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INFLUENCE OF STRUCTURE ON THE CIRCULAR DICHROISM OF METHYL-SUBSTITUTED 1,3,4-TETRAHYDROBENZ[b]AZEPIN-2-ONES

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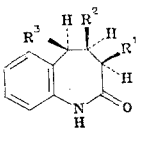
UDC 541.653:543.422.6:547.891.2

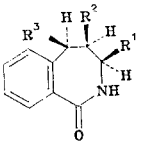
The chirooptical properties of methyl-substituted 1,3,4,5-tetrahydrobenz[b]azepin-2-ones have been studied. A considerable increase in the intensity of the Cotton effect (CE) in the 240-250 nm region with an enlargement of the lactam ring has been observed. The sign of this CE for seven-membered benzolactams correlates with the type of conformation of the lactam ring. A change in the nature of the conjugation (passage from lactams of the benzamide type $-C_6H_4-CO-NH-$ to lactams of the anilide type $-C_6H_4-NH-CO-$) leads to an inversion of the signs of the CEs in the 230-250-nm region.

The chirooptical properties of cyclic amides — lactams — have been described in fairly great detail in the literature (see, for example, [1-3]), unlike the benzolactams containing an aromatic chromophore (of the benzamide or anilide type) fixed to the ring and conjugated with the amide chromophore. We have previously studied a number of compounds of the benzamide type [4] with different sizes of the lactam ring [5] and different positions of the asymmetric center in seven-membered benzolactams [6].

In the present investigation, in order to establish the influence of the type of conjugation on the chirooptical properties of the benzolactams, we have studied the UV spectra and the circular dichroism (CD) of seven-membered benzolactams of the anilide type with different positions of the asymmetric center: R-(+)-3-methyl-, R-(−)-4-methyl-, and S-(−)-5-methyl-1,3,4,5-tetrahydrobenz[b]azepin-2-ones (I, II, and III, respectively), the synthesis of which we have described in preceding papers [7, 8].



I–III



IV–VI

R-(+)-I $R^1=CH_3$, $R^2=R^3=H$; *R*-(−)-II $R^2=CH_3$, $R^1=R^3=H$; *S*-(−)-III $R^3=CH_3$, $R^1=R^2=H$; *R*-(−)-IV $R^1=CH_3$, $R^2=R^3=H$; *R*-(+)-V $R^2=CH_3$, $R^1=R^3=H$; *S*-(+)-VI $R^3=CH_3$, $R^1=R^2=H$

When the CD spectra of the benzolactams obtained were measured in ethanol and in isooctane, it was found that the sign and magnitude of the observed Cotton effects (CEs) did not depend on the polarity of the solvent.

M. V. Lomonosov Moscow State University. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 97-100, January, 1984. Original article submitted April 19, 1983.

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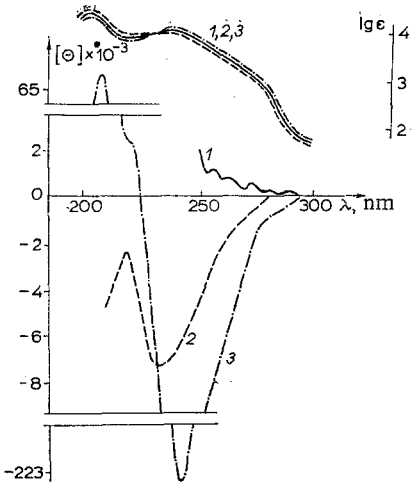


Fig. 1. UV and CD spectra in ethanol: 1) the R-(+)-3-methyl derivative (I); 2) the R(—)-4-methyl derivative (II); 3) the S-(—)-5-methyl derivative (III) of 1,3,4,5-tetrahydrobenz[b]azepin-2-one.

The CD spectra of the seven-membered benzolactams (I-III) showed two CEs: a weak aromatic CE in the 275-285 nm region due to the ^1L_b absorption band of the aromatic chromophore [the corresponding absorption band in the UV spectra appears in the form of an inflection at 275 nm (log ε 3.0)], and a considerably stronger CE in the 230-240-nm region connected with an optically active absorption band of the anilide grouping (Fig. 1).

The low optical purity of the 3-methyl isomer (I) [7] did not permit the quantitative measurement of the anilide CE, but the shape of the CE curve of compound (I) below 250 nm in ethanol and isooctane indicates the existence of a positive CE in this region of the spectrum. In the UV spectrum of all three benzolactams the corresponding absorption band appeared in the form of a distinct maximum in the 240-nm region (log ε 4.1).

For the 5-methyl isomer (III), we measured the strong short-wave CE in the 210-nm region apparently due to a second optically active absorption band of the aromatic chromophore (^1L_a band). The existence of a strong CE in the region below 220 nm is also shown by the shape of the CD curve of the 4-methyl isomer (II), but the sharp increase in absorption in the short-wave region of the spectrum did not permit a reliable determination of the position of this maximum. An absorption band corresponding to this CE appeared in the UV spectra of all three benzolactams at 204 nm.

A comparison of the chirooptical properties of five-membered [5] and six- and seven-membered [4-6] benzolactams of the benzamide and anilide types with the same positions of the asymmetric center relative to the chromophore showed a considerable increase in the intensity of the CE in the 230-250 nm region with an expansion of the lactam ring (thus, for R-(—)-4-methyl-3,4-dihydro-2H-1-quinolone in ethanol, $[\theta]_{237} = -6720°$ [9], and for S-(—)-5-methyl-1,-3,4,5-tetrahydrobenz[b]azepin-2-one (III), $[\theta]_{242} = -223{,}100°$). In the UV spectra of the benzolactams of the anilide type investigated under the same conditions a hypsochromic shift took place ($\Delta\lambda_{max}$ 10 nm) with a decrease in the intensity of the corresponding absorption band (Δ log ε 0.1).

It may be assumed that the observed differences are due to a distortion of the planar conjugated system of amide and aromatic chromophores with an increase in the size of the lactam ring. The conformational mobility of six-membered benzolactams is limited: Five of the atoms of the lactam ring lie in one plane, and only one — the $C_{(3)}$ — carbon atom can depart from this plane. The conformational contribution due to the dissymmetry of the lactam ring is not so considerable for six-membered as for seven-membered benzolactams.

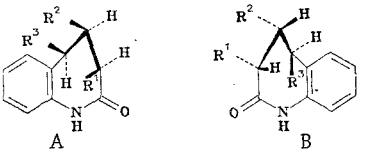
The tetrahydrobenz[b]azepin-2-ones (I-III; benzolactams of the anilide type) and the tetrahydrobenz[c]azepin-1-ones (IV-VI) (benzolactams of the benzamide type) studied previously [5, 6] exhibit some general features: The CE in the 240-250-nm region for the 3- and 5-methyl isomers is considerably greater than that for the 4-methyl isomers (we do not consider 3-methyl-1,3,4,5-tetrahydrobenz[b]azepin-2-ones, the optical purity of which was low).

One of the possible reasons for this fact may be the remoteness of the asymmetric $C_{(4)}$ carbon atom from the two ends of the conjugated chromophore. The second and, apparently main reason is the conformational composition of the seven-membered benzolactams. In these com-

Compound	Type of preferred conformation	Sign of the CE in the 240-250 nm region (ethanol, isooctane)
R-(+)-I	B	+
R-(−)-II	(A)	−
S-(−)-III	A	−
R-(−)-IV	B	−
R-(+)-V	(A)	+
S-(+)-VI	A	+

pounds, because of an increase in the conformational mobility of the seven-membered lactam ring the possibility is created of a lack of coplanarity of the amide group and the aromatic ring [10], which leads to the appearance of an intrinsically dissymmetric chromophore.

The chirality of this chromophore is different for the two possible stable conformations A and B (identical for the anilide and benzamide types of lactams):



A B

The large values of the CE for the 3- and 5-methyl isomers shows the presence in these compounds of one preferred conformation which determines the sign and magnitude of the observed CEs. The conclusion concerning the predominance of one conformation or the other can be drawn on the basis of the configuration of the benzolactams and the preferred quasi-equatorial orientation of the methyl group.

In the case of the (R)-3-methyl isomers (I) and (IV), the quasi-equatorial orientation of the methyl group is achieved in conformation B and for the (S)-5-methyl isomers (III) and (V) this is the case for conformation A. The signs of the CEs of the seven-membered benzolactams in the 240-250 nm region correlate with the types of conformations of the lactam ring (Table 1). For compounds of anilide type, a negative sign at 240-250 nm corresponds to the A conformer and a positive sign to the B conformer; for compounds of the benzamide type, the signs of the CEs of the corresponding conformers are the opposite (+ for A; − for B).

In the case of the 4-methyl isomers, apparently, two conformations of the lactam ring with close energies exist whose contributions to the optical activity cancel one another out, which explains the small values of the CEs. The sign of the CEs of the 4-methyl isomers indicates some predominance of conformer A, making a positive contribution to the rotation in the case of a benzamide-type chromophore and a negative contribution in the case of an anilide-type chromophore.

The reversal of the signs of the CEs for the benzolactams with the same type of conformation with a change in the nature of the conjugation (—C_6H_4—NH—CO— in compounds (I-III) and —C_6H_4—CO—NH— in compounds (IV-V)) is obviously connected with a change in the direction of the electronic transition. On the basis of a study of the UV and CD spectra, the optically active absorption band in the anilides in the 242-247 nm region (log ε 4.1) is assigned to a charge-transfer band (a CTB) in the anilide chromophore (see, for example [11]). Information on the benzamide chromophore is less clear. Some authors [11] assign the CE in the 225-250 nm region to a CTB in the benzamide chromophore, and others to the $n \rightarrow \pi^*$ transition in the benzamide chromophore [12]. A consideration of the CTBs in the anilide and the benzamide chromophore on the basis of the theory of this type of transition indicates different directions of electron transfer. In the case of anilides, the electrons pass from the p-orbital of the donor substituent (the nitrogen of the amide group) to the π^*-orbital of the aromatic nucleus, and in the case of the benzamides the direction of transfer is the opposite, from the aromatic nucleus to the acceptor substituent (carbonyl group).

The values of the Hammett constants of the substituents $NHCOCH_3$ and $CONH_2$ [13] and also the results that we have obtained from a mass-spectral study of isomeric benzolactams of the anilide and benzamide types [8, 14] indicate a decrease in the conjugation of the amide group

with the aromatic nucleus in the benzamide chromophore as compared with the anilide chromophore. This is confirmed by an investigation of the chiroоptical properties of benzolactams of the anilide and benzamide types with the same size of lactam ring and the same position of the asymmetric center in it. Thus, for the six-membered compounds studied previously, on passing from the 3,4-dihydro-2-quinolones [9] to the corresponding 3,4-dihydro-1-isoquinolones [4], a hypsochromic shift of the maximum appears (from 250 nm to 230 nm), and also a decrease in its intensity ($\Delta\varepsilon$ 300-800). In the case of the seven-membered compounds, the differences in the UV spectra are even more considerable: While for tetrahydrobenz[b]azepin-2-ones (I, II, and III) a sharp maximum is observed in the 240-nm region (log ε 4.1), for the tetrohydrobenz-[c]azepin-1-ones (IV, V, and VI) [5, 6] the corresponding band does not appear at all. There are also differences in the spectropolarometric behaviors of the compounds of the anilide and benzamide types, although these are less considerable than in the UV spectra. A somewhat greater intensity of the "characteristic" CE (in the 240-250-nm region) is observed for compounds of the anilide type and also the above-mentioned inversion of the sign of the CE in the seven-membered benzolactams.

A comparison of the chiroоptical properties and results of the mass-spectral investigation of the isomeric benzolactams of the benzamide and anilide types permits the assumption that the deciding contribution to the CE at 230-250 nm is made in both cases by the charge-transfer band, although the question of the nature of the benzamide CE cannot be regarded as having been definitively answered.

EXPERIMENTAL

CD spectra were taken on a JASCO J-20 spectropolarimeter in cells 1, 0.5, and 0.1 mm thick. UV spectra were taken on a Cary-219 spectrophotometer.

R-(+)-3-Methyl-1,3,4,5-tetrahydrobenz[b]azepin-2-one (I). The synthesis and the characteristics of the IR and UV spectra and the CE in isooctane have been given in a preceding paper [7]. CD in ethanol (c 0.04) [θ] (λ, nm): 0 (300), 46 (282), 640 (270), 365 (268), 1050 (252), 1370 (250), 1920 (240).

The synthesis and details of the IR and mass spectra of R-(−)-4-methyl- and S-(−)-5-methyl-1,3,4,5-tetrahydrobenz[b]azepin-2-ones (II and III) have been given by Terent'ev et al. [8].

R-(−)-4-Methyl-1,3,4,5-tetrahydrobenz[b]azepin-2-one (II). UV spectrum in ethanol: λ_{max}, nm (log ε): 275 (inflection, 3.0); 239 (4.1). CD in ethanol (c 0.01) [θ] (λ, nm): 0 (300), 211 (285), 0 (280), −7220 (233); (c 0.001): −2100 (220), −5280 (210).

S-(−)-5-Methyl-1,3,4,5-tetrahydrobenz[b]azepin-2-one (III). UV spectrum in ethanol, λ_{max}, nm (log ε): 275 (inflection, 2.96), 238 (4.13), 219 (3.83). CD in ethanol (c 0.03) [θ] (λ, nm): 0 (300), −178 (285), −6090 (260); (c, 0.003): 152,170 (250), −223,100 (242), −76,090 (230), 0 (225), 35,510 (220), 55,800 (210), 65,940 (208), 0 (202). CD in isooctane (c 0.006) [θ] (λ, nm): 0 (300), −8750 (270), −173,490 (245), 0 (230), 27,160 (223), 95,040 (208), 75,430 (205).

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PREPARATION AND PROPERTIES OF AZINIUM SALTS OF THE 2-PYRAZOLINE SERIES

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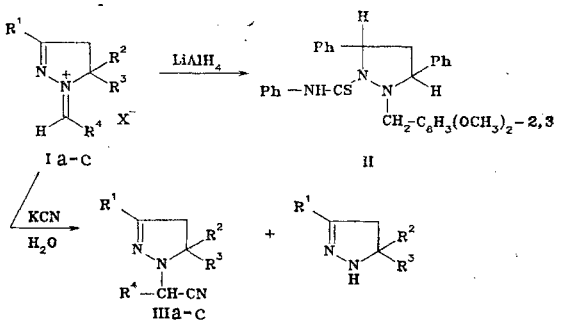
UDC 547.772.2:542.942.4

Azinium salts containing pyrazoline fragments have been obtained by the reaction of 2-pyrazolines with aromatic and heteroaromatic aldehydes, acetylacetone, and acetoacetic ester in the presence of H_2SnCl_6 and HBF_4. Reactions of nucleophilic addition to the multiple bonds and also some cycloaddition reactions among the arylidene derivative have been studied. From the azinium salts of a series of β-dicarbonyl compounds have been obtained previously unknown enamino carbonyl compounds of the 2-pyrazoline series.

Up to the present time, the synthesis of only a few representatives of azinium salts of the 2-pyrazoline series [1] and their hydrolysis [2, 3] and reduction [4] has been described. On studying the possibility of activating the C=N bond in 2-pyrazolines to the attack of nucleophilic agents, we turned to a more detailed study of the properties of this class of compounds. In addition to the fact that this system consists of a model of a pyrazoline ring activated at the $N_{(1)}$ atom, it contains two C=N groups the reactivities of which may differ sharply. As the object of investigation we selected two types of azinium salts: the benzylidene salts (Ia-g, Table 1), which permitted us to study the reactivities of the azinium systems themselves, and the condensation products of salts of 2-pyrazolines with β-dicarbonyl compounds — acetoacetic ester and acetylacetone (IV and V in Table 1) — which enables us to study mutual influence in a system of conjugated bonds. In addition to the preparation of hexachlorostannates by known methods [1, 2], we obtained the tetrafluoroborates in a two-phase system.

In the PMR spectra of the benzylidene derivative (I) obtained, the signals of all the protons of the pyrazoline ring were shifted downfield in comparison with the free 2-pyrazolines. Thus, the signal of the 5-H proton was shifted into the 6.2-ppm region as compared with 4.5 ppm, and the signals of the 4-H protons into the 3.8-4.5 ppm region as compared with 2.8-3.2 ppm for the free pyrazoline. The IR spectra of the salts (I) each contained two different bands of the vibrations of the C=N and $C=N^+$ bonds, in the 1600-cm^{-1} regions, regions, respectively.



I, III a $R^1=R^2=R^3=CH_3$, $R^4=Ph$, $X=1/2\ SnCl_6^{2-}$; b $R^1=R^2=Ph$, $R^4=C_6H_3(OCH_3)_2$-2,3, $X=BF_4^-$; c $R^1=CH_3$, $R^2=R^4=Ph$, $X=BF_4^-$

M. V. Lomonosov Moscow State University. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 101-105, January, 1984. Original article submitted August 2, 1983.

0009-3122/84/2001-0085$08.50