7-Amino-2,4-diphenylpyrido[1,2-f]phenanthridinium Perchlorate (IVe). A 2 g sample of perchlorate V [8] was dissolved in 1 liter of absolute methylene chloride, and the solution was irradiated in a photoreactor in an argon atmosphere for 3 h. The solvent was then removed by distillation. The resulting dark-red crystalline residue was identified as a mixture of starting azomethine V (10%), with R_f 1, a compound with unestablished structure (10%, with R_f 0.85, 7-(p-nitrobenzylamino)-2,4-diphenylpyrido[1,2-f]phenanthridinium perchlorate (VII) (35%) with R_f 0.27, and perchlorate IV (30%) with R_f 0.78 [Al_2O_3, chloroform—acetone—nitromethane (4:1:1)]. Data on perchlorate IV are presented in Table 3. IR spectrum: 3390 cm^{-1} (NH_2).

7-(p-Nitrobenzylamino)-2,4-diphenylpyrido[1,2-f]phenanthridinium Perchlorate (VII). This compound was obtained as yellow prisms with mp 110°C (from ethanol). IR spectrum: 3330 (NH) and 1545 cm^{-1} (NO_2). PMR spectrum: 2.22 (s, NH) and 4.2 ppm (s, CH_2). Found: C 68.1; H 5.0; Cl 5.8%. $C_{36}H_{26}ClN_3O_6$. Calculated: C 68.4; H 4.9; Cl 5.7%.

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CONFORMATIONAL STUDY OF CHIRAL HETEROCYCLIC ENAMINO KETONES*

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UDC 541.653:547.831

An assumption regarding the existence of a homoconjugation effect involving enaminoketo and phenyl groups as a result of the drawing together in space of their π orbitals was made on the basis of circular dichroism (CD) data and an examination of the preferred conformations of two-ring enamino ketones with α-phenylethyl and α-benzylethyl substituents. A study of enamino ketones with a chiral alkyl substituent attached to the nitrogen atom made it possible to confirm this assumption.

A study of the chiral-optical properties of two-ring cisoid enamino ketones I and II, which have α-phenylethyl or α-benzylethyl substituents attached to the nitrogen atom, by optical rotatory dispersion (ORD) and circular dichroism (CD) has made it possible to make an assumption regarding the drawing together in space of the π orbitals of the phenyl and enaminoketo chromophores separated by two and three σ bonds, i.e., manifestation of a homoconjugation effect [2, 3].

For a further study of the nature of the enaminoketo chromophore, which has a cis-s-trans configuration, and its geometry for an evaluation of the contribution of homoconjugation to optical rotation we investigated model compounds — cisoid two-ring enamino ketones III with

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TABLE 1. Spectral Characteristics of Enamino Ketones IIIa-c

Compound	UV spectrum		CD	
	λ_{max}, nm	ε	λ_{max}, nm	[θ]°
IIIa	310[a] 330[b] 322[c] 315[d]	12800 15050 26100 15100	338 330 335 315	+8900 +7580 +11000 +12860
IIIb	316[a] 336[b] 330[c] 322[d]	11700 17810 16100 12000	335 335 336 323	+9080 +7980 +10540 +5715
IIIc	318[a] 338[b] 331[c] 317[d]	14900 18400 14700 10800	335 340 337 310—320	+2500 +6760 +8940 +7310

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[a] In heptane. [b] In alcohol. [c] In acetonitrile. [d] In CF_3COOH.

TABLE 2. Properties of the Enamino Ketones

Compound	mp, °C	IR spectrum, cm^{-1}		Found, %		Empirical formula	Calc., %		PMR, δ, ppm	M^+	Yield, %
		C=O	C=C	C	H		C	H			
IIIa	125—126*	1640	1585	51,4*	5,2*	$C_{12}H_{19}NO \cdot C_6H_3N_3O_7$*	51,2*	5,2*	1,23 (t), **CH_3**CH_2 1,6 (d), **CH_3**CH 3,7 (m), NCH_2 4,0 (m), CH	193	25
IIIb	135—136*	1638	1560	52,5*	5,4*	$C_{13}H_{21}NO \cdot C_6H_3N_3O_7$*	52,3*	5,5*	0,83 (t), **CH_3**CH_2 1,07 (d), **CH_3**CH 3,15 (m), NCH_2 3,77 (q d), CH	207	27
IIIc	67—68	1620	1550	76,6	10,5	$C_{14}H_{23}NO$	76,8	10,5	1,25 (t), **CH_3**CH_2 1,55 (d), **CH_3**CH 3,65 (t), NCH_2 4,23 (m), CH	221	40

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*Data for the picrates.

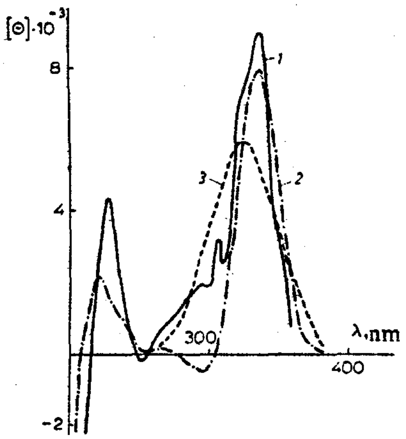


Fig. 1

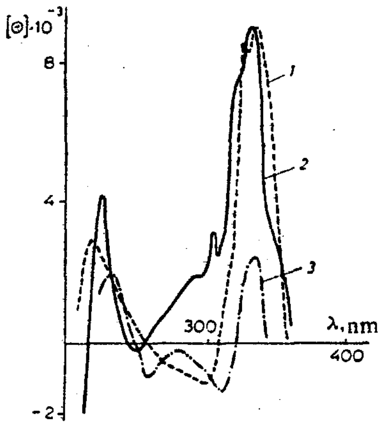


Fig. 2

Fig. 1. CD curves of enamino ketones IIIa (1), IIIb (2), and IIIc (3) in heptane.

Fig. 2. CD curves of enamino ketone IIIb in heptane (1), alcohol (2), and trifluoroacetic acid (3).

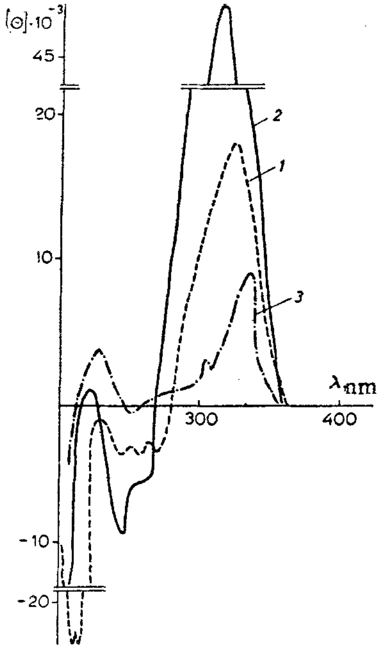
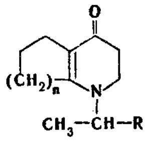


Fig. 3. CD curves of enamino ketones Ib (1), IIb (2), and IIIb (3) in heptane.

a chiral alkyl substituent attached to the nitrogen atom. Their synthesis was accomplished by a general method [2], and their compositions and structures were confirmed by the results of elementary analysis and by means of mass spectrometry and other spectral methods (Table 2).



I–III a-c

a $n=1$; b $n=2$; c $n=3$; I $R=C_6H_5$; II $R=CH_2C_6H_5$; III $R=C_2H_5$

Only one intense absorption maximum at 310-330 nm with log ε > 4 is observed in the UV spectra of enamino ketones IIIa-c (Table 1); this band undergoes a bathochromic shift as the polarity of the solvent increases, and this made it possible to ascribe it to a $\pi \to \pi^*$ transition in the enaminoketo chromophore.

The CD spectra of all of the enamino ketones in solvents with different polarities were studied. A positive very unsymmetrical band at 338 nm, which corresponds to the $\pi \to \pi^*$ transition of the enaminoketo chromophore, and a short-wave positive band at 228 nm are observed on the CD curve of 1-sec-butyl-4-keto-$\Delta^{9,10}$-octahydroquinoline (IIIb) in heptane (Fig. 1). In addition to the two indicated Cotton effects (CE), another negative CE is observed at 300 nm on the CD curves of five- and seven-membered analogs IIIa and IIIc. It is difficult to assign the short-wave transitions without a detailed study of model compounds; however, both effects vanish in trifluoroacetic acid. The polarity of the solvent does not introduce substantial changes in the trend of the CD curves or in the CE (Table 1). One should note the absence of a bathochromic shift of the $\pi \to \pi^*$ band of the enaminoketo chromophore as the polarity of the medium increases, as displayed in the UV spectra. There is also no correlation of the positions of the CE in the UV and CD spectra for enamino ketones IIIa-c.

An examination of molecular models shows that both rings in these compounds exist in the half-chair conformation; in conformity with the literature data, this makes it possible to regard the enaminoketo chromophore as an internally chiral chromophore. Our calculation of the rotational force of the $\pi \to \pi^*$ band for enamino ketone IIIc (the minimum value of the molecular ellipiticity), $R \approx 0.9 \cdot 10^{-39}$, also confirms this sort of nature for the chromophore.

A decrease in the molecular ellipticity of the positive transition band is observed for the investigated enamino ketones IIIa-c in all solvents as the size of the carbocycle increases (Table 1), during which the magnitude of absorption (ε) for this series, on the other hand, increases as the size of the carbocycle increases; this constitutes evidence for more favorable conditions for conjugation in enamino ketone IIIc. This in turn decreases the degree of distortion of the chromophore and leads to a decrease in the molecular ellipticity.

The greater coplanarity of the chromophore in enamino ketone IIIc also follows from an examination of the IR spectral data. The decrease in the frequencies of the stretching vibrations that characterize the enaminoketo chromophore is maximal in the case of the seven-membered analog (Table 2).

A comparison of the molecular ellipticities of the band of the $\pi \rightarrow \pi^*$ transition in enamino ketones I-III showed that they undergo a significant decrease when a sec-butyl substituent is incorporated at the nitrogen atom; this confirms the previously expressed assumption [3] regarding the existence of homoconjugation in enamino ketones I and II (Fig. 2).

The sign of the CE of the $\pi \rightarrow \pi^*$ band in the spectra of the investigated two-ring enamino ketones with different substituents attached to the nitrogen atom can be used to determine the absolute configuration of the amine: a positive CE is observed for amines with an S configuration.

EXPERIMENTAL

The UV spectra of the compounds were recorded with a Cary-15 spectrophotometer. The IR spectra of mineral oil suspensions and films of the compounds were recorded with a UR-20 spectrometer. The PMR spectra of solutions of the compounds in CCl_4 were recorded with Varian-T60 and XL-100 spectrometers with hexamethyldisiloxane as the external standard. The mass spectra were recorded with an MKh-1303 spectrometer. The ORD and CD spectra were obtained with a Jasco J-20 spectropolarimeter.

(+)-(S)-2-Aminobutane was obtained by resolution of racemic 2-aminobutane by the method in [4] and had bp 62-63°C and $[\alpha]_D^{20}$ + 7.8° (without a solvent) (according to the data in [4], this compound has bp 62°C and $[\alpha]_D^{20}$ + 7.80).

Methyl β-(N-sec-Butylamino)propionate. An 8.6-g (0.1 mole) sample of freshly distilled methyl acrylate was added dropwise to a solution of 9.14 g (0.125 mole) of (+)-(S)-2-aminobutane in 60 ml of absolute CH_3OH, and the reaction mixture was stirred for 3 h and allowed to stand overnight. The alcohol was removed, and the residue was vacuum distilled to give 14.5 g (90%) of the amino ester with bp 84°C (15 mm), n_D^{20} 1.4305, and $[\alpha]_D^{20}$ + 12.5° (without a solvent). IR spectrum (thin layer): 1746 ($COCH_3$) and 3330 cm^{-1} (NH). Found: C 60.8; H 10.9%. $C_8H_{17}NO_2$. Calculated: C 60.3; H 10.8%.

The enamino ketones were obtained by the method described in [3].

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