

THE C-H...O and C-H...N INTRAMOLECULAR HYDROGEN BONDS IN  
BETAINEALDEHYDES OF AZOLES CONTAINING THE PYRIDINIUM CATION

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UDC 547.821.3'789.3'783.  
04:543.422.25

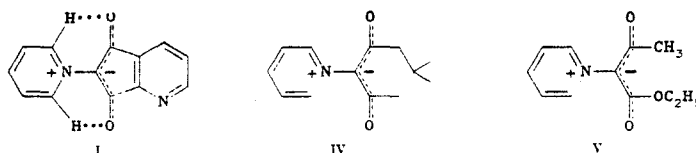
The comparison of the values of the chemical shifts of the pyridinium protons in the ylides of  $\beta$ -dicarbonyl compounds and in betainealdehydes of thiazole and imidazole established the presence of the intramolecular C-H...O and C-H...N hydrogen bond between the  $\alpha$ -protons of the pyridinium and the oxygen atoms of the formyl group and the nitrogen of the amide fragment in the anionoid part of the betaine. The conclusion was confirmed by the varying influence of the effects of protonation on the character of the deshielding of the  $\alpha$ - and  $\gamma$ -protons.

The hydrogen bonds of the C-H...O and C-H...N type pertain to the most studied group, whereby the intermolecular hydrogen bonds (InterMHBS) were chiefly investigated. At the same time, there are individual communications on the investigations of intramolecular hydrogen bonds (IntraMHBS).

As is known [1] (p. 197), the weak interaction may arise between the acceptor and the CH group attached to the ammonium nitrogen atom. Such C-H...O bonds with distances of 3.2-3.3 Å are observed in the crystals of aminoacids and peptides [2]. The possible role of the C-H...O-C interactions, influencing the intra-layer packing of the carboxylic acids and amides in the crystalline state, was considered in the review [3].

In the series of internal organic salts, the formation of IntraMHBS between the  $\alpha$ -protons of the pyridinium cation and the oxygen atoms of the anionoid part in the betaines (ylides) of 2-(N-pyridinium)-1,3-indandiones (I) in the crystalline state [4] and solutions [5] was previously shown in the works of Neiland and coauthors.

A comparative study of the values of the chemical shifts of the pyridinium protons in the indicated ylides and model compounds [ylides of 1,3-cyclohexanedione (IV) and acetoacetic ester (V)] was carried out to confirm the presence of the IntraMHBS in the ylides of (I) by the authors [5] using the method of PMR spectroscopy. It should be expected that when the IntraMHBS are formed, the signals of the protons participating in the formation of the H-bond with electron-donors containing an unshared electron pair should appear at lower fields than in the case of the compounds of close structure but lacking the IntraMHBS [6] (p. 5), [7] (p. 506)]. Such a marked paramagnetic shift ( $\Delta H_1 = 0.94...1.26$  ppm in  $\text{CDCl}_3$  and  $0.36...0.94$  ppm in  $\text{DMSO-D}_6$ ) of the signals of the pyridinium  $\alpha$ -protons in the ylides of the type (I) by comparison with the data for the model ylides (IV) and (V) indicates in favor of the IntraMHBS (Table 1).



Having taken the data of the work [5] as a basis, we examined the possible existence of the IntraMHBS in the betainealdehydes (II) and (III), the synthesis of which was previously described by us [8]. If there are no doubts on the possible formation of the intramolecular H-bond in the ylide (I), first of all due to structural factors [4] (the molecule is almost

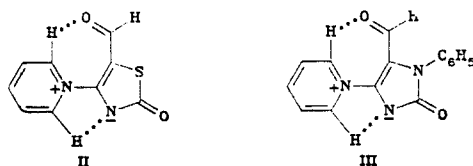
Institute of Physico-organic Chemistry and Carbon Chemistry, Academy of Sciences of the Ukrainian SSR, Donetsk 340114. Translated from *Khimiya Geterotsiklicheskikh Soedinenii*, No. 5, pp. 626-628, May, 1989. Original article submitted July 23, 1987; revision submitted February 25, 1988.

TABLE 1. Chemical Shifts of the Protons of the Pyridinium Cation in Betainealdehydes of the Azoles (II) and (III) and the Ylides of  $\beta$ -Dicarbonyl Compounds (I), (IV), and (V)

| Compound | Solvent              | $\delta$ , ppm* |          |      | $\Delta H_{rel} = \sigma(\alpha_H) - \sigma(\gamma_H)$ |
|----------|----------------------|-----------------|----------|------|--|
|          |                      | 2-H, 6-H        | 3-H, 5-H | 4-H  |  |
| I        | DMSO-D <sub>6</sub>  | 9,73            | 8,16     | 8,36 | 1,37   |
| II       | DMSO-D <sub>6</sub>  | 9,58            | 8,30     | 8,84 | 0,74   |
|          | CF <sub>3</sub> COOH | 9,32            | 8,47     | 9,05 | 0,27   |
| III      | DMSO-D <sub>6</sub>  | 9,50            | 8,35     | 8,75 | 0,75   |
|          | CF <sub>3</sub> COOH | 9,15            | 8,31     | 8,83 | 0,32   |
| IV       | DMSO-D <sub>6</sub>  | 8,62            | 7,97     | 8,40 | 0,22   |
| V        | DMSO-D <sub>6</sub>  | 8,67            | 7,97     | 8,47 | 0,20   |

\*The values of the chemical shifts are indicated relative to TMS.

coplanar), then this did not seem evident for the betaines (II) and (III) since the formation of such IntraMHBs in them is possible under the condition of finishing the structure together with the flat five-membered ring with the participation of the nitrogen atom of the amide fragment, the "non-classical" seven-membered ring involving the oxygen of the aldehyde group. However, as Pimentel showed [9], the optimal linear configuration is not a necessary condition for the formation of the IntraMHBs, and is not achieved in the majority of cases.



Taking into consideration the structural differences of ylides and betaines, the observed paramagnetic shift of the signals of the 2-H and 6-H pyridinium protons in the betaines (II) and (III) (Table 1), by analogy with the ylide (I) and in contrast to the model compounds (IV) and (V) [the  $\Delta H_i(\alpha)$  are equal to 0.96 and 0.88 ppm correspondingly by comparison with the ylide (IV) and 0.91 and 0.83 ppm by comparison with the ylide (V)], can be explained not by the formation of the IntraMHBs but by the stronger electron-acceptor influence of the anionoid portion in the betaines; this should lead to the deshielding of the  $\alpha$ -protons also caused by the presence of the IntraMHBs. The breaking of the IntraMHBs should be expected when the anionoid portion in the betaines (II) and (III) is protonated (the spectrum in CF<sub>3</sub>COOH). Consequently, the shift of the signals of the pyridinium  $\alpha$ -protons to high magnetic field should also be expected; this also in fact occurs. On the other hand, the resonance of the  $\beta$ - and  $\gamma$ -protons, which do not participate in the forming of the IntraMHBs, appears at lower fields, and is therefore characterized by the increased (by the action of protonation) electron-acceptor influence of the azole part on the deshielding of the indicated protons.

Attention is also drawn to the fact that the difference in the values of the chemical shifts of the  $\alpha$ - and  $\gamma$ -protons, conditionally designated by us as  $\Delta H_{rel}$ , differs significantly for the compounds having the hydrogen bond (I)-(III) and the compounds lacking the hydrogen bond (IV), (V). When the betaine (II) is protonated, the  $\Delta H_{rel}$  (0.27 ppm) approximates in value to the  $\Delta H_{rel}$  for the compounds (IV) and (V) (0.22 and 0.20 ppm correspondingly) without the IntraMHBs; this may be a unique test for the determination of the intramolecular H-bond in ylides and betaines. The differences in the values of the  $\Delta H_{rel}$  in the case of the ylide (I) and the betaines (II) and (III) are evidently determined to a significant extent not by the higher stability of the IntraMHBs in the ylide (I), but by the shielding of the pyridinium  $\gamma$ -protons on account of the delocalization of the negative charge in the ylide with the participation of the C(4) atom of the pyridine ring. However, the quantitative parameters of the IntraMHBs require further study.

## EXPERIMENTAL

The spectra of the compounds (II) and (III) were recorded on the BS-487C (80 MHz) spectrometer. The concentration of the solutions was  $1 \cdot 10^{-1}$  M. The internal standard was TMS.

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## INFRARED ABSORPTION OF 4,5-DIHYDROINDENO[1,2-b]PYRIDINES

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UDC 547.828'665:543.422.4

Individual Infrared spectroscopic absorption bands in the double bond region have been assigned to specific, nonequivalent  $\beta$ -ketoenamine structural fragments, i.e., to atomic groups in which the carbonyl is included in a cyclic oxoindenodihydropyridine system or to a ketoenamine group with a nonrigid carbonyl-containing substituent.

There are literature reports [1, 2] of the IR spectra of 4,5-dihydroindeno[1,2-b]-pyridines with different electron accepting  $\beta$ -substituents (I), the interpretation of the individual bands in the double bond region being particularly difficult [1]. The same also relates to the IR spectra of acyclic  $\beta$ -ketoenamine compounds [3].

The aim of this study was to assign the absorption bands in the double bond region of the IR spectra to specific nonequivalent  $\beta$ -ketoenamine structural fragments, i.e., to  $\text{NC}=\text{C}=\text{O}$  atomic groups in which the carbonyl group is included in a cyclic oxoindenodihydropyridine system or to ketoenamine groups with a nonrigid  $\beta$ -carbonyl substituent (see next page).

A comparison was made of the IR spectra of the 4,5-dihydroindeno[1,2-b]pyridines Ia-l and of their oxidized forms IIa-d with a change in the carbethoxy group  $\beta$ -substituent of oxygen for sulfur or the cyclic oxo group for sulfonyl or thiocarbonyl (Table 1).

For substances of type I or II there was carried out a) a progressive elimination of individual structural elements, b) comparison of the spectral characteristics of oxygen containing 5-oxo-4,5-dihydroindeno[1,2-b]pyridine esters (Ia, b), thio (I, II d, e, h) or thione

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