Table I. ^{13}C NMR Chemical Shifts for Enol Forms of 1,3-Diketones (**1a–7a**) and Those for Their Methyl Ethers (**1b–7b**)[a]

state[b]	C1	C2	C3	C4[c]	C5[c]	C6[c]	C7[c]	C8[c]	C9[c]	Me[d]	MeO
1a solid	205.8	102.9	186.6	44.3	33.8	49.3	31.6	25.8			
1a soln	185.6	102.3	185.6	46.0	31.4	46.0	27.5	27.5			
1b $CDCl_3$	199.2	100.6	176.8	42.3	32.1	50.3	27.8	27.8			55.3
2a solid	202.7	109.6	174.9	43.4	32.6	49.3	30.5	25.5		7.5	
					33.4	50.5	31.6	26.8		8.3	
2a soln	182.0	108.4	182.0	46.3	30.6	46.3	27.4	27.4		6.0	
2b $CDCl_3$	198.1	112.9	169.8	38.3	31.5	49.6	28.1	28.1		6.6	54.7
3a solid	204.1	104.9	186.1	30.5	21.1	35.9					
3a soln	186.7	103.6	186.7	31.7	20.3	31.7					
3b $CDCl_3$	199.0	101.7	178.2	28.3	20.7	36.2					55.0
4a solid	201.5	112.3	177.8	30.5	22.0	37.4				9.2	
4a soln	*e*	109.6	*e*	32.1	19.9	32.1				6.2	
4b $CDCl_3$	198.4	114.2	171.7	24.3	20.4	35.7				6.7	54.7
5a solid	196.3	126.0	173.4	129.0	131.1	129.1	129.1	129.1	131.1		
5a soln	178.3	120.8	178.3	131.5	128.6	127.0	126.0	127.0	128.6		
5b $CDCl_3$	190.1	122.3	169.7	129.9	128.9	127.5	127.1	127.5	128.9		62.4
6a solid	194.7	122.5	170.7	127.8	131.6[f]	130.4	137.3	130.4	132.4[f]	19.6	
			173.1				139.1			21.6	
6a soln	178.2	120.7	178.2	128.4	128.4	127.7	135.2	127.7	128.4	20.1	
6b $CDCl_3$	190.1	122.3	169.4	126.8	128.7	128.2	136.8	128.2	128.7	20.8	62.3
7a solid	194.6	122.7	170.3	122.7	132.0[f]	111.9	160.2	118.2	133.8[f]	55.3	
	196.3		173.4		134.7[f]				134.7[f]	56.2	
7a soln	178.3	120.4	178.3	123.8	129.7	113.0	157.9	113.0	129.7	54.8	
7b $CDCl_3$	190.2	121.8	169.3	122.1	130.8	112.9	158.3	112.9	130.8	54.7	62.3

[a] Chemical shifts are given in units of ppm from $(CH_3)_4Si$. [b] States for measurements: solid, measured in solids at room temperature; soln. measured in $(CD_3)_2SO$ solutions at 393 K for **1a**, **3a**, and **5a–7a**, and at 423 K for **2a**; $CDCl_3$, measured in $CDCl_3$ solutions at room temperature. [c] Carbon atoms C4–C9 correspond to carbon atoms C1′–C6′, respectively, for **5–7**. [d] The 4′-methoxyl carbon atom for **7**. [e] Not observed. [f] Assignments may be interchanged.

NaCl and dried over anhydrous Na_2SO_4. The solvent was evaporated and the residual oil was distilled under reduced pressure to give **5b**.

In a similar manner as above, **6b** and **7b** were prepared from **6a** and **7a**, respectively, with the reaction temperature at 0 °C for **6b** and 30 °C for **7b**.

NMR Spectra. Isotropic ^{13}C NMR spectra in solids at room temperature were measured on a home-built spectrometer operating at 15.0 MHz for **1a** and **3a** and at 22.6 MHz for **2a** and **4a–7a** by using the CPMAS techniques with mixing times of 1–5 ms, repetition times of 1–50 s, and a sample-spinning frequency of ca. 3 kHz. ^{13}C chemical shifts in the solids were calibrated in units of ppm relative to $(CH_3)_4Si$ as described previously.[3] ^{13}C NMR spectra in solutions were recorded on a JEOL FX-90Q spectrometer operating at 22.6 MHz for **1a** and **3a** or on a JEOL GX-400 spectrometer operating at 100.5 MHz for **2a**, **4a–7a**, and **1b–7b**. Concentrations of the solutions were 0.7 mol kg^{-1} in $(CD_3)_2SO$ for **1a–7a** or 1.0 mol kg^{-1} in $CDCl_3$ for **1b–7b**. ^{1}H NMR spectra for **5b** in solutions at room temperature were taken on a JEOL PS-100 spectrometer operating at 100 MHz.

Results and Discussion

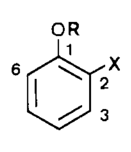
A. Estimation of ^{13}C Chemical Shifts for Isolated Enol Forms of 1,3-Diketones. The ^{13}C chemical shifts for enol forms of the 1,3-diketones (**1a–7a**) in solids and in $(CD_3)_2SO$ solutions, and those for the methyl ethers (**1b–7b**) in $CDCl_3$ solutions, are collected in Table I. Two different values for each carbon atom are ascribed to independent molecules in the solid state. For 1,3-diketones existing in enol forms in $(CD_3)_2SO$ solutions, the ^{13}C chemical shifts of their C1 and C3 carbon atoms could not be determined definitely, because their resonance signals were very broad at room temperature owing to fast proton exchange with solvent molecules; freezing of the solutions prevented the observation of low-temperature ^{13}C spectra. Consequently, the ^{13}C spectra for **1a**, **3a**, and **5a–7a** were measured at 393 K and those for **2a** and **4a** at 423 K. The coalescent signals of the C1 and C3 carbon atoms for **1a–3a** and **5a–7a** were observed, but the signal for **4a** remained broad.

The C1, C2, and C3 carbon atoms in the enol forms of **1a–7a** and those of **1b–7b** form a conjugated system with a hydroxyl or methoxyl group at the 3-position. Recently, Takegoshi et al.[10,11] have determined ^{13}C chemical shift tensors for **1a** and tetraacetylethane, which is an intramolecularly hydrogen-bonded enol of a 1,3-diketone, and have found that the chemical shift tensors of the C2 and C3 carbon atoms in **1a** are close to those of the aromatic carbon atoms bonding with a hydrogen atom and a hydroxyl group, respectively, on the basis of the directions of the principal axes. We have, therefore, taken advantage of substituent effects on ^{13}C chemical shifts of aromatic carbon atoms in order to estimate the ^{13}C shifts of the C1, C2, and C3 carbon atoms in isolated, non-hydrogen-bonded enol forms of **1a–7a**.

Table II. ^{13}C NMR Chemical Shift Differences between Phenol (**8a**) and Anisole (**8b**) and Those between 2-Methylphenol and (**9a**) and 2-Methylanisole (**9b**) in $CDCl_3$ Solutions[a]

atom	**8a–8b**	**9a–9b**
C1	-4.5	-4.1
C2	1.5	-2.6
C3	0.3	0.5
C6	1.5	5.1

[a] Values are given in units of ppm. Positive values represent downfield shifts for phenols.



	X	R
8a	H	H
8b	H	Me
9a	Me	H
9b	Me	Me

Table II collates the chemical shift differences between phenol (**8a**) and anisole (**8b**) and those between 2-methylphenol (**9a**) and 2-methylanisole (**9b**) in concentrations of 1 mol kg^{-1} in $CDCl_3$ solutions. Variation of the ^{13}C shift of each carbon atom in **8a** and **9a** is maximally 0.4 ppm, ranging in concentration from 0.2 to 1.6 mol kg^{-1}, and that in **8b** and **9b** is at most 0.1 ppm, ranging in concentration from 0.25 to 2.0 mol kg^{-1}. Both variations are small enough to be negligible in the following considerations. The ^{13}C chemical shifts of the C1, C2, and C3 carbon atoms in the isolated enol forms of **1a–7a** are obtained by adding the ^{13}C chemical shift differences for the C3, C2, and C1 carbon atoms in Table II to the ^{13}C chemical shifts of the C1, C2, and C3 carbon atoms, respectively, in the corresponding methyl ethers **1b–7b**. Correction terms for **1b** and **3b** are derived from the ^{13}C chemical-shift differences for **8**, while those for **2b**, **4b**, and **5b–7b** are from **9** to take the effects of the 2-substituents into account. For

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Structure-Dependent Intermolecular Hydrogen Bond Effects on ^{13}C NMR Chemical Shifts in Enol Forms of 1,3-Diketones

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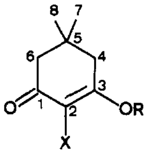
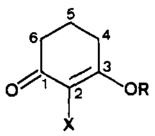
Abstract: We measured solid-state ^{13}C NMR chemical shifts for the enol forms of seven 1,3-diketones, which are intermolecularly hydrogen-bonded in the solid state: dimedone (**1a**), 2-methyldimedone (**2a**), 1,3-cyclohexanedione (**3a**), 2-methyl-1,3-cyclohexanedione (**4a**), 2-phenylmalondialdehyde (**5a**), 2-(4′-methylphenyl)malondialdehyde (**6a**), and 2-(4′-methoxyphenyl)malondialdehyde (**7a**). From the ^{13}C chemical shifts of their methyl ethers (**1b–7b**) in solution, the ^{13}C chemical shifts of the corresponding enols in the isolated, non-hydrogen-bonded state were estimated to obtain individual chemical shift changes due to hydrogen bonding. The downfield shift for the carbonyl (C1) carbon atom, ΔC1, in **1a** (6.3 ppm) is comparable to that in **5a** (5.7 ppm), consistent with similar O···O hydrogen bond lengths for both compounds. The downfield shift for the enol (C3) carbon atom, ΔC3, is always larger than the corresponding ΔC1. The ratio $\Delta C3/\Delta C1$ for **1a** having infinite helical hydrogen bonds is 2.3, whereas that for **5a** possessing infinite planar zigzag hydrogen bonds is 1.5, reflecting differences in the hydrogen bond structure. The structure-dependent downfield shift is examined by the change in charge density for model systems obtained from molecular orbital calculations. On the basis of the $\Delta C3/\Delta C1$ values, we conclude that the helical hydrogen bond structure holds for **3a** and it is still maintained on substitution of the 2-hydrogen atom in **1a** and **3a** by a methyl group.

From stereochemical aspects it is of much interest to investigate how ^{13}C NMR chemical shifts are affected by conformationally different hydrogen bonds. In the solid state, intermolecular hydrogen bonds in the enol form of dimedone (**1a**), 5,5-dimethyl-1,3-cyclohexanedione, are known to make infinite helices[1,2] with an O···O hydrogen bond distance of 2.593 Å.[1] In a preliminary study,[3] we found that the average of the ^{13}C chemical shifts of the carbonyl (C1) and enol (C3) carbon atoms in the solid state of **1a** moves significantly downfield from their ^{13}C chemical shift in $(CD_3)_2SO$ solutions, owing to the intermolecular hydrogen bonding in the solid. The hydrogen bond structure of solid 2-phenylmalondialdehyde (**5a**), which is a noncyclic 1,3-diketone existing also as an enol in the solid state, as determined by X-ray crystallography,[4] is different from that of **1a**: the intermolecular hydrogen bonds of **5a** form infinite planar zigzag chains rather than helices, but the O···O distance (2.577 Å) is only slightly shorter than that in **1a**.

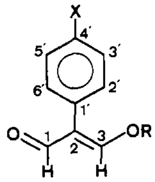
In order to investigate the hydrogen-bonding effects on the ^{13}C chemical shifts in detail, it is necessary to distinguish the individual effects on the shifts for the C1 and C3 carbon atoms in the enols. The chemical shifts of the C1 and C3 carbon atoms in the isolated, non-hydrogen-bonded enol forms can hardly be determined in solution, due to rapid enol–enol tautomerism. Therefore, in the present work, we have attempted to make an estimate of the individual chemical shifts in the isolated, non-hydrogen-bonded enol forms from those of the corresponding methyl ethers, with appropriate corrections, and have elucidated the structure-dependent hydrogen-bonding effects on the ^{13}C chemical shifts.



	X	R
1a	H	H
1b	H	Me
2a	Me	H
2b	Me	Me



	X	R
3a	H	H
3b	H	Me
4a	Me	H
4b	Me	Me



	X	R
5a	H	H
5b	H	Me
6a	Me	H
6b	Me	Me
7a	OMe	H
7b	OMe	Me

The intermolecular hydrogen bonds in α-methyl- or α,γ-dimethyltetronic acid, which can be regarded as an enol of a five-membered cyclic 1,3-diketone with a methyl group at the 2-position, form infinite planar zigzag chains in the crystalline state.[5,6] Then, a question is raised as to whether the structural change of hydrogen bonds from helices to zigzag chains is brought about by introduction of a methyl group to the 2-position in **1a**, which has a six-membered ring structure. Accordingly, we have measured the ^{13}C chemical shifts of 2-methyldimedone (**2a**), 1,3-cyclohexanedione (**3a**), and 2-methyl-1,3-cyclohexanedione (**4a**). Effects of para (4′) substituents of the phenyl ring in **5a** on the hydrogen bond structure are also examined by ^{13}C chemical shifts of 2-(4′-methylphenyl)malondialdehyde (**6a**) and 2-(4′-methoxyphenyl)malondialdehyde (**7a**).

Finally, we have carried out ab initio molecular orbital calculations to confirm the structure-dependent hydrogen-bonding effects on ^{13}C chemical shift on the basis of charge densities at carbon atoms in model systems.

Experimental Section

Materials. Commercially available diketones **1a** and **3a** were used. **4a** was prepared from **3a** by the method of Born et al.[7] and was recrystallized from water: mp (uncorrected) 211.0–214.0 °C [lit.[7] mp 210 °C]. **2a** was likewise obtained from **1a** but was recrystallized from $CHCl_3$–benzene: mp (uncorrected) 164.0–165.0 °C [lit.[8] mp 163–165.5 °C]. **5a–7a** were synthesized by the procedure of Coppola et al.[9] and were purified by sublimation under reduced pressure for **5a** and **7a** and by recrystallization from $CHCl_3$–benzene for **6a**. **5a**: mp (uncorrected) 95.0–96.0 °C [lit.[9] mp 92–95 °C]. **6a**: mp (uncorrected) 132.0–133.0 °C [lit.[9] mp 129–132 °C]. **7a**: mp (uncorrected) 150.0 °C [lit.[9] mp 146–148 °C].

The methyl ethers **1b–4b** were prepared by addition of diazomethane, generated from *N*-methyl-*N*′-nitro-*N*-nitrosoguanidine and aqueous KOH at 0 °C, to the corresponding diketones **1a–4a** dissolved in dioxane and were purified by distillation under reduced pressure.

5b was prepared as follows. To a stirred solution of 1.04 g of **5a** in 15 mL of *N,N*-dimethylacetamide at 0 °C was added by portions 560 mg of ca. 50% NaH washed with petroleum ether. After the mixture was stirred for 45 min at 0 °C, 1 mL of methyl iodide was added and the solution was stirred for 5 h. Then the reaction mixture was poured into water and extracted by ether. The extract was washed with aqueous

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Table III. ^{13}C NMR Chemical Shifts of the C1, C2, and C3 Carbon Atoms in Enol Forms of 1,3-Diketones (**1a**–**7a**) and Their Variations due to Hydrogen Bonding[a]

atom	solid[b]	soln[c]	isolated[d]	ΔC[e]	ΔC3/ ΔC1[f]
1a					
C1	205.8		199.5	6.3	2.3
C2	102.9	102.3 (0.2)	102.1	0.8	
C3	186.6		172.3	14.3	
C1,3	196.2	185.6 (−0.3)	185.9	10.3	
2a					
C1	202.7		198.6	4.1	2.2
C2	109.6	108.4 (−1.9)	110.3	−0.7	
C3	174.9		165.7	9.2	
C1,3	188.8	182.0 (−0.2)	182.2	6.6	
3a					
C1	204.1		199.3	4.8	2.6
C2	104.9	103.6 (0.4)	103.2	1.7	
C3	186.1		173.7	12.4	
C1,3	195.1	186.7 (0.2)	186.5	8.6	
4a					
C1	201.5		198.9	2.6	3.9
C2	112.3	109.6 (−2.0)	111.6	0.7	
C3	177.8		165.7	10.2	
C1,3	189.7	*g*	183.3	6.4	
5a					
C1	196.3		190.6	5.7	1.4
C2	126.0	120.8 (1.1)	119.7	6.3	
C3	173.4		165.6	7.8	
C1,3	184.9	178.3 (0.2)	178.1	6.8	
6a					
C1	194.7		190.6	4.1	1.6[h]
C2	122.5	120.7 (1.0)	119.7	2.8	
C3	170.7, 173.1		165.3	5.4, 7.8	
C1,3	183.3	178.2 (0.2)	178.0	5.3	
7a					
C1	194.6, 196.3		190.7	3.9, 5.6	1.4[h]
C2	122.7	120.4 (1.2)	119.2	3.5	
C3	170.3, 173.4		165.2	5.1, 8.2	
C1,3	183.7	178.3 (0.3)	178.0	5.7	

[a] Values except for ΔC3/ΔC1 are given in units of ppm. Values for C1,3 denote averages of the chemical shifts of the C1 and C3 carbon atoms. [b] Chemical shifts in solids. [c] Chemical shifts in $(CD_3)_2SO$ solutions. Differences between the chemical shifts in solutions and those in the isolated state are given in parentheses. [d] Chemical shifts for enols in the isolated non-hydrogen-bonded state obtained by the method in the text. [e] Differences between the chemical shifts in the solids and those in the isolated state. Positive values stand for downfield shifts. [f] The ratio of the variation for the C3 carbon atom (ΔC3) to that for the C1 carbon atom (ΔC1). [g] Not observed. [h] Average values of the ratios for two different combinations.

1a–**7a**, variations of the ^{13}C chemical shifts of the C1, C2, and C3 carbon atoms in the solid state from those in the isolated state, thus evaluated, are assembled in Table III together with ΔC3/ΔC1, which is the ratio of the downfield shift for the C3 carbon atom (ΔC3) to that for the C1 carbon atom (ΔC1).

B. Hydrogen Bond Effects for Enol Forms of Cyclic 1,3-Diketones. The estimated values for the ^{13}C chemical shifts of the C2 carbon atoms and the averages of those of the C1 and C3 carbon atoms in the isolated enol forms of **1a**–**4a** agree very well with the corresponding chemical shifts obtained in $(CD_3)_2SO$ solutions: differences between them are at most 1.9 ppm. This supports the validity of the present estimation, implying that the ^{13}C chemical shifts of the C1 and C3 carbon atoms in $(CD_3)_2SO$ solutions are scarcely influenced by hydrogen bonding with the solvent molecules.

Comparing the ^{13}C shifts in the solids with the estimated values for the isolated state, we can see pronounced downfield shifts for both C1 and C3 carbon atoms (maximally 14.3 ppm) due to the intermolecular hydrogen bonding in the solid state. It should be noted that ΔC3 is always larger than the corresponding ΔC1, whereas ΔC2 is small (at most 1.7 ppm). The ratio ΔC3/ΔC1 for **1a** is 2.3. Although both ΔC1 and ΔC3 for **3a** are smaller than the corresponding values for **1a**, the ratio (2.6) remains almost unchanged. Substitution of the 2-hydrogen atom in **1a** and **3a** by a methyl group decreases ΔC1 by 2.2 ppm and ΔC3 by 5.1 and 6.0 ppm for **1a** and **3a**, respectively. Thus, the ratio for **2a** (2.2) is similar to that for **1a**, while the ratio for **4a** (3.9) is somewhat larger than that for **3a**.

Table IV. Solvent Effects on ^{1}H NMR Chemical Shifts of the H1 and H3 Protons in **5b** at Room Temperature[a]

solvent	H1	H3
$(CD_3)_2SO$	9.27	7.53
$CDCl_3$	9.33	7.02
CCl_4	9.20	6.87
C_6D_6	9.17	6.15

[a] Chemical shifts are given in units of ppm from $(CH_3)_4Si$.

C. Geometries of 2-Arylmalondialdehydes in Solutions. The olefin part of **5a**–**7a** may take two configurations in solutions: trans and cis with respect to the carbonyl and hydroxyl groups. The cis configuration makes it possible to take the intramolecularly hydrogen-bonded structure, which is observed for dibenzoylmethane (**10**) in the solid state.[12] The hydroxyl proton of **10** resonates in an extremely downfield region both in $CDCl_3$ and in $(CD_3)_2SO$, due to the strong intramolecular hydrogen bonding. The ^{1}H chemical shifts of the hydroxyl proton (δ_{OH}) are 17.0 ppm in $CDCl_3$ and 17.2 ppm in $(CD_3)_2SO$. For **1a**, which cannot form intramolecular hydrogen bonds, δ_{OH} in $CDCl_3$ is 6.42 ppm, whereas that in $(CD_3)_2SO$ is 10.9 ppm. On the contrary, for **5a**, δ_{OH} is 14.2 ppm in $CDCl_3$, implying intramolecular hydrogen bonding, but is 11.5 ppm in $(CD_3)_2SO$, similar to the value for **1a** in the same. Hence, the contribution of the intramolecular hydrogen bonding for **5a** in $(CD_3)_2SO$ is small, and so the configuration of the enol olefin in $(CD_3)_2SO$ should be trans.

Since the solvent (*N*,*N*-dimethylacetamide) used for the preparations of **5b**–**7b** is an aprotic polar one like dimethyl sulfoxide, the configuration of the olefin part of **5b**–**7b** is expected to be trans. Table IV lists the ^{1}H chemical shifts of the H1 and H3 protons of **5b** in various solvents. While the chemical shift of the H1 proton remains nearly constant, that of the H3 proton varies extensively from solvent to solvent. The chemical shift of the H3 proton is affected by the magnetic anisotropy of the carbonyl group.[13] The position of the H3 proton relative to the carbonyl group varies sensitively with conformations about the C1–C2 bond in various solvents. This variation is much larger in the trans configuration than in the cis configuration. Thus, the trans configuration for **5b** is supported. The additivity rule for ^{1}H chemical shifts of olefins[14] gives 7.33 and 8.04 ppm in CCl_4 solutions for the chemical shifts of the H3 proton of **5b** in the trans and cis configurations, respectively, also in favor of the trans configuration (see Table IV). Consequently, the ^{13}C chemical shifts for the enol forms of **5a**–**7a** in the isolated state calculated from those of **5b**–**7b** in $CDCl_3$ solutions can be good references to evaluate the chemical shift changes due to hydrogen bonding.[15]

D. Hydrogen Bond Effects for Enol Forms of 2-Arylmalondialdehydes. The observed ^{13}C chemial shifts of the C1, C2, and C3 carbon atoms for **5a**–**7a** in $(CD_3)_2SO$ solutions are also well reproduced by the above-mentioned method (section A), as shown in Table III, indicating that molecular structures of **5a**–**7a** in this solvent are similar to those of their methyl ethers in $CDCl_3$ solutions. Comparing the ^{13}C chemical shifts of the C1, C2, and C3 carbon atoms for **7a**–**9a** in the solids with the corresponding shifts thus estimated, we can also see noticeable downfield shifts for the ^{13}C resonance lines of the C1 and C3 carbon atoms. Although ΔC3 is still larger than ΔC1, the ratio ΔC3/ΔC1 reduces to ca. 1.5, which is characteristic of this system and smaller than that for **1a** (2.3). The resonance positions of the C2 carbon atoms in the solids are downfield by 3–6 ppm compared with the estimated values. This may partly be ascribed to the correction value for the ^{13}C chemical shift of the C2 carbon atom, because the olefin

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(15) The ^{13}C chemical shifts of the C1, C2, and C3 carbon atoms in C_6D_6 solutions at room temperature are 189.9, 122.6, and 170.0 ppm, only slightly different from the corresponding chemical shifts in $CDCl_3$ solutions.

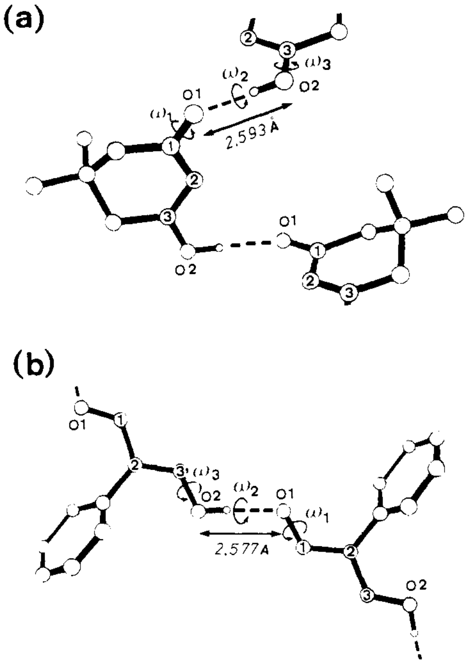

Figure 1. Hydrogen bond structures for enol forms of two 1,3-diketones in the solid state determined by X-ray crystallography: (a) dimedone (**1a**) at 291 K adapted from ref 1; (b) 2-phenylmalondialdehyde (**5a**) at 111 K adapted from ref 4.

part of **5**–**7** is not involved in a cyclic system as that of **1**–**4**. The large value for ΔC2 may also be attributed to different conformations for **5**–**7** in solids and in solutions; the aromatic ring of **5a** is twisted from the plane involving the conjugated C1, C2, and C3 carbon atoms in the crystalline state, while the two conjugated systems are not fixed at this conformation in solutions.

E. Structure-Dependent Hydrogen Bond Effects. The intermolecular hydrogen bonds of **1a** and **5a** in the solid state as revealed by X-ray crystallography are illustrated in Figure 1. The hydrogen bonds of **1a** form infinite helices:[1] the O1···O2 distance is 2.593 Å, the C1–O1···O2 angle is 129.7°, and the dihedral angles are −0.4°, 75.9°, and 14.8° for the C2–C1–O1···O2 (ω_1), C1–O1···O2–C3 (ω_2), and O1···O2–C3–C2 (ω_3) angles, respectively. On the other hand, those for **5a** make infinite planar zigzag chains:[4] the O1···O2 distance is 2.577 Å, the C1–O1···O2 angle is 119.0°, and the dihedral angles are 179.8°, 179.6°, and −177.9° for ω_1, ω_2, and ω_3, respectively.

The intramolecular difference in their hydrogen bond structures is whether the OH bond is cisoid (in **1a**) or transoid (in **5a**) with respect to the enol olefin. The close ΔC1 values for **5a** (5.7 ppm) and **1a** (6.3 ppm) seem to reflect the similarity of their hydrogen bond lengths. A notable difference in the downfield shifts for **1a** and **5a** appears in ΔC3. Since the magnitude of the downfield shift depends on the O···O hydrogen bond distances in similar compounds,[16] the ratio ΔC3/ΔC1 may serve as a marker for the hydrogen bond structure. For infinite helical hydrogen bonds, as in **1a**, the ratio exceeds 2, whereas it is 1.5 for infinite planar zigzag-chain hydrogen bonds, as in **5a**. From the similarity of the ratios for **1a** and **3a**, the hydrogen bond structure for **3a** is considered to be unaltered from that for **1a**. In spite of the hydrogen bond lengthening (ΔC1 = 4.1 ppm) expected for the replacement of the 2-hydrogen atom in **1a** by a methyl group (**2a**), the ΔC3/ΔC1 value (2.2) suggests that the hydrogen bonds remain unaltered. Molecules of **4a** seem to take a helical structure with a hydrogen bond distance longer than that for **3a** (ΔC1 = 2.6 and ΔC3/ΔC1 = 3.9 ppm). On the other hand, the hydrogen bond structures for **6a** and **7a** are similar to that for **5a**, though the O···O distance for **6a** is slightly longer than, but that for **7a** is similar to, that for **5a**.

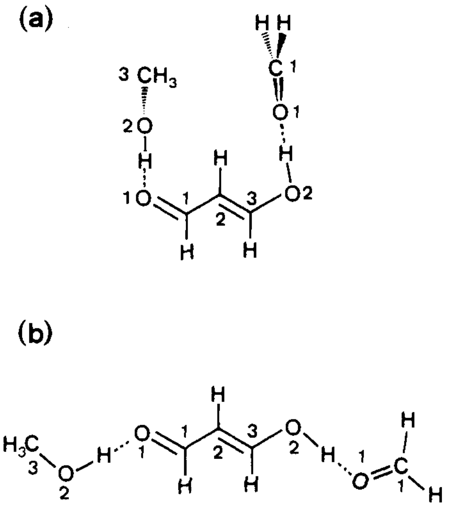

Figure 2. Two models for the structure of 3-hydroxyacrolein (**11**) hydrogen bonded with methanol and formaldehyde employed for ab initio molecular orbital calculations: (a) the helix model; (b) the zigzag-chain model.

It is well-known that the ^{13}C chemical shift of a carbon atom incorporated in a conjugated system reflects the charge density at the carbon atom.[17] We have performed ab initio molecular orbital calculations with the STO-3G basis set to elucidate how the charge density of the carbon atom reflects the hydrogen bond structure. As models for the present systems, we employ simple hydrogen bond systems consisting of *trans*-3-hydroxyacrolein (**11**) hydrogen bonded with methanol and formaldehyde to construct a helix and a zigzag chain as illustrated in Figure 2: the C2–C1–O1···O2, C1–O1···O2–C3, and O1···O2–C3–C2 dihedral angles are 0.0°, 90.0°, and 0.0°, respectively, for the former model, but are 180° for the latter. Standard values[18] are used for the intramolecular bond lengths and angles, and the O1···O2 distance, the C1–O1···O2 angle, and the O1–H···O2 angle are assumed to be 2.60 Å, 120.0°, and 180.0°, respectively. Variations of the charge densities at the C1, C2, and C3 carbon atoms in **11** due to hydrogen bonding are estimated by comparing those with the corresponding values averaged over the two conformations for **11** in the isolated state. The increases of the charge densities at the C1, C2, and C3 carbon atoms are 0.021, −0.030, and 0.016, respectively, in the helix model, and 0.022, −0.007, and 0.009, respectively, in the zigzag-chain model. The downfield shifts for the C1 and C3 carbon atoms due to hydrogen bonding are supported by the increases of their charge densities: the charge density at the C1 carbon atom in the helix model increases as much as that in the zigzag-chain model, whereas the charge density at the C3 carbon atom in the former model is larger than that in the latter. Thus, a larger ΔC3/ΔC1 ratio is predicted for the former model. The charge density at the C2 carbon atom, however, predicts an upfield shift, particularly for the helical model, in conflict with the experimental behavior. These effects should, of course, be examined by more rigorous quantum mechanical treatments of the ^{13}C chemical shieldings.

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