STEREOCHEMISTRY OF NITROGEN HETEROCYCLES.

70. CONFORMATION OF 1-BENZOYL-t-2-METHYL-t-5-BENZOYLOXY-r-9-H-CIS-DECAHYDROQUINOLINE AND THE NATURE OF ITS COMPLEX WITH BENZOIC ACID

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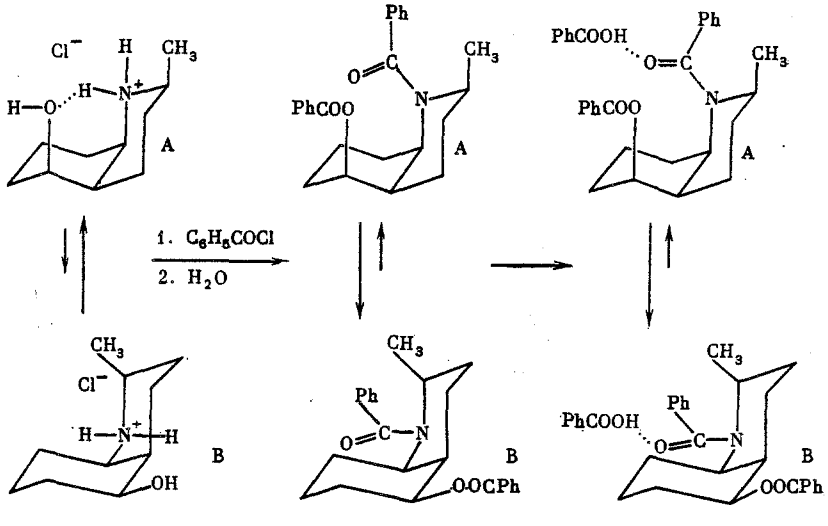
547.581.2

In the continuation of the study of the stereochemistry of 4- and 5-substituted decahydroquinolines [1-3], an investigation of the structure of 1-benzoyl-t-2-methyl-t-5-benzoyloxy-r-9-H-cis-decahydroquinoline (II) and its 1:1 complex with benzoic acid (BA) (III) was carried out. The hydrochloride of t-2-methyl-t-5-hydroxy-r-9-H-cis-decahydroquinoline (I) [4-6] exists in the conformation (IA) with the intramolecular hydrogen bond; the charge on the nitrogen is delocalized to a significant degree in consequence of this. Therefore, when (I) is benzoylated by the method of [7] (heating with benzoyl chloride), the main reaction product is found to be not the benzoate ester but the amidoester (II), which is isolated in the free form or as the complex with benzoic acid (BA) (III).



(I) (II) (III)

The mass spectrum of (II) has the molecular ion of mass 377 and the fragment ions (M—1)$^+$, (M—15)$^+$, and (M—105)$^+$ corresponding to the removal of the H and CH$_3$ in the α-position to the N atom, and the PhCO groups, as well as the rearrangement ion with the m/z 122 corresponding to the removal of BA. The IR spectrum contains the absorption bands of the ester (1715 cm^{-1}) and amide (1628 cm^{-1}) oxo groups and the C—C double bonds of the Ph rings (1585 and 1603 cm^{-1}). The PMR spectrum in the region of $\sim$7 ppm contains the signals from 10 aromatic protons. The signal of the proton at the C^5 atom is a doublet of triplets (δ from TMS 5.06 ppm, J = 10.5, 5.0, and 5.0 Hz); this demonstrates the axial orientation of the H atom and the equatorial orientation of the PhCOO substituent. On the basis of these data, the conformation (IIB) can be assigned to it, taking into account the configurational relation of (II) with the initial aminoalcohol (I) [4].

Therefore, (II) is similar in its structure to the previously investigated 1-benzoyl-t-2-methyl-4-oxo-r-9-H-decahydroquinoline [2] and 1-benzoyl-t-2-methyl-t-4-hydroxy-r-9-H-cis-decahydroquinoline [3] existing in the conformation with the diaxial disposition of the α,α'-substituents at the piperidine ring (the C^{11}H$_3$ substituent at the C^2 atom and the C^{8}H$_2$ group), since the alternative conformation (IIA) with the equatorial orientation of these substituents

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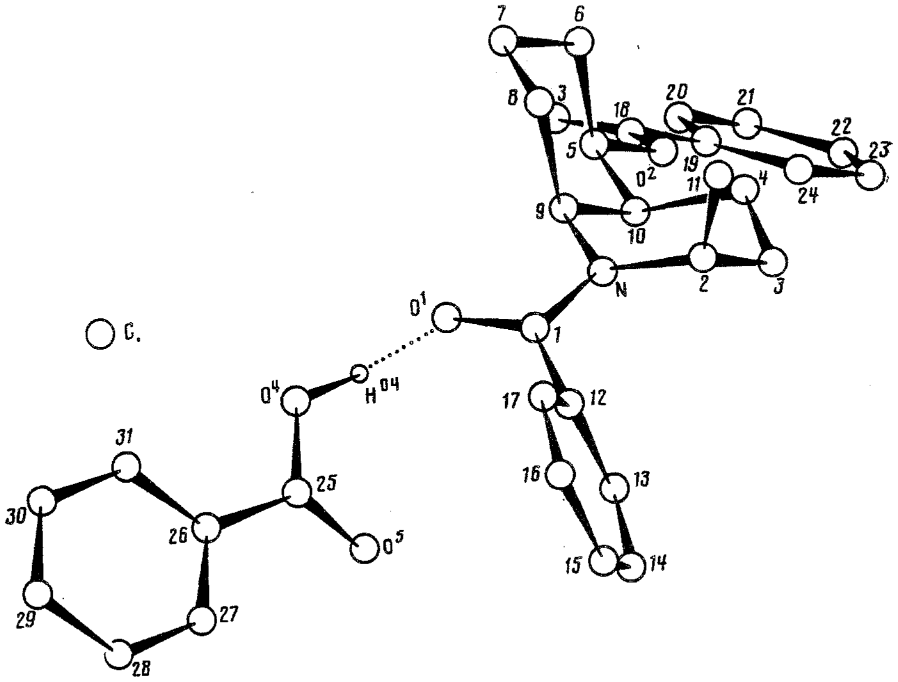

Fig. 1. The structure of the complex (III).

is energetically less favorable due to the steric hindrance for the conjugation of the CO group of the PhCO substituent with the unshared electron pair (UEP) of the N atom.

The molecular ion is absent from the mass spectrum of the complex (III). However, the ions of the amidoester (II) with the m/z 377 and of BA with the m/z 122 are present, whereby the latter is present in a significantly higher amount than in the mass spectrum of (II). This permits the assumption that the heating of (III) in the mass spectrometer proceeds with its thermal decomposition to (II) and BA. Salts of the type of hydrochlorides and complex compounds behave in such a way. The fact that (II) is readily isolated from compound (III) by its treatment with an aqueous-alcoholic solution of potassium carbonate and by the chromatography on Al_2O_3 also indicates that (II) and BA are not connected by a covalent bond.

The PMR spectrum of compound (III) has the signals of 15 aromatic protons; this corresponds to the 1:1 ratio of (II) and BA. The proton at the C^5 atom is identified in the spectrum as a doublet of triplets (J = 10.4, 5.2, and 5.2 Hz) with the chemical shift of 4.88 ppm; this indicates the existence of the decahydroquinoline fragment in the conformation (IIIB) but not (IIIA).

The IR spectrum of (III) contains intensive bands with frequencies of 1715 cm^{-1} (the CO group of the ester substituent) and 1568 cm^{-1}, a broad band in the region of 2400-2800 cm^{-1}, and weak bands of the C=C vibrations of the Ph ring with the frequencies of 1589, 1600, and 1630 cm^{-1}. The band at 1568 cm^{-1} occurs in the range of frequencies characteristic of the anion of BA (1550-1610 cm^{-1}). This permits the proposition that an acid-base interaction takes place between (II) and BA with the formation of the salt, and that the band with the frequency of 1568 cm^{-1} corresponds to the carbanion; the absorption in the region of 2400-2800 cm^{-1} corresponds to the vibrations of O^+—H. However, there is doubt as to whether the amide, which is a very weak base, can form a salt with a weak acid such as benzoic acid. It can be proposed that the donor-acceptor interaction does not go as far as the salt formation, and (III) is a complex compound in which the BA is connected by an H-bond with the CO group of the amide. The frequency of the absorption of the amide CO group should decrease both with the protonation and in the formation of the H-bond [8], whereby the absorption frequency of the CO group of the acid in the first case should decrease to the frequency of the CO group of the anion, and in the second case by substantially less. With the object of clarifying whether the band with the frequency of 1568 cm^{-1} is complex, the Raman spectrum was recorded. However, there is only one band of medium intensity at 1561 cm^{-1} in the Raman spectrum besides the strong absorption band of the CO group of the ester (1718 cm^{-1}) and the very strong band of the vibrations of the Ph ring (1604 cm^{-1}).

TABLE 1. Coordinates of the Atoms ($\times 10^4$; $\times 10^3$ for the H atom) in the Structure of (III)

Atom	*X*	*Y*	*Z*	Atom	*X*	*Y*	*Z*
O^1	3886,4(8)	493(2)	1269(1)	C^{14}	3739(2)	1796(4)	−1914(3)
O^2	5544,9(8)	2852(2)	4677(1)	C^{15}	4272(2)	1506(4)	−2353(2)
O^3	5481,5(9)	1166(2)	5921(2)	C^{16}	4762(2)	1346(3)	−1777(2)
O^4	3299,6(9)	−1575(2)	345(2)	C^{17}	4728(1)	1463(3)	−713(2)
O^5	3902(1)	−1794(3)	−966(2)	C^{18}	5747(1)	2134(3)	5498(2)
N	4390,2(9)	2572(2)	1529(2)	C^{19}	6324(1)	2657(3)	5840(2)
C^1	4444(1)	1579(3)	903(2)	C^{20}	6563(1)	2086(4)	6749(2)
C^2	4592(1)	4007(3)	1122(2)	C^{21}	7104(2)	2545(5)	7078(3)
C^3	5149(1)	4480(3)	1670(2)	C^{22}	7409(2)	3563(4)	6515(3)
C^4	5127(1)	4329(3)	2834(2)	C^{23}	7177(1)	4126(4)	5617(3)
C^5	4981(1)	2390(3)	4526(2)	C^{24}	6631(1)	3680(3)	5287(2)
C^6	4488(1)	3100(3)	4827(2)	C^{25}	3464(1)	−2148(3)	−520(2)
C^7	3911(1)	2563(4)	4381(2)	C^{26}	3064(1)	−3311(3)	−920(2)
C^8	3879(1)	2922(3)	3228(2)	C^{27}	3161(4)	−3868(4)	−1900(3)
C^9	4401(1)	2275(3)	2648(2)	C^{28}	2808(2)	−4942(5)	−2283(3)
C^{10}	4989(1)	2753(3)	3103(2)	C^{29}	2363(2)	−5457(5)	−1689(4)
C^{11}	4116(2)	5168(3)	1172(3)	C^{30}	2266(2)	−4933(5)	−710(3)
C^{12}	4193(1)	1704(3)	−238(2)	C^{31}	2617(2)	−3834(4)	−329(3)
C^{13}	3697(1)	1890(4)	−834(2)	H^{04}	363(2)	−84(5)	38(3)

The x-ray structural investigation of (III) was performed to clarify the nature of its complex. It was established that (III) (Fig. 1) actually has the cis-coupling of the piperidine and cyclohexane fragments with the axial orientation of the $C^{11}H_3$ and C^8H_2 substituents in the piperidine ring and the equatorial orientation of the 5-benzoyloxy group in the carbocycle (the conformer B). "The angle of coupling" between the $C^2C^3C^{10}C^9$ [the plane P_1 is achieved with the accuracy of 0.025(3) Å] and $C^6C^7C^9C^{10}$ [the plane P_2 is achieved with the accuracy of 0.018(3) Å] planes comprises 132.2°. This value significantly exceeds the corresponding angles of 128.1° in cis-decalin (IV) [9] and 127.4° in t-2-methyl-t-5-hydroxy-r-9-H-cis-decahydroquinoline (V) [1], practically coincides with the value of 130.3° and 132.0° in two independent molecules of N-benzoyl-t-2-methyl-4-oxo-r-9-H-cis-decahydroquinoline (VI) [2], and is appreciably less than the 134.7° in N-benzoyl-t-2-methyl-t-4-hydroxy-r-9-H-cis-decahydroquinoline (VII) [3]. The change in the "angle of coupling" in the order (IV) ≈ (V) < (VI) ≈ (III) < (VII) is explained by the development of steric stress caused by the repulsion between the axial substituents. Thus, this angle is the lowest in the molecules of (IV) and (V), not having axial substituents (not considering the C^8H_2 axial methylene group which is common to all the compounds considered). On account of the 1,3-diaxial interaction of the CH_3 and CH_2 groups in the molecules of (III) and (IV), the angle increases to $\sim$132° and reaches the highest value in the molecule of (VII), where there is also the repulsion between the OH group of the piperidine ring and the C^6H_2 group of the carbocycle besides the three paired 1,3-diaxial interactions between the OH, CH_3, and CH_2 groups.

We previously [3] investigated the influence of the interaction of the axial substituents on the bond and torsion angles of the piperidine ring in derivatives of N-acylpiperidines and decahydroquinolines. The C^2NC^9 angle in (III) is increased to 120.3(2)° as is also the case in the molecules of (V), (VII), and N-benzoyl-2,6-dimethylpiperidine (VIII) [10] with the Me substituents in the axial positions. At the same time, the endocyclic CNC angle comprises 112.0-114.3° in the N-acylpiperidines not having the axial substituents in the 2 and 6 positions. The angle of deflection of the C^2NC^9 plane from the P_1 plane in the molecule of (III) comprises 41.6° and is in good conformity with the values of 42.0° in the molecule of (VII), whereas the angle of deflection of the $C^3C^4C^{10}$ plane from the P_1 plane (52.0°) is somewhat higher than in (VII) (48.0°) due to the absence of the bulky substituent in the axial position at the C^4 atom in (III). On the whole, the torsion angles in the piperidine ring of the molecule of (III) conform well with the corresponding values in the molecules of the N-acylpiperidines and decahydroquinolines [3].

As in the case of the amide structures which we previously investigated [2, 3], the UEP of the N atom participates in the conjugation with the CO group in the molecule of (III). The dihedral angles between the $NC^1C^2C^9$ and $C^1O^1NC^{12}$ planes (the P_3 plane) comprises 11.5°; the angle between P_3 and the Ph ring (C^{12}–C^{17}) comprises 68.5°.

The bond lengths and bond angles in the molecule of (III) are the regular ones [1-3] with the exception of the $C^1{=}O^1$ bond [1.252(3) Å], which exceeds the lengths of the corresponding bonds in the structures of (VI) (cf. 1.230 Å) and (VII) [1.238(5) Å]. The difference in the bond lengths of C=O in the N-benzoyl groups is explained by the participation of the carbonyl O atom in intermolecular H-bonds of varying stability. The O atom of the carbonyl of the amide group in the complex (III) participates in the very stable H-bond with the OH group of BA [O^4—H^{O4} is 1.02(4) Å, O^4...O^1 is 2.614(3) Å, and H^{O4}...O^1 is 1.74(4) Å; the O^4—H^{O4}...O^1 angle is 163(3)°]. In the structure of (VII) [3], the less stable intermolecular H-bond C=O...H—O is realized with the hydroxy group in the position 4 [O...O is 2.796(5) Å], but H-bonds are absent from the structure of (VI).

The geometrical parameters of the O-benzoyl group and the BA molecule are in good accord with the parameters typical of the esters of BA (cf. the review [11]); the geometrical parameters of the amide group in the molecule of (III) (besides the C=O bond length) agree, within the limits of accuracy, with the parameters typical of amides and particularly benzamides (cf. the review [12]).

EXPERIMENTAL

The IR spectra were recorded on the UR-20 spectrophotometer using tablets with KBr. The PMR spectra were recorded on the Tesla BS-487C spectrometer (80 MHz) in C_2HCl_5 using the internal standard of HMDS. The thin layer chromatography was performed on Al_2O_3 (II-III activity) with dioxane as the eluent.

The mixture of 8.22 g of (I) and 8.43 g of C_6H_5COCl was heated at 120°C for 1 h on Wood's alloy. The reaction product, which is a glassy mass, was dissolved in 20 ml of H_2O and extracted with diethyl ether. After the drying of the ether extracts with Na_2SO_4 and the removal of the solvent, 6.84 g (34%) of the complex (III) were obtained. The colorless crystals had the mp 126-127°C (from diethyl ether). The PMR spectrum (C_2HCl_5) at 94°C was as follows (δ, ppm, J, Hz): 1.20 d, 7.0 ($2\text{-}CH_3$), 2.25 sh/br 22 (4-He), 4.30 sh/br 26 (2H + 9H), 4.95 d 12, t (5.5-H_e), 7.27, and 7.92 ppm (3Ph). The R_f was 0.87. Found: C 74.6, H 6.8, and N 3.1%. $C_{24}H_{27}O_3N \cdot C_6H_5COOH$. Calculated: C 74.8, H 6.6, and N 2.8%.

When 0.4 g of (III) was held in an aqueous—alcoholic solution of potassium carbonate at room temperature for a day, with the subsequent extraction with ether, the drying of the ether extracts, and the removal of the solvent, 0.25 g (83%) of (II) was obtained as colorless crystals with the mp 120-121°C (from CCl_4). The PMR spectrum (C_2HCl_5) at 92°C was as follows (δ, ppm, J, Hz): 1.02 d, 7 ($2\text{-}CH_3$), 2.19 d, 10, q 5 (4-H_e), 4.23 sh/br 29 (2H + 9H), 4.88 sh/br 22 (5-H_e), 7.29, and 7.88 ppm (2Ph). The R_f was 0.87. Found: C 76.1, H 6.9, and N 3.4%. $C_{24}H_{27}O_3N$. Calculated: C 76.4, H 7.2, and N 3.7%.

The aqueous solution was acidified with HCl, and the BA was extracted with ether. After recrystallization, 0.12 g of BA, which did not show a depression of the melting point in a sample mixed with the known material, was obtained. The x-ray structural analysis was as follows: the crystals of (III) were monoclinic; at 20°C, a = 22.954(1), b = 9.180(1), and c = 12.911(1) Å; β = 90.13(1)°; V = 2720.5 Å; d_{calc} = 1.22 g/cm³; Z = 4; $C_{24}H_{27}NO_3 \cdot C_6H_5COOH$; space group $P2_1/n$.

The cell parameters and the intensities of the 2302 independent reflections with $F^2 \geqslant 4\sigma$ were measured on a four-circle automatic Hilger-Walls diffractometer (λCuK_α, graphite monochromator, θ/2θ-scanning, $\theta \leqslant 66°$). The structure was decoded by the direct method using the MULTAN program and was specified by the full-matrix MNK in the anisotropic approximation. All the H atoms were shown in the difference synthesis and were included in the specification with the isotropic approximation. The final R-factor comprised 0.041 (R_w = 0.047). The calculations were performed on an Eclips S/200 computer using the INEXTL program [13]. The coordinates of the atoms are presented in Table 1.

CONCLUSION

The main product of the benzoylation of the hydrochloride of t-2-methyl-t-5-hydroxy-r-9-H-cis-decahydroquinoline, which exists in the conformation with the intramolecular H-bond, is the amidoester which can form a stable 1:1 complex with benzoic acid having the strong OH... O=CN H-bond. The amidoester thereby exists in the conformation with the diaxial disposition of the substituents in the α,α'-positions of the piperidine ring.

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MAGNETOOPTICAL PROPERTIES IN THE ANILINIUM SERIES USING COTTON–MOUTON EFFECT DATA

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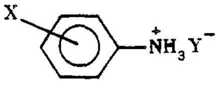
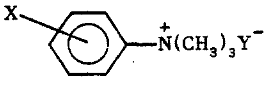
The Cotton–Mouton effect has not previously been applied to investigation of electrolytes, and manifestation of the action of charged substituents on the magnetic anisotropy has not been investigated. It is well known that the average electrical characteristics, polarizability, and magnetic susceptibility of ions vary greatly in comparison with those for electrically neutral particles, substantially declining in cations and increasing in anions [1]. It is of interest to follow the effect of excess charge on the corresponding anisotropic properties. With this aim we determined the total polarizabilities, susceptibilities, and Cotton–Mouton molar constants (CMC) of some anilinium salts in water, containing a strongly anisotropic organic cation and an inorganic anion of spherical symmetry


(I) - (V)


(VI), (VII)

$X = H$, $Y = Cl^-$ (I); $X = H$, $Y = ClO_4^-$ (II); $X = p\text{-}CH_3$, $Y = Cl^-$ (III); $X = p\text{-}Br$, $Y = Cl^-$ (IV); $X = o\text{-}Br$, $Y = Cl^-$ (V); $X = H$, $Y = I^-$ (VI); $X = p\text{-}Br$, $Y = I^-$ (VII). The latter in consequence of its isotropy cannot introduce a contribution to the molar CMC if it is in solutions in the form of independent particles.

A correct investigation of the properties of charged particles is possible only when the condition of total dissociation of the ions is fulfilled. In connection with the fact that the CMC are additive in mixtures

$$
{}_mC_c n_1 + {}_mC_a n_1 + {}_mC_{c+a} n_2 = {}_mC_{\exp}
$$
$$
\sum n_i = 1
$$

while the CMC of the isotropic anion is close to zero, in the absence of association ($n_2 = 0$) the relation

$$
{}_mC_c = {}_mC_{\exp}
$$

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