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STERIC EFFECT OF SUBSTITUENTS ON THE NATURE OF THE CHROMOPHORE IN $\Delta^{9,10}$-OCTAHYDRO-4-QUINOLONES*

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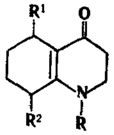
The study of the behavior of cisoid two-ring ketones from substituted cyclohexanones and (—)-menthone was continued. The steric effect of a bulky substituent attached to the 8-C atom of the quinolone system on the conformation of the molecule was established; this effect leads to disruption of the conjugation of the p-electron pair of the nitrogen atom in the enamino ketone portion of the chromophore.

During a comparison of the spectral characteristics of 1-butyl-5-methyl-8-isopropyl-$\Delta^{9,10}$-octahydro-4-quinolone (Ia) [2] and the previously investigated two-ring enamino ketones IV [3, 4] we observed a shift of 70 nm to the short-wave region of the band of the $\pi \rightarrow \pi^*$ transition in the UV spectrum of Ia. This change in the spectral behavior evidently may be associated with the steric effect of the substituent in the carbocyclic ring on the conformation of the molecule. In this connection we investigated a number of enamino ketones (I-III) containing various substituents in the 1, 5, and 8 positions of the octahydroquinoline system.



I-IV

I a R=C_4H_9, R^1=CH_3, R^2=$CH(CH_3)_2$; b R=$CH_2C_6H_5$, R^1=CH_3, R^2=$CH(CH_3)_2$; II R=$CH_2C_6H_5$, R^1=H, R^2=$CH_2CH(CH_3)_2$, III a R=$CH_2C_6H_5$ R^1=CH_3, R^2=H; b R=$CH_2C_6H_5$, R^1=H, R^2=CH_3; IV R^1=R^2=H; a R=$CH(C_6H_5)CH_3$; b R=$CH(C_2H_5)CH_3$

Two-ring cisoid enamino ketones I-III were obtained by the methods described in [3, 4]. Their compositions and structures were confirmed by the results of elementary analysis and PMR spectroscopic data (Table 1). The mass spectral fragmentation of the enamino ketones confirms their structures and is characteristic for compounds of this series [2].

It should be noted that the UV spectra of enamino ketones IV in heptane are characterized by the band of a $\pi \rightarrow \pi^*$ transition of the enamino ketone chromophore at 305-315 nm. In contrast to this, the band of the $\pi \rightarrow \pi^*$ transition in the UV spectra of enamino ketones I obtained from (—)-menthone appears at 240 nm, and an inflection is also observed at 280-310 nm (Fig. 1).

In the IR spectra of compounds I, II and III, IV we also observed these differences; in enamino ketones III and IV bands appeared at 1540-1560 and 1620-1630 cm^{-1}, characteristic of the stretching vibrations of the conjugated C=C bond and the carbonyl group. In the spectra of compounds I and II these bands converge strongly at 1638 and 1670 cm^{-1}.

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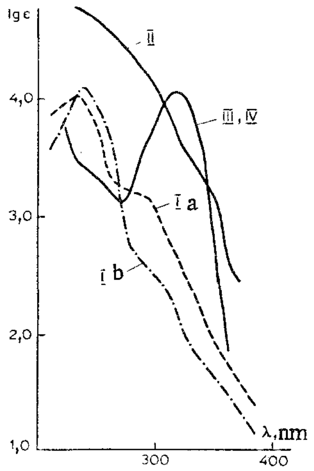

Fig. 1. UV spectra of the enamino ketones in heptane.

TABLE 1. Properties of the Enamino Ketones

Compound	Found, %		Empirical formula	Calc., %		IR spectrum, ν, cm^{-1}		M	PMR spectrum, δ, ppm	Yield, %
	C	H		C	H	C=O	C=C			
Ia	77,1	11,1	$C_{17}H_{29}NO$	77,5	11,1	1670	1638	263	1—1,4 (m), 3,8 (t), 5,3 (t)	50
Ib	80,4	9,3	$C_{20}H_{27}NO$	80,8	9,2	1672	1648	297	0,4—1,0 (m), 4,8 (s), 5,1 (s), 7,2 (s)	30
II	80,8	9,0	$C_{20}H_{27}NO$	80,8	9,2	1670	1647	297		30
IIIa	80,0	7,8	$C_{17}H_{21}NO$	80,0	8,3	1620	1550	255		50
IIIb	79,8	8,4	$C_{17}H_{21}NO$	80,0	8,3	1630	1550	255		50

It is apparent from an examination of the UV spectral data for enamino ketones IIIa,b and IVb in heptane that the introduction of a methyl group in the 5 (IIIa) or 8 (IIIb) position and a sec-butyl group in the 1 position (IVb) of the quinolone system does not lead to a shift in the maximum of the $\pi \rightarrow \pi^*$ transition of the enamino ketone chromophore. However, the band of a $\pi \rightarrow \pi^*$ transition at 310 nm vanishes in the UV spectrum of enamino ketone II with an isobutyl substituent in the 8 position, and only an inflection at 260-265 nm is observed (Fig. 1). This change in the character of the spectral data for enamino ketones I and II confirms our assumption regarding the change in the conformation of the molecule and, consequently, the nature of the enamino ketone chromophore: The volume of the isopropyl and isobutyl groups in the 8 position may lead to deformation of the two-ring system and disruption of the conjugation of the p-electron pair of the nitrogen atom in the enamino ketone chromophore. In other words, the electron pair of nitrogen deviates from conjugation with the π electrons of the double bond and the carbonyl group. Our observed spectral characteristics of enamino ketones I and II very much recall the spectral behavior of the α,β-unsaturated carbonyl chromophore [5].

EXPERIMENTAL

The IR spectra of the compounds were recorded with a UR-20 spectrometer. The UV spectra were recorded with a Cary-15 spectrophotometer. The PMR spectra of solutions of the compounds in CCl_4 were recorded with a Varian T-60 spectrometer with hexamethyldisiloxane as the internal standard. The mass spectra were obtained with an MKh-1303 mass spectrometer.

Methyl β-(N-methylamino)propionate [6], with bp 55°C (11 mm), was obtained in 50% yield.

Methyl β-(N-butylamino)propionate [7], with bp 92-94°C (10 mm) and n_D^{20} 1.4329, was obtained in 88% yield.

Methyl β-(N-benzylamino)propionate [8], with bp 144-146°C (7 mm) and n_D^{20} 1.5169, was obtained in 85% yield.

(−)-Menthone, with bp 94°C (17 mm), n_D^{20} 1.4502, and $[\alpha]_D^{20}$ −28°, was obtained in 76% yield by oxidation of l-menthol with a chromic acid mixture [9].

2-Isobutylcyclohexanone was obtained by refluxing 0.1 mole of 1-pyrrolidinyl-1-cyclohexene and isobutyl iodide in absolute CH_3OH for 5 h. The methanol was removed by distillation, 80 ml of 2 N HCl was added to the dry residue, and the mixture was refluxed for 1.5 h. It was then cooled and extracted with ether, and the ether extract was washed with water and dried over Na_2SO_4. The solvent was removed, and the residue was vacuum distilled to give 4.6 g (30%) of a product with bp 87-88°C (13 mm) and n_D^{20} 1.4525 (bp 77-78°C, 5 mm [11]).

The enamino ketones (Table 1) were obtained by the methods in [2-4].

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SPECTRAL-LUMINESCENCE AND GENERATION CHARACTERISTICS OF 1-R-VINYL-3-ARYL(HETERYL)BENZO[f]QUINOLINES

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The absorption and fluorescence spectra and the fluorescence quantum yields of 1-R-vinyl derivatives of benzo[f]quinoline containing aryl and 2-, 4-, and 6-quinolyl groups in the vinylene grouping and in the 3 position were studied. The relationship between the spectral-luminescence characteristics and the structures of the molecules was examined. It was established that solutions of compounds that contain a dimethylamino group attached to the phenyl ring give forced emission when they are excited with the second harmonic of a ruby laser. The effect of the solvent on the spectral-luminescence and generation characteristics of the indicated compounds was investigated.

Continuing our research on the effect of the structural factors on the spectral-luminescence properties of benzo[f]quinoline derivatives [1, 2], we investigated 1-R-vinyl-3-aryl(heteryl)benzo[f]quinolines. The latter were obtained by reaction of arylidene-2-naphthylamine with α,β-unsaturated ketones [3, 4] and by condensation of 1-methyl derivatives of benzo[f]quinoline with aldehydes or anils of the aromatic and heterocyclic series [5, 6].

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