Spectroscopic detection of the *endo*-enol form of 2-acetylcyclopentane-1,3-dione

V. G. Avakyan,[a]* V. V. Gromak,[b] and A. Ye. Yatsenko[a]

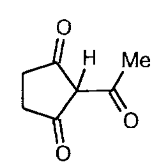
[a]*Institute of Petrochemical Synthesis, Russian Academy of Sciences, 29 Leninsky prosp., 117912 Moscow, Russian Federation. Fax: +7 (095) 230 2224*

[b]*Institute of Bioorganic Chemistry, Byelorussian Academy of Sciences, 5/2 ul. Zhodinskaya, 220141 Minsk, Belaruss. Fax: +7 (017) 263 6772*

According to vibrational spectroscopic data, in the gas phase at 280 °C and in crystals prepared by sublimation, 2-acetylcyclopentane-1,3-dione was established to exist not as trione **1** but as the enol-form **2** with an *exo*-cyclic C=C bond (ν(C=C) = 1593 cm^{-1}) and an intramolecular hydrogen bond. The enol **3** prepared by crystallization from CCl_4 is also stabilized by an intramolecular H-bond but has an *endo*-cyclic C=C bond (ν(C=C) = 1545 cm^{-1}). In a trichloroethylene solution, both the *exo*- and *endo*-enol forms co-exist, and the percentage of the latter is ~11 %. The frequencies in the vibrational spectra have been assigned using the normal coordinate calculation of **2**, **3**, and their OD-analogs. The mechanism of tautomer transfer is discussed in terms of PMO theory.

Key words: tautomerism of β,β′-tricarbonyl compounds; *exo*- and *endo*-enol forms of 2-acetylcyclopentane-1,3-dione.

Enol-enol tautomerism is one of the characteristic properties of both β-diketones and β,β′-triketones, which are synthones for the preparation of numerous biologically active compounds.[1] Moreover, in contrast to the diketo-forms of β-diketones, which exist in equilibrium with enols,[2] the triketo-forms are postulated only as short-lived intermediates, occurring during the interconversions of the triketone enol-forms.[3] Meanwhile, information on the presence of one or the other tautomer is important in the investigation of the mechanism of β,β′-triketone reactions. The 2-acetylcyclopentane-1,3-dione (ACPD) molecule, which may exist principally in three tautomeric forms **1**, **2**, and **3**, is a good model of β,β′-triketones with a rigid skeleton.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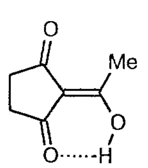
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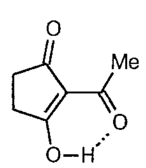
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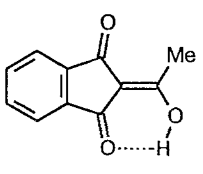
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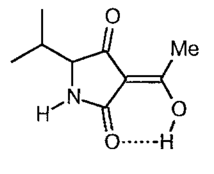
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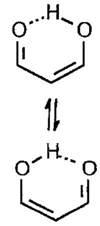
6, **6′**

The intramolecular H-bond energy in ACPD has been recently determined by us using IR-spectroscopic method,[4] based on the assumption that the substance exists in form **2**. The bands observed in the spectrum of a CCl_4 solution at 2967, 1711, 1634, and 1593 cm^{-1} have been assigned, respectively, to ν(OH)(H-bonded), ν(C=O)(free), ν(C=O) (H-bonded), and ν(C=C) of the *exo*-enol form, although, earlier, it was considered[5] that ACPD exists in form **3**. The ACPD **2** form is in agreement with the idea that the stability[6] of cyclopentane derivatives having C=C double bonds in the *exo*-position is greater than that of the isomer cyclopentenes (Dieckmann—Cohn rule) and also with the results of ACPD quantum-chemical calculations[7] according to which *exo*-enol **2** was found to be more thermodynamically stable than triketo form **1** and *endo*-enol **3** by 5.2 and 5.3 kcal mol^{-1}, respectively. Additionally, the ACPD analogs, 2-acetylindane-1,3-dione (**4**) (see Ref. 8) and 5-isopropyl-3-acetylazolidine-2,4-dione (**5**) (see Ref. 9), have an *exo*-enol structure in the crystalline state.

The structures of both enol forms **2** and **3** differ only by the position of the double bond, therefore the possibility should not be ruled out that their vibrational frequencies are close to one another and the spectrum of **3** can not be distinguished because of the superposition of the bands. Consequently, not knowing the frequencies of **3**, it was impossible to judge the tautomer properties of ACPD with complete confidence.

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Table 1. Experimental frequencies (ν/cm^{-1}) of the *exo*-enol form (**2**) of 2-acetylcyclopentane-1,3-dione (ACPD), its deuterio analog (**2**-d_1), and also the *endo*-enol form (**3**) of ACPD

2 RAMAN[b]	**2**[a] IR[c]	**3**[a] IR[d]	**2** IR[e]	**2**-d_1 IR[e]	**2** RAMAN[b]	**2**[a] IR[c]	**3**[a] IR[d]	**2** IR[e]	**2**-d_1 IR[e]
—	3055 m wi	—	(3442 v v w)	—	1219 w	1220 w	1220 m	—	—
—	—		2967 v w	2967 v w	—	—	—	1199 m	—
—	2965 v w	2951 m wi	—	—	1165 w wi	1165 m	1160 s wi	(1197 w)	—
2943 m	—	—	(2945 w)	—	1100 w wi	1100 sh	—	—	1095 m
—	2929 v w	—	2928 v w	2928 v w	—	—	—	—	1060 v w
2921 s	—	—	—	—	1025 v w	1021 w	1020 m	1027 w	1030 v w
—	—	—	2895 w wi	—	1001 m wi	—	1000 sh	994 v w	—
—	—	—	2849 v w	2849 v w	—	—	—	—	975 w
—	—	—	2821 v w	2820 v w	985 v w	985 v w	984 w	982 v w	982 sh
—	—	—	—	2060 w wi	—	940 sh	—	940 m	930 v w
1697 v s	1698 v s	1704 v s	1711 v s	1710 v s	931 m	935 w	932 w	(936 m)	915 v w
			(1726 s)		—	886.5 w	884 m	(840 v w)	—
1635 v w	1638 v s	1640 v s	1634 v s	1635 v s	816.5 v w	825 w	820 m	824 v w	—
			(1642 v.s)		676.5 s	—	—	—	—
1570 v s	1575 v s	—	1593 v s	1537 s	—	655 w	648 m wi	652 w	640 v w
			(1603 v s)		—	—	—	—	625 v w
1545 sh	1543 w sh	1546 m	—	—	593.5 w	592 m	595 w	590 w	590 w
1435.5 w	1430 s	—	1439 m	1440 s	560 m	560 v w	561 w	555 v w	550 v w
—	—	1420 s	1427 s	1426 m	525 w wi	525 v w	525 w	—	535 v w
			(1429 m)		—	—	483 v w	475 w	475 v w
1412 m	1408 w sh	—	1410 m	1410 w	458 m	460 m	456 m	—	465 v w
1396.5 m	1396 v w	—	1390 v w	1390 v w	381 w	380 w wi	433 v w		
1357.5 w	1360 m	—	1367 m	1365 m	318 w	320 m wi			
			(1367 m)		—	265 w wi			
—	1330 sh	—	1340 sh	—	—	223 v w			
1315.5 m	1317 m	1316 m	1331 m	1320 m	—	202 v w			
			(1328 sh)		119 v w	—			
1280 m	1277 m	1276 m	—	—	—	106 v w			
1250 w	1256 w	1256 m	—	1265 v w	90.5 v w	—			
—	1235 v w	—	1234 m		56 v w	—			

Notes. The following abbreviations were used: w — weak, wi — wide, m — medium, s — strong, v — very, sh — shoulder. [a] Preferred content of forms **2** or **3** in the crystalline samples. [b] Crystal substance, sublimated sample. [c] Sublimated sample in KBr pellet, polyethylene matrix. [d] Crystalline film on Ge plate. [e] Solution in CCl_4. The vibrational frequencies of the enol **2** gas-phase are given in brackets.

In the present work, using the experimental and theoretical methods of vibrational spectroscopy it became possible to detect the *endo*-enol form **3** and to estimate its content.

Experimental

2-Acetylcyclopentane-1,3-dione was prepared by the method in Ref. 10, and purified by vacuum sublimation just before the spectra were taken. The deuteration of the enol proton was performed by azeotropic distillation[11] of excess D_2O from a solution of ACPD in CCl_4. IR spectra were recorded with the spectrometers: Specord M-82, UR-20, FT-IR Perkin Elmer 1725X, and Far-IR Nicolet 20F. The study of the low temperature IR spectrum of ACPD carried out with a Carl Zeiss vacuum cryostat at the temperatures 90—273 K demonstrated that lowering the temperature does not lead to any detectable changes in the spectra, aside from the usual narrowing and minor shifts of bands.

The gas phase IR spectrum of ACPD was recorded with a HP 5965 FT-IR Fourier IR spectrometer attached as a monitor to a HP 5890 ser 2 gas-chromatograph through a capillary column (50 m length, phase SE-30) through which the ACPD solution in acetone was passed in an isothermal regime. Retention time was equal to 6.48 min at 280 °C in a flow cell (l = 10 cm), the spectrum registration regime was 4 scan sec^{-1}.

The Raman spectra of ACPD were registrated with Coderg AR-300 and Ramanor U-1000 Ar^+ laser spectrometers (the wave length of exciting radiation — 4841 and 5154 Å, respectively). The greatest distinction between the IR and Raman spectra obtained is that, in the latter, the band at 1640 cm^{-1} assigned to ν(C=O) of the H-bonded keto group exhibits a very low intensity, whereas, in the IR spectrum, the intensity of this band is comparable to ν(C=O) of the free keto-group. The experimental vibrational frequencies of **2**, **2**-d_1, and **3** are given in Table 1.

Calculation methods. Mathematic deconvolution of the IR band envelope in the 1750—1500 cm^{-1} range of the IR spectrum of a ACPD solution in trichloroethylene (C = 0.1035 M, l = 0.011 cm) was carried out using the program "Spectrum" (Institute of Bioorganic Chemistry, Byelorussian Academy of Sciences) allowing for digital registration of the necessary spectral region. The spectral band characteristics are given in Table 2.

Table 2. Characteristics of IR spectral bands calculated during deconvolution of the band envelope in the region 1750—1500 cm^{-1}

ν/cm^{-1}	$\Delta\nu_{1/2}$ /cm^{-1}	D* /10^3 L mol^{-1} cm^{-2}	A**	Assignment	Enol
1709.4	15	0.64	8.4	ν(C=O) (free)	**2**
1689.7	18	0.050	0.79	ν(C=O) (free)	**3**
1667.5	23	0.058	1.72	ν(C=O) (H-bonded)	**3**
1633.9	29	0.51	13.00	ν(C=O) (H-bonded)	**2**
1591.3	38	0.48	16.02	ν(C=C) (*exo*-)	**2**
1546.6	30	0.048	1.27	ν(C=C) (*endo*-)	**3**

* Optical density, $\ln(I_0/I)$. ** Apparent integral intensity calculated by Eq. $A = (1/Cl)(D \cdot \Delta\nu_{1/2})$.

The normal coordinate analysis of ACPD and ACPD-d_1 for structures **2** and **3** was carried out using the program set[12] adapted for a PC AT by O. V. Fateyev (Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow). The atomic coordinates necessary for the calculation of the elements of a kinematic coefficient matrix, G, were determined by means of the optimization of the ACPD structure in the process of the quantum-chemical AM1 calculation (see Ref. 7). For the approximation of F matrix elements, the force constants obtained from the calculations of the cyclopentane[13,14] and malonic aldehyde *cis*-enol[15] vibrational spectra were used. The force constants of the alicyclic moiety of **2** and **3** were not further changed. For the achievement of the best agreement between the calculated and experimental frequencies in the spectral region assigned to hydroxy and carbonyl groups, the starting force constants were refined using partial derivatives of the frequencies with respect to the force constants, *i.e.*, the so-called reciprocal vibrational problem (RVP) was solved. The calculated ACPD vibrational frequencies and the experimental frequency assignments are given in Table 3. The force constants calculated by solving RVP are presented in Table 4.

Results and Discussion

Observation of the exo- and endo-enol forms of ACPD

The simplest enol molecule, malonic aldehyde, is known to exist as a planar chelate cycle **6** and **6'** having C_s symmetry. Both enol forms are equivalent, but their interconversion occurrs by tunnel proton transfer.[15] In the IR absorption spectrum of the chelate cycle **6**, three intense bands are observed at 2960 cm^{-1} (ν(OH)), 1655 cm^{-1} (ν(C=O)), and 1593 cm^{-1} (ν(C=C)). In the ACPD molecule, the enol chelate cycle is condensed with a five-membered ring. This fact results in the structural non-equivalence of enol forms **2** and **3**. A rise in the intercyclic strain usually leads[2,16] to a decrease in the ν(C=C) frequency, therefore, one would expect that the frequency of the *endo*-cyclic double bond in the spectrum of **3** would be lower than ν(C=C) of the *exo*-cyclic bond in the spectrum of **2**. The comparison of IR spectra of a crystalline sample of ACPD obtained in different manners demonstrates that, indeed, in the region 1650—1500 cm^{-1}, bands which may be assigned to the absorption of *exo*- and *endo*-cyclic C=C double

Table 3. Interpretation of the vibrational spectrum of *exo*-enol form (**2**) of 2-acetylcyclopentane-1,3-dione

ν/cm^{-1}		Assignments
Calculation	Experiment	
2976	2967	ν(CH_2), ν(CH_3)
2970	—	ν(CH_2), ν(CH_3)
2967	—	ν(CH_2), ν(CH_3)
2948	2928	ν(CH_2), ν(CH_3)
2942	—	ν(CH_2), ν(CH_3)
2897	2895	ν(CH_2), ν(CH_3)
2896	2885	ν(CH)
1713	1711	ν(C=O)(free)
1635	1634	ν(C=O)(H-bonded)
1592	1593	ν(C=C), δ(C—OH)
1442	1439	α HCH (in cycle)
1435	1427	α HCH, δ(C—OH)
1398	1410	α HCH
1393	1390	α HCH (CH_3)
1362	1360	α HCH (CH_3)
1347	1340	ν(C=C), δ(C—OH)
1340	1330	α HCH (CH_3), δ OCC
1314	1315	β CCH (CH_3)
1255	1255	β CCH_2 w
1232	1234	β CCH_2 w, ν(C—C)
1222	1220	β CCH (in cycle)
1197	1195	ν (C—C) (in cycle)
1139	1165	ν (C—C) (in cycle)
1110	1095	β CH_2 w (in cycle)
1036	1050	τ CH_2 (in cycle)
1017	1030	ν CC, δ(CC=O) (CO free)
995	1001	β CCH (CH_3)
956	985	β CCH_2 (CH_3)
938	940	ρ(C_2C=O)
872	887	ν(C—O), ν(C—CH_3)
723	824	β CCH_2 ρ
632	648	δ(CC=O), δ(OC—CH_3)
624	595	ν(C—C)(in cycle), δ(CC=O)
568	555	γ(C—CC)(in cycle)
548	525	τ(O=C—C=C)
497	483	γ CCC (in cycle)
460	458	τ C=C
432	433	β(C=CO), δ(CC=O)(H-bonded)
386	381	γ(C=C—C)
327	317	ν(O...H), γ CCC (in cycle)
238	223	τ(O...H—O=C)
192	202	γ(C=C—CH_3), γ(C—C=C)
165	119	ρ(C_2C=C)
163	90	τ(C=C—C—OH)
79	56	δ(O—H...O)

Notations. The following symbols are used for the notations of vibrational co-ordinates: ν — stretching vibrations, α — deformation vibrations of HCH angles, β — deformation vibrations of CCH angles, γ — deformation vibrations of CCC angles, δ — deformation vibrations of other angles, τ — torsion vibrations, ρ — rocking deformation, w — wagging vibrations of the CCH_2 group.

Table 4. Force constants ($K/10^6$ cm^{-2}) of *exo*- и *endo*-enol forms of ACPD (**2** and **3**)

Force constant	2(3)*
F(C=C)	11.05 (11.00)
F(C=O, free)	16.22 (16.28)
F(C=O, H-bonded)	14.70 (15.30)
F(C—C)	7.30
F(C—O)	8.11
F(O—H)	7.80 (7.78)
F(H...O)	0.28
F(COH)	1.305 (1.00)
F(O—H...O)	0.08
f(C=C, COH)	0.06
f(C=C, C—C)	0.36
f(C=C, C—O)	0.36
f(C=O, C—C)	0.61
f(C=O, O...H)	0.05
f(C=C, CCO)	0.90
f(C=C, CCC)	0.94

* Force constants of form **3** are given if they are different from those of **2**.

bonds are observed. Thus, in the IR spectrum of ACPD purified by sublimation (KBr pellets), an intense band is found at 1575 cm^{-1} (1593 cm^{-1} in CCl_4) with a shoulder at 1543 cm^{-1}, whereas in the IR spectrum of ACPD precipitated either on a germanium or KBr plate from a concentrated solution in CCl_4 or methanol, the intensity of the 1546 cm^{-1} band increases distinctly, although the background level in the frequency region 1560—1590 cm^{-1} remains sufficiently high. Assuming that the band at 1575 cm^{-1} (1593 cm^{-1} in CCl_4) is assigned to ν(C=C) of the *exo*-cyclic bond, and the band at 1546 cm^{-1} is that of ν(C=C) of the *endo*-cyclic bond, we concluded that, as the result of sublimation, a crystalline phase consisting of a tautomer mixture in which **2** predominates significantly is formed, while through evaporation of solutions, a crystalline phase with an increased content of **3** dominates.*

The detection of the shoulder at 1565 cm^{-1} in the IR spectrum of the liquid diketo-analog of ACPD, 2-acetylcyclopentanone, is also associated[2] with *endo*-enol. The *exo*-enol form of this substance absorbs at 1660 cm^{-1} (ν(C=O)(H-bonded)) and 1615 cm^{-1} (ν(C=C)) and it is found in equilibrium with the diketo-form[2] (bands at 1710 cm^{-1}, *exo*-cyclic C=O group, 1740 cm^{-1} ν(C=O) of the acetyl group). In the IR spectrum of gas phase ACPD at 280 °C, one would expect an increase in the content of the thermodynamically less stable forms **1** and **3**. However, in this spectrum, only the ν(C=C) band at 1603 cm^{-1} and the single band of free C=O groups at 1726 cm^{-1} are observed, which correspond to pure *exo*-enol **2**.

* This tautomer reveals higher volatilability than **2** because **3** is sublimated during registration of the spectrum.

Heating to 280 °C is probably insufficient to break the intramolecular H-bond, the energy of which was estimated to be equal to 6.6 kcal mol^{-1}.[4] This follows from the lack of an O—H band in the 3600 cm^{-1} region, although the spectral registration was specially performed with a more than tenfold increase in sensitivity, and the weak band at 3442 cm^{-1} assigned to the first overtone of ν(C=O) — 1726 cm^{-1}, is easily visible.

The relative content of tautomers in solution

The percent of form **3** in the solution was determined by mathematic deconvolution of the spectral band envelope into its components. It turned out that the observable spectral curve in the frequency region 1750—1500 cm^{-1} of the IR spectrum of a solution of ACPD in trichloroethylene is an envelope of six absorption bands belonging, according to the frequencies, to both enol forms **2** and **3**.

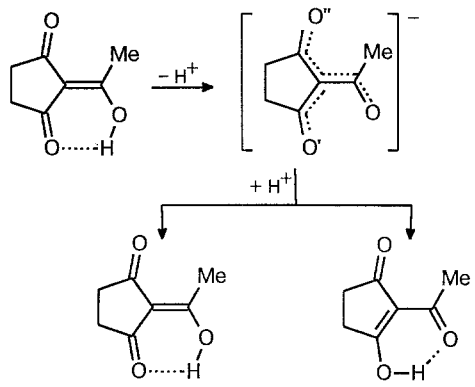
The comparison of the apparent integral intensities of the ν(C=O) bands shows that, assuming the equality of the extinction coefficients for both forms, the percentage of form **3** in trichloroethylene does not exceed 11 %. From the analysis it follows that the distances between the maxima of the bands belonging to the free (1709.4 and 1689.7 cm^{-1}) and H-bonded (1667.5 and 1633.9 cm^{-1}) carbonyl groups, respectively, are close to the order of magnitude of the halfwidths of these bands. Therefore, the bands belonging to **3** are usually not seen against the background of the strong bands of the major tautomer **2**, whereas, the ν(C=C) bands (1593 and 1546 cm^{-1}) of both forms can be recognized in the spectra of the crystals, in which these bands are narrower than in the solution spectra.

Assumed mechanism of tautomer conversion

All enolized β,β′-triketones are known to exhibit acidic properties and to be able to dissociate to give anionic forms. In particular, ACPD as an acid (pK_a = 3.78) is comparable in strength to formic acid (pK_a = 3.75) (see Ref. 18). Therefore, it is believed that, in solutions of protic solvents as well as in aprotic solvents at high concentrations of the β,β′-tricarbonyl compound, interconversion between the enol forms of the β,β′-tricarbonyl compound proceeds *via* an intermolecular proton exchange mechanism (Scheme 1).

As a result of ACPD dissociation, an anion containing three negatively charged oxygen atoms is formed. During the protonation of this anion, *endo*-enol may be formed in two cases (during protonation of cyclic O-atoms), but *exo*-enol is formed only once (during protonation of the acetyl O-atom). Assuming equiprobable protonation, the ratio of *endo*- and *exo*-enols would be 2 : 1. Protonation belongs to the category of charge-controlled reactions.[19] Therefore, using the negative charge values on each of the three oxygen atoms as

Scheme 1



reactive indices, we estimated the relative amount of each enol form in terms of perturbation MO theory (PMO).[20]

The calculation of the charge distribution was carried out by the AM1 method for the completely optimized geometry of the ACPD anion[7] (Table 5). It turned out that the maximum negative charge is centered on the O"-atom, whereas the charges on both the O'- and O-atoms are close one to another.

The relative percentage of enols forming during protonation of each of the three O-atoms was calculated from the equation (see Ref. 21):

$$n_i = \{1 + \Sigma\exp[-\Delta E_{ij}/(kT)]\}^{-1},$$
$$i \neq j = 1, 2, 3,$$

where the energy differences, $\Delta E_{ij} = E_{Q(i)} - E_{Q(j)}$, and E_Q are the electrostatic interaction energies calculated in the PMO approximation from the equation: $E_{12} = q_1 q_2/\varepsilon R_{12}$, q_1 is the negative charge on the O-atom, and q_2 is the positive charge of proton ($+1e^-$), ε is the dielectric constant of the solvent, R_{12} is the distance between particles (taken equal to 2.5 Å). The calculation was carried out for two solvents: CCl_4 and CH_2Cl_2 (ε = 2.23 and 4.7 D, respectively[18]).

As can be seen from the results obtained (see Table 5), owing to the difference of the charges and depending on the dielectric constants of the solvent, the percentage of the *endo*-form may reach ~94 %. However, the real content of **3** in solutions is about tenfold less. This may be explained by the lower thermodynamic stability of *endo*-enol, by the low efficiency of proton exchange in aprotic solvents at low ACPD concentrations, and by the influence of the medium, which promotes stabilization of the less polar form **2**, whose dipole moment, according to the calculation, is equal to 0.4 D, whereas μ_3 = 2.8 D (see Ref. 7).

Table 5. Charges on oxygen atoms of the ACPD anion (q), electrostatic interaction energy of O atoms with proton (E_Q), relative content of the *endo*-enol form of ACPD in CCl_4 and CH_2Cl_2 (n)

Solvent	Atom O	q/e^-	E_Q /kcal mol^{-1}	n (%)
CCl_4	O"	−0.439	−26.1	81.5
	O'	−0.393	−23.4	7.8
	O	−0.411	−24.5	18.5
CH_2Cl_2	O"	−0.439	−12.4	93.8
	O'	−0.393	−11.1	< 1
	O	−0.411	−11.6	5.4

The dramatic shift of the equilibrium in favor of the more polar form **3** takes place with the significant increase in the concentration of the sample during solvent evaporation. In this case, proton exchange efficiency increases leading to an increase in the contents of the more polar molecule **3** in the medium, and having a stabilizing effect on the *endo*-enol form of ACPD.

Intramolecular conversion of **2** into **3** is possible by two paths: either by means of a direct proton transfer reaction or by tunnel proton transfer between O-atoms with subsequent redistribution of electronic density as it occurs in the malonic aldehyde molecule. Probably neither of reactions is realized for ACPD because the former reaction requires high activation energy estimated,[22] *e.g.*, for **4** as 35 kcal mol^{-1}, while the tunnel proton transfer is forbidden due to the high energy difference (> 5 kcal mol^{-1}) between the ground state energies of **2** and **3**.

Interpretation of vibrational spectra of enols 2 and 3

The validity of the assignment of ν(C=C) band on which the spectroscopic identification of both tautomers **2** and **3** was based, was verified by the isotope substitution method. In the IR spectrum of malonic aldehyde, the ν(C=C) band at 1593 cm^{-1} is shifted to 1534 cm^{-1} after replacing the H at O and at the C(2)-atom with D. Therefore, one would expect that, in the spectra of the structurally non-eqvivalent enol forms **2** and **3**, the ν(C=C) bands would be sensitive to variable degrees of deuteration of the hydroxyl proton.

The normal coordinate analysis indicated that the frequency shift of ν(C=C) in the transition from enol **2** (1592 cm^{-1}) to **2**-d_1 (1531 cm^{-1}) may amount to 61 cm^{-1}, while the similar transition from **3** (1547 cm^{-1}) to **3**-d_1 (1527 cm^{-1}) leads to a 20 cm^{-1} shift only.

The deuteration of the enol proton in *exo*-enol **4** resulted in a fairly substantial shift (47 cm^{-1}). From a comparison of the CCl_4 solution spectra of ACPD (ν(C=C) = 1593 cm^{-1}) and ACPD-d_1 (1537 cm^{-1}) (see Table 1) it can be seen that the ν(C=C) shift amounts*

* To receive a confirmation for the ν(C=C) of the *endo*-enol is considerably more difficult, because the enol **3** is always crystallized in the mixture with the enol **2**. Therefore, during deuteration which occurs never completely, the mixture of four compounds (**2**, **2**-d_1, **3**, and **3**-d_1) is always formed, the bands ν(C=C) of which are overlapped in the spectrum.

to 57 cm^{-1}, therefore, the band at 1593 cm^{-1} needs to be assigned to the *exo*-cyclic double bond.

The complete interpretation of the vibrational spectra of the *exo*- and *endo*-enol forms was carried out using the results of the normal coordinate analysis of **2**, **2**-d_1, **3**, and **3**-d_1. The vibrational frequencies of **2** and **3** appeared to be rather close, therefore, in Table 3, only the frequency assignment of enol **2** is given. The minor difference between the force constants of both ACPD forms obtained by solving the RVP (see Table 4) demonstrates that the vibrational frequency changes occurring in the transition from **2** to **3** are caused by changes in kinematics.

The calculation of the potential energy distribution during vibrations shows that the contribution of δ(OH) to ν(C=C) of **2** (1593 cm^{-1}) reaches 30 %, while the contribution of δ(OH) to the C=C *endo*-cyclic vibration of **3** (1547 cm^{-1}) is less than 1 %. Hence it is clear why the replacement of the enol proton with deuterium leads to a significant shift of the ν(C=C) band in the spectrum of *exo*-form **2**-d_1 in contrast to *endo*-form **3**. At the same time, the interpretation of the spectra in the range below 1500 cm^{-1} represented here needs to be considered as tentative. A comparison of the spectra shows that going from **2** to **3** not only lowers the ν(C=C) frequency, it also decreases the intensity of the band at 1362 cm^{-1} assigned by the calculation to α(HCH) bending of the Me group. However, in the spectrum of the sample containing with predominantly **3**, the suitable band is absent while the calculation does not predict a change in the frequency of this vibration.

* * *

The spectroscopic experiments perfomed by us allowed the *endo*-enol form of ACPD to be detected and indicate that the tautomeric properties of ACPD agree with the Dieckmann—Cohn rule. Namely, the *exo*-enol tautomer is the most thermodynamically stable and is abundant in solution, in the vapor phase, and in crystals obtained by sublimation. A shift of the tautomeric equilibrium to the side of the ACPD *endo*-enol form takes place only during fast crystallization from a solution.

The results of quantum-chemical calculations do not contradict experimental data demonstrating the higher thermodynamic stability of **2**, because at differences in energies between forms **2** and **1** as well as forms **2** and **3** equal to more than 5 kcal mol^{-1} (see Ref. 7) the percentage of the less stable tautomer at 280 °C does not exceed 1 % (of the lowest limit of reliable detection), but the bands of **1** and **3** are missing from the gas phase absorption spectrum at this temperature. Consequently, unlike 2-acetylcyclopentanone, the diketo-form of which is found in equilibrium with *exo*- and *endo*-enols, the triketo form of ACPD is not observed even at sufficiently high temperatures (280 °C). It is to be noted that the dicarbonyl form of malonic aldehyde has also not yet been detected in either the vapor or crystalline phases.

Comparison of the ^{13}C NMR spectra in the region of the chemical shifts of the enol and ketone groups of ACPD (see Refs. 4, 24) and **4** (see Ref. 22) which is an authentic enol, points merely to the similarity of these structures. Therefore, it is premature, in our view, to assume that ACPD exists solely as *endo*-enol[5,24] since there is no data on the NMR spectra of authentic **2** and **3**.

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