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EFFECT OF THE HETEROATOM OF A BENZO[b]-ANNELATED FIVE-MEMBERED HETERORING ON THE STRUCTURE AND PROPERTIES OF AN AMINOVINYL KETONE FRAGMENT INCLUDED IN THE RING

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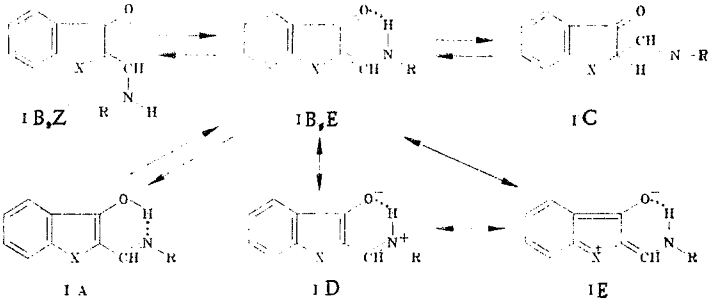
An analysis of the results of theoretical and physicochemical studies of and x-ray diffraction data for a series of aminovinyl ketones — derivatives of hydroxy aldehydes of benzo[b]-annelated five-membered heterosystems — is presented. In addition to the peculiarities of the aminovinyl ketone fragment, the effect of the heteroatom of the five-membered ring on the structure and properties of aminovinyl ketones, which consists in direct electronic conjugation of the ring carbonyl group with the heteroatom, was ascertained.

Studies carried out by means of electronic, IR, and PMR spectroscopy [1-3] and x-ray diffraction analysis [4-6] have made it possible to establish and confirm, by means of the results of quantum-chemical calculations [7], the preferableness of an aminovinyl ketone structure (B) for the potentially tautomeric molecules of the I type in the solid phase and in various solvents, regardless of the external conditions (temperature, irradiation). It has also been shown that some types of aminovinyl ketones exist in solutions in the form of two (E and Z) equilibrium forms [2, 8-10], and opinions regarding the preferableness of the $O^{-}{-}CR{=}CR{-}CH{=}N^{+}HR$ zwitter-ion structure in the aminovinyl ketone fragment have been expressed [10-13].



In the present communication we attempted to evaluate the peculiarities of the structure of compounds of the I type and their derivatives as a function of the properties of the structural links, particularly the X group of the five-membered ring. The IB molecules may exist in the form of Z-IB and E-IB isomers [with an intramolecular hydrogen bond (IMHB)], each of which, as a consequence of the effects of conjugation of the electron-acceptor carbonyl group, contains a certain degree of contribution of canonical forms D and E. Structure D reflects π polarization in the tautomeric chain. The contribution of the E form, which corresponds to π interaction of the C=O and X groups, will increase with an increase

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in the electron-donor character of the X group, evidently in the order $CO < CH_2 < O < S < Se < NCH_3$. Electron shifts in cases D and E create excess negative charge on the oxygen carbonyl atom, thereby promoting the formation of a strong IMHB as compared with keto form B, in which the formation of a ring with an IMHB is less likely. Let us note that heterocycles that contain S, Se, and NMe as the X group are aromatic. This should stabilize the annelated quasi-aromatic ring with a hydrogen bond.

It might be assumed that the influence of the corresponding electronic effects should affect the actual bond lengths in the molecules, as well as the physicochemical properties of the I systems. In order to detect this dependence we analyzed the structural and physicochemical characteristics of compounds that we have previously investigated. The bond lengths in the tautomeric aminovinyl ketone fragment, calculated for N-phenyl compounds I (R = Ph) by the Pariser—Parr—Pople (PPP) method within the Dewar σ, π parametrization [7], and the corresponding data from x-ray diffraction analysis [4-6]* are presented in Table 1. The three-dimensional structures of the molecules are reflected in the writing of the formulas (Table 1). One may note that the calculated bond lengths do not convey the effect of the X group. On the other hand, the x-ray diffraction data provide evidence for the contribution of conjugated structures D (III and V) and E (IV) to the distribution of the bonds; the dominating role belongs to keto enamine form B. In fact, with the exception of the III molecule (possibly as a consequence of the effect of nitrophenyl substituent R), the C=O bond is elongated in IV and V as compared with II, which corresponds to its considerable polarization. The carbonyl group in II displays the greatest degree of double bond character. The distance between the $C_{(2)}$ and $C_{(3)}$ atoms is appreciably shorter in III than in II and particularly IV. The double bond character of the exocyclic $C_{(3)}=C_{(4)}$ bond is most pronounced in II and IV. The III molecules contain a stronger $C_{(4)}-N_{(5)}$ bond than II and IV structures. Thus, in conformity with the electron-donor character of heteroatom X in the II-IV molecules, the contribution of dipolar structures D and E increases. This is the reason for the existence of the aminovinyl ketone fragment of II in the Z configuration with an intermolecular hydrogen bond and of the aminovinyl ketone fragments of III and IV in the E configuration with an IMHB. Judging from the NH...O=C distances, all of the hydrogen bonds are quite strong (Table 1). The aminovinyl ketone of the indandione series (V) is an interesting model that combines E- and Z-tautomeric chains in a single molecule. The $O_{(1)}=C_{(2)}$ group is included in a "forcedly" (for steric reasons) formed ring with an IMHB. Its bond parameters provide evidence for the evident contribution of dipolar form D. The other "free" $C_{(6)}=C_{(7)}$ group has appreciably greater double bond character, and the $C_{(6)}=C_{(3)}$ distance is 0.016 nm longer than the $C_{(2)}-C_{(3)}$ bond (Table 1).

The above-noted structural peculiarities are reflected in the physicochemical properties of the II-V molecules, as evidenced by the data presented in Table 2 for N-phenyl derivatives. The constants for 2-(N-phenylaminomethylene)-indan-3-one (VI), crystals of which have not been subjected to x-ray diffraction analysis, are also included in Table 2. However, following the logic set forth above, in connection with the sp^3-hybridized X = CH_2 group and the absence of conjugation of the E type, one may propose for the VI molecules Z-keto enamine structure B in the solid phase with a small contribution of the dipolar D form and with parameters close to those of benzofuran analog II. The frequencies of the stretching vibrations of the bonds of the tautomeric frgment are a sensitive indicator of the fine structures of the II-VI molecules. The conjugated bonds that are not tied up in a ring wih an IMHB are least polarized. The high-frequency vibrations at 1715 and 1700 cm^{-1} in the spectra of II and V and, probably, VI (1695 cm^{-1}) correspond to them. Polarization of the orbitals in the III-V molecules leads to a substantial decrease in the frequencies of the stretching vibrations of the keto enamine fragment. Let us note that this effect is not a consequence of a decrease in the strain of the five-membered ring in connection with an increase in the size of the X groups, since, according to the data from x-ray diffraction analysis, the magnitude of the ring angle at the carbonyl carbon atom does not vary over a wide range — from 102.4° in II to 108.9° in III [4-6].

According to quantum-chemical calculations by the Pariser—Parr—Pople (PPP) method, the long-wave band in the electronic absorption spectra of II-VI reflects redistribution of the

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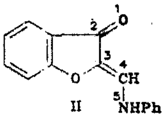
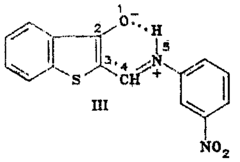
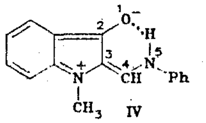
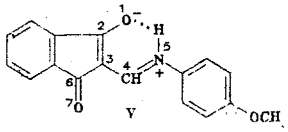
*The x-ray diffraction analysis was carried out by L. O. Atovmyan and S. M. Aldoshin (Branch of the Institute of Chemical Physics, Academy of Sciences of the USSR, Chernogolovka).

TABLE 1. Experimental and Calculated Bond Lengths of the Tautomeric Fragments of II-V

Compound	Bond length,* nm				
	$O_{(1)}-C_{(2)}$	$C_{(2)}-C_{(3)}$	$C_{(3)}=C_{(4)}$	$C_{(4)}-N_{(5)}$	$(N_{(5)})$ $H\cdots O_{(1)}$
 II	0,1220 (0,1265)	0,1458 (0,1460)	0,1345 (0,1352)	0,1358 (0,1407)	0,207
 III	0,1195 (0,1264)	0,1452 (0,1465)	0,1367 (0,1351)	0,1342 (0,1413)	0,195
 IV	0,1248	0,1478	0,1353	0,1352	0,184
 V	0,1237 ($O_{(7)}=C_{(6)}$ 0,1224) (0,1262)	0,1439 ($C_{(6)}-C_{(3)}$ 0,1455) (0,1465)	0,1380 (0,1358)	0,1328 (0,1403)	0,208

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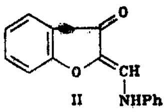
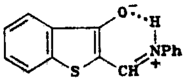
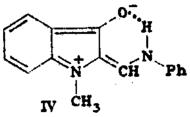
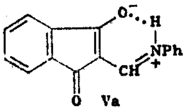
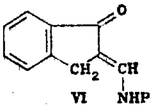
*The calculated values are indicated in parentheses. In the case of III and V the values for molecules with unsubstituted N-phenyl rings are presented.

π charge from the aminomethylene part of the molecule to the electron-acceptor carbonyl groups [7]. The effect of the X fragment, which consists in drawing together of the S_0 and S_1 levels as its electron-donor character increases, is evident from the data in Table 2. A bathochromic shift of the maximum of the long-wave band ($\Delta\lambda_{max}$ 150 nm) is noted on passing from indandione molecules V (X = CO) to indole molecules IV (X = NCH_3) through VI, II, and III; this is explained by an increase in the polarization of the systems.

The weak-field shift of the signals of the NH protons in the PMR spectra reflects the considerable contribution of zwitter-ion form D, in contrast to the slightly polarized aminovinyl ketones, which have chemical shifts (CS) δ_{NH} 4-6 ppm [1]. Regardless of which form of hydrogen bond predominates in solutions of I, the strongest NH bond is noted in the II, V, and VI molecules. In direct relationship to this, the same aminovinyl ketones with a very slight contribution of dipolar form D have the lowest acidities (Table 2). All of the data presented in Table 2 for VI make it possible to assume the real proposed structure, which contains the least contribution of dipolar form D with a trans configuration of the aminovinyl ketone fragment in the solid phase.

In discussing the structure of systems I, we did not take into account the steric factors of the X group, which should not be significant and may be reflected only in the stabilities of the E and Z isomers in molecules of the IV type. An increase in the electron-donor character of the R group attached to the nitrogen atom in I leads to strengthening of the N-H bond, a decrease in acidity [14], and an increase in the polarization of the C=O group. Electron-accetor R groups increase the NH acidity and decrease the overall effective negative charge on the carbonyl fragment. Replacement of the exocyclic oxygen atom by sulfur leads to aminovinyl thiones. Since a less electron-accepting (than C=O) but more polarizable C=S group arises in the molecules, the previous reasoning is also acceptable in this case. The role of dipolar structures in aminovinyl thione molecules is significant. Evidence for this is provided by the increased (as compared with ketones) acidities of the thiones [14], strengthening of the IMHB, the results of x-ray diffraction analysis [18], and other facts [19]. The sulfur atom in the aminovinyl thione anion is a softer nucleophilic center than the oxygen atom in amino ketones.

TABLE 2. Physicochemical Characteristics of II-VI

Compound	ν, cm^{-1} (in mineral oil)	λ_{max}·nm ($\varepsilon \cdot 10^{-3}$)	δ_{NH} (in DMSO), ppm [14]	pK$_d$ (in acetonitrile) [14]
 II	1715 [16]	417 (31,0) [16]	10,15	23,78
 IIIa	1660 [15]	445 (26,5) [15]	10,30	23,49
 IV	1675 [17]	520 (25,4) [17]	10,0	—
 Va	1645 1700 [17]	370 (36,9) [17]	11,10	23,21
 VI	1695 [17]	390 (30,3) [17]	9,43	25,29

Thus, in addition to other factors, the effect of heteroatom X of the five-membered ring on the structure and properties of aminovinyl ketones of the I type was ascertained.

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