B) A mixture of 1 g (2.5 mmole) of salt X and 8 ml of a 40% K_2CO_3 solution was refluxed for 4 h, after which it was cooled, and the precipitate was removed by filtration, washed with water, and dried to give 0.56 g (74.7%) of shiny pale-yellow plates with mp 155-156° (from ligroin). The product was identical to the product obtained by method A.

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CONFORMATIONAL STUDY OF CHIRAL CISOID ENAMINO KETONES*

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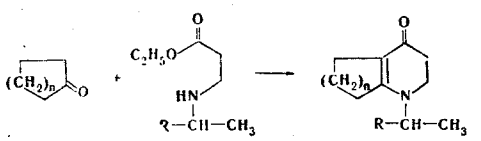
A study of a number of chiral cisoid cyclic enamino ketones by the circular dichroism method showed that they contain an inner disymmetric chromophore. The presence of homoconjugation of the phenyl and enamino ketone chromophores as a result of the drawing together of their π orbitals in space was also established.

In an investigation of chiral cisoid cyclic enamino ketones by the optical rotatory dispersion method in the case of III and IV we established [2] that the character of the rotatory dispersion curves reflects the nature of the cis-enamino ketone chromophore. To obtain further information regarding the three-dimensional structures of the enamino ketones we synthesized a series of compounds (III-VIII) and investigated them by the circular dichroism (CD) method. The enamino ketones necessary for the study were obtained by condensation of cycloalkenones with optically active β-aminopropionic acid esters in the presence of catalytic amounts of trifluoroacetic acid:



n=1, 2, 3 I, II III-VIII

I R=C_6H_5; II R=$CH_2C_6H_5$; III n=1, R=C_6H_5; IV n=2, R=C_6H_5; V n=3, R=C_6H_5; VI n=1, R=$CH_2C_6H_5$; VII n=2, R=$CH_2C_6H_5$; VIII n=3, R=$CH_2C_6H_5$

The UV spectroscopic data indicate the presence in the products of an enamino ketone chromophore, the absorption maximum of which in all cases is found at 310-330 nm. A bathochromic shift as the polarity of the solvent increases and a large extinction coefficient (log $\varepsilon > 4$) are observed for this absorption band, and this

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TABLE 1. Spectral Characteristics of Enamino Ketones III-VIII

Compound	n	R	UV spectrum		CD	
			λ_{max}, nm	(ε)	λ_{max}, nm	(θ)
III	1	C_6H_5	310[a]	(14580)	320[a]	(+22700)
			320[b]	(10000)	318[b]	(+17810)
			340[c]	(21000)	330[c]	(+27810)
IV	2	C_6H_5	315[a]	(15840)	324[a]	(+18590)
			328[b]	(14040)	327[b]	(+37900)
			338[c]	(19120)	337[c]	(+43400)
V	3	C_6H_5	319[a]	(16530)	330[a]	(+14000)
			320[b]	(11960)	323[b]	(+48600)
			340[c]	(21800)	342[c]	(+45300)
VI	1	$CH_2C_6H_5$	318[a]	(13030)	313[a]	(+12820)
			315[b]	(10680)	316[b]	(+42250)
			340[c]	(18330)	336[c]	(+47700)
VII	2	$CH_2C_6H_5$	315[a]	(12200)	315[a]	(+49000)
			324[b]	(19160)	338[b]	(+57800)
			338[c]	(23250)	322[c]	(+68400)
VIII	3	$CH_2C_6H_5$	310[a]	(18200)	309[a]	(+42850)
			315[b]	(12800)	313[b]	(+54900)
			332[c]	(16430)	332[c]	(+45130)

[a] In heptane.
[b] In CF_3COOH.
[c] In methanol.

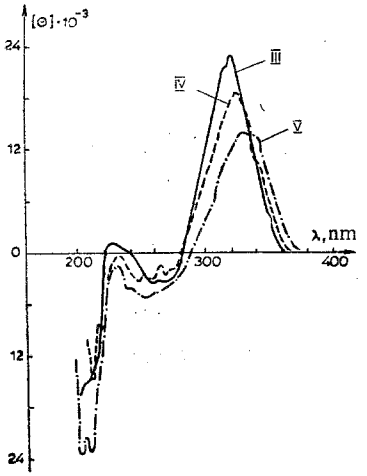


Fig. 1. Circular dichroism of enamino ketones III-V in heptane.

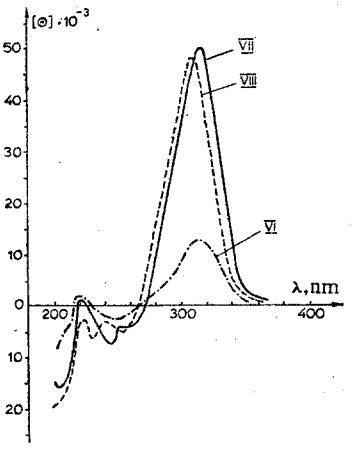


Fig. 2. Circular dichroism of enamino ketones VI-VIII in heptane.

makes it possible to assign this maximum to a $\pi-\pi^*$ transition of the enamino ketone chromophore. The band of the phenyl chromophore appears as a shoulder at 240-250 nm, but this is not true for all of the compounds.

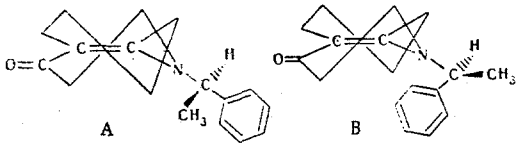
The presence of a chiral substituent at nitrogen in the investigated enamino ketones makes its electron transitions optically active and converts the enamino ketone chromophore to strictly a dissymmetric chromophore. This in turn creates the possibility for the determination, by means of CD curves, of the change in the three-dimensional structure of the chromophore and, consequently, of the investigated enamino ketones.

An examination of three-dimensional models of six-membered enamino ketone IV shows that the conformation in which both rings have half-chair forms is the most favorable one. Free rotation of the phenylethyl substituent is substantially hindered, as confirmed by an analysis of the PMR spectrum of N-benzyl-Δ^9-octahydro-4-quinoline, in which one observed nonequivalence of the protons of the methylene group of the N-benzyl substituent (quartet, δ, 4 ppm), which attests to retarded rotation of the benzyl group [3]. An examination of molecular models of enamino ketones III and V-III showed that their construction is similar to that of IV, but a different degree of distortion of the heterocyclic ring as a function of the size of the carbocycle is observed.

The CD curves of solutions of enamino ketones III-VIII in solvents with differing polarities were investigated. Three Cotton effects (CE) are observed on the CD curve of enamino ketone IV in heptane: a strong positive effect with a maximum at 324 nm corresponding to a $\pi \rightarrow \pi^*$ transition of the enamino ketone chromophore, a low-intensity negative effect at 250 nm, which we assigned to the ^1L_b band of the aromatic chromophore, and a strong negative effect at 210 mm, which is apparently the result of mixing of the ^1L_a transition of the aromatic chromophore and the $n \rightarrow \sigma^*$ transition of the enamino ketone (Fig. 1). Only a longwave positive CE associated with a $\pi \rightarrow \pi^*$ transition of the enamino ketone chromophore with a peak at 339 nm and a valley at 300 nm is observed on the DC curve. The midpoint of this CE practically coincides with the maximum of the positive band of the $\pi \rightarrow \pi^*$ transition in the CD spectrum. Correlation of the band of the $\pi \rightarrow \pi^*$ transition in the UV and CD spectra is also observed. The trends of the CD curves of enamino ketones III and V-VIII in heptane are similar, but the molecular ellipticity values change (Table 1), and there is a slight change in the position of the maxima ($\Delta\lambda$ 5-9 nm).

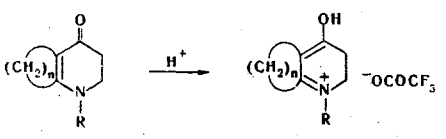
One should note the decrease in the absolute value of the molecular ellipticity of the positive band of $\pi \rightarrow \pi^*$ transition as the size of the carbocyclic ring increases ($\theta_{III} = +22{,}700$, $\theta_{IV} = +18{,}590$, and $\theta_V = +14{,}000$). On the other hand, the magnitude of the absorption for this series increases as the size of the carbocycle increases ($\varepsilon_{III} = 14{,}580$, $\varepsilon_{IV} = 15{,}835$, and $\varepsilon_V = 16{,}530$). This increase in the absorption constitutes evidence for more favorable conditions for conjugation in the enamino ketone chromophore. Inasmuch as the chromophore system simultaneously becomes more planar, this reduces the degree of dissymmetry of the chromophore and leads to a decrease in the molecular ellipticity. Internally, the dissymmetric nature of the enamino ketone chromophore is also confirmed by our calculation of the rational force [4], which is on the order of 10^{38}.

From an analysis of models, for enamino ketone III-VIII one can propose the existence of two preferred conformations A and B:



The existence of enamino ketone molecules preferably in conformation B may make an additional contribution to rotation as a result of the drawing together in space of the π orbitals of both chromophores, i.e., through homoconjugation [5]. To verify this possibility we investigated enamino ketones VI-VIII, which have a benzylethyl substituent attached to the nitrogen atom. The phenyl ring and the enamino ketone chromophore in these compounds are separated by three σ bonds, and the configuration of the asymmetric center remained S. An examination of the molecular models of enamino ketones V-VIII showed that the benzylethyl group has much greater spatial freedom and may be situated almost parallel to the enamino ketone chromophore in such a way that their electron clouds interact. This sort of interaction should lead to changes in the absorption of the individual chromophores. The CD data in heptane (Fig. 2) were investigated for enamino ketones VI-VIII, and an increase in the molecular ellipticity of the positive band of the $\pi \rightarrow \pi^*$ transition was noted. The magnitude of the molecular ellipticity of the negative CD based at 250 nm, which corresponds to the ^1L_b transition of the aromatic chromophore, also increases for enamino ketones VII and VIII as compared with the ellipticity of the same transition in enamino ketones IV and V. In other respects, the trend of the CD curves of enamino ketones VI-VIII is similar to the trend of the curves for III-V. In conformity with these data, the increase in the molecular ellipticities of the examined bands is associated with homoconjugation of the phenyl and enamino ketone chromophores.

The trend of the CD curve in trifluoroacetic acid for enamino ketones III-VIII does not change appreciably, although, in conformity with [6], they exist in the O-protonated form, i.e., the nature of the chromophore changes:



An appreciable increase in the ellipticity of the $\pi \rightarrow \pi^*$ band (Table 1), which is apparently associated with noncoplanarity of the enolimine structure that develops (Fig. 3), was observed for all of the enamino ketones except five-membered III and VI on protonation. The existence of noncoplanarity gives rise to a

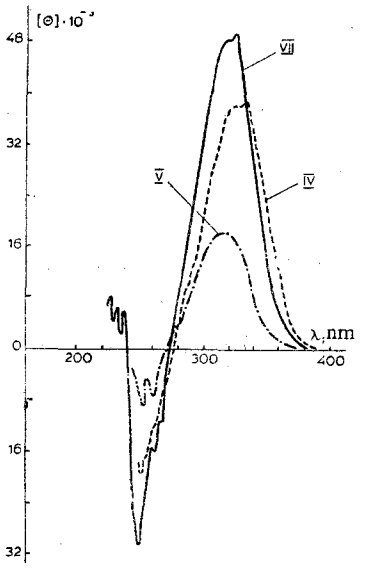


Fig. 3

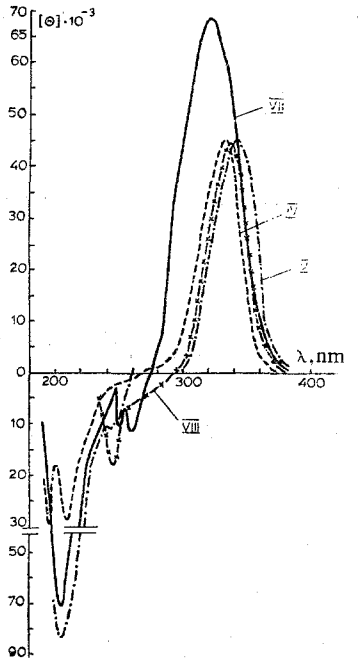


Fig. 4

Fig. 3. Circular dichroism of enamino ketones IV, V, and VII in trifluoroacetic acid.

Fig. 4. Circular dichroism of enamino ketones IV, V, VII, and VIII in methanol.

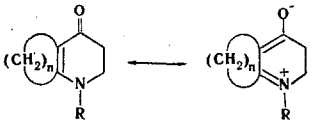
TABLE 2. Properties of Enamino Ketones V-VIII

Compound	mp, °C	IR spectrum, ν, cm^{-1}		Empirical formula	Found, %		Calc., %		M*	Yield, %
		C=O	C=C		C	H	C	H		
V	70—71	1610	1540	$C_{18}H_{23}NO$	80,1	8,5	80,4	8,6	269	40
VI	126—127	1595	1530	$C_{17}H_{21}NO$	79,2	8,5	79,9	8,3	255	54
VII	124—125	1615	1550	$C_{18}H_{23}NO$	79,9	8,5	80,3	8,6	269	61
VIII	99—100	1620	1560	$C_{19}H_{25}NO$	80,1	8,6	80,6	8,9	283	57

*The molecular weights (M) were determined by mass spectrometry.

decrease in the conjugation and, consequently, the intensity of the absorption but leads to an increase in the chirality of the enolimine chromophore, which is manifested maximally in seven-membered enamino ketone V.

The increase in the ellipticity of the $\pi \rightarrow \pi^*$ band of the enamino ketones in methanol is also associated with a contribution to rotation of the chiral dipolar mesomeric form – the aza analog of cisoid dienes [7,8] (Fig. 4):



n = 3,4,5

EXPERIMENTAL METHOD

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

Ethyl β-N-(α-Benzylethyl)aminopropionate (II). A 10.8-g (0.11 mole) sample of ethyl acrylate was added dropwise with stirring to 9.9 g (0.07 mole) of (+)-S-α-benzylethylamine in 108 ml of absolute alcohol, and the mixture was stirred at room temperature for 2 h and allowed to stand overnight. The solvent was removed, and the residue was vacuum distilled to give 13.9 g (84%) of ester II with bp 107-109° (1 mm), $[\alpha]_D$ +16.9° (without a solvent), d_4^{20} 0.8975, and n_D^{20} 1.5005. Found: C 71.3; H 9.2; N 6.0%. $C_{13}H_{21}NO_2$. Calculated: C 71.7; H 9.0; N 6.0%.

Enamino Ketones III-VIII (Table 2). These compounds were obtained by the method in [2] by refluxing 0.01 mole of the amino ester and 0.15 mole of the cycloalkanone in absolute xylene in the presence of a few drops of trifluoroacetic acid in an apparatus with a Dean–Stark trap for 3-9 h. The pure compounds were isolated with a column filled with activity II Al_2O_3 and successive elution with benzene, benzene–ethyl acetate (1 : 1), and ethyl acetate.

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