SPECTROSCOPIC STUDY OF HYDROGEN BONDING IN AMINOANTHRAPYRIDONES*

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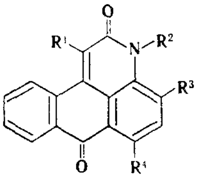
UDC 668.8:547.837:6:543.422.4:541.571.9

By an analysis of the IR spectra of solutions of aminoanthrapyridones in chloroform it was demonstrated that the primary and secondary amino groups in the 1 and 6 positions form an intermolecular hydrogen bond with the CO groups; the amino groups in the 6 position form a stronger hydrogen bond. An anomalous form of the absorption band of the stretching vibrations of the NH group was detected in the IR spectrum of 6-n-hexylamino-3-ethylanthrapyridone. The long-wave band in the electronic spectra of aminoanthrapyridone is related to the band of charge transfer of the unshared pair of electrons of the amino nitrogen atom to the π system of the rings.

Aminoanthrapyridone derivatives have long been used as dyes, and they have recently found application as luminophores [2]. However, up until now the dependence of the spectral characteristics of anthrapyridone derivatives on their structure has remained practically unstudied. There are only a few studies of descriptive characters [2-5]. In the present paper we examine the IR and electronic absorption spectra of amino derivatives of anthrapyridone (I-VIII, Tables 1-3).



It has been shown that anthrapyridone (X) to a certain degree retains the properties of anthraquinone and α-pyridone [1]. Proceeding from this, one should expect that the amino group in the 6 position of anthrapyridone will interact with the anthrapyridone system in a manner similar to the interaction in α-aminoanthraquinone [4] and should be tied up in an intramolecular hydrogen bond (IHB). The amine nitrogen atom will be close to an sp^2 state, which will create favorable conditions for electron transition with charge transfer from the $2p_z$ orbital of the nitrogen atom to the anthrapyridone system; this transition is responsible for the color of the dye. The indicated character of the interaction should show up in the vibrations of the functional groups (C = O, NH), that participate in the formation of the IHB and in the $p_z \to \pi^*$ charge-transfer band in the electronic spectra.

It is seen from Table 1 that one band at 1649 cm^{-1} is observed in the spectrum of a solution of 6-piperidino-3-methylanthrapyridone (I) in the region of the stretching vibrations of the CO bonds (ν_{CO}). The certain decrease in the ν_{CO} frequency in I

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*Communication VI from the series "Structures and Properties of Dyes." See [1] for communication V.

Scientific-Research Institute of Organic Intermediates and Dyes, Moscow. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1357-1363, October 1974. Original article submitted November 28, 1972; revision submitted December 24, 1973.

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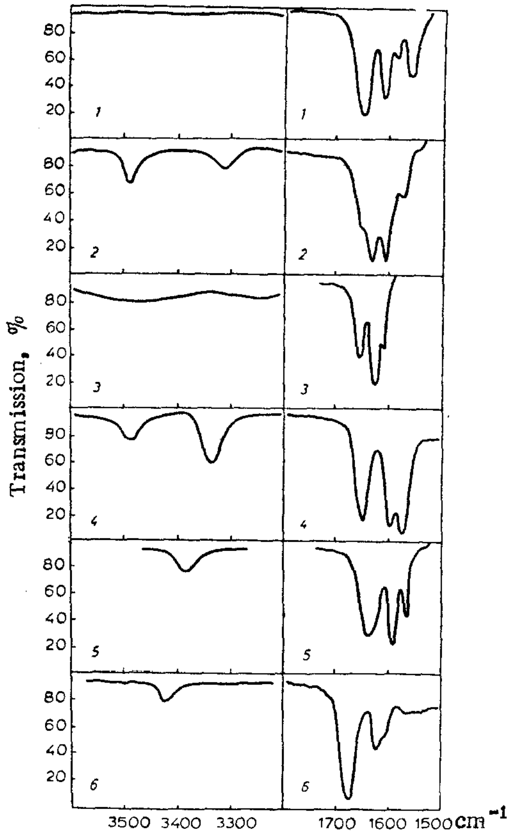


Fig. 1. IR spectra of anthrapyridone derivatives in chloroform: 1) 6-piperidino-3-methylanthrapyridone (I); 2) 6-amino-3-methylanthrapyridone (II); 3) 6-n-hexylamino-3-methylanthrapyridone (III); 4) 1-amino-3-methylanthrapyridone (IV); 5) 1-n-hexylamino-3-methylanthrapyridone (VI); 6) 4-isopropylanthrapyridone (VII).

as compared with N-methylanthrapyridone (IX, 1667 cm^{-1}) can be explained by conjungation of the amino group with the aromatic system. The ν_{CO} bands in the spectra of solutions of 6-amino- and 6-n-hexylamino-3-methylanthrapyridone (II, III) are split into two components. The splitting of the ν_{CO} band may be due to the formation of an IHB between the amino group and the adjacent keto group, which is characteristic for the previously investigated 1-aminoanthraquinones [6], and Fermi resonance. The keto group is tied up in the formation of an IHB in II and III, while the amide $C=O$ group is free. Inasmuch as the intensity (A_{CO}) of the band of the amide group is higher by a factor of almost 3 than the intensity of the keto band [1], the high-frequency ν_{CO} band should be more intense. However, the reverse ratio of the intensities is observed in the spectra (Fig. 1). The redistribution of the intensities of the components of the $C=O$ band is possibly explained by Fermi resonance.

The stretching vibrations of the primary amino group of II give two bands (ν_s and $\nu_{as NH_2}$) in the spectrum, while the secondary amino group of III gives one diffuse ν_{NH} band. On subsequent dilution, the position and intensity of these bands are retained, and new bands do not appear. The deviation in the experimentally found ν_{sNH_2} values from the values calculated from the empirical expression below [7] may be a criterion of the association of the amino group (in particular, through IHB):

$$\nu_{s\,NH_2}=345.5+0.876\nu_{as\,NH_2}. \qquad (1)$$

These deviations are 95 cm^{-1} for 6-amino-3-methylanthraphyridone (II) and 42 cm^{-1} for 1-aminoanthrapyridone. It has been pointed out [8] that the $\Delta\nu_{NH_2} = \nu_{as} - \nu_s$ value increases as the strength of the IHB of the amino group increases. The $\Delta\nu_{NH_2}$ value in the spectrum of II is twice that in the spectrum of 2-aminoanthraquinone and 11 cm^{-1} larger than in the spectrum of 1-aminoanthraquinone (170 cm^{-1}). It must therefore be assumed that the energy of the IHB in II is greater than in 1-aminoanthraquinone.

The anomalous behavior of the ν_{NH} band in the IR spectrum of 6-n-hexylamino-3-methylanthrapyridone (III) should be noted. A diffuse band at 3150-3500 cm^{-1} (Fig. 1) is observed in the region of stretching vibrations of the NH bond in place of a distinct absorption band.

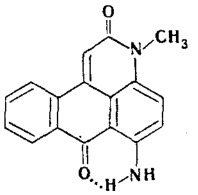
The integral intensities (A) and half widths ($\Delta\nu_{1/2NH_2}$) of the absorption bands of the stretching vibrations of the amino groups in the IR spectrum of II differ from the values observed in the spectra of α-aminoanthraquinone. The chief difference consists in the increase in A_{NH_2} and $\Delta\nu_{1/2NH_2}$ of the band of the asymmetrical vibration by a factor about two in the spectrum of II.

Thus, on the basis of the behavior of the ν_{CO} and ν_{NH_2} absorption bands and the experimentally found spectral characteristics in dilute $CHCl_3$ solutions, it can be concluded that the amino group in the 6 position of anthrapyridone forms a strong IHB with the adjacent keto group; this bond has a higher energy than in the case of α-aminoanthraquinone.

TABLE 1. Frequencies, Integral Intensities, and Half-Widths of the Bands of the Stretching Vibrations of CO and NH Groups in the IR Spectra of Aminoanthrapyridones in $CHCl_3$

Compound	R	ν, cm^{-1}	$A \cdot 10^{-4}$ liters/mole $\cdot$ cm^2	$\Delta\nu_{1/2}$, cm^{-1}	Assignment	Preparative methods
I	$R^2=CH_3$	1649 ± 2	8,3	23,7	νCO amide +	—
	$R^4=C_5H_{10}N$				+Ketone	
	$R^1=R^3=H$	1662 ± 2 (CCl_4)	—	—		
II	$R^2=CH_3$	1636 ± 1			νCO ketone	11
	$R^4=NH_2$	1653 ± 3*			νCO amide	
	$R^1=R^3=H$	3301 ± 3	1,3	42,1	ν_sNH_2	
		3482 ± 3	1,8	28,8	$\nu_{as}NH_2$	
III	$R^2=CH_3$	1652 ± 2			νCO amide	12
	$R^4=C_6H_{13}NH$	1623 ± 3			νCO ketone	
	$R^1=R^3=H$	3150—3500			νNH	
IV	$R^2=CH_3$	1661 ± 1	5,7	23,5	νCO	13
	$R^4=R^3=H$	1643*	6,1			
	$R^1=NH_2$	3363 ± 2	1,8	29,4	ν_sNH_2	
		3485 ± 2	1,0	32,5	$\nu_{as}NH_2$	
V	$R^2=R^4=R^3=H$	1651 ± 2	10,0	26,1	νCO	12
	$R^1=C_6H_{13}NH$	1659 ± 2 (CCl_4)	10,2			
		3340 ± 3	1,9	42,5	νNH amine	
		3393 ± 3	1,4	27,5	νNH amide	
VI	$R^2=CH_3$	1633 ± 2	7,8	40,0	νCO	12
	$R^4=R^3=H$	3338 ± 3	1,7	42,5	ν(NH...OC)	
	$R^1=C_6H_{13}NH$					
VII	$R^2=R^4=R^1=H$	1663 ± 2	9,8	15,0	νCO	1
	$R^3=CH(CH_3)_2$	3385 ± 4	1,4	20,5	νNH	
VIII	$R^2=CH_3$	1626 ± 2	9,9	24,7	νCO	12
	$R^4=R^1=C_6H_{13}NH$	1660 †				
	$R^3=H$	3305 ± 3	1,7	45,0	νNH	

*Overlaps with the band of δ_{NH_2} deformation vibrations.
†Shoulder.



An asymmetric ν_{CO} band at 1661 cm^{-1} with a shoulder at 1643 cm^{-1} and two bands of symmetrical and asymmetrical vibrations with $\Delta\nu_{NH_2}$ = 122 cm^{-1} are observed in the IR spectrum of 1-amino-3-methylanthrapyridone (IV) (Table 1) in $CHCl_3$. The difference in the frequencies of the indicated absorption bands in the spectra of IV as compared with the spectra of II is explained by the different position of the amino group in the molecule and the different possibilities of formation of an IHB. In II the amino group may form a 6-membered ring, while in IV the amino group may form a 5-membered ring, which is usually characterized by a weaker IHB than the six-membered ring [8]. Comparing the $\Delta\nu_{NH_2}$ values in the series β-aminoanthraquinone (90 cm^{-1}), which does not form an IHB, 2-chloro-3-aminoanthraquinone (101 cm^{-1}) [9], which forms a weak IHB of the NH...Cl type, IV (122 cm^{-1}), and II (181 cm^{-1}), it can be concluded that the strength of the IHB increases in the indicated order. The A_{sNH_2} integral intensity in the spectrum of IV is approximately twice that of A_{asNH_2}, while the $\Delta\nu_{1/2NH_2}$ half-widths are approximately identical.

One ν_{CO} band of the amide and carbonyl groups is observed in the IR spectrum of a solution of V in $CHCl_3$ and in CCl_4. The absence of a distinctly expressed splitting of the ν_{CO} band in the spectrum can be explained by the rather weak IHB (H...O=C). The following two bands are observed in the ν_{NH} region of 1-n-hexylaminoanthrapyridone (V) in $CHCl_3$ solution: 3340 cm^{-1}, which is related to ν_{NH} of the amino group, and 3393 cm^{-1}, which is related to ν_{NH} of the cyclic amide group (Table 1). This is confirmed

TABLE 2. Frequencies of the Vibrations in the IR Absorption Spectra of Anthrapyridone Derivatives in the Crystalline State

Compound*	ν_{NH}	ν_{ArH}	ν_{CH_2}, ν_{CH_3},	ν_{CO}	$\nu_{C=C}$	δ_{CH_3}, δ_{CH_2},	ν_{C-N}	σ_{CH}	Other bands
I		3060, 3080	2856 m, 2803 m	1653 vs	1505 w, 1568 s	1435 m 1463 m	1295 m 1275 m 1225 m 1200 w	713 w 735 m 915 m	1220 m 1245 m 1282 m 1318 w
II	3165, 3090 w 3440 s	3093 w	2880 m, 2950 s	1655 sh 1630 s	1448, 1466 1545 m	1425 w 1450		758 m 782 s 823 w 870 m 899 w	1275 w 1298 m 1318 w 1342 w 1390 w
III	3150—3500	3045 w 3055 w	2865 m, 2898 w 2935 m, 2960 w	1625 vs, 1650	1445 w 1473 w 1515 s	1445 sh 1473 m	1268 m 1295 m 1320 w 1385 s	725 w 840 w 758 w 895 m 789 s 805 m 807 sh	1267 s 1295 s 1320 m 1385 s
V	3310 w		2845 2862 2925 w 2956	1655 s		1432 w 1459 1469 1498		688 w 711 m 733 m 765 m 784 w 792 w 879 w	1233 w 1248 1297 w 1312 1348 1363 1372
VI	3308 s		2855 m 2926 m 2954 m	1650 s 1663	1513 s 1568 s 1596 s	1420 m 1473 s 1460 sh	1279 w 1333 w 1315 w 1353 sh	682 w 712 m 737 w 768 s 830 w	1198 w 1280 w 1315 w 1343 w 1363 m
VIII	3320 vs 3315 vs	3085 3066 w	2875 w 2953 2880 m 2890 m 2952 m 2980 m	1622 vs	1438 m 1488 m			705 m 770 m 805 m 838 w 885 w	1225 w 1255 w 1290 m 1312 m 1345 s 1365 w
IX		3070 w	2825 w 2890 w 2945 w	1660 vs	1470 sh 1480 m 1605 w 1500 w 1635 w	1431 m		695 m 786 710 m 829 722 m 773 875	1186 w 1325 1212 vs 1350 1262 vw 1370 w 1398 w 1312 w
X	3110—3500 2600—3250	3065 3016		1642	1445 m 1552 m 1465 w 1597, 1508 m			703 s 779 s 733 m 750 w 831 w 868 m	1189 w 1310 w 1245 w 1298 m 1349 m 1381 w

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*Compound IX is 3-methylanthrapyridone, while X is anthrapyridone. The following abbreviations were adopted in the table: vs is very strong, s is strong, m is medium, w is weak, vw is very weak, and sh is shoulder.

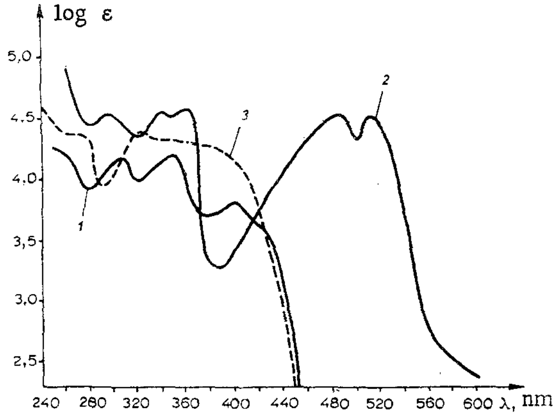

Fig. 2. Electronic spectra (c $5 \cdot 10^{-4}$M): 1) 3-methylanthrapyridone in chloroform; 2) 6-amino-3-methylanthrapyridone (II) in chloroform; 3) II in concentrated H_2SO_4.

by the observation of a band at 3385 cm^{-1} in the spectrum of a solution of 4-isopropylanthrapyridone (VII), which has only an amide NH group, and by the presence of a group at 3338 cm^{-1} in the spectrum of 1-n-hexylamino-3-methylanthrapyridone (VI), which has only an amine NH group. It should be noted that the ν_{CO} band in the spectra of V and VII, which contains an amide NH group, is ~10 cm^{-1} higher than in the spectra of compounds that have a methyl group attached to the ring-nitrogen atom. The A_{CO} integral intensities in the spectra of V and VII lie within the limits of 10 units.

The position of the ν_{CO} band, which is due to vibrations of amide and ketone CO groups, in the IR spectrum of 1,6-di(n-hexylamino)-3-methylanthrapyridone (VIII) is markedly reduced as compared with ν_{CO} in the spectra of the monoamino derivatives (Table 1). This can be explained by the formation of an IHB and by the electron-donor capacity of amino nitrogen atoms. One distinct band with an intensity of 1.7 units, which is close to A_{NH} in the spectrum of VI (Table 1), is observed in the spectrum of VIII in the ν_{NH} region. Consequently, this band can be assigned to vibrations of the NH group in the 1 position. The vibration of the NH group in the 6 position is manifested as a diffuse band, as in the spectrum of III. The observed diffuse character of the ν_{NH} band in the spectrum of 6-n-hexylamino-3-methylanthrapyridone (II), in analogy with νOH...X, for example, in the spectrum of α-hydroxyanthraquinone, may be explained by the symmetrical orientation of the proton with respect to the nitrogen and oxygen atoms.

The ν_{CO} values in the spectra of crystalline samples change only slightly in passing to the spectra of solutions. The ν_{NH} absorption band in the crystalline samples appears as a complex system of bands at 3100-3440 cm^{-1} with several maxima (Table 2).

A shoulder of medium intensity at 1655 cm^{-1} and an intense band at 1630 cm^{-1}, which is probably overlapped with the band of the vibrations of the aromatic rings (Table 2), are observed in the spectrum of II in the crystalline state. The closeness of the ν_{CO} values in the spectra of II in the crystalline state and in solution attest to the similarity of the character of the interaction of the ketone group and the NH bond in the different states.

A broad absorption region is observed in the region of the stretching vibrations of the amino group in the spectrum of crystals of II. The complication in the region of absorption of the NH_2 group is due to strong intermolecular hydrogen bonds. Just as in the spectrum of a solution, a diffuse band is observed in the spectrum of 6-n-hexylamino-3-methylanthrapyridone (III) in the region of the stretching vibrations of the NH group; this provides evidence for the identical character of the hydrogen bonding in the crystalline state and in solution.

A characteristic feature of the electronic spectra of 6-aminoanthrapyridones as compared with the spectra of unsubstituted anthrapyridone is the intense band at 510-550 nm (Fig. 2 and Table 3).

Proceeding from the assumption that anthrapyridones to a certain extent have the properties of anthraquinones and benzathrones, the long-wave band can be assigned to transfer of the charge of the unshared pair of electrons of the amine nitrogen to the vacant orbitals of the aromatic anthrapyridone system, which are usually designated $p_z \to \pi^*$. The assignment of this band is proved by its disappearance when the compounds are protonated in concentrated H_2SO_4 (Fig. 2). As pointed out above, the appearance of a $p_z \to \pi^*$ band is possible if the amine nitrogen atom is close to the sp^2 state. The formation of an IHB of the NH...O=C type promotes transition of the amine nitrogen to the sp^2 state.

TABLE 3. Electronic Spectra of Amino Derivatives of Anthrapyridone in Chloroform

Compound	λ_{max}, nm	log ε
I	260, 342, 392, 410, 530	4,53; 4,01; 3,36; 3,30; 3,97
II	294, 340, 360, 483, 511	4,14; 4,53; 4,56; 4,49; 4,50
III	260, 300, 350, 520, 550	4,60; 3,99; 3,99; 4,07; 4,13
VIII	250, 371, 423, 520	3,86; 3,07; 3,28; 3,36

Inasmuch as protonation of the investigated compounds is realized only in concentrated sulfuric acid, it must be assumed that the amine nitrogen atom interacts strongly with the aromatic rings, and this sharply reduces the basicity of the amino group. It should be noted that two $p_z \to \pi^*$ transition bands with $\Delta\lambda_{max}$ 40 nm are observed in the long-wave region of the spectra of 6-aminoanthrapyridones.

Thus the character of the interaction of the amino group in the 6 position with the benzene rings is basically similar to the interaction of the amino group in α-aminoanthraquinone [10], while the character of the interaction of the amino group in the 1 position differs substantially.

EXPERIMENTAL

The IR spectra of crystalline samples (KBr pellets) and chloroform solutions of the compounds were recorded with a UR-20 spectrometer. The integral intensities of the absorption bands were measured by the Bourgin method [7]. The solutions were diluted to $1 \cdot 10^{-3}$ M. The layer thicknesses of the solutions ranged from 0.1-1.0 cm. The accuracy in the measurement of the frequencies of the absorption maxima in the range of an NaCl prism was ±2 cm^{-1}, while the accuracy in the range of an LiF prism was ±4 cm^{-1}. The accuracy in the measurement of the integral intensities of the absorption bands was ±10%.

The electronic spectra were measured with an SF-4A spectrophotometer in quartz cuvettes with a layer thickness of 1 cm with $5 \cdot 10^{-4}$ M chloroform solutions. The measurements were made through each 5-nm interval, and the positions of the maxima were additionally refined.

The citations to the methods for the preparation of II-VIII are indicated in Table 1.

6-Piperidino-3-methylanthrapyridone (I). A 5-g sample of 6-bromo-3-methylanthrapyridone and 50 ml of piperidine were refluxed for 30 min, after which the mixture was diluted with water, and the precipitate was removed by filtration and washed with water to give a product with mp 225-226° (from white spirit) in 95% yield. Found: N 7.9%. $C_{22}H_{20}N_2O_2$. Calculated: N 8.1%.

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