INTEGRAL INTENSITIES OF THE IR BANDS OF THE SKELETAL VIBRATIONS OF THE AROMATIC RING IN THE 1480-1630 cm^{-1} REGION OF THE APORPHINE ALKALOIDS AND SOME OF THEIR DEHYDRO DERIVATIVES

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UDC 547.6

We have previously shown that in biphenyl derivatives the ortho effect lowers the integral intensity ($A \cdot 10^4$ $mole^{-1} \cdot liter \cdot cm^{-2}$) in the region mentioned [1]. The aporphine alkaloids with substituents in positions 4 and 5 of rings A and B of the biphenyl system differ in the amplitude of the Cotton ORD curves [2], the positions of the maxima in the UV spectra [3, 4], and the chemical shifts of the signals of the aromatic protons in the NMR spectra [5] from alkaloids in which these positions are free.

It was of interest to study the influence of the nature of the substituents and their spatial arrangement on the magnitude of the integral intensities of the bands of the skeletal vibrations of the aromatic ring in the 1480-1630 cm^{-1} region in the aporphine alkaloids. The results of our measurements of A for nine aporphine alkaloids and two dehydro derivatives are given in Table 1. It can be seen from the table that aporphine alkaloids with substituents in positions 4 and 5 have a smaller integral intensity (compounds 5-13) than 3,6-dimethoxyaporphine [4]. This change in the integral intensity in the region mentioned can obviously be explained by the spatial and electronic interactions of the substituents of rings A and B of the biphenyl system.

In alkaloids with a free position 4 (5-10), the integral intensities depend on the nature of the substituents in ring B. For compounds 6-9, the changes of A_{tot} are within the limits of error of the measurements [$A_{tot} = (4.0\text{–}4.4) \cdot 10^4$ pr. units].

However, the replacement of the two methoxy groups in positions 2 and 3 of ring B by a methylenedioxy group leads to a fall in the total integral intensity. Thus, for example, in glaucine (9), $A_{tot} = 4.1 \cdot 10^4$ pr. units, and in nantenine (10), $A_{tot} = 3.2 \cdot 10^4$ pr. units. The lowest value of A of the bands studied in the 1480-1630 cm^{-1} region, in remerine (5), is explained by the absence of a substituent in ring B (see Table 1).

It is known that biphenyls with OH groups in the ortho positions can form two types of intramolecular hydrogen bonds: with the unshared pair of electrons of the oxygen (OH...O) and with the π electrons of the neighboring aromatic nucleus (OH...π) [6-9].

The changes in the intensities of the bands of compounds (11-13), which form intramolecular hydrogen bonds, are caused by the different natures of the spatial interactions of the 4,5-substituents [in bulbocapnine (12), $A_{tot} = 1.7 \cdot 10^4$ pr. units, and in isocorydine (11) $A_{tot} = 3.0 \cdot 10^4$ pr. units]. These alkaloids also differ by the ν_{OH} frequencies in the region of the stretching vibrations of an associated hydroxy group.

As follows from Table 2, in the region mentioned of the spectrum of isocorydine (11) there is one broad absorption band at about 3250 cm^{-1} which can be assigned to a OH...O interaction [6, 7]. In the spectrum of bulbocapnine (12) there are two absorption bands, at about 3440 and 3540 cm^{-1}.

The low-frequency, broader, absorption band, as in the orthohydroxybiphenyls, corresponds to a OH...O intramolecular association, and the high-frequency, narrower, band to the (OH...π) type of hydrogen bond formed between the OH group of one ring and the π electrons of the adjacent ring [5-9]. The absence

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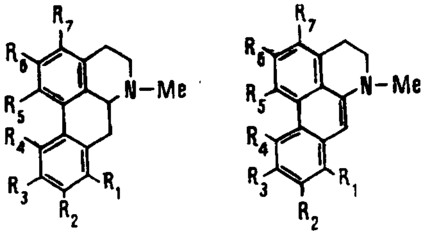
Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR. Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 646-649, September-October, 1973. Original article submitted July 20, 1972.

TABLE 1. Integral Intensities of the IR Bands of the Skeletal Vibrations of the Aromatic Ring in the 1480-1630 cm^{-1} Region of the Aporphine Alkaloids and Some of Their Dehydro Derivative



Compound	ν, cm^{-1}	$A_1 \cdot 10^4$ $mole^{-1} \cdot liter \cdot cm^{-2}$	ν, cm^{-1}	$A_2 \cdot 10^4$ $mole^{-1} \cdot liter \cdot cm^{-2}$	ν, cm^{-1}	$A_3 \cdot 10$ $mole^{-1} \cdot liter \cdot cm^{-2}$	$\Sigma A = A_1 + A_2 + A_3$
Biphenyl (1)	1560	Tr.	1690	0,12	—	—	0,12
Fluorene (2)	—	—	1600	0,11	—	—	0,11
Phenanthrene (3)	—	—	1595	0,16	—	—	0,16
I. Positions 4 and 5 free							
3,6-Dimethoxyaporphine (4) $R_3=R_6=-OCH_3$	1510	2,0	—	—	1585 1610	4,20	6,20
II. Position 4 free							
Remerine (5) $R_5=R_6=-OCH_2-O$	1510	0,70	—	—	1610 1630	0,70	1,40
Thalicmine (6) $R_5=R_6=-O\cdot CH_2-O$ $R_2=R_3=-OCH_3$	1510	2,10	—	—	1610 1630	1,80	3,90
Thalicmidine (7) $R_2=R_3=R_6=$ $-OCH_3 R_5=OH$	1510	1,90	—	—	1615	2,20	4,10
Thalicsimidine (8) $R_2=R_3=R_5=R_6=R_7=OCH_3$	1510	2,0	—	—	1615	2,40	4,40
Glaucine (9) $R_2=R_3=R_5=R_6=OCH_3$	1515	1,90	—	—	1605 1590	2,20	4,10
Nantenine (10) $R_2=R_3=O-CH_2-O$ $R_5R_6=O-CH_3$	1510	1,40	—	—	1584 1615	1,75	3,20
III. Positions 4 and 5 substituted							
Isocorydine (11) $R_3=OCH_3$; $R_4=OH$; $R_5=R_6=OCH_3$	1495	1,10	1585 1575	1,90	—	—	3,00
Bulbocapnine (12) $R_3=OCH_3$; $R_4=OH$ $R_5=R_6=O-CH_2-O$	—	—	1580	0,78	1610 1630	0,92	1,70
Isothebaine (13) $R_4=R_6=OCH_3$ $R_5=OH$	1490	1,40	—	—	1600 1580	2,10	3,50
Dehydroglaucine (14)	1520	2,70	—	—	1605 1620	4,80	7,50
Dehydrothalicmine (15)	1510	3,20	—	—	1590 1610	2,20	5,40

of OH...π interaction in isocorydine (11) is explained by the fact that the angle of rotation of the rings of the biphenyl system of this molecule is smaller than that of bulbocapnine (12).

Thus, the values of the total integral intensities of the aporphine alkaloids of group II depend on the nature of ring B and in the alkaloids of group III they depend on the nature of the spatial interaction of the 4,5-substituents.

In the dehydro derivatives (compounds 3, 14, and 15), an increase in the number of π bonds leads to a rise in A_{tot}, as can be seen from Table 1. For example, in dehydroglaucine (14), $A_{tot} = 7.40 \cdot 10^4$ pr. units, i.e., almost 1.5 times the figure for glaucine (9).

Consequently, the results obtained enable the role of substituents in the change of the integral intensities of the bands of the skeletal vibrations of the aromatic ring in the 1480-1630 cm^{-1} region to be explained and provide the possibility for the identification of the series of aporphine alkaloids studied from the value of A.

TABLE 2. Region of the Stretching Vibrations of the OH Group in the Aporphine Alkaloids

Compound	Associated OH, solvent CCl_4		$A \cdot 10^4$ pr. units $_{OH...O}$	$A \cdot 10^4$ pr. units $_{OH...\pi}$	$A \cdot 10^4$ pr. units $\nu_{C=C}$
	OH...O	OH...π			
Isocorydine (11)	3250	—	4,10	—	3,0
Bulbocapnine (12)	3440	3540	2,30	2,50	1,70
Isothebaine (13)	3360	3540	3,80	2,70	3,5

EXPERIMENTAL

The IR spectra were recorded on a UR-10 double-beam infrared spectrophotometer in the 1650-1480 cm^{-1} region with a NaCl prism and in the 3000-3600 cm^{-1} region with a LiF prism. Chloroform and carbon tetrachloride were used as the solvents. The spectral slit width between 1480 and 1650 cm^{-1} was 8 cm^{-1}. The rate of scanning was 32 cm^{-1}/min. The work was performed with nondemountable standard cells with NaCl windows and thicknesses of the absorbing layers of 0.0178, 0.038, and 0.060 cm, and also with quartz cells with a thickness of the absorbing layer of 1 cm.

The integral intensities were calculated by Bourgin's method [10]. The error in the intensity measurements was ±10%.

SUMMARY

1. The integral intensities of the bands of the skeletal vibrations of the aromatic ring in the 1480-1630 cm^{-1} region of nine aporphine alkaloids and two of their dehydro derivatives have been measured.

2. The value of A_{tot} of the aporphine alkaloids of group II depends on the nature of the substituents in ring B, and in the alkaloids of group III on the nature of the intramolecular H bonds of the 4,5-substituents.

3. The increase in the number of π bonds in the dehydro derivatives leads to a rise in A_{tot}.

LITERATURE CITED

1. É. L. Kristallovich, G. P. Moiseeva, and M. R. Yagudaev, Uzb. Khim. Zh., No. 2, 41 (1971).
2. C. Djerassi and K. Mislow, Exper., 18, 53 (1962).
3. A. W. Sangster and K. Stuart, Chem. Rev., 65, 1 (1965).
4. M. Shamma and S. G. Yao, J. Org. Chem., 36, 21, 3253 (1971).
5. W. H. Baarschers and R. R. Arndt, J. Chem. Soc., 4778 (1964).
6. W. F. Baitinger and P. R. Schleyer, J. Amer. Chem. Soc., 87, 14, 3168 (1965).
7. H. Musso and S. Grunelius, Chem. Ber., 3101 (1959).
8. M. Oki and K. Akashi, Bull. Chem. Soc. Japan, 44, No. 6, 1683 (1971).
9. M. Musso and H. Matthiens, Chem. Ber., 94, 356 (1961).
10. D. G. Bourgin, Phys. Rev., 29, 794 (1927).