Solid-State NMR Study of the Tautomerism of Acetylacetone Included in a Host Matrix

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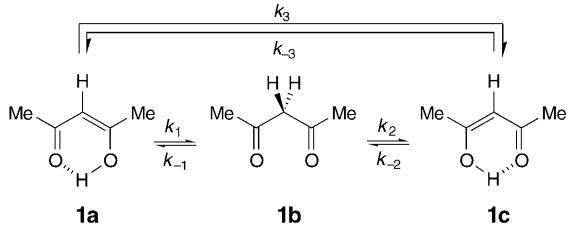
Dedicated to Professor *Rolf Huisgen* on the occasion of his 85th birthday

The tautomerism of the enol form of acetylacetone (= pentane-2,4-dione; **1**) inside a host cavity has been studied by means of solid-state ^{13}C-NMR spectroscopy (SSNMR) using the variable-temperature CPMAS technique. It appears that the enol form, 4-hydroxypent-3-en-2-one (**1a**), exists in an equilibrium with an identical tautomer (**1c**) trough O–H ··· O proton transfer. The experimental results (energy barrier and chemical shifts) were rationalized by means of MP2 and GIAO calculations.

1. Introduction. – In a broad sense, one might consider that organic chemistry rests on few pillars such as the tetrahedral structure of sp^3 C-atoms, the aromaticity of benzene, the *Diels–Alder* reaction, or the keto–enol equilibrium [1–4]. Although theoreticians prefer malonaldehyde (to avoid the conformational degrees of freedom of the Me groups), acetylacetone (**1**) is the 'paradigm' of tautomerism. This compound can exist in the three tautomeric forms **1a–c**, two of which, 4-hydroxypent-3-en-2-one (**1a**,**c**) are degenerate, the other being pentane-2,4-dione (**1b**) (*Scheme 1*).

Scheme 1



The identity of **1a** and **1c** can be circumvented by exchanging one CH_3 group by CD_3, or by placing the molecule inside an asymmetric cavity. Otherwise, the equilibrium is usually discussed as involving only **1a** and **1b**. The thermodynamic aspects of this process are well understood (solvent and temperature effects on the equilibrium constant between the keto and the enol forms ($K_{ke} = k_1/k_{-1} = k_{-2}/k_2$)). Since it involves the cleavage of a C–H bond, the equilibrium is slow on the NMR time-

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scale, but its kinetics aspects are not known. This is so because the transition state (TS) is not an intramolecular one (TS_{intra}), but probably also involves solvent molecules (TS_{inter}; *Fig. 1*).

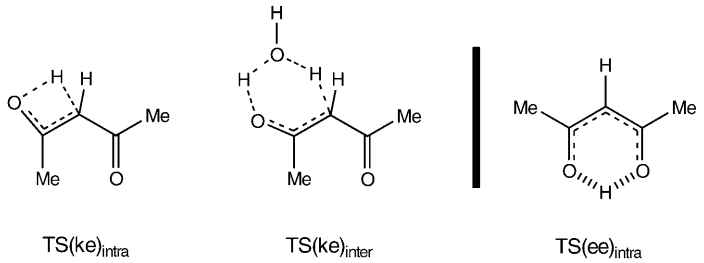


Fig. 1. *Intra-* vs. *intermolecular transition states of the keto–enol* (ke) *and the enol–enol* (ee) *forms of acetylacetone* (**1**)

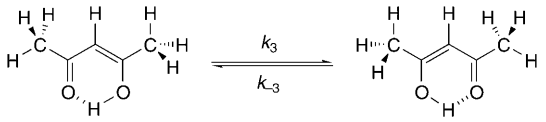
The equilibrium **1a**/**1c** ($K_{ee} = k_3/k_{-3}$) is rapid on the NMR timescale, but, being intramolecular, its transition state, TS(ee), is easily calculable by quantum-chemical methods. The keto–enol equilibrium constant ($K_T = K_{ke} = [\mathbf{1b}]/[\mathbf{1a}] = [\mathbf{1b}]/[\mathbf{1c}]$), easy to determine by NMR, has been used to study solvent effects [5], relationships between NMR and IR [6], electronic effects (for other substituents) [7][8], as well as pressure and temperature effects [8][9]. The kinetics part of the proton transfer through the intramolecular H-bond between **1a** and **1c** ($k_3 = -k_{-3}$; $K_{ee} = [\mathbf{1a}]/[\mathbf{1c}] = 1$) remains unknown. Crystallographers have discussed the strength of this H-bond, and *Gilli et al.* [10] have introduced the *resonance-assisted hydrogen-bond* (RAHB) concept for these compounds, although it has been shown for malonaldehyde that the magnetic properties are not consistent with this concept [11]. There is one aspect of the equilibria represented above that is qualitatively known: the rate constants k_1 and k_{-1}. The activation energy should be, on one hand, high enough since the keto form **1b** and the enol tautomers **1a**,**c** always appear in ^{1}H-NMR spectra as narrow signals, on the other hand, it cannot be too high because the equilibrium is very rapidly attained in solution, which means that the free energy of activation, $\Delta G^{\ddagger}$, lies between 65 and 85 kJ mol^{-1}. This explains why, using low temperature HPLC, both tautomers give rise to two different peaks [12]. Concerning the keto–enol tautomerism, neither the forward (k_1) nor the reverse reaction (k_{-1}) can take place without at least a trace of acid or base, ruling out a *direct* H-shift from the C- to the O-atom or *vice versa* [13][14]. As expected from a mechanism in which the C–H bond is broken in the rate-determining step, isotopomers of the type CO–CD_2–CO have shown D-isotope effects of *ca.* 5 in both the base- [15] and the acid-catalyzed [16] processes.

Temperature effects on the keto–enol tautomerism have been reported by *True* and co-workers using gas-phase ^{1}H-NMR [17]. The enol tautomer **1a** (or **1c**) is the most stable, as present in condensed phases at a given temperature. For the gas-phase, the following values have been reported: ΔH^0(enol–keto) = –19.5 kJ mol^{-1}, ΔS^0(enol–keto) ≈ 33 J mol^{-1} K^{-1} [17].

It should be noted that the **1a**/**1c** equilibrium involves not only the migration of H^+ through the H-bond, but probably a rotation of both Me groups. Unless the Me groups

in **1** have identical conformations, they must rotate by 60° for the equilibrium to be degenerate (*Scheme 2*).

Scheme 2



1a **1c**

Moon and *Kwon* [18] published an important theoretical paper based on experimental ^{17}O-NMR chemical shifts: the average chemical shift of the two O-atoms in **1a**, corresponding to a rapid **1a**/**1c** equilibrium, is $\delta(^{17}O)$ 274 ppm relative to gaseous H_2O determined in neat liquid [19]. The best result is obtained at the MP2/6-31+G**//B3LYP/6-31G** level, with $\delta(^{17}O)$ values of 418.5 (C=O) and 151.2 (C–OH), thus, on average, 284.85 ppm[2]). Finally, it should also be noted that, in the case of benzoylacetone (=1-phenylbutane-1,3-dione), ^{13}C-CPMAS NMR, combined with accurate neutron-diffraction studies, have shown that the nondegenerate enol–enol equilibrium corresponds to a double-minimum potential, as reported by *Oliveri* and co-workers [20][21].

2. Results and Discussion. – We will describe our results concerning the tautomerism of acetylacetone (**1**) in four sections. First, NMR studies with solutions of **1** will be presented; second NMR experiments with **1** adsorbed on solid supports are described; third, a complex between **1** and a suitable host is probed; and, finally, theoretical investigations will be discussed.

2.1. *Solution-NMR Studies.* Although the ^{1}H- and ^{13}C-NMR chemical shifts and the percentage of the tautomers in **1** have been described several times, we preferred to determine our own values. The data given in *Table 1* were consistent with those of previous works [5][22].

The ^{17}O-NMR chemical shifts of the neat compound are 575.5 ppm for **1b**, and 275.9 ppm for **1a**,**c**. These values are close to those reported for the corresponding benzene solution (566 and 274 ppm, resp.) [19].

2.2. *NMR Studies in the Presence of Solid Supports.* We have already studied the possibilities offered by silica and alumina for recording ^{13}C-NMR spectra of solid samples [23], a technique originally introduced by *Günther* and co-workers [24]. When a sample of **1** and *Silica Gel 60* (0.040–0.063 mm, 230–400 mesh) was mixed by mechanical grinding, we obtained ^{13}C-CPMAS NMR data very similar to the solution ^{13}C-NMR data given in *Table 1.* The SiO_2/**1** spectrum is shown in *Fig. 2*,*a*. From integration of the Me signals, a 70:30 ratio **1a**/**1b** (or **1c**/**1b**) was determined (*Inset*). Since, in all cases, **1** on solid support exists exclusively in the enol form (see below), we concluded that acetylacetone impregnated in silica exists, from a chemical point of view, in the 'solution' state, eventually with some residual 'solvent-like' effect, since, in solution (*Table 1*), the **1a**/**1b** (or **1c**/**1b**) ratio is 80/20.

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[2]) HF/HF and B3LYP/B3LYP Calculations, even with larger bases, yield worse values.

Table 1. *^{1}H- and ^{13}C-NMR Data of the Keto–Enol Tautomers of Acetylacetone in Solution*. Sample: neat, or 50 µl of **1** in 0.6 ml of the appropriate solvent; δ in ppm.

	Neat	$CDCl_3$	(D_6)DMSO
^{1}H-NMR:			
Me (**1b**)	2.32	2.11	2.13
CH_2 (**1b**)	3.76	3.66	3.67
Me (**1a**,**c**)	2.14	2.00	2.01
CH (**1a**,**c**)	5.69	5.66	5.66
OH (**1a**,**c**)	15.73	15.54	15.55
1b/**1a**,**c**	20 : 80	16 : 84	40 : 60
^{13}C-NMR:			
Me (**1b**)	29.6	30.7	30.6
CH_2 (**1b**)	57.4	58.4	57.8
CO (**1b**)	201.6	201.9	203.3
Me (**1a**,**c**)	23.7	24.7	24.5
CH (**1a**,**c**)	99.7	100.3	100.5
CO (**1a**,**c**)	190.9	191.1	191.2

When aluminum oxide (*Alox 90*, active neutral, 0.063–0.200 mm, 70–230 mesh) was used as support, the spectrum of **1** (*Fig. 2*,*b*) turned out to be very different from the previous one. Compound **1** was found to be 100% in the enol form **1a**,**c**, thus probably being 'solid', but present in several conformations, since there were at least four chemically different CH groups.

2.3. *NMR Studies of a Host/Guest Complex*. We have already used CPMAS-SSNMR for studying host–guest complexes with respect to proton transfer. In the case of pyrazole complexed by 1,1-bis(2,4-dimethylphenyl)but-2-yn-1-ol, we used both solid-state ^{13}C/^{15}N-NMR and X-ray crystallography [25]. The structure and proton disorder of the three-component crystal formed by, *e.g.*, 3(5)-methyl-4-nitropyrazole, (−)-(*R*,*R*)-*trans*-4,5-bis[hydroxy(diphenyl)methyl]-2,2-dimethyl-1,3-dioxolane, and toluene was described [26]. Also, the complexes between 1,1′-binaphthyl-2,2′-dicarboxylic acid and pyrazoles have been investigated, including an example of manual sorting of conglomerate crystals (triage) [27].

A search in the *CSD* dictionary (Vers. 5.25; updated July 2004) [28] revealed several compounds in which acetylacetone (**1**) acts as 'solvate' (because of its low molecular weight and being liquid at room temperature). In all these compounds, it exists in the tautomeric form **1a**,**c**: CUXQER, a holmium complex containing **1** and H_2O; DPHEAD, a 2 : 1 : 1 bis(diphenylhydantoin) (**2**)/9-ethyladenine (**3**)/acetylacetone (**1**) solvate; HADJUS, 1,1-bis(*p*-hydroxyphenyl)cyclohexane/**1** clathrate monohydrate [29]; HADKAZ, (−)-(*R*,*R*)-*trans*-4,5-bis[hydroxy(diphenyl)methyl]-2,2-dimethyl-1,3-dioxolane/**1** clathrate; IBOWAX, *N*,*N*'-bis(*p*-nitrophenyl)-(1*R*,2*R*)-diaminocyclohexane/**1** solvate; KEJMER, an iron complex containing **1**; QASGAS, 6-formyl-2-trifluoromethylperimidine/**1** solvate), and TITZEB, 1,1′-binaphthyl-2,2′-dicarboxylic acid/**1** solvate [30]. Besides, *Boese et al.* investigated the structure of **1** at low temperatures (110 and 210 K; *CSD* entries LIWPIQ and LIWPIQ01, resp.). At these temperatures, **1** exists as a dynamic mixture of **1a** and **1c** (double-well potential) [31].

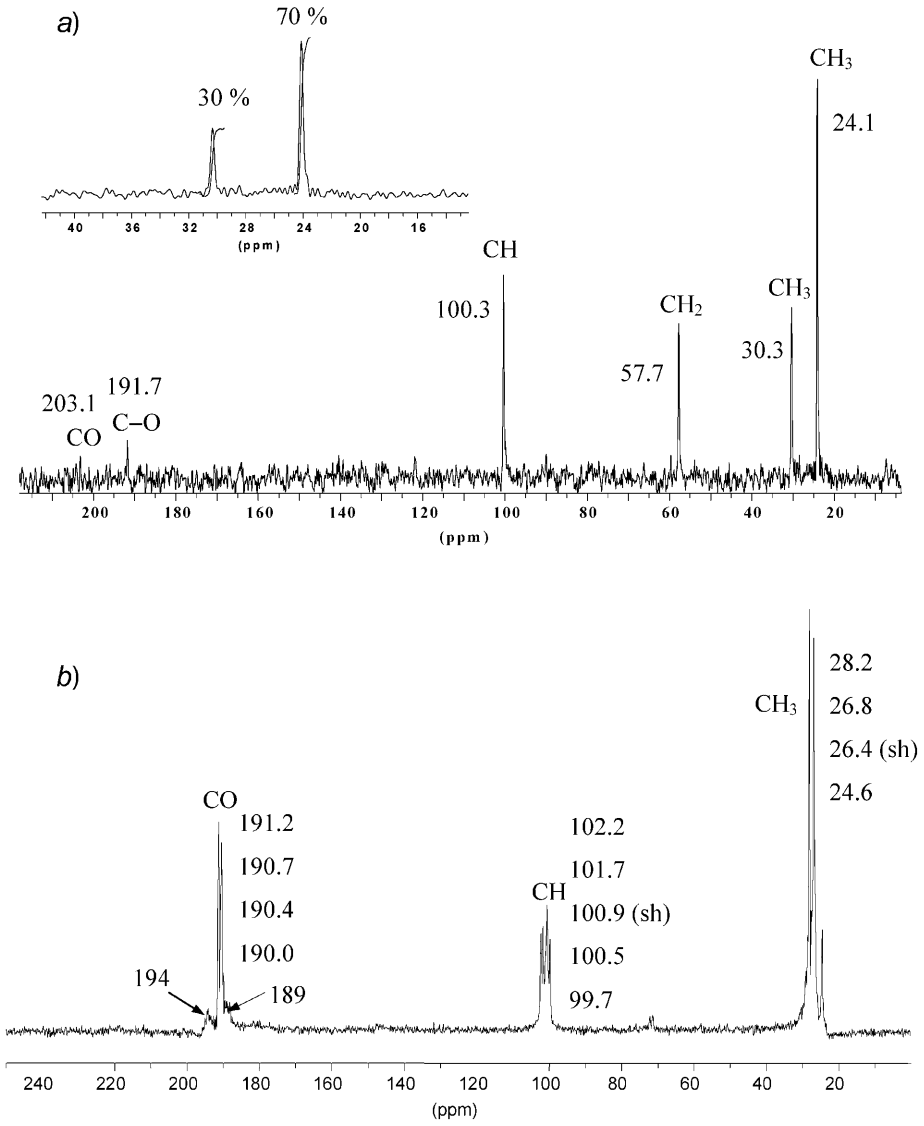

Fig. 2. *^{13}C-CPMAS NMR Spectrum of* **1** *in the presence of* a) *SiO_2 and* b) *Al_2O_3 solid supports.* The inset shows the expanded Me region of **1** on SiO_2.

We selected the DPHEAD structure (*Fig. 3*) [32] to start our studies of acetylacetone complexes. *Camerman et al.* described the H-bonded complex of 5,5-diphenylhydantoin (**2**) and 9-ethyladenine (**3**) crystallized from acetylacetone (**1**), DPHEAD, with an asymmetrical unit consisting of two molecules of **2**, one molecule of **3** and one solvent molecule [32]. X-ray determination reveals that one N(1)–H of **2** binds to the N(1) of **3** in a *Watson–Crick* mode while the second N(3)–H of **2** links to

the N(3) of **3** to form a **2**/**3** 2:1 intermolecular complex. All three molecules in the complex also form self-associated cyclic dimers through pairs of H-bonds (*Fig. 3*). The acetylacetone molecules adopt the enol form **1a**(**c**) with an asymmetric intramolecular H-bond and do not participate in any H-bond with molecules of **2** and **3**. However, a closer examination of the structure[3]) revealed that **1a** (or **1c**) is not floating in a void determined by the hydantoin **2** (=5,5-diphenylimidazolidine-2,4-dione) and 9-ethyladenine (**3**), but has its Me groups interacting with the π system of the Ph rings of **2** and the O–H ··· O H-atom of **1a** (or **1c**) close to the N-atom of the 6-NH_2 group of **3**. The fact that the O ··· N distances are 3.19 Å (OH) and 3.41 Å (C=O) probably explains why the H-atom lies 0.36 Å above the molecular plane [31][32], rendering the six-membered H-bonded pseudo-cycle nonplanar (*Fig. 3*).

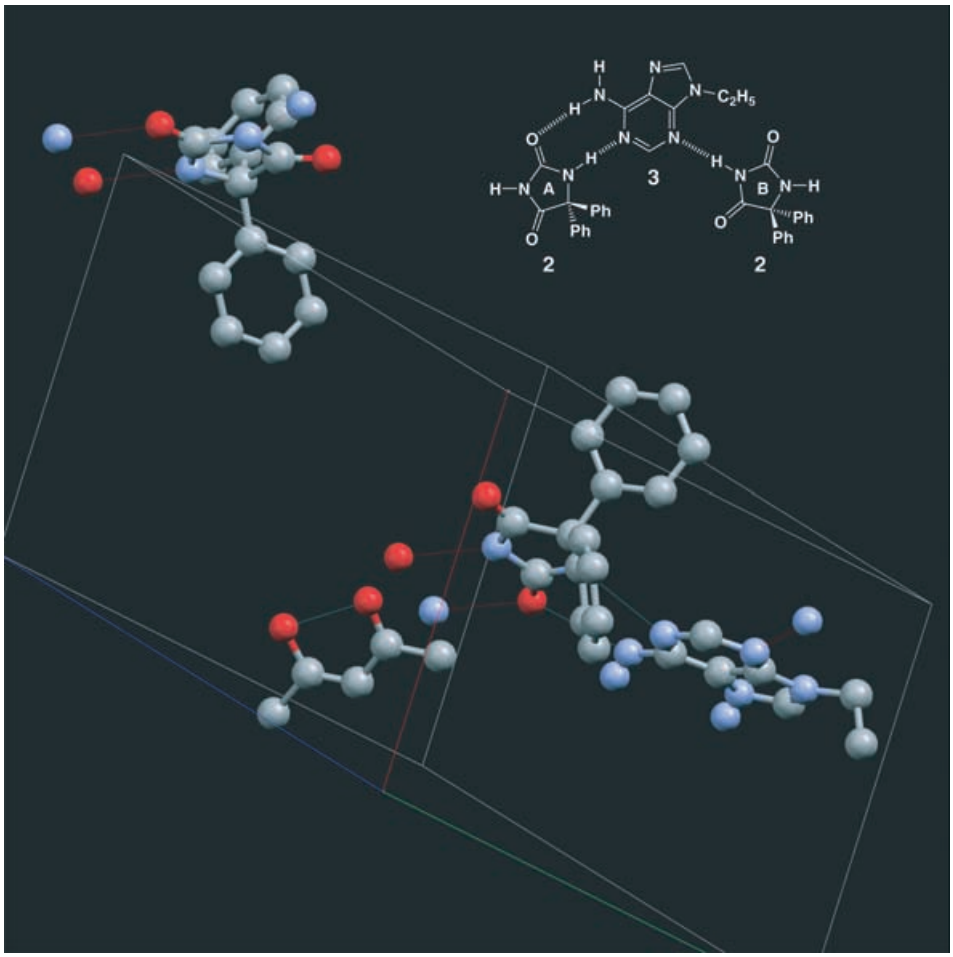

Fig. 3. *A view of the unit cell of the* **2**/**3**/**1** *2:1:1 complex* (DPHEAD, see text)

[3]) In the CSD, H-atom positions are provided only for **1a** (**1c**).

2.3.1. *Static Aspects.* The 100.73-MHz ^{13}C-CPMAS NMR spectrum of the DPHEAD 2:1:1 complex **2/3/1** at 300 K indicated that **1** exists as a dynamically averaged mixture of the degenerate enol forms **1a** and **1c**, and the broadened lines for the C–O and Me groups indicated an exchange regime. The spectrum also indicated two chemically different molecules **2**, with a splitting for each signal of the imidazolidine-2,4-dione ring. This could be rationalized in terms of two different C(2), C(4), and C(5) atoms, respectively, experiencing, in turn, the effect of the Ph groups in two different crystallographic conformations (four signals; *Table 2*). The part of the spectrum corresponding to the adenine **3** showed the expected signals (*Table 3*). The assignments given in *Tables 2* and *3*, although made independently by means of 2D-NMR correlations based on the values obtained in solution, were consistent with the literature data for **2** [33] and those of the *N*-Me congener of **3**[4]) [34].

Table 2. *^{13}C- and ^{15}N-CPMAS NMR Data of* **2**, *either Free or in the DPHEAD Complex.* At 300 K; δ in ppm. Primed atoms refer to the Ph rings.

	C(4)	C(2)	C(1′)	C(2′–6′)	C(5)	N(1)	N(3)
Free	176.0	157.0	140.4	128.5 (3′,5′)	71.9	– 267.8	– 230.8
		156.5	138.7	126.5 (4′), 128.5 (2′,6′)	71.4	– 272.0[a])	– 234.1[a])
Complex	175.9	159.7	141.2	129.5, 129.0	73.5	– 262.4[b])	– 233.1[b]) (A)
	175.6	158.1	139.6	128.6, 127.8	72.9	– 269.5[b])	– 228.6[b]) (B)
	174.7	157.5	139.0	126.6	71.5		
	174.4				71.0		

[a]) In (D_6)DMSO solution. [b]) Two values since two nonequivalent molecules.

Table 3. *^{13}C- and ^{15}N-CPMAS NMR Data of* **3**, *either Free or in the DPHEAD Complex.* At 300 K; δ in ppm.

	C(6)	C(2)	C(4)	C(8)	C(5)	CH_2	Me
Free	156.4	149.1	149.1	138.6	119.5	41.6	16.5
Complex	159.7	151.1	148.1	144.1	118.9	38.7	16.7
	N(7)	N(1)	N(3)	N(9)	NH_2		
Free	– 143.3	– 149.3	– 152.6	– 208.5	– 290.2		
Free[a])	– 140.5	– 144.9	– 154.9	– 214.7	– 299.6		
Complex	n.d.[b])	n.d.	n.d.	n.d.	– 289.5		

[a] In (D_6)DMSO solution. [b]) Not detected.

The assignment of the ^{15}N-NMR signals of **2** to the two specific molecules (A and B in *Fig. 3*) in the complex is based on the known effects of H-bonds on ^{15}N-NMR chemical shifts [35].

2.3.2. *Dynamic Aspects.* To slow the fast tautomeric equilibrium between the two degenerate enol forms **1a** and **1c**, variable-temperature ^{13}C-CPMAS NMR experiments were performed. As indicated in *Fig. 4*, two sharp signals for the C–O and Me groups

4) For 9-(cyclohexylmethyl)adenin, see K. S. Schmidt, R. K. O. Sigel, D. V. Filippov, G. A. van der Marel, B. Lippert, J. Reedijk, *New J. Chem.* **2000**, *24*, 195.

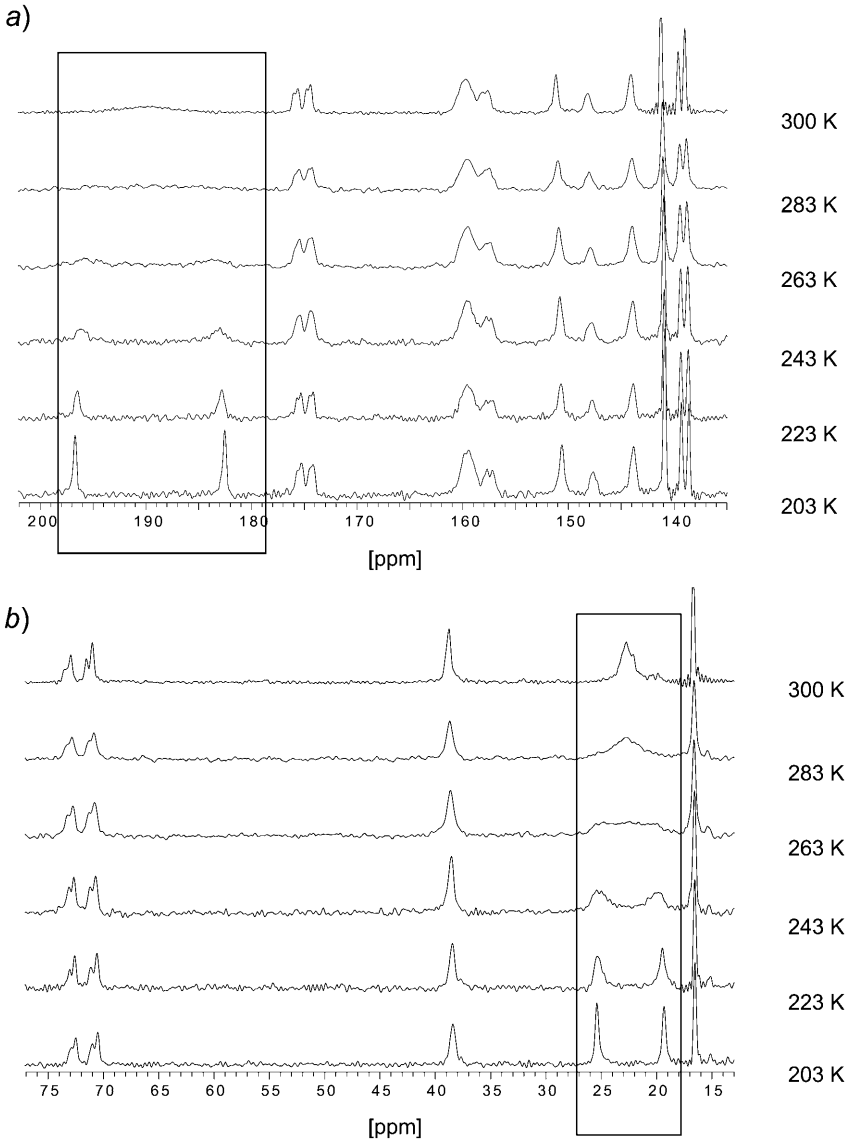

Fig. 4. *^{13}C-CPMAS Variable-temperature NMR spectra of* **1** *in the DPHEAD complex* (see *Fig. 3*). *a*) 135–200 ppm; *b*) 15–75 ppm.

were observed at 203 K, and the lines broadened and coalesced into a single line, when the temperature was raised.

We calculated the kinetics parameters k with *Brucker* WIN Dynamics as 40 (203 K), 400 (243 K); 1350 (263 K), 3000 (283 K), and 8500 s^{-1} (323 K). Linear regression afforded $\Delta H^{\ddagger} = 22.8\ (\pm 0.9)$ kJ mol^{-1} and $\Delta S^{\ddagger} = -98\ (\pm 4)$ J mol^{-1} K^{-1} ($r^2 = 0.994$), which corresponds to $\Delta G^{\ddagger} = 50.7$ kJ mol^{-1} at 283 K.

2.4. *Computational Experiments.* Calculations of **1** were performed at the MP2/6-311 + G** level. For the different geometries, absolute shieldings were calculated within the GIAO approximation. The optimized geometry of **1a**,**c** corresponds to a planar structure (excluding four H-atoms of the Me groups) of C_s symmetry, which is the most-stable tautomer (more stable by 6.1 kJ mol^{-1}). One H-atom of the Me group near the C=O function lies in the molecular plane in a synperiplanar disposition, and one H-atom of the Me group near the OH function lies in the molecular plane in a antiperiplanar disposition. The diketo tautomer **1b** belongs to the C_2 spatial group, and both Me groups have a H-atom in synperiplanar disposition. The O ··· O distance in **1a**,**c** and in **1b** are 2.546 and 4.185 Å, respectively. The first value agrees with both experimental results and elaborate calculations: 2.381 [36] and 2.512 Å [37] by electron diffraction; 2.547 Å by X-ray diffraction at 110 K [31], and 2.535 Å by X-ray diffraction of DPHEAD [32]; and 2.549 or 2.548 Å by MP2/D95 + + ** [38] or MP2(FC)/6-311 + + G(2d,2p) [39] calculations, respectively. For **1b**, *Karle et al.* [36] experimentally determined the O ··· O distance as 2.767 Å, the calculated values [38] being 4.046 and 3.559 Å for the more- and the less stable forms, respectively. Our calculated value for the O ··· O distance was 4.185 Å, close to that of the most-stable minimum reported previously [38]. In our view, the results of *Karle* and co-workers [36] are dubious; not even the percentages of **1a**,**c** and **1b** agree with those reported by *True* and co-workers at the same temperature [17]. Contrary to *Dannenberg* and *Rios* [38], who questioned their own calculations, we think that *Karle*'s structure actually represent an *average* conformation between mirror-like compounds having much longer O ··· O distances.

The calculated absolute shieldings σ of the O-atoms of **1a**,**c** and **1b** were determined as 183.573 (C=O), −132.584 (C−OH), and −264.484 ppm (both C=O groups), respectively. Since H_2O at the same level has a σ value of 344.523 ppm, the previous values can be transformed into calculated chemical shifts δ of 160.95, 477.11 (average 319.03), and 609.01 ppm. These have to be compared with the experimental $\delta(^{17}O)$ values: 275.90 (average) and 575.50 ppm. Including H_2O, they are fit to *Eqn. 1* ($n = 3$, $r^2 = 0.999$):

$$\delta(^{17}O)_{exp} = (0.928 \pm 0.023) \cdot \delta(^{17}O)_{calc} \quad (1)$$

The two signals of **1a**,**c** should appear at $\delta(^{17}O)$ 412.9 and 139.2, the first one being close to that of *Moon* and *Kwon* [18] (418.5 ppm), but the second one being quite different (151.2).

The calculated ^{13}C-NMR absolute shieldings of **1a**,**c** are in perfect agreement ($r^2 = 0.999$) with the experimental solid-state NMR data ($\sigma_{TMS} = 198.8327$ ppm):

$$\delta(^{13}C)_{CPMAS} = (198.8327 \pm 2.2015) - [(1.0187 \pm 0.0164) \cdot \sigma(^{13}C)] \quad (2)$$

The barrier for the proton transfer between **1a** and **1c** ($k_3 = k_{-3}$) *via* transition state TS(ee) has been calculated many times but never determined experimentally. It includes the rotational barrier of both Me groups, from syn- to antiperiplanar, and *vice versa*, by a 60° rotation. The following classical barriers have been reported (in kJ mol^{-1}): 11.1 (this work, MP2/6-311 + G**), 10.5 (MP2/D95 + + **) [38], 14.3 (MP2(FC)/6-311 + + G(2d,2p)) [39], 14.6 (HF/6-31G*) [40], and 19.1 (CISD + Q)

[41]. *Hinsen* and *Roux* [40] carried out calculations considering a classical model with quantum proton (9.6 kJ mol^{-1}) and the fully quantum model (5.7 kJ mol^{-1}).

Since the barrier we have determined is $\Delta H^{\ddagger} \approx 23$ kJ mol^{-1}, it appears that acetylacetone (**1**) inside the cavity provided by the DPHEAD complex has a much higher enol–enol barrier than in the gas phase. One possibility is that the structure of **1a** in the complex is highly asymmetric, and that after H-transfer (→ **1c**) the resulting structure has a different energy. However, two arguments speak against this hypothesis. First, in *Fig. 4*, the signals of the Me and C=O groups are not split (if **1a** and **1c** were different, four signals would be expected); second, when the population deviates from 1:1, the coalescence spectra would show two lines, and not a single one [42]. It is probable that the populations of **1a** and **1c** are not exactly 1:1, but this does not rationalize the considerable increase of the barrier. In our opinion, this increase is due to distortion of the geometry of **1a**,**c**, which destabilizes the corresponding transition state. For such an assumption speaks the observation that the proton migrates outside the molecular plane.

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Experimental Part

Chemistry. All compounds were commercially available and used without further purification. The host–guest complex [32] was prepared by dissolving 150 mg of **2** and 50 mg of **3** in 6 ml of **1** under heating. To assure clathrate formation, the soln. was placed into a heated water bath, and the resulting crystals of the host–guest complex were collected by filtration, and dried at r.t. The 2:1:1 stoichiometry was checked by ^{1}H-NMR solution spectroscopy and by thermogravimetric analysis (*Seiko TG/DTA* apparatus). In the latter case, the sample was equilibrated first at 30°, and then heated at a rate of 3°/min in a N_2 flow.

NMR Experiments. Solution-NMR spectra were recorded on a *Bruker DRX-400* apparatus (9.4 Tesla, 400.13 (^{1}H), 100.62 (^{13}C), 54.26 (^{17}O), and 40.56 MHz (^{15}N)). Chemical shifts δ (in ppm) are given rel. to residual solvent signals ($CDCl_3$: 7.26 (^{1}H), 77.0 (^{13}C); (D_6)DMSO: 2.49 (^{1}H), 39.5 (^{13}C). For ^{17}O- and ^{15}N-NMR, D_2O (0.00) and nitromethane (0.00) were used as external standards. Coupling constants *J* (in Hz) were accurate within ±0.2 (^{1}H) and ±0.6 Hz (^{13}C). 2D ^{1}H,^{1}H-gs-COSY and Inverse-proton-detected-heteronuclear-shift-correlation spectra, gs-HMQC (^{1}H,^{13}C), gs-HMBC (^{1}H,^{13}C), gs-HMQC (^{1}H,^{15}N), and gs-HMBC (^{1}H,^{15}N) were obtained using standard pulse sequences [43].

Solid-state ^{13}C- (100.73 MHz) and ^{15}N (40.60 MHz) CPMAS NMR spectra were obtained on a *Bruker WB-400* spectrometer at 300 K, using a 4-mm DVT probehead. Samples were carefully packed in a cylindrical 4-mm zirconia rotor, with Kel-F end-caps and the standard CPMAS; the TPPM decoupling pulse sequence was used. ^{13}C-NMR Spectra were originally referenced to a glycine sample, and then, the chemical shifts were re-calculated to Me_4Si (for C=O, δ(glycine) 176.1); and ^{15}N-NMR spectra were re-calculated to $^{15}NH_4^+Cl^-$, and then converted to the $MeNO_2$ scale by the relationship δ (^{15}N, $MeNO_2$) = δ(^{15}N, NH_4Cl) – 338.1 ppm. Typical acquisition parameters for ^{13}C-CPMAS: spectral width, 40 kHz; acquisition time, 30 ms; contact time, 2 ms; spin rate, 12 kHz. To assign in the solid state the C-atom signals, we run non-quaternary suppression (NQS) experiments by conventional cross-polarization, and during the acquisition, the decoupler was switched off for a very short time (25 μs) [44]. For ^{15}N-CPMAS NMR, the following parameters were used: spectral width, 40 kHz; acquisition time, 35 ms; contact time, 6 ms; spin rate, 6 kHz.

Variable-Temperature Experiments: A *Bruker BVT-3000* temperature unit was used to control the temp. of the cooling gas stream, and an exchanger was used to achieve low temperatures. To avoid problems at low temperatures caused by air moisture, anh. N_2 was used as bearing, driving, and cooling gas. The rotational frequencies were *ca.* 12 kHz, and we used boron nitride caps.

Ab initio *Calculations.* The structures of the compounds discussed in this paper were optimized at the MP2/6-311 + G** level [45][46] with the Gaussian 98 suite of programs [47]. In all cases, the minimum-energy

geometries were confirmed by frequency calculations at the same level. Absolute shielding values σ were calculated for these geometries within the GIAO approximation [48][49].

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