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.

LITERATURE CITED

1. H. Ratajczak and W. J. Orville-Thomas, Molecular Interactions [Russian translation], Mir, Moscow (1984).
2. L. Leiserowitz, Acta Cryst., 32, 775 (1976).
3. R. E. Marsh, S. Ramacumar, and K. Vencatasan, Acta Cryst., 22, 66 (1976).
4. V. F. Kaminskii, R. P. Shibaeva, and O. Ya. Neiland, Zh. Strukt. Khim., 17, 898 (1976).
5. O. Ya. Neiland, R. B. Kampare, D. É. Prikule, and É. É. Liepin'sh, Khim. Geterotsikl. Soedin., No. 3, 379 (1979).
6. I. P. Gragerov, V. K. Pogorelyi, and I. F. Franchuk, The Hydrogen Bond and Rapid Proton Exchange [in Russian], Nauk. Dumka, Kiev (1978).
7. J. W. Emsley, J. Feeny, and L. Sutcliffe, High Resolution NMR Spectroscopy [Russian translation], Vol. 1, Mir, Moscow (1968).
8. R. O. Kochkanyan, A. N. Zaritovskii, G. I. Belova, and S. N. Baranov, Khim. Geterotsikl. Soedin., No. 2, 278 (1975).
9. G. C. Pimentel and A. L. McClellan, The Hydrogen Bond [Russian translation], Mir, Moscow (1964), p. 462.

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

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Individual Infrared spectroscopic absorption bands in the double bond region have been assigned to specific, nonequivalent β-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 β-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 acylic β-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 β-ketoenamine structural fragments, i.e., to NC=C–C=O atomic groups in which the carbonyl group is included in a cyclic oxoindenodihydropyridine system or to ketoenamine groups with a nonrigid β-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 β-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, IId, e, h) or thione

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TABLE 1. IR Spectra and Integrated Intensities of Absorption Bands near 6μ in Dihydroindenopyridines Ia-l, III, and Indenopyridines IIa-d

Compound	ν, cm^{-1}		A, practical units	ΣA, practical units
	in Vaseline mull	in $CHCl_3$		
Ia	1704, 1670, 1634	1691, 1651	6,23; 1,94	8,18
Ib	1696, 1670, 1637	1690, 1652	6,26; 1,64	7,90
Ic*	1670, 1631	1693, 1647	2,40; 2,10	4,60
Id	1673, 1646, 1634	1695, 1648	3,10; 2,49	7,39
Ie	1678, 1650, 1640	1694, 1650	2,68; 4,70	7,38
If	1676, 1632	1700, 1640	4,02; 1,80	5,82
Ig	1675, 1625	1685, 1634	3,10; 2,71	5,81
Ih	1677, 1641, 1623 sh	1687, 1646	3,00; 5,10	8,10
Ij	1697, 1662	1695, 1667	3,90; 0,50	4,40
Ik*	1696, 1661	1695, 1668	3,80; 0,40	4,20
Iℓ*	1660, 1639	—		
	1660, 1603	—		
IIa	1720	1720	8,00; 7,20	8,00
IIb	1733, 1717	1725		7,20
IIc	1720, 1665	1720, 1666	3,23; 3,20	6,46
IId	1724, 1668	1725, 1668	3,22; 3,38	6,60
III	—	1677, 1627	2,40; 0,70	3,10

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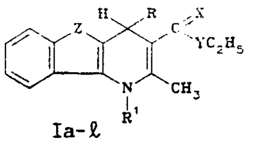
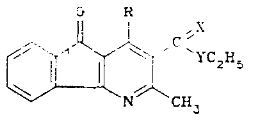
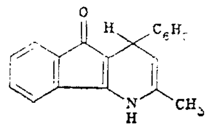
*Insufficiently soluble in chloroform.



Ia-ℓ



IIa-d



III

Compound	R	R^1	X	Y	Z
Ia	C_6H_5	H	O	O	C=O
Ib	$C_6H_3(OCH_3)_2$-2,3	H	O	O	C=O
Ic	C_6H_5	H	S	O	C=O
Id	C_6H_5	H	O	S	C=O
Ie	$C_6H_3(OCH_3)_2$-2,3	H	O	S	C=O
If	C_6H_5	H	O	O	C=S
Ig	C_6H_5	CH_3	S	O	C=O
Ih	C_6H_5	CH_3	O	S	C=O
Ii	$C_6H_4OCH_3$-4	H	O	O	SO_2
Ij	$C_6H_3(OCH_3)_2$-2,3	H	O	O	SO_2
Ik	C_6H_5	H	O	S	SO_2
Iℓ	C_6H_5	H	S	O	SO_2
IIa	C_6H_5		O	O	
IIb	$C_6H_3(OCH_3)_2$-2,3		O	O	
IIc	C_6H_5		O	S	
	$C_6H_3(OCH_3)_2$-2,3		O	S	

(Ic, g) esters, and c) exchange of the oxo group in the cyclic fragment for sulfonyl (Ii-ℓ) and thiocarbonyl (If). Through these it has been shown that solid state Ia-e,g,h have two absorption bands near 1640 and 1670 cm^{-1} (Table 1, Fig. 1) attributable to the oxoindenodihydropyridine fragment.

The β-ketoenamine structural fragment with a carbethoxy substituent (Ia,b) gives rise to a band near 1700 cm^{-1}. By contrast the thiol esters Id,e show this band at approximately 1650 cm^{-1} in agreement with the lowering of carbonyl frequencies when thiol esters are compared with their oxygen analogs [4-6]. Thione esters have only absorptions for the oxoindenodihydropyridine fragment at 1630 and 1670 cm^{-1} (Figs. 1 and 2). The cyclic benzosulfonyldihydropyridines residue is responsible for absorption in the region 1660-1670 cm^{-1} and solid If has a band at 1676 cm^{-1} in agreement with [7].

A shift (Table 1, Figs. 2 and 3) is observed in both absorption bands of the cyclic oxoindenodihydropyridine fragment to 1650 and 1690 cm^{-1} in chloroform solution with an integrated intensity of about two practical units (see Experimental) for each band. The

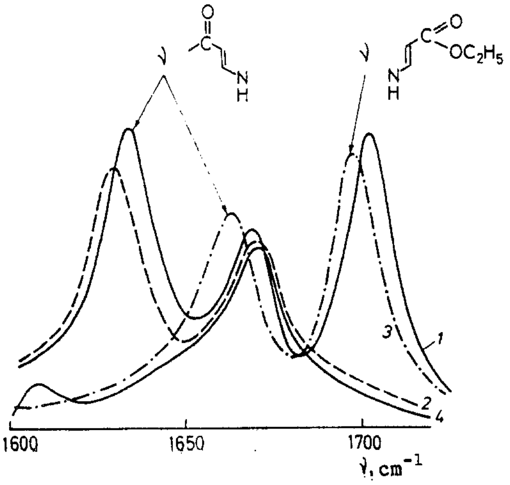


Fig. 1

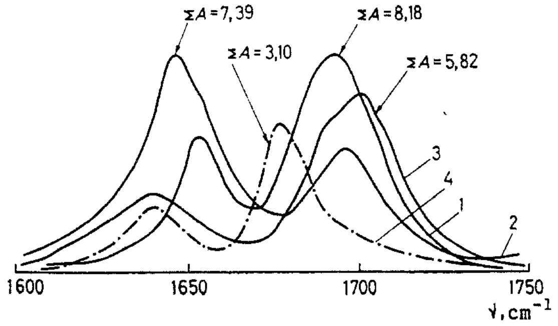


Fig. 2

Fig. 1. IR spectra in the double bond region for dihydroindenopyridines I in Vaseline mull: 1 = Ia, 2 = Ic, 3 = Ii, 4 = Iℓ.

Fig. 2. Integrated intensities for the carbonyl group absorptions in the dihydroindenopyridines I and III in chloroform: 1 = Ia, 2 = Id, 3 = If, 4 = III.

ketoenamine fragment with the carbethoxy substituent gives rise to the 1690 cm^{-1} absorption with integrated intensity about four units. This maximum is combined with the high frequency absorption of the cyclic fragment to form one intense maximum of intensity approximately six units (Figs. 2, 3).

For the thiol esters Id, Ie the maximum absorption for the ketoenamine fragment with an (ethylthio)carbonyl group is at 1650 cm^{-1} (Fig. 2) and coincides with the low frequency absorption of the cyclic fragment.

The β-unsubstituted III has absorption maxima at 1627 and 1677 cm^{-1} which is basically assigned to the cyclic ketoenamine fragment but If absorbs at 1700 cm^{-1} with A = 4.02 units which is assigned to the ketoenamine fragment with a carbethoxy group.

Measurements of the integral intensities of the IR maxima for Ia-j, IIa-d, and III confirm their assignment to the corresponding structural elements.

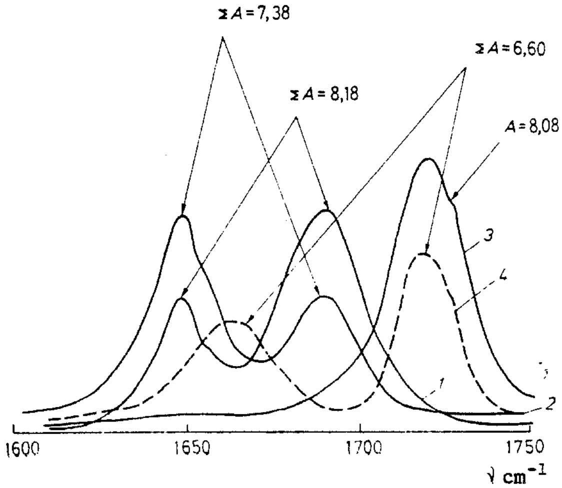


Fig. 3. Integrated intensities for the carbonyl group absorptions in the dihydroindenopyridines I and their oxidized analogs II in chloroform: 1 = Ia, 2 = Id, 3 = IIa, 4 = IIc.

Comparison of the integral intensities of the oxidized forms of the oxygen esters IIa,b shows that the absorption bands of the carbonyl groups coincide and appear as a single intense maximum at 1720 and 1725 cm^{-1} correspondingly with A = 8.0 and 7.2 units (Table 1, Fig. 3). By contrast, the thiol esters IIc and IId have carbonyl bands for $-COSC_2H_5$ at 1665 cm^{-1} and a separate oxo group maximum for the cyclic benzoyl group fragment at 1720 and 1725 cm^{-1} correspondingly with A = 3.22 practical units.

Thus the dihydroindenopyridines examined preserve an approximately additive relationship for the integral intensities of the β-ketoenamine fragments with a dominant contribution from the carbonyl group vibration. The numerical values for the absorption maxima integral intensities of the structural units studied varied between 3.4 and 4.4 practical units.

EXPERIMENTAL

IR Spectra were taken on a Specord 75-IR instrument for suspensions in paraffin mulls and for solutions in chloroform ($2.5-8.0 \times 10^{-3}$ molar, thickness 0.04 cm).

Integral intensities were calculated by the Wilson-Wells method using the corrections described by Ramsay [9] and are reported in practical units (1 practical unit = 10^4 liter·$mole^{-1}$·cm^{-2}).

The starting dihydroindenopyridines Ia-h and indenopyridines IIa-d were obtained by [2, 7, 10], the 1,4-dihydrobenzothieno[3,2-b]pyridine-5,5-dioxides Ii-ℓ by [10, 11] and III by [12].

LITERATURE CITED

1. É. I. Stankevich and G. Ya. Vanag., Zh. Org. Khim., 1, 815 (1965).
2. B. A. Vigante, Ya. Ya. Ozols, and G. Ya. Dubur, Izv. Akad. Nauk Latvian SSSR, Ser. Khim., No. 6, 707 (1980).
3. Ya. F. Freimanis, Chemistry of Enaminoketones, Enaminoimines, and Enaminothiones, Zinatne, Riga (1974).
4. B. A. Vigante, Ya. Ya. Ozols, G. Ya. Dubur, Yu. I. Beilis, E. M. Belash, and V. V. Prezhdo, Khim. Geterotsikl. Soedin., No. 2, 219 (1982).
5. S. Oae, Chemistry of Organic Compounds of Sulfur, Khimiya, Moscow (1975), p. 139.
6. A. W. Baker and G. H. Harris, J. Am. Chem. Soc., 82, 1923 (1952).
7. V. K. Lusis, D. Kh. Mutsenietse, and G. Ya. Dubur, Khim. Geterotsikl. Soedin., No. 5, 709 (1986).
8. S. P. Valtere, Structure and Tautomeric Conversions of β-Dicarbonyl Compounds, Zinatne, Riga (1977), p. 88.
9. D. A. Ramsay, J. Am. Chem. Soc., 74, 72 (1952).
10. B. A. Vigante, Ya. Ya. Ozols, and G. Ya. Dubur, USSR Patent No. 1198067, Byul. Izobr., No. 46, 102 (1985).
11. R. R. Dubure, B. A. Vigante, Ya. Ya. Ozols, and G. Ya. Dubur, Khim, Geterotsikl. Soedin., No. 11, 1563 (1986).
12. E. Ya. Ozola and G. Y. Vanag, Khim. Geterotsikl. Soedin., No. 1, 103 (1969).