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INTEGRAL INTENSITIES OF THE IR BANDS OF THE SKELETAL VIBRATIONS OF THE AROMATIC RING IN THE 1480-1630 cm^{-1} REGION AND THE UV SPECTRA OF THE APORPHINE ALKALOIDS

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UDC 547.944/945+547.856.1

The integral intensities of the skeletal vibrations of the aromatic rings of 12 aporphine alkaloids have been measured. It has been established that with an increase in the twisting of the C_1–C_{11} bond (cos Q) caused by the different natures of the spatial interaction of the 1,11-substituents ΣA decreases.

We have previously shown that the total integral intensities (ΣA 10^4 liter·mole·cm^{-2}) of the skeletal vibrations of the aromatic rings of aporphine alkaloids depend on the nature of the intramolecular hydrogen bonds of the 1,11-substituents [1]. However, no estimate was made of the spatial influence of a methylenedioxy group on the resonance interaction of the two phenyl rings of the biphenyl system of the aporphine alkaloids. In view of the fact that the series of aporphine alkaloids investigated has been supplemented by new compounds containing this substituent in the 1,2 or the 9,10 positions, the possibility has arisen of continuing the study of the total integral intensities of the absorption bands in the 1480-1630 cm^{-1} region and making a comparison with the characteristics of the UV spectra.

As can be seen from Table 1, the integral intensities in remerine (ΣA = 1.40), nantenine (ΣA = 3.20), and domesticine (ΣA = 3.00) are smaller than in glaucine (ΣA = 4.10). This gives grounds for considering that in aporphines with unsubstituted positions 11 [2, 6], because of its noncoplanarity with the nucleus A, a methylenedioxy group ($-O-CH_2-O-$) leads to a decrease in the values of ΣA.

Among the aporphines with a substituted position 11 the lowest value of ΣA is found for bulbocapnine (ΣA = 1.70), which distinguishes it from isothebaine, isocorydine, and corydine. Apparently, a methylenedioxy group noncoplanar with rings A and D increases the degree of twisting of the phenyl rings A and D of the biphenyl system of the bulbocapnine molecule.

The results of a study of the UV spectra of ortho-bridged biphenyls has revealed a link between the intensity of the absorption band at about 270 nm and the interplanar angle of the two phenyl rings [2-6], which is expressed by the relation

$$\cos^2 Q = \frac{E}{E_0},$$

where E is the extinction coefficient at the maximum of the absorption of the sample under

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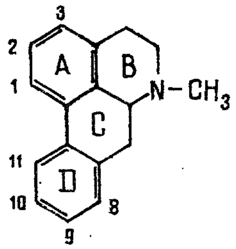
Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 495-498, July-August, 1984. Original article submitted July 4, 1983.

0009-3130/84/2004-0467$08.50

TABLE 1. ΣA of the Vibrations of the Absorption Bands of the Aporphine Alkaloids in the 1480-1630 cm^{-1} Region



Compound	ν_s, cm^{-1}	$A_s \cdot 10^4 \cdot$ liter $\cdot$ $mole^{-1} \cdot cm^2$	$\nu_{as} + \nu_{as'}$	$\Sigma A_{as} = A_{as} + A_{as'}$	$\Sigma A = A_s + A_{as} + A_{as'}$
C_{11}-Unsubstituted					
N-Methylasimilobine (I) R $R_1 = OMe$; $R_2 = OH$	1520	1,20	1590 1610	1,80	3,0
Remerine (II) R_1, $R_2 = O-CH_2-O$	1510	0,70	1610 1630	0,70	1,40
Glaucine (III) R_1, R_2, R_9, $R_{10} = OCH_3$	1515	1,90	1590 1605	2,20	4,10
Domesticine (IV) $R_1 = OH$, $R_2 = OMe$, $R_{9,10} = O-CH_2-O$	1500	1,50	1610	1,65	3,15
Thalicmine (V) $R_{1,2} = O-CH_2-O$, $R_{9,10} = OCH_3$	1510	2,10	1610 1630	1,80	3,90
Nantenine (VI) $R_{1,2} = OCH_3$, $R_{9,10} = O-CH_2-O$	1510	1,40	1584	1,75	3,20
Isoboldine (VII) $R_{1,9} = OH$, $R_{2,10} = OCH_3$	1510	1,50	1590 1605	2,70	4,20
N-Methyllaurotetanine (VIII) $R_{1,2,10} = OCH_3$, $R_9 = OH$	1510	1,20	1590 1610	2,50	4,40
C_{11}-Substituted					
Isothebaine (IX) $R_1 = OH$, $R_{2,11} = OCH_3$	1490	1,40	1580 1600	2,10	3,50
Isocorydine (X) $R_{1,2,10} = OCH_3$, R_{11}-OH	1495	1,10	1575 1585	1,90	3,00
Corydine (XI) $R_1 = OH$, $R_{2,10,11} = OCH_3$	1495	0,98	1595 1600	1,80	2,80
Bulbocapnine (XII) $R_{1,2} = O-CH_2-O$, $R_{10} = OCH_3$; $R_{11} = OH$	—	—	1580 1610 1630	1,70	1,70

TABLE 2. UV Spectra of Ortho-Bridged Diphenyls and the Aporphine Alkaloids

Compound	λ_{max}, nm	E	$\frac{E}{E_0}$	$\cos^2 Q = \frac{E}{E_0}$	Q, deg	ΣA
Fluorene (I)	260	19000	1	1	0	0,11
9,10-Dihydrophenanthrene	264	17000	0,90	0,95	18	
Dimethoxydihydrophenanthrene (III)	272	13580	0,71	0,84	32	
	272	19000	1	1	0	3,50
Isothebaine (IX)	268	15100	0,80	0,89	26	3,00
Isocorydine (X)	270	14330	0,74	0,86	30	3,00
Corydine (XI)	270	10000	0,52	0,73	42	1,70
Bulbocapnine (XII)*					(39)	

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*A value Q = 39° has been obtained by x-ray structural analysis [6].

investigation; and E_0 is the extinction coefficient at the maximum of the absorption of a standard with Q = 0°.

Making use of this relation and the parameters of the UV spectra, we have calculated the interplanar angles Q for the 11-substituted aporphine alkaloids relative to fluorene as standard (Table 2).

It can be seen from Table 2 that the interplanar angle decreases in the following sequence: bulbocapnine (Q = 42°) > isocorydine, corydine (Q = 30°) > isothebaine (Q = 0°), and ΣA increases correspondingly.

EXPERIMENTAL

IR spectra were recorded on a UR-20 double-beam infrared spectrometer in the 1480-1650 cm^{-1} region (NaCl prism). Chloroform was selected as the solvent. The spectral slit width in the 1480-1630 cm^{-1} region was 8 cm^{-1}. The rate of scanning was 40 cm^{-1}/min. Integral standard NaCl cells with thicknesses of the absorbing layer of 0.0176, 0.038, and 0.060 (0.1 ± 0.1 cm) were used. The integral intensities were measured by Bougin's method [7]. The error of the intensity measurements was ±10%.

SUMMARY

1. The integral intensities of the skeletal vibrations of the biphenyl system of 12 aporphine alkaloids in the 1480-1630 cm^{-1} region (ΣA) have been measured.

2. It has been shown that the $-O-CH_2-O-$ group lowers the ΣA values of the aporphine alkaloids.

3. A comparison of ΣA with UV spectra have shown that an increase in the angle of rotation of rings A and D of the biphenyl system (Q) of the 11-substituted aporphine alkaloids is due to the steric effect of the methylenedioxy group.

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