic data,[5,8] solely the *endo*-enol structure is attributed to ACPD. However, study of the structure of ACPD by vibrational spectroscopy[9] showed that the compound is crystallized as two types of crystals, one of which is mainly the *exo*-enol and in the other the *endo*-enol predominates.

In solution, an isomeric mixture is present in which the *exo*-enol prevails (~90 %), whereas it is the only observed tautomer in the vapor phase (up to 300 °C).

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In a solution of ATA in $CDCl_3$, all four enols were detected by NMR, among which, as one would suppose, the pair of tautomers **1b** and **2b** predominates. In solvents of acidic nature, an equilibrium between forms **2a** and **1a** exists, whereas in DMSO-d_6 and pyridine, an equilibrium between **2b** and **1b** is observed. However, in all solvents except $CDCl_3$, only one set of signals characterized by averaged values of the chemical shifts is observed in the NMR spectra of the mentioned tautomeric pairs. This fact is caused by sufficiently fast (in the NMR time scale) **1**—**2** tautomeric interconversion hindering the investigation of the enol-enol tautomerism in this series by the specified method.

Meanwhile, exact data on the isomeric composition of ATA and its analogs under different conditions are necessary to find the correlation between a structure and biological activity.

In the present work, we studied the structure of ATA in different aggregate states by IR and Raman spectroscopy, whereby the presence of the both tautomers of ACPD has been detected previously. In addition, we attempted to estimate the relative thermodynamic stability of all four isomeric forms using the experimental data arrived at in the work and the results of both *ab initio* calculation of 3-formyltetronic acid (**A**, R = H, FTA) (the simpler model of ATA) and semiempirical calculation of ATA by AM1 along with a molecular mechanics calculation of ATA.

Experimental

The IR spectra of ATA in solid phase and solutions were recorded with UR-20, Perkin Elmer 571, Specord M-82, and IR-Fourier Perkin Elmer 1725-X FTIR spectrometers. Resolution was improved by recording the second derivative of the spectrum. Crystalline samples were pressed in pellets with KBr, or the spectra of a diffuse reflection were obtained by the condensation of substances from a solution onto a stainless steel disk. The spectra thus registered differ from those of pellets both in the frequencies of some vibrations and in the narrower width of the bands.

The spectral measurements of ATA solution in CH_2Cl_2 at low temperatures were carried out with an UR-20 instrument using a Karl Zeiss standard vacuum cryostat. The accuracy of temperature measurements was ±2 °C.

The IR spectra of substances in a gas phase were recorded with a Hewlett-Packard 5965A FT-IR Fourier IR spectrometer attached as a monitor to an HP 5890 ser 2 gas chromatograph. A solution of ATA in acetone was passed through a capillary column (50 m length, phase SE-30) of the chromatograph in an isothermal regime. The temperature in a flow cell (l = 10 cm) was varied in the interval from 180 to 300 °C; the regime of the recording of the spectrum was 4 scan s^{-1}.

The Raman spectra of crystalline samples were recorded with Coderg AR-300 and Ramanor U-1000 spectrometers (the wavelength of the exciting radiation of the Ar^+ laser was 4841 and 5154 Å, respectively); the accuracy of the measurement of the Raman shift ($\Delta\nu$) was ±3 and ±0.5 cm^{-1}, respectively.

The NIR Raman spectra of ATA were recorded with a Perkin-Elmer 1725-X FTIR spectrometer equipped with a Nd-YAG Spectron laser that works in a continuos regime on a TEM_{00} mode. The wavelength of the exiting radiation of a Raman spectrum was 1.064 μ (9398 cm^{-1}). The scattered light from a sample was focused by the lens systems into the input of a Jakinos' interferometer by a 180° scheme. Elimination of the plasma lines of the Nd-YAG laser and the 632.8 nm line of the He-Ne laser on which an interferometer works was achieved with filters. As a result of the use of the filters, the minimal value of $\Delta\nu$ was 200 cm^{-1}. A transistor InGaAs (indium arsenide doped by gallium) diode was used as the detector. The Raman spectra of substances placed in a glass capillary were recorded with a resolution of 4 cm^{-1}. Comparison of the Raman spectra excited by different lighr sources showed no principal differences between them, although the quality of the

Table 1. Experimental frequencies (ν/cm^{-1}) of the vibrations of 3-acetyloxolane-2,4-dione

Raman (solution)	IR (solution)	Raman (solid)	IR (solid)	IR (gas)[a]	IR (gas)[b]
2996 v.s	3028 m	2976 w	—	2953 w	2994 w
—	—	2930 v.s	—	—	—
1771 s	1771 v.s	—	1780 v.s	1798 v.s	—
1743 s	—	—	—	—	1768 v.s
—	—	1723 v.s	—	1720 v.s	1723 w
1700 w	1699 v.s	1689 v.w	—	—	—
1682 w	1673 m.b	1667 w	1667 s.b	1674 m	
1655	—	—	—	1626 v.s	1636 v.s
1608 v.s.b	1608 v.s.b	—	1594 s.b	—	—
—	—	1569 v.s	—	—	1562 v.s
—	—	1471 w	1470 sh	—	—
—	—	—	—	—	1453 m
1439 s	1430 m	1425 s	1433 m	1426 m	1416 m
—	1393 m.b	—	—	1400 s	—
1361 m	1354 w	1373 w	1388 m.b	—	—
—	—	—	—	—	1355 s
1328 m	1329 w	1342 w	1338 w	1335 m	—
—	—	1294 m	1300 sh	—	—
1240 m.b	1233 w.b	—	1250 w	—	1251 m
—	1217 v.s	1225 m	—	1199 s	1200 w
1192 m.b	1197 m.	1185 m	1187 w.b		
—	—	1153 m.b	1160 sh	—	—
1039 w	1047 m	1049 w	1047 s	1044 s	—
—	1023 m.b	—	—	—	—
1003 m	—	1009 m.b	1009 m	—	1009 sh
—	—	—	—	—	993 m
960 w	960 w	941 w	970 w	—	—
—	869 w.b	900 v.w	888 m	899 w	
—	—	—	—	—	826 w
—	—	—	765 w	—	—
718 v.s		734 v.s	717 w	710 w	716 w
689 w	—	—	—	—	—
—	—	662 s	667 m	—	—
620 m	—	641 w	—	—	—
—	—	—	—	—	598 m
569 m	—	577 m	575 w	—	—
—	—	530 w	—	—	526 w
477 m	—	452 m	485 w	—	—
442 w	—	—	—	—	—
395 w	—	390 w.b	—	—	—
343 w	—	308 w	—	—	—

[a, b] The first and second peaks on chromatogram, respectively.

spectra was significantly higher when using an infrared laser. The experimental vibrational frequencies are given in Table 1.

Calculation methods. The quantum chemical calculation of isomeric forms **1a—2b** of FTA was carried out by an *ab initio* method with a 3-21G standard valence basis set and complete optimization of geometry using a MONSTERGAUSS-81 program modified for the application in a SCO XENIX system with a TANDON 386 PC.

The calculation of the spatial structure and heats of formation ($\Delta_f H^\circ$) of ATA isomeric forms **1a—2b** was performed by the AM1 method with complete optimization of geomatry using a MOPAC program with the same computer. The calculation of the relative stability of isomeric forms **1a—2b** by the method of molecular mechanics was carried out with the MMX-88 program on a PC/AT-286 using a set of standard parameters and taking account π-conjugation. The results obtained are given in Table 2.

Results and Discussion

Relative stability of the isomers. Theoretical data. Comparison of the results of quantum chemical calculation of FTA isomers (Table 2) shows that both *exo*-enols are close in thermodynamic stability (ΔE is of the order of kT) and are energetically preferential to *endo*-enols. The calculated energetic difference between structures **1a** and **1b** (0.6 kcal mol^{-1}) is too small to decide with confidence which of the compounds is more stable. However, it should be expected that structure **1b,** in which a lactonic carbonyl takes part in formation of intramolecular H-bonds, is less preferable, because lactones are believed to form weaker H-bonds in comparison to ketones.

The *endo*-enols are more distinguished energetically than the *exo*-enols, the conformer **2a** being more stable (by 3.1 kcal mol^{-1}). The results of the calculation of four ATA enol forms by the semiempirical AM1 method agree with the data of the *ab initio* calculation of FTA. Both *exo*-enols having approximately equal heats of formation are energetically more profitable than *endo*-enols, of the latters a structure **2a** is more preferable than a form **2b**. The same series of stabilities was found when using the method of molecular mechanics for their estimation, although the excessive low relative stability of **2b** seems to be erroneous. Thus, it follows from the calculations of FTA and ATA, that *exo*-enols **1a** and **1b** should be the main observable tautomers of ATA and **2a** is more preferable among two *endo*-forms.

Table 2. Total (E_{total}/au) and relative (ΔE/kcal mol^{-1}) energies of isomers FTA and ATA calculated by *ab initio* method (FTA) and AM1 and MMX (ATA).

Isomer	E_{total}	ΔE		
		ab initio[a]	AM1[b]	MMX[b]
1a	−488.37504	0.6	0	0
1b	−488.37601	0	0.1	0.4
2a	−488.37096	3.2	7.2	2.9
2b	−488.36602	6.3	9.5	24.1

[a] R = H. [b] R = Me.

Order of the diagnostic frequencies of ATA. For identification of the ATA isomers, it is necessary to distinguish reliably the bands in spectra assigned to ν(C=O) of the lactone and keto groups and the bands assigning to ν(C=C) of C=C bonds located in *exo-* and *endo*-positions. According to the literature data, the lactone group has considerably higher ν(C=O) frequencies (>1750 cm^{-1}) than usual keto-group (1700—1720 cm^{-1}).[15,16] Additionally, the vibrational frequencies of ν(C=C) of bonds located in *exo*-position of five-membered cycle are more sensitive to the deuteration of the enol fragment. For example, the band assigned to ν(C=C) is observed at 1545 cm^{-1} in the IR spectrum of ACPD-d_1,whereas in the spectrum of ACPD-h_1, it is found at 1600 cm^{-1} (see Ref. 9). Hence, the following order of the frequencies was taken in the basis of interpretation of experimental spectra: $(\nu(\text{C=O})_{\text{lactone}})_{exo}$ > $(\nu(\text{C=O})_{\text{lactone}})_{endo}$ > $(\nu(\text{C=O})_{\text{ketone}})$, and $(\nu(\text{C=C})_{exo}$ > $(\nu(\text{C=O}))_{endo}$.

The interpretation of the vibrational spectrum of ATA. The assignment of the frequencies in the diagnostic region of spectrum are represented in detail in Table 3. The experimental data available are deficient to give the complete assignments of the frequencies for all four isomers. Therefore, they should be considered as preliminary.

IR spectra of ATA vapor. The relative stability of the tautomers and rotamers of ATA. The IR spectra of ATA vapors were obtained by passing a solution of the substance in acetone through a gas chromatograph connected with a Fourer IR-spectrometer. On the chromatogram, two peaks were found with the retention times of 12.2 and 14.4 min (at 180 °C) and — 3.7 and 3.8 min (at 300 °C), respectively. The area of the first peak changed dependently on the temperature from 96.6 % at 180 °C to 95.2 % at 300 °C, whereas the area of the second peak changed from 3.4 to 4.8 %, respectively.

The IR spectrum (see Table 1) having two very strong ν(C=O) bands at 1798 cm^{-1} and 1720 cm^{-1} whose relative intensity is almost independent of changing temperature from 180 to 300 °C, corresponds to the more intense peak on the chromatogram (with the less retention time). The first band corresponds to ν(C=O) of the free lactone keto group of isomer **1a**, whereas the second band belongs to ν(C=O) of isomer **1b**. The strong band at 1626 cm^{-1} is assigned to the ν(C=C) of the *exo*-cyclic C=C bond of both compounds. Therefore, the first peak on chromatogram corresponds to the mixture of the *exo*-enols of ATA **1a** and **1b**.

The less intense peak of the chromatogram (with greater retention time) corresponds to the band in the IR spectrum of ν(C=O) of free lactone keto group observed at 1768 cm^{-1}. The weak band at 1723 cm^{-1} of

Table 3. Assignments of vibrational frequencies of 3-acetyloxolane-2,4-dione

Calculation[9]*	Experiment	Assignment
2976	2989	ν (CH$_2$, CH$_3$)
2967	2960	ν (CH$_2$, CH$_3$)
2948	2930	ν (CH$_2$, CH$_3$)
2942	2918	ν (CH$_2$, CH$_3$)
2897	—	ν (CH$_2$, CH$_3$)
2896	?	ν (OH)
—	1798	ν (C=O), lactone **(1a)**
—	1768	ν (C=O), lactone (**2a**)
—	1723	ν (C=O), free **(2b)**
1713	1720	ν (C=O), free (**1b**)
—	1674	ν (C=O), H-bonded **(1a)**
1668	1667	ν C=O), H-bonded **(2b)**
—	1655	ν (C=O), H-bonded **(1b)**
1635	1636	ν (C=O), H-bonded **(2a)**
—	1626	ν (C=C), δ (C—OH)(**1b**)
1592	1613	ν (C=C), δ (C—OH)(**1a**)
—	1569	ν (C=C), (**2b**)
1546	1562	ν (C=C), (**2a**)
1442	1430	α (HCH in cycle)
1435	1425	α (HCH), δ (C—OH)
1398	1400	α (HCH)
1393	1393	α (HCH)(CH$_3$))
1362	1361	α (HCH) (CH$_3$))
1347	1340	δ (C-OH), ν (C=C),
1340	1328	α HCH (CH$_3$), δ (OCC)
1314	1298	β (CCH (CH$_3$))
1255	1240	β$_w$(CCH$_2$)
1232	1234	β$_w$(CCH$_2$), ν (C—C)
1222	1217	β (CCH$_2$), ν (CO, in cycle)
1197	1197	ν (C—C, in cycle)
1139	1153	ν (C—C, in cycle)
1095	1047	β$_w$ (CH$_2$, in cycle)
1036	1023	τ (CH$_2$, in cycle)
1017	1003	ν (C—C), δ (CC=O (CO free))
995	993	β (CCH (CH$_3$))
956	960	β (CCH$_2$(CH$_3$))
938	941	ρ (C$_2$C=O)
872	869	ν (C—O), ν (C—CH$_3$)
723	718	β$_r$ (CCH$_2$)
632	667	δ (CC=O), δ (OC—CH$_3$)
624	620	ν (C—C, in cycle), δ (C—C=O)
568	569	γ (CCC, in cycle)
548	530	τ (O=C—C=C)
497	485	γ (CCC, in cycle)
460	477	τ (C=C)
432	442	β (C=CO), δ (CC=O H-bonded)
386	395	γ (C=C—C)
327	347	ν (O...H), γ (CCC, in cycle)
238	308	τ (O...H—O=C)
192	—	γ (C=C—CH$_3$), γ (C—C=C)
165	—	ρ (C$_2$C=C)
163	—	τ (C=C—C—OH)
79	—	δ (O—H...O)

Note. The following symbols are used for the notations of vibrational coordinates: ν — stretching vibrations, α — deformation vibrations of HCH angles, β — deformation vibrations of C—C—H angles, γ — deformation vibrations of C—C—C angles, δ — deformation vibrations of other angles, τ — torsion vibrations, r — rocking deformation, w— wagging vibrations of the C—CH$_2$ group.

* The data calculated for ACPD.

free C=O group appears in the spectrum only at the temperature about 300 °C, whereas the band of ν(C=C) is found at 1562 cm^{-1}. It means that a pair of *endo*-enols **2a** and **2b** conforms to the less intense peak on chromatogram, and an appreciable temperature sensitivity of the relative intensities of the bands of both C=O groups testifies to a high energetic difference of these compounds.

The calculation by Boltzmann's formula of the relative content of all four ATA isomers at 300° C using the differences of the total energies calculated for FTA results in the following composition of a gas phase, %: **1b** — 60.4, **1a** — 35.5, **2a** — 3.8, **2b** — 0.02. It agrees, as a whole, with the chromatographic data on the overall content of the *exo-* and *endo*-tautomeric pair of ATA and with a visual estimation of the intensities of the diagnostic band in the spectra corresponding to the first and second chromatographic peaks.

Therefore, from the data mentioned it follows that both *exo*-forms are approximately thermodynamically equivalent and considerably more stable than *endo*-forms of ATA which, in turn, are essentially distinguished in their stability.

IR- and Raman spectra of solutions. The isomeric composition of the substance. By the comparison of the IR- and Raman spectra of ATA in a solution in CHCl$_3$, it was revealed that the frequencies of the IR bands and Raman lines at 1771 cm^{-1} (ν(C=O) of lactone carbonyl) and 1608 cm^{-1} (ν(C=C)) coincide in the diagnostic region. The strong IR band at 1699 cm^{-1} corresponds to the weak Raman line at 1700 cm^{-1}, whereas the analog of the Raman line at 1743 cm^{-1} was not found in the IR spectrum of a solution in CHCl$_3$. The shoulder in this region (1745 cm^{-1}) is observed in the IR spectrum of ATA solution in CCl$_4$, whereas the other bands have the frequencies 1781, 1702, 1673 and 1613 cm^{-1} close to frequencies for the gas phase.

Taking into account that the frequencies of keto groups non-bonded by intramolecular H-bond are sensitive significantly to the influence of medium, being shifted in a low frequency region on going from a gas to a solution, we assumed that the bands at 1798 и 1720 cm^{-1} in the IR spectrum of ATA vapor (the first peak on the chromatogram) correspond to the pair of bands at 1771 and 1700 cm^{-1} in the spectrum of a solution, whereas the IR band at 1768 cm^{-1} (the second peak on the chromatogram) conforms to the Raman line at 1743 cm^{-1}. Thus, using as a guide the frequencies of free carbonyl groups one may conclude that both *exo*-enols **1a** and **1b**, along with a minor amount of *endo*-form **2a**, are contained in solutions of $CHCl_3$ and CCl_4.

The lack of a line in the vicinity of 1560 cm^{-1} in Raman spectrum casts some doubt on the reliability of this conclusion. However, a very wide band observed in the spectrum at 1608 cm^{-1} which consists clearly of several components allows one to assume that the line assigned to ν(C=C) underwent a high frequency shift.

The fact that the Raman lines observed in the interval 1690—1630 cm^{-1} and assigned to ν(C=O) of carbonyl groups which participate in the formation of intramolecular H-bond are very weak, should not be surprising. It is known[18] that these lines have a low intensity in the Raman spectra of the enol forms of alicyclic β-diketones (acetylacetone, benzoylacetone, *etc.*).

For the estimation of the relative stabilities of isomers in solutions, the spectral measurements were carried out at low temperature. CH_2Cl_2 was used as the solvent, in which the frequencies of ATA are close to those of its solution in $CHCl_3$. The experiments showed that the intensity of the band in the vicinity of 1700 cm^{-1} is lowered, and the band at 1771 cm^{-1} is shifted to a low frequency part of a spectrum as the temperature decreases to −100 °C. After annealing a frozen solution, only three wide bands (at 1758, 1671 и 1605 cm^{-1}) closed by the nature to the bands in the IR spectrum of ATA in KBr pellet remained in IR spectrum. Taking into account the sensitivity of the frequencies to the influence of medium, we assumed that the spectrum of annealed crystal corresponds to *exo*-enol **1a** which is, consequently, the most stable form of ATA in a condensed phase, whereas the disappearance of the band in the vicinity of 1700 cm^{-1} with decreasing the temperature indicates a less thermodynamic stability of the second *exo*-enol form.

The deuteration of the enol fragment in ATA caused the band ν(C=C) (1613 cm^{-1} in the IR spectrum of ATA-h_1) in the IR spectrum of ATA-d_1 in CCl_4 to reveal at 1582 cm^{-1}, *i.e.*, a deuterium shift was 51 cm^{-1}, and the band at 1745 cm^{-1} in the spectrum of ATA-d_1 in CCl_4 assigned to *endo*-enol **2a** became more pronounced than that in the spectrum of ATA-h_1, in which it was observed like a shoulder.

These data confirm the assignment of the band at 1613 cm^{-1} to the *exo*-enol C=C bond in **1a** as well as the presence of *endo*-enol **2a** in the solution.

Thus, the parallel study of IR and Raman spectra shows that solutions in $CHCl_3$ and CCl_4 at ambient temperatures contain at least three isomers of ATA, among which the pair of *exo*-enols **1a** and **1b** predominates considerably. From two *endo*-enols, there is only a minor amount of form **2a** in the solutions. When decreasing a temperature, isomer **1b** disappears. Hence, it follows that the series of the relative stability of the isomeric forms of ATA in the solutions is: **1a** > **1b** > **2a** > **2b**, in agreement with the results of calculations.

Our data are completely inconsisted with the results obtained by NMR method. Based in these data, 17 percent of isomer **1a**, 30 percent of its rotamer **1b**, 19 percent of tautomeric form **2a**, and 34 percent of **2b** are believed to be present in $CHCl_3$ in which signals assigned to group CH_2 and CH_3 protons are splitted on doublets, *i.e.*, a series of stability, according to NMR spectrum, looks as follows: **2b** > **1b** > **2a** > **1a**. The reason of discrepancy between the data of vibrational and NMR spectra seems to be caused by the fact that the signals in NMR spectrum were assigned by analogy with 5,5-dimethylacetylcyclohexane-1,3-dione. In our opinion, such analogy is improper because *endo*-enol forms are known to be more preferable than *exo*-enol forms for six-membered cyclic β,β'-triketones, whereas for the compounds studied the sequence of stability is opposite.[19,20]

Moreover, the comparison of the proposed interpretation of the vibrational spectra of ATA with the literature data on the IR spectra of wide set of its homologs and analogs [5] demonstrates that the low frequency limit for ν(C=C) of five-membered cyclic β-di- and β,β'-triketones, *e.g.*, for 4,4-dimethyl-2-acetylcyclopentane-1,3-dione, reaches 1585 cm^{-1} (IR spectrum of the solution in CCl_4). Meanwhile, for six- and seven-membered cyclic β,β'-triketones the frequencies of ν(C=C) are 20 cm^{-1} lower. In our view, it confirms an opinion that the five-membered triketones exist as *exo*-enols, whereas six-membered ones are in the form of *endo*-enols.[19,20]

IR and Raman spectra of crystalline ATA. The difference between the solid phase IR and Raman spectra of ATA in the diagnostic region is, in our view, of particular interest. From Table 1 it follows that IR spectrum corresponds to *exo*-enol **1a** (the bands at 1787, 1667, and 1594 cm^{-1}), whereas the Raman spectrum corresponds to the least stable *endo*-enol **2b** (the lines at 1723 and 1569 cm^{-1}), and this result is independent of the energy of radiation exiting Raman spectrum. Unfortunately, we did not find proper explanation of this fact.

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