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EFFECT OF HYDROGEN BONDING ON THE ROTATIONAL BARRIERS OF PARTIAL DOUBLE BONDS—I

2,6-DIFORMYLPHENOLS

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Abstract—Variable temperature PMR spectra of 2,6-diformylphenols were measured, and the rotational barrier heights around the C_{Ar}—C_{Formyl} bonds were determined to be 10·9 kcal/mole for the *p*-Me derivative and 11·1 kcal/mole for the *p*-Me derivative and 11·1 kcal/mole for the *p*-Cl derivative. The difference between the above values and the barrier height of *ortho*-unsubstituted benzaldehydes are *a priori* attributed to the intramolecular O—H—O=C hydrogen bond energies. A brief discussion on these values is given.

The intramolecular H-bond is formed between the OH and CO groups if the two groups are suitably situated in the molecule. And the intramolecular H-bond of this type has been extensively investigated by IR, UV and NMR spectroscopy and also by dipole moment measurement.[1] However, the H-bond energies of the O--H—O=C intramolecular H-bonding are not clearly known.

The coplanar conformations of the formyl groups of 2,6-diformylphenols are stabilized by the intramolecular H-bonding in addition to the energy of conjugation common with the benzaldehydes without H-bonds. Thus, the rotational barrier of the formyl groups in these aldehydes should be higher than those of the normal benzaldehydes. The difference in potential barrier heights can be related to the intramolecular H-bond energies, even if there remain some ambiguity arising from the uncertainty in the conformation of the transition state of the internal rotation.

In order to decide the rotational barrier height of the formyl group which participates in the intramolecular H-bond the PMR spectra of 2,6-diformylphenols were measured at various temperatures, and compared with the results previously reported on *p*-substituted benzaldehydes.[2]

RESULTS AND DISCUSSION

4-Substituted 2,6-diformylphenols were prepared and their PMR spectra were determined at various temperatures between the room temperature and − 73° in chloroform-d. Some typical spectra were illustrated in Fig 1 for *p*-Me derivative. The spectrum of the *p*-Me derivative at room temperature consists of four singlet peaks (2·37, 7·65, 10·02 and 11·28 ppm from the TMS signal) which can be assigned, in the order of decreasing field, to the three Me protons, the two ring protons, the two formyl protons and the OH proton. The three singlets at 7·78, 10·01 and 11·36

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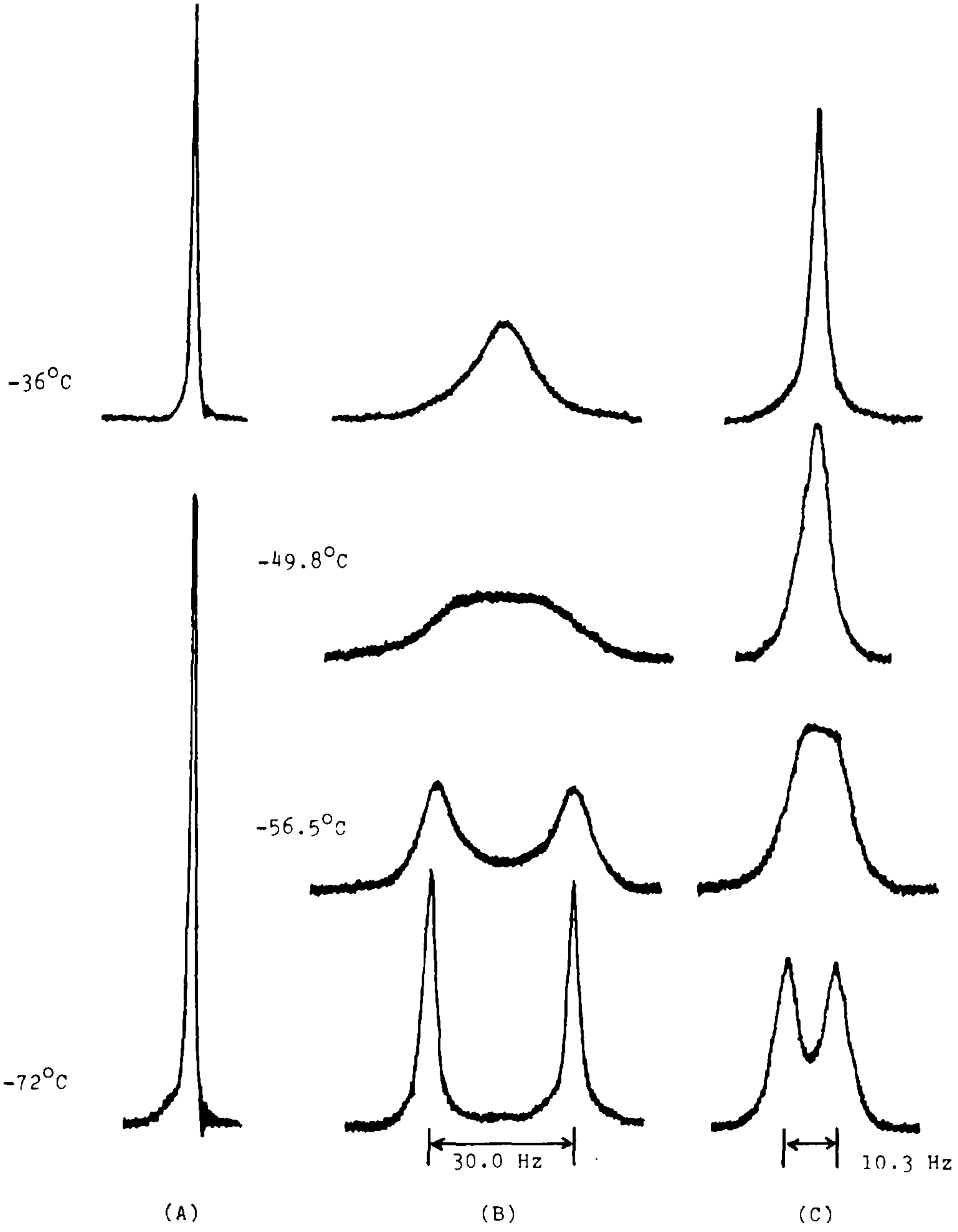
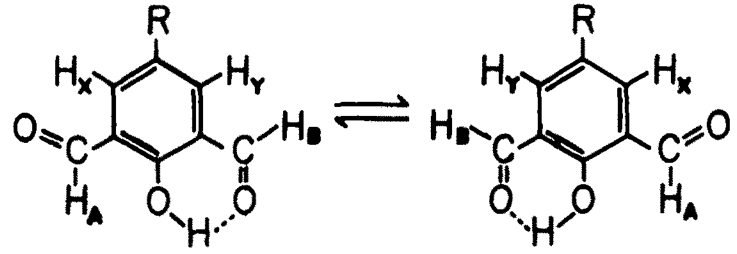


Fig 1. The proton magnetic resonance spectra at 60 MHz of 2,6-diformyl-4-methylphenol at various temperatures. (A) hydroxyl proton, (B) formyl protons and (C) protons on the aromatic ring.

ppm of the *p*-chloro derivative are also assigned to the ring protons, the formyl protons and the OH proton, respectively. Thus, the proton signals of the two formyl protons (designated by H_A and H_B in formula (1)) and the two ring protons (designated by H_X and H_Y in formula (1)) were both observed as two singlets at higher



temperatures because of the rather fast rotation of both formyl groups. As the temperature decreases, the half life of a planar confrontation becomes longer until the two formyl protons (H_A and H_B) and the two ring protons (H_X and H_Y) can be identified individually by PMR. Thus, the two singlets gradually split into the two doublets as shown by the spectra b, c and d in Fig 1.

By the analysis of the line shapes of these signals, the exchange rate constants at various temperatures were estimated using some well established methods previously reported. Here, the peak separation measurement,[3] the peak intensity ratio measurement,[4] the Takeda and Stejskal's method[5] and the line shape simulation method[6] were employed and compared. The exchange rate constant k and the half life τ obtained by the analysis were tabulated in Table 1. The log k *vs* $1/T$ plots give the activation parameters shown in Table 2 (where T is the absolute temp). The activation energy values E_a calculated from the half life values of formyl protons by the different methods coincide each other within experimental errors and concluded to be 10·9 ± 1·0 kcal/mole for *p*-methyl derivative and 11·1 ± 1·0 kcal/mole for *p*-chloro derivative by averaging these values. The other thermodynamic quantities of activation derived from these values were listed in Table 3.

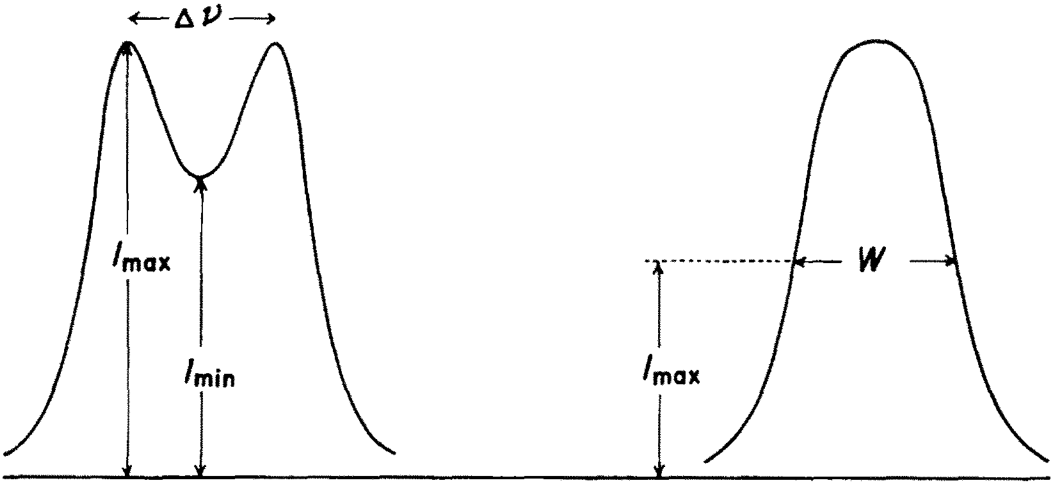


FIG. 2

The activation energy value can be assumed roughly the sum of the rotational barrier of benzaldehyde and the additional stabilization energy caused by the intramolecular H-bond. The rotational barrier of the formyl group in benzaldehyde can

TABLE 1. RATE CONSTANTS k AND HALF-LIFE VALUES τ FROM THE LINE SHAPES OF THE PROTON SIGNALS OF THE FORMYL GROUPS AT VARIOUS TEMPERATURES

Temperature (°C)	Peak separation* $\Delta\nu$ (Hz)	Peak intensity* ratio, I_{max}/I_{min}	Half width* W (Hz)	Half life† τ (10^{-2} sec)	Rate constant† k (sec^{-1})
(a) 4-*Methyl-2,6-diformylphenol*					
−32·5			5·70	[0·37]	[274]
−39·0			7·95	[0·50]	[202]
−40·5			13·87	[0·79]	[126]
−45·0			21·25	[1·08]	[92·4]
−49·0			27·75	[1·33]	[75·4]
−49·3			29·62	[1·40]	[71·6]
−49·8 = T_c			30·25	[1·54]	[65·0]
−50·0	13·5			1·68	59·5
−50·8	17·3	1·07		1·84 (1·74)	54·3 (57·4)
−55·2	25·5	1·67		2·86 (2·48)	35·0 (40·3)
−58·2	28·9	4·64		4·27 (4·43)	23·4 (22·5)
−62·0	29·6	13·3		5·59 (7·7)	17·9 (13·0)
−66·7	29·8			9·62	10·4
−73	30·0 = $\nu_A - \nu_B$				
(b) 4-*Chloro-2,6-diformylphenol*					
−26·5			3·60	[0·28]	[356]
−28·5			5·70	[0·43]	[230]
−31·0			6·75	[0·51]	[197]
−34·5			7·65	[0·57]	[174]
−38·2			12·9	[0·87]	[115]
−41·2			20·9	[1·22]	[82·0]
−43·2 = T_c			28·4	[1·58]	[63·2]
−45·5	21·0	1·32		2·23 (2·11)	44·8 (47·5)
−47·2	25·0	2·06		3·24 (2·99)	30·9 (33·5)
−48·8	25·3	2·12		3·31 (3·04)	30·2 (32·9)
−50·5	27·0	4·25		4·93 (4·48)	20·3 (22·3)
−52·5	27·5	5·70		6·25 (5·26)	16·0 (19·0)
−54·5	27·9	7·13		8·40 (5·88)	11·9 (17·0)
−56·5	28·31				
−66·0	28·35 = $\nu_A - \nu_B$				

* These quantities are defined as shown in Fig. 2. A: below the coalescence temperature. B: above the coalescence temperature.

† The half life and the rate constant from the measurement of the peak separation. Those from the intensity ratio value and from the half width value above the coalescence temperature are also tabulated in ( ) and in [ ], respectively.

TABLE 2. THE ENERGIES OF ACTIVATION FROM THE $\log_{10}k$ *vs* $1/T$ PLOTS OF THE RATE CONSTANTS OBTAINED BY VARIOUS METHODS

Compound	Energy of activation (kcal/mole) from $\Delta\nu$	 from I_{max}/I_{min}	 from W
4-Methyl	11·33 ± 1·0	11·24 ± 1·0	10·15 ± 1·0
4-Chloro	11·70 ± 1·0	10·74 ± 1·0	10·97 ± 1·0

TABLE 3. ACTIVATION ENTHALPIES AND ENTROPIES FOR THE RESTRICTED ROTATION ABOUT THE C_{Ar}—C_{Formyl} BONDS OF 2,6-DIFORMYLPHENOLS

Compound	T_c(CHO) (°K)	ΔF^* (kcal/mole)	E_a (kcal/mole)	ΔH^* (kcal/mole)	ΔS^* (e.u.)
Methyl	223·4	11·3 ± 0·1	10·9 ± 1·0	10·5 ± 1·0	−3·6 ± 2·0
Chloro	230·0	11·5 ± 0·1	11·1 ± 1·0	10·7 ± 1·0	−3·5 ± 2·0

regard *a priori* as the increase in resonance energy caused by the conjugation between the aromatic ring and the CO group, and determined experimentally to be 7·9 ± 1·0 kcal/mole by Anet *et al.*[2] The barrier height of the *p*-Me and *p*-Cl derivatives of 2,6-diformylphenol are nearly the same values and the difference from the unsubstituted benzaldehyde is 3·4–3·6 kcal/mole, which is attributable to the stabilization energy caused by the H-bond. The O—H···O=C intermolecular H-bond energies of phenols to oxygen acceptors were determined with a series of phenol-carboxylic ester-inert solvent ternary systems and the estimated enthalpies of H-bond formation varies from 3·3 to 6·7 kcal/mole[7] depending upon the structures of the donors and acceptors and to the solvent polarity. The H-bond energy obtained in this investigation is somewhat smaller than that expected from the higher stability of the chelated forms of *o*-hydroxyphenyl-carbonyl compounds concluded from the IR and NMR studies.[8] The smaller values may be justified by the remaining conjugation in the transition state and by the polarity of the solvent used.

The coalescence in the aromatic protons (H_X and H_Y) also gives activation parameters nearly equal with those obtained from the formyl protons, but the non-equivalent H_X and H_Y protons should give an AB quartet signal because of the small spin–spin coupling between the two nuclei. Thus, the analysis of the temperature dependent spectra becomes more complicated.

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