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INTRAMOLECULAR HYDROGEN BOND IN ENOL FORM OF 3-SUBSTITUTED-2,4-PENTANEDIONE

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Abstract—The 3-substituent effect on the enolic ring of 2,4-pentanedione has been investigated. A linear relationship between the chemical shifts of the enolic proton and the chelated carbonyl stretching vibrations has been found for the various highly enolized 3-substituted-2,4-pentanediones. The stronger electron-withdrawing resonance effect of the substituent at 3-position results in the lower magnetic field shift of the enolic proton and the lower frequency shift of the chelated carbonyl stretching. Semi-empirical Hückel calculations have been performed to enable discussion of the electronic effect of the substituents.

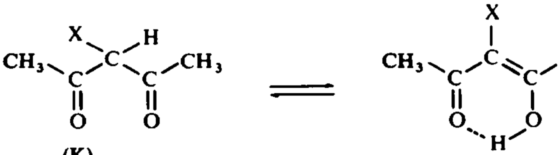
INTRODUCTION

IN SPITE of extensive work on the tautomerism of β-diketones, no conclusions have been made for the substituent effect on the enolic ring of β-diketones.[1] The quasi aromatic character proposed by Shigorin[2] has been examined and put in question by the recent NMR study.[3] It is of particular interest to study the effect of substituent on the chelate system, involving an intramolecular H-bond, in connection with this problem.

The present paper reports the first attempt at elucidating the electronic effect of various 3-substituents on the enolic ring of 2,4-pentanedione (acetylacetone) including newly prepared β-diketones.

RESULTS AND DISCUSSION

β-Diketones exist as mixtures of the keto (K) and enol (E) tautomers. The ratio of the enol and keto tautomers can be determined by the integration of the relative intensities of the —CHX— (K form) and the —OH (E form) or those of the $—CH_3$(K) and $—CH_3$(E).[1, 4] Complete enolizations have been confirmed from the absence of the signals for —CHX— and the free carbonyl stretching in CCl_4 except for **I**, **II**, **III** and **IV**. Table 1 lists proton chemical shifts of the 3-substituted-2,4-pentanediones. The NMR spectrum of **XII** indicates three enolic isomers, in which both the carbonyls of acetyl and formyl groups act as the proton acceptors.[5]



(K) (E) (1)

X=H (I), Cl (II), $—CH{=}CH—CH_3$ (III), $—CH{=}CH—C_2H_5$ (IV), —CN (V), $—NO_2$ (VI), —SCN (VII), $—SCH_3$ (VIII), $—COCH_3$ (IX), $—COOCH_3$ (X), $—COOC_2H_5$ (XI), —CHO (XII)

TABLE 1. NMR SPECTRA OF THE 3-SUBSTITUTED-2,4-PENTANEDIONES

(τ values, J values in c/s in parentheses)

	Substituent	Enol		Keto		Others†	Enol (%)	Method of prep
		—OH	CH_3(E)	—CHX—	CH_3(K)			
I	H	−5·84	7·98	6·50	7·64	H (4·54 s)	96	
II	Cl	−5·55	7·70	5·27	7·66		92	Ref 6
III	$—CH^{\alpha}=CH^{\beta}—CH_3$	−6·61	7·92	—	7·88	H^{α} (4·09 m), H^{β} (4·50 m) CH_3 (8·20 d; J = 5·8)	93	Ref 7
IV	$—CH^{\alpha}=CH^{\beta}—CH_2—CH_3$	−6·60	7·85	—	7·80	H^{α} (3·50 m), (H^{β} (4·20 m) CH_2 (7·90 m) CH_3 (9·10 t; J = 7·5)	93	Ref 8
V	—CN	−6·90	7·58	—	—		100	Ref 9
VI	$—NO_2$	−6·95	7·54	—	—		100	this work
VII	—SCN	−7·10	7·48	—	—		100	Ref 10
VIII	$—SCH_3$	−7·08	7·67	—	—	CH_3 (7·86 s)	100	this work
IX	$—COCH_3$	−7·40	7·81	—	—	CH_3 (7·65 s)	100	Ref 11
X	$—COOCH_3$	−7·97	7·65	—	—	CH_3 (6·25 s)	100	Ref 12
XI	$—COOCH_2CH_3$	−8·10	7·74	—	—	CH_2 (5·75 q; J = 7·5) CH_3 (8·67 t; J = 7·0)	100	Ref 12
XII	—CHO*	−8·51	7·55	—	—	H (0·03 s)	100	Ref 16

* The chemical shifts are listed here for the enolic form (E)

† Symbols; s, d, t, q and m denote singlet, doublet, triplet, quartet, and multiplet, respectively. Values of the chemical shifts are given for the enol form

TABLE 2. THE OBSERVED FREQUENCIES OF THE CHELATED C=O STRETCHING AND THE DOUBLE BOND (X=Y) STRETCHING OF THE SUBSTITUENTS

No of compd	$\nu_{C=O \cdots H}$, (cm^{-1})	$\nu_{X=Y}$, (cm^{-1})
I	1623	
II	1618	
III	1607	1607,† $\nu_{C=C}$ of $-CH=CH-CH_3$
IV	1603	1603,† $\nu_{C=C}$ of $-CH=CH-C_2H_5$
V	1598	
VI	1595	1530, $\nu_{as(NO_2)}$;* 1350, $\nu_{s(NO_2)}$*
VII	1580	
VIII	1575	
IX	1580	1680, $\nu_{C=O}$ of $-COCH_3$
X	1555	1710, $\nu_{C=O}$ of $-CO_2CH_3$
XI	1560	1720, $\nu_{C=O}$ of $-CO_2C_2H_5$
XII	1550	1677, $\nu_{C=O}$ of $-CHO$

* ν_s and ν_{as} denote the symmetric and asymmetric stretching respectively.

† The C=C stretchings are overlapped with the chelated C=O stretching.

Table 2 shows the observed bond stretching frequencies of the C=O bond and the conjugated double bond (X=Y) of the substituents. As a matter of fact, a conjugative interaction between the enolic ring and the substituent is evidently confirmed by the shift of $\nu_{X=Y}$ towards lower frequency relative to that in the non-conjugated system.[13] The chemical shift of the O—H proton has been known to be occasionally influenced by concentration. Therefore, we have determined the value τ°_{OH} by an extrapolation of the observed τ_{OH} to zero concentration in order to evaluate the strength of the H-bond. Fig 1 shows the plot of τ_{OH} against the concentration. The chemical shifts of the O—H protons show no appreciable change upon dilution. Those of **I** and **VI** exhibit slight shift to lower field due to intermolecular interactions.[14]

Fig 1 shows the plot of τ°_{OH} against $\nu_{C=O}$. The linear relationship indicates that the stronger H-bond results in the shift of $\nu_{C=O}$ to lower frequency and the downfield shift of τ°_{OH}. A similar trend has been found for β-diketones[15] and β-triketones.[16]

If the enolic ring can be considered as a non-benzenoid aromatic, we may expect a similar substituent effect in benzenoid systems. However, the order of the substituent effect can not be related to Hammett parameters (*para*-σ or σ^-). It is supposed that this trend is better explained in terms of a mesomeric effect rather than an inductive effect. The electron-withdrawing substituent decreases the electron density of the enolic oxygen through conjugation, resulting in a stronger H-bond and more delocalization of the π-electrons of the enolic ring.

Among β-diketones, it is particularly interesting to notice that the substitution of the methylthio group causes complete enolization and the down-field shift of the enolic proton in comparison with acetylacetone. Although the electronegativity of the sulphur atom is smaller than that of chlorine, the enolic ring of **VIII** is more stabilized than that of **II** in view of the delocalization of the π-electrons and the stronger intramolecular hydrogen bond. This extraordinary stabilization of the enolic ring is possibly due to the participation of the 3d orbitals of sulphur in the ground state. Consequently, the sulphur atom directly attached to the enolic ring may act as an electron-withdrawing group through a pπ–dπ conjugation.[17]

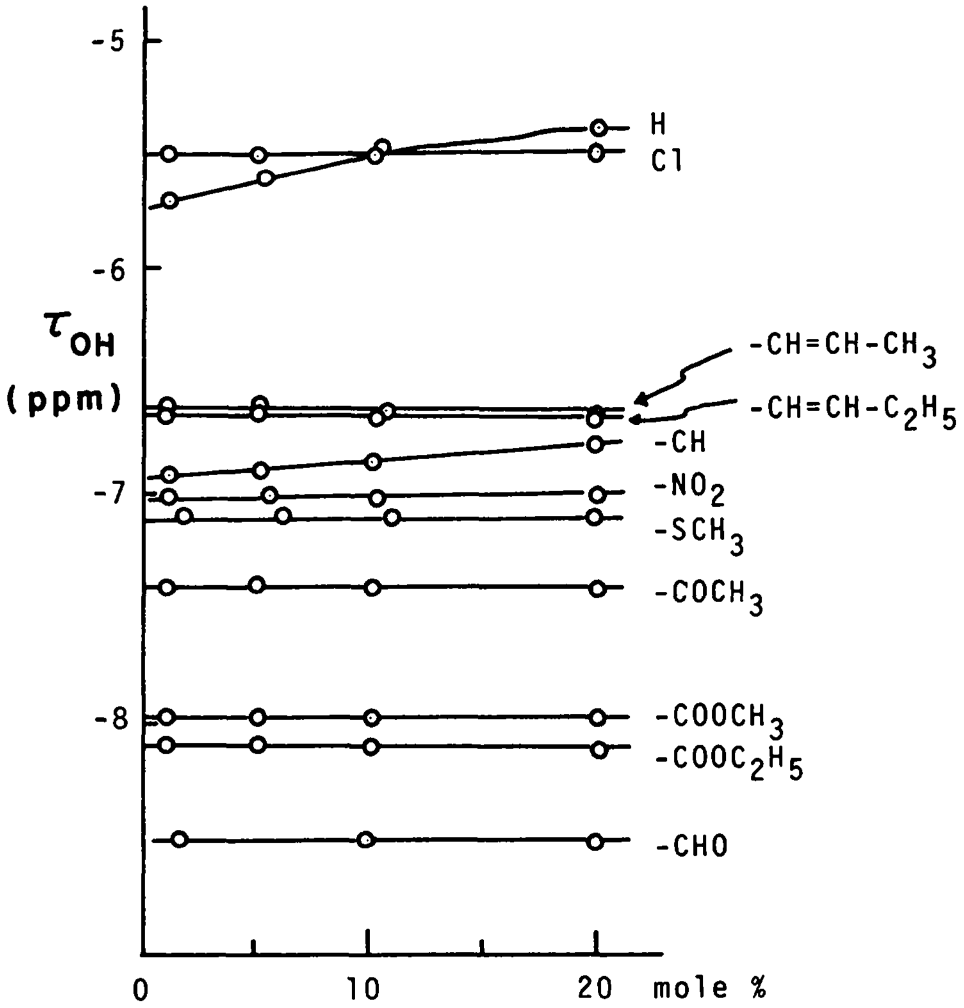


FIG 1. Chemical shift (τ_{OH}) of the OH proton as a function of the concentration of 3-substituted-2,4-pentanediones in CCl_4.

TABLE 3. PARAMETERS USED IN THE HMO CALCULATIONS[18,19]

Coulomb integrals	Resonance integrals	
$\alpha_{=O} = \alpha_C + 1{\cdot}2\,\beta_{CC}$	$\beta_{C=O} = 2\beta_{CC}$	$\beta_{-N=C} = \beta_{CC}$
$\alpha_{-O-} = \alpha_C + 2\,\beta_{CC}$	$\beta_{C-O} = 0{\cdot}9\,\beta_{CC}$	
$\alpha_{-N=} = \alpha_C + 1{\cdot}5\,\beta_{CC}$		
$\alpha_{-N<} = \alpha_C + 0{\cdot}5\,\beta_{CC}$	$\beta_{N-O} = 0{\cdot}8\,\beta_{CC}$	
$\alpha_{Cl} = \alpha_C + 1{\cdot}8\,\beta_{CC}$	$\beta_{C-Cl} = 0{\cdot}4\,\beta_{CC}$	

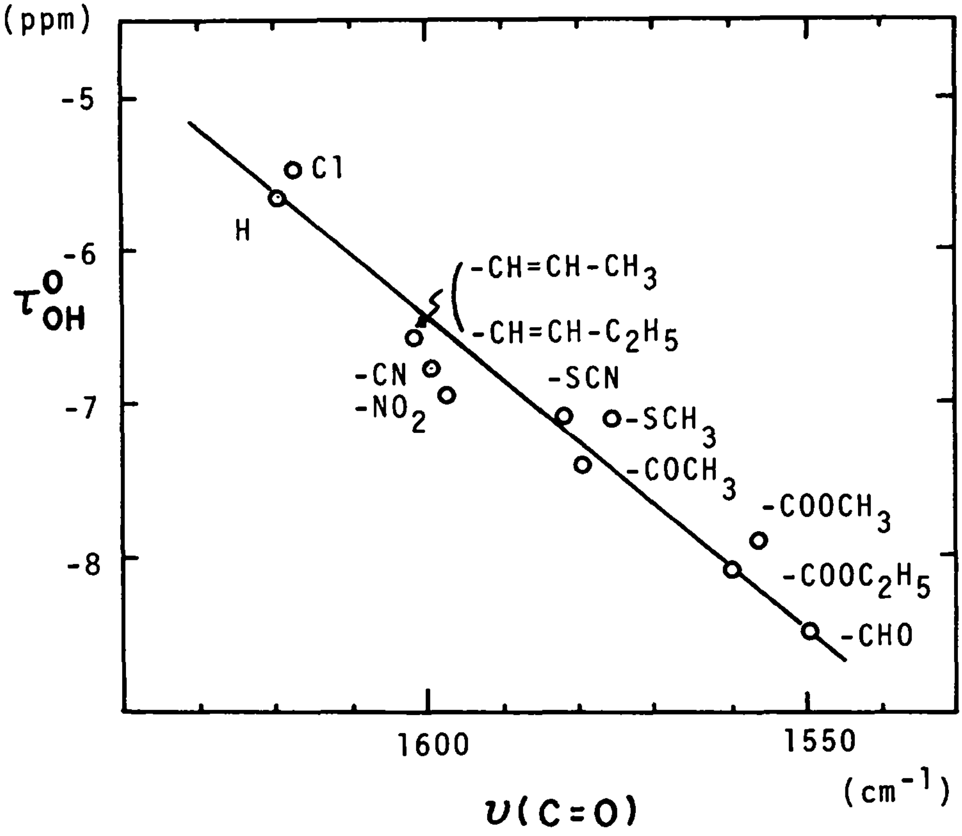
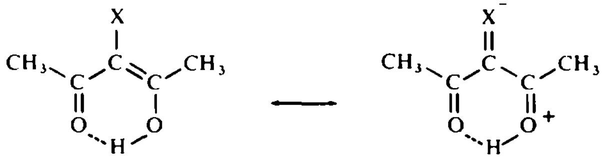


FIG 2. Plot of chemical shift (τ°_{OH}) of OH proton at infinite dilution against C=O stretching frequency.

Since the mesomeric effect is rather important than the inductive effect as mentioned above, a Hückel Molecular Orbital calculation has been attempted to elucidate this conjugated π-system. The parameters used here are summarized in Table 3. The results of the calculations may support the above interpretation. A linear relationship exists between the π-electron densities of the enolic oxygen and the chemical shifts of the OH protons as shown in Fig 3. In our previous work, the out-of-plane deformation of the O—D (π_{OD}) can be related to the double bond character of the C—O being evaluated from the extent of delocalization of the π-electrons of the enolic ring.[20] The vibration of π_{O-D} can be expressed as a torsion about the C—O bond. A parallelism has also been found between τ°_{OH} and the π-bond order of the C—O bond (Fig 3). This suggests that the intramolecular hydrogen bond is strongly associated with π-conjugation of the enolic ring.

Consequently, mesomeric effects through the enolic ring cause migration of the π-electron from the —OH to the substituent group resulting in a decrease of diamagnetic shielding of the enolic hydrogen nucleus by its own electron. The decrease of the charge density on the O—H oxygen bring the enolic proton at equilibrium to closer proximity with the C=O oxygen. The ionic structure **B** may contribute a stabilization of the enolic ring in the ground state.



A B

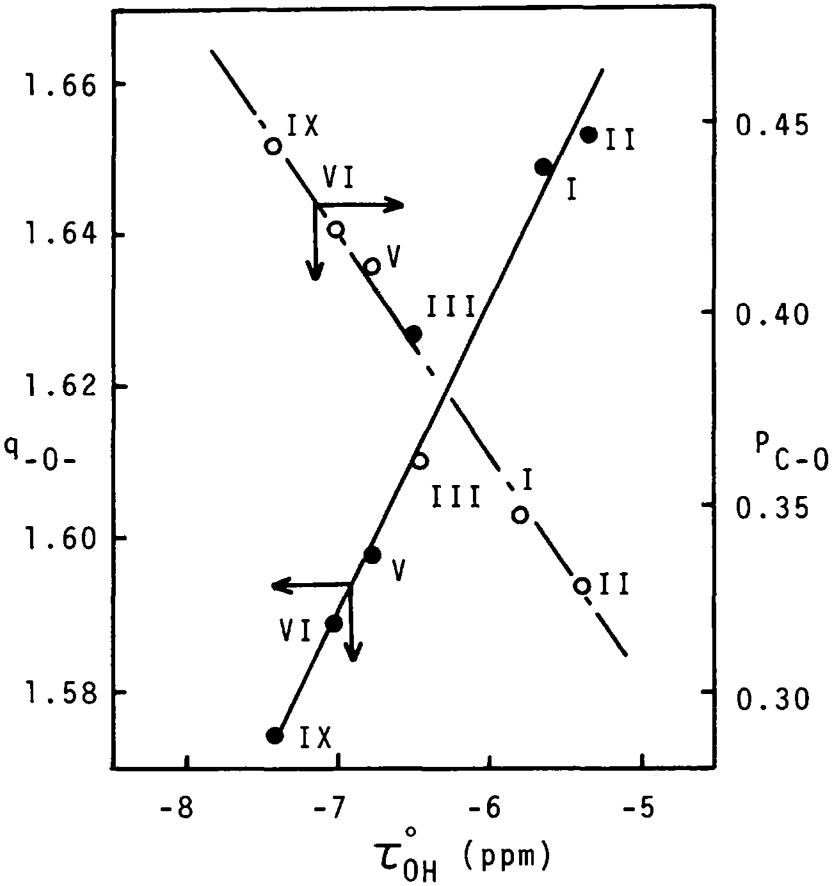


FIG 3. Correlation of τ°_{OH} with electron density at enol oxygen (q_{-O-}) and π-bond order of the C—O (P_{C-O}).

EXPERIMENTAL

A Preparation of compounds

3-Nitro-2,4-pentanedione VI. Bis-(3-nitro-2,4-pentanediono)-Cu(II) was prepared according to the method of Collman *et al.*[21] The finely pulverized complex (15·0 g) suspended in 150 ml of $CHCl_3$ was shaken with 150 g of EDTA diammonium dissolved in 150 ml of water, until the green colour of the $CHCl_3$ layer disappeared. The $CHCl_3$ soln was washed with a small amount of water and dried over anhyd Na_2SO_4. After removing $CHCl_3$, distillation gave 12·2 g (87·7 %) of diketone as a pale yellow liquid; b.p. 72·5–73·0° (8 mm). (Found: C, 41·39; H, 4·99; N, 9·75 Mol. wt. by mass spectrum 145. $C_5H_7O_4N$ requires: C, 41·39; H, 4·86; N, 9·65%, M.W. 145) Collman *et al*[21] have reported that hydrolysis of bis-(3-nitro-2,4-pentanediono)-Cu(II) with a mineral acid yields an intractable oily material. We have followed their procedure and isolated colourless crystals, confirmed as nitroacetone; m.p. 46·3° (lit[22] 46·5°).

3-Methylthio-2,4-pentanedione **VIII**. A soln of methylmercaptane (7·5 g) in MeOH (20 ml) was added dropwise to the stirred mixture of **II** (19·0 g) and pyridine (12·0 g) at 0°. The reaction mixture was further stirred for 2 hr at room temp. After MeOH was removed under vacuum, pyridine hydrochloride crystallized from the soln was removed by filtration. CCl_4 (100 ml) was added to the filtrates.

The CCl_4 soln was separated from solid material, washed with water, and dried over anhyd Na_2SO_4 overnight. The distillation gave a pale yellow liquid (4·6 g), b.p. 75·0–75·7° (16 mm). (Found: C, 49·45; H, 6·80; S, 22·21 M.W by mass spectrum 146. $C_6H_{10}O_2S$ requires: C, 49·31; H, 6·85; S, 21·92%, M W. 146).

The other β-diketones were prepared according to the methods listed in Table 1. Acetylacetone was as commercially available and was purified by distillation under N_2.

B Spectral measurements

Proton magnetic resonance spectra in CCl_4 soln were recorded on a Jeolco JNM SH-60 spectrometer using TMS as an internal reference. Concentration was changed from approx 20% to approx 1% at 25°. A Jasco DS-402G spectrophotometer was used to obtain the infrared spectra (4000–800 cm^{-1}) in CCl_4 at 25°. Mass spectra were obtained with a Hitachi Model RMS-4 mass spectrometer.

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