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HEXAHYDRO-8-ISOQUINOLONES WITH ELECTRON-ACCEPTOR SUBSTITUENTS IN POSITION 4

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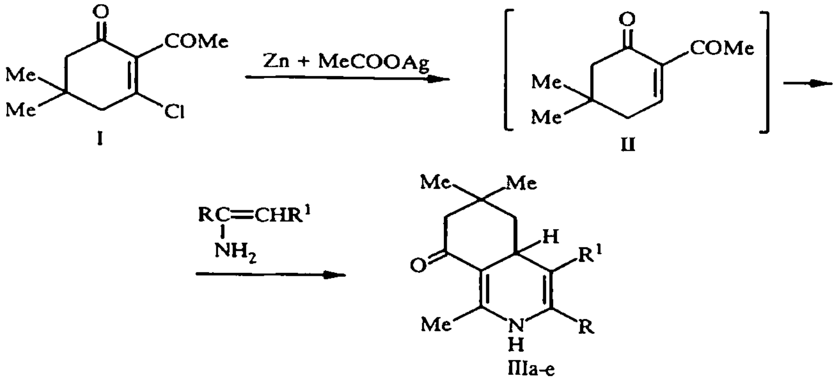
By the interaction of 2-acetyl-5,5-dimethyl-2-cyclohexen-1-one with certain nitroenamines, a number of hexahydro-8-isoquinolones with a nitro group in position 4 have been obtained; potentials of their electrochemical oxidation have been determined, and a possible mechanism and manifestation of structural effects in this process have been suggested and discussed. The structure of 1,3,6,6-tetramethyl-4-nitro-2,4a,-5,6,7,8-hexahydro-8-isoquinolone has been established by means of x-ray diffraction analysis.

Derivatives of hexahydro-8-isoquinolone with electron-acceptor substituents (nitro or ethylthiocarbonyl groups) in position 4 represent a group of compounds that have not been investigated adequately, namely hydrogenated nitrogen heterosystems containing a β-aminovinylcarbonyl structural fragment in which the keto group is fixed in the s-cis-configuration with respect to the double bond. In the work reported here, we synthesized and studied new representatives of this class of compounds.

Hexahydroisoquinolones III were synthesized by heating the intermediate 2-acetyl-5,5-dimethyl-2-cyclohexen-1-one (II) with enamine compounds in methanol. The ketone II was obtained by hydrogenolysis of 2-acetyl-3-chloro-5,5-dimethyl-2-cyclohexen-1-one (I) through the action of zinc activated with silver acetate [1-3].



a) $R = H, R^1 = NO_2$; b) $R = Me, R^1 = NO_2$; c) $R = Me, R^1 = COSEt$;
d) $R = Me, R^1 = COOEt$; e) $R = Me, R^1 = COMe$

In the electronic spectra of compounds IIIa,b,c, which were synthesized here for the first time, there are long-wave absorption bands with maxima at 455, 448, and 421 nm, respectively (Table 1) – bands that are characteristic for compounds of the hexahydroisoquinolone series [2]. In the spectra of compound IIIc, we found a 23-nm bathochromic shift of the long-wave maximum relative to the oxygen-containing analog, indicating a stronger conjugation of the ethylthiocarbonyl substituent with the β-aminovinyl system [2, 4].

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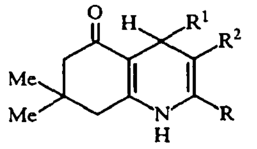
TABLE 1. Spectral Characteristics of Compounds IIIa-c

Compound	Electronic spectra, λ_{max}, nm (and ε)	IR spectrum, cm^{-1}	PMR spectrum (DMSO-d_6), δ, ppm (and J, Hz)
IIIa	208 (9000), 234 (10000), 264 (8200), 455 (2000)	1325, 1370, 1415, 1510, 1608, 1652, 1685, 3180, 3240	1,01 & 1,14 (two s, 3H & 3H, 6-$(CH_3)_2$; 2,16 (s, 3H, 1-CH_3); 1,53 & 2,40 (two dd, 1H and 1H, *J*–13 & 12, 5-CH_a & 5-CH_e); 2,18 & 2,38 (AB, two d, 1H & 1H, *J*–18, 7-CH_a & 7-CH_e); 4,10 (dd, *J*–12 & 4, $C_{(4a)}H$); 6,31 (br.s, 1H, NH); 7,62 (d, 1H, *J*–6, 3-CH)
IIIb	210 (7200), 264 (6400), 305 (4400), 448 (7800)	1375, 1460, 1482, 1595, 1615, 1628, 1680, 3065, 3330	0,95 & 1,07 (two-s, 3H & 3H, 6-$(CH_3)_2$; 1,45 and 2,25 (two dd, 1H & 1H, *J*–12 & 11,5, 5-CH_a; *J*–12 & 4, 5-CH_e); 2,15 & 2,35 (two s, 3H & 3H, 1,3-2CH_3); 2,17 & 2,38 (AB, two d, 1H & 1H, *J*–18, 7-CH_2); 4,15 (dd, *J*–11,5 and 4, $C_{(4a)}H$); 5,77 (br.s, 1H, NH)
IIIc	210 (8400), 252 (7600), 283 (5600), 421 (4400)	1310, 1370, 1382, 1480, 1560, 1590, 1655, 1673, 2950, 3310	0,93 & 1,05 (two s, 3H & 3H, 6-$(CH_3)_2$; 2,06 and 2,18 (two s. 3H & 3H, 1,3-2-CH_3); 2,04 and 2,33 (AB, two d, 1H & 1H, *J*–16, 7-CH_a & 7-CH_e): 1,27 (t, 3H, CH_2CH_3); 1,50 & 2,01 (t and dd), H & 1H, *J*–12, 5-CH_a & 5-CH_e); 2,96 (q, 2H, SCH_2); 3,92 (dd, 1H, *J*–12 and 2,2, $C_{(4a)}H$); 5,17 (br.s, 1H, NH)

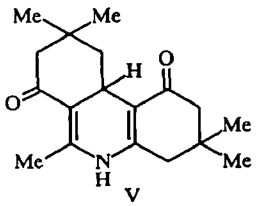
In the IR spectra of compounds IIIa-c in the region of stretching vibrations of double bonds and NH groups, there are absorption bands that are characteristic for the enaminocarbonyl fragment and the nitro or ethylthiocarbonyl group (Table 1).

In the PMR spectra we observe characteristic signals from the structural fragments of the hydrogenated isoquinolones III. The chemical shifts and multiplicity of the proton signals confirm the structures postulated for these substances. The most characteristic feature is the presence of a signal from the methine proton in the γ-position of the 1,4-dihydropyridine fragment, in the form of a double doublet at about 4 ppm, and also a singlet signal from NH-group protons in weaker fields (Table 1).

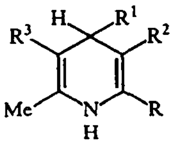
This reaction that we have described is the sole method that is known for the synthesis of derivatives of hexahydro-8-isoquinolone III, which, in contrast to the hydrogenated quinolones IV [5, 6], are not among the substances that can be obtained by known methods. This new method of preparation expands the possibilities of modifying hydrogenated nitrogen-containing heterosystems with a 1,4-dihydropyridine fragment.



IV



V



VI

IV a) R = R^1 = Me; R^2 = NO_2; b) R = R^1 = Me; R^2 = COOEt; c) R = R^1 = Me; R^2 = COMe;
d) R = H, R^1 = Me; R^2 = NO_2; e) R = H, R^1 = Ph; R^2 = NO_2

VI a) R = Me, R^1 = H, R^2 = R^3 = COOEt; b) R = Me, R^1 = H, R^2 = R^3 = COMe;
c) R = R^1 = Me, R^2 = R^3 = COOEt; d) R = R^1 = Me, R^2 = R^3 = COMe;
e) R = Me, R^1 = Ph, R^2 = R^3 = COOEt; g) R = Me, R^1 = Ph, R^2 = R^3 = COMe ;
h) R = H, R^1 = Me, R^2 = NO_2, R^3 = COMe; i) R = H, R^1 = Ph, R^2 = NO_2, R^3 = COMe;
j) R = Me, R^1 = Ph, R^2 = NO_2, R^3 = COOEt

With the aim of synthesizing new hydrogenated quinolones IVa,d,e and monocyclic 1,4-dihydropyridines VIh,i with a nitro group in the β-position (some of which we needed for a study of electrochemical oxidation), we carried out the condensation of the potassium salts of nitroacetaldehyde and nitroacetone with the corresponding aldehyde and 5,5-dimethyl-1,3-cyclohexanedione. As a result, we obtained the quinolones IVa,d,e, in which the keto group is fixed in the s-trans-configuration with respect to the double bond. By a modification of the Hantzsch reaction, we obtained monocyclic 1,4-dihydropyridines with a nitro group in the β-position (VIh,i), while the previously described compounds IV and VI were

TABLE 2. Spectral Characteristics of Compounds IVa,d,e and VIh,i

Compound	Electronic spectra, λ_{max}, nm (and ε)	IR spectrum cm^{-1}	PMR spectrum (DMSO-d_6), δ, ppm (and J, Hz)
IVa	205 (8800), 272 (10800), 425 (8000)	1610, 1640, 1660, 3180, 3300	0,9...1,0 (m 9H, 7-$(CH_3)_2$, 4-CH_3); 2,18 (d, 2H, 8-CH_2); 2,33 (d, 2H, 6-CH_2); 2,42 (s, 3H, 2-CH_3); 4,09 (q, 1H, 4-CH); 9,56 (s, 1H, N—H)
IVd	205 (10000), 256 (10000), 287 sh.(8000), 430 (9200)	1610, 1640, 1660, 3100, 3200, 3260	0,9...1,0 (m 9H, 7-$(CH_3)_2$, 4-CH_3); 2,19 (s, 2H, 8-CH_2); 2,33 (s, 2H, 6-CH_2); 4,09 (q, 1H, 4-CH); 7,93 (s, 1H, 2-CH); 9,89 (s, 1H, N—H)
IVe	205 (16000), 233 (10400), 263 (8000), 423 (9200)	1610, 1640, 1680, 3240	0,87 (s, 3H, 7-CH_3); 1,02 (s 3H, 7-CH_3); 2,08 (s, 2H, 8-CH_2); 2,16 (s, 2H, 6-CH_2); 5,14 (s, 1H, 4-CH); 7,20 (s, 5H, 4-C_6H_5); 8,11 (s, 1H, 2-CH); 10,11 (s, 1H, N—H)
VIh	205 (8400), 258 (8800), 294 sh.(6400), 432 (9400)	1610, 1645, 1680, 3120, 3250	1,18 (d, 3H, 4-CH_3); 2,27 (s, 3H, 6-CH_3); 2,36 (s, 3H, 5-$COCH_3$); 4,29 (q, 1H, 4-CH); 6,53 (d, 1H, N—H); 7,73 (d, 1H, 2-CH)
VIi	205 (15200), 232 (10400), 287 (7400), 430 (8600)	1600, 1640, 1680, 3100, 3200	2,16 (s, 3H, 6-CH_3); 2,24 (s, 3H, 5-$COCH_3$); 5,29 (s, 1H, 4-CH); 7,24 (s, 5H, 4-C_6H_5); 7,96 (d, 1H, *J*-6, 2-CH); 9,91 (d, 1H, *J*-6, N—H)

TABLE 3. Half-Wave Potentials ($E_{1/2}$) and Number of Electrons (p) per Molecule That Are Involved in Electrochemical Oxidation of Compounds III-VI

Compound	$E_{1/2}$, V	Number of electrons, p	Compound	$E_{1/2}$, V	Number of electrons, p
IIIa	+0,76	1,0	VIa	+0,73	1,5
IIIb	+0,78	1,6	VIb	+0,50	1,0
IIIc	+0,68	1,0	VIc	+0,76	1,1
IIId	+0,63	1,0	VId	+0,70	1,2
IIIe	+0,54	1,0	VIe	+0,79	1,1
IVa	+1,16	1,0	VIg	+0,80	~1,2*
IVb	+0,90	1,4	VIh	+1,03	1,6
IVc	+0,72	1,1	VIi	+1,10	1,6
IVd	+1,08	1,6	VIj	+1,22	1,0
IVe	+1,19	1,4			
V	+0,77	1,2			

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*Difficult to measure wave height, owing to further oxidation of primary product.

synthesized by known methods [5, 6]. In Table 2 we have summarized the spectral characteristics of compounds of the IV and VI types that were obtained here for the first time.

Processes of electrochemical oxidation of hexahydro-8-isoquinolones had not been studied previously; therefore, with the aim of determining the influence of structural factors on electrochemical oxidation in this series of compounds, we determined their oxidation potentials, and also determined for comparison the oxidation potentials of the corresponding s-trans-fixed quinolones IV and the oxidation potentials of pentamethyldecahydrophenthridine-1,7-dione (V) and a series of monocyclic 1,4-dihydropyridines VI.

From an examination of the results of electrochemical oxidation, we found that the influence of β-substituents of the dihydropyridine fragment of compounds III and IV on the variation of potential was the same as in the oxidation of monocyclic 1,4-dihydropyridines [7-10]. The introduction of the strong electron-acceptor nitro group into the β-position of compounds III and IV increases the electrochemical oxidation potential by 0.15 and 0.26 V in comparison with the effect of

TABLE 4. Bond Lengths (d) and Bond Angles (ω) in Molecule of IIIb

Bond	*d*, Å	Angle	ω, deg
$N_{(1)}$—$C_{(2)}$	1,35(1)	$C_{(2)}$—$N_{(1)}$—$C_{(6)}$	121,9(1)
$N_{(1)}$—$C_{(6)}$	1,40(1)	$C_{(3)}$—$C_{(2)}$—$N_{(1)}$	119,7(1)
$C_{(2)}$—$C_{(3)}$	1,32(2)	$C_{(3)}$—$C_{(2)}$—$C_{(12)}$	128,3(1)
$C_{(2)}$—$C_{(12)}$	1,53(2)	$N_{(1)}$—$C_{(2)}$—$C_{(12)}$	112,0(1)
$C_{(3)}$—$N_{(13)}$	1,46(2)	$C_{(2)}$—$C_{(3)}$—$N_{(13)}$	122,1(1)
$C_{(3)}$—$C_{(4)}$	1,48(2)	$C_{(2)}$—$C_{(3)}$—$C_{(4)}$	123,8(1)
$C_{(4)}$—$C_{(5)}$	1,51(1)	$N_{(13)}$—$C_{(3)}$—$C_{(4)}$	114,0(1)
$C_{(4)}$—$C_{(7)}$	1,54(1)	$C_{(3)}$—$C_{(4)}$—$C_{(5)}$	111,0(1)
$C_{(5)}$—$C_{(6)}$	1,32(1)	$C_{(3)}$—$C_{(4)}$—$C_{(7)}$	116,5(1)
$C_{(5)}$—$C_{(10)}$	1,44(2)	$C_{(5)}$—$C_{(4)}$—$C_{(7)}$	109,5(1)
$C_{(6)}$—$C_{(11)}$	1,50(2)	$C_{(6)}$—$C_{(5)}$—$C_{(10)}$	121,7(1)
$C_{(7)}$—$C_{(8)}$	1,51(2)	$C_{(6)}$—$C_{(5)}$—$C_{(4)}$	121,5(1)
$C_{(8)}$—$C_{(16)}$	1,53(2)	$C_{(10)}$—$C_{(5)}$—$C_{(4)}$	116,3(1)
$C_{(8)}$—$C_{(9)}$	1,55(2)	$C_{(5)}$—$C_{(6)}$—$N_{(1)}$	120,3(1)
$C_{(8)}$—$C_{(17)}$	1,55(2)	$C_{(5)}$—$C_{(6)}$—$C_{(11)}$	128,5(1)
$C_{(9)}$—$C_{(10)}$	1,56(1)	$N_{(1)}$—$C_{(6)}$—$C_{(11)}$	111,0(1)
$C_{(10)}$—$O_{(18)}$	1,23(1)	$C_{(8)}$—$C_{(7)}$—$C_{(4)}$	115,5(1)
$N_{(13)}$—$O_{(15)}$	1,21(1)	$C_{(7)}$—$C_{(8)}$—$C_{(16)}$	110,0(1)
$N_{(13)}$—$O_{(14)}$	1,23(1)	$C_{(7)}$—$C_{(8)}$—$C_{(9)}$	110,7(1)
		$C_{(16)}$—$C_{(8)}$—$C_{(9)}$	105,6(1)
		$C_{(7)}$—$C_{(8)}$—$C_{(17)}$	113,1(1)
		$C_{(16)}$—$C_{(8)}$—$C_{(17)}$	107,5(1)
		$C_{(9)}$—$C_{(8)}$—$C_{(17)}$	109,6(1)
		$C_{(8)}$—$C_{(9)}$—$C_{(10)}$	108,3(1)
		$O_{(18)}$—$C_{(10)}$—$C_{(5)}$	125,2(1)
		$O_{(18)}$—$C_{(10)}$—$C_{(9)}$	120,6(1)
		$C_{(5)}$—$C_{(10)}$—$C_{(9)}$	114,1(1)
		$O_{(15)}$—$N_{(13)}$—$O_{(14)}$	124,3(1)
		$O_{(15)}$—$N_{(13)}$—$C_{(3)}$	116,9(1)
		$O_{(14)}$—$N_{(13)}$—$C_{(3)}$	118,6(1)

an ethoxycarbonyl substituent, and by 0.24 and 0.44 V in comparison with an acetyl substituent (Table 3). Replacement of the methyl group in the α-position by a hydrogen atom in the β-nitro derivatives IIIa and IVd facilitates the oxidation to a slight degree. The s-cis-fixed compounds III are oxidized more readily not only in comparison with their s-trans analogs, but also in comparison with 1,4-dihydropyridines with the corresponding nonfixed β-substituents (Table 3).

The tricyclic compound V has $E_{1/2}$ at +0.77 V, which is 0.05 V above $E_{1/2}$ of the s-trans-fixed hydrogenated quinolone IVc with a nonfixed β-acetyl substituent. In this case, the β-aminovinylcarbonyl fragment of compound V with an endocyclic s-cis-fixed carbonyl group hinders the electrochemical oxidation to a greater degree than the same fragment with a nonfixed acetyl group. However, any examination of the oxidation potentials and other physicochemical properties of 1,4-dihydropyridines with nonfixed carbonyl-containing β-substituents in comparison with the potentials of their analogs having an endocyclic carbonyl group (hydrogenated quinolones and isoquinolones) is rather arbitrary, since the properties of the latter group depend also on the size and stereochemistry of the ring [11].

A comparison of the electrochemical oxidation potentials of the quinolones IIIa and IVd, which are unsubstituted in the α-position, with the monocyclic derivative VIh indicates that for compound IIIa, the potential is considerably lower than for the monocyclic derivative VIh; for compound IVd, the potential is slightly greater than that of compound VIh. An analogous picture is observed when comparing compounds IIIb and IVa with VIj, substituted in the α-position with a methyl group.

In all of the compounds that have been studied, when an acetyl substituent is replaced by an ethoxycarbonyl substituent in the β-position of the heterocycle, we observed a change in the electrochemical oxidation potential that was the opposite of what was expected on the basis of the change in magnitude of the Hammett σ-constant. Such a phenomenon, when it was observed in a study of the electrochemical oxidation of derivatives of 1,2-dihydropyridine [12], was explained by assuming that the hindrance to the oxidation of the ethoxycarbonyl derivatives is due to an inductive effect of the field F, determined by the Swain–Lapton constant [13]. We can assume that this sort of explanation is also valid for the compounds investigated in the present work.

TABLE 5. Principal Torsion Angles in Molecule of IIIb

Angle	τ, deg	Angle	τ, deg
$C_{(6)}$—$N_{(1)}$—$C_{(2)}$—$C_{(3)}$	11(2)	$C_{(4)}$—$C_{(7)}$—$C_{(8)}$—$C_{(9)}$	-18(2)
$N_{(1)}$—$C_{(2)}$—$C_{(3)}$—$C_{(4)}$	-1(2)	$C_{(7)}$—$C_{(8)}$—$C_{(9)}$—$C_{(10)}$	60(1)
$C_{(2)}$—$C_{(3)}$—$C_{(4)}$—$C_{(5)}$	-10(2)	$C_{(6)}$—$C_{(5)}$—$C_{(10)}$—$O_{(18)}$	-21(2)
$C_{(2)}$—$C_{(3)}$—$C_{(4)}$—$C_{(7)}$	116(1)	$C_{(4)}$—$C_{(5)}$—$C_{(10)}$—$O_{(18)}$	167(1)
$C_{(3)}$—$C_{(4)}$—$C_{(5)}$—$C_{(6)}$	12(2)	$C_{(6)}$—$C_{(5)}$—$C_{(10)}$—$C_{(9)}$	160(1)
$C_{(7)}$—$C_{(4)}$—$C_{(5)}$—$C_{(6)}$	-118(1)	$C_{(4)}$—$C_{(5)}$—$C_{(10)}$—$C_{(9)}$	-12(2)
$C_{(7)}$—$C_{(4)}$—$C_{(5)}$—$C_{(10)}$	54(1)	$C_{(8)}$—$C_{(9)}$—$C_{(10)}$—$O_{(18)}$	136(1)
$C_{(10)}$—$C_{(5)}$—$C_{(6)}$—$N_{(1)}$	-176(1)	$C_{(8)}$—$C_{(9)}$—$C_{(10)}$—$C_{(5)}$	-46(1)
$C_{(4)}$—$C_{(5)}$—$C_{(6)}$—$N_{(1)}$	-4(2)	$C_{(2)}$—$C_{(3)}$—$N_{(13)}$—$O_{(15)}$	170(1)
$C_{(2)}$—$N_{(1)}$—$C_{(6)}$—$C_{(5)}$	-8(2)	$C_{(4)}$—$C_{(3)}$—$N_{(13)}$—$O_{(15)}$	-6(2)
$C_{(3)}$—$C_{(4)}$—$C_{(7)}$—$C_{(8)}$	-165(1)	$C_{(2)}$—$C_{(3)}$—$N_{(13)}$—$O_{(14)}$	-5(2)
$C_{(5)}$—$C_{(4)}$—$C_{(7)}$—$C_{(8)}$	-38(2)	$C_{(4)}$—$C_{(3)}$—$N_{(13)}$—$O_{(14)}$	178(1)

TABLE 6. Coordinates of Nonhydrogen Atoms ($\times 10^4$), and Standard Deviations, in Molecule of IIIb

Atom	x	y	z
$N_{(1)}$	1028(9)	6775(10)	823(5)
$C_{(2)}$	-102(14)	7048(11)	689(5)
$C_{(3)}$	-934(11)	6280(11)	766(6)
$C_{(4)}$	-708(10)	5107(11)	987(6)
$C_{(5)}$	592(10)	4854(12)	988(6)
$C_{(6)}$	1380(11)	5660(12)	933(5)
$C_{(7)}$	-1247(12)	4745(12)	1684(7)
$C_{(8)}$	-756(11)	3673(12)	1992(7)
$C_{(9)}$	-99(12)	2982(12)	1436(7)
$C_{(10)}$	921(12)	3713(13)	1147(6)
$C_{(11)}$	2682(11)	5583(11)	1020(6)
$C_{(12)}$	-237(12)	8287(10)	489(6)
$N_{(13)}$	-2157(12)	6509(11)	598(6)
$O_{(14)}$	-2434(8)	7472(8)	423(5)
$O_{(15)}$	-2823(8)	5711(8)	595(5)
$C_{(16)}$	-1759(12)	2918(12)	2241(8)
$C_{(17)}$	64(13)	3885(12)	2615(7)
$C_{(18)}$	1906(7)	3307(7)	1060(5)

The heights of the polarographic waves of compounds III-VI are either one-electron, or they correspond to a fractional number of electrons (see Table 2). On the ring electrode, we did not observe even one case of reversibility of the oxidation process. This means that the primary products of electrooxidation, i.e., the cation radicals, undergo rather rapid conversions; in the case of a one-electron wave, the cation radicals are probably destroyed with discharge of a hydrogen atom and the formation of a pyridinium cation, while in the case of a fractional wave of electrons, two parallel paths are possible for destruction of the cation radicals, with discharge of either a hydrogen atom or a proton and subsequent oxidation of the pyridinyl radical to pyridine, as was demonstrated previously in [14]. This hypothesis is supported experimentally by the reduction waves of the pyridinium cation that are observed on the ring electrode (in the interval of potentials from −0.6 to −1.2 V) and of pyridine (in the interval from −1.7 to −2.2 V). We do not find any clear relationship between the change in height of the polarographic waves and the structure of the compounds; however, it is evident that the introduction of a nitro group into the β-position of the heterocycle, in all cases other than compound IVa, leads to an increase in the height of the electrochemical oxidation wave. The introduction of a strong electron-acceptor substituent into the molecule hinders detachment of the first electron; however, in the state of a cation radical, it accelerates the process of subsequent oxidation with detachment of a second electron, as a result of a change in the electronic or steric structure of the particle.

In order to establish the steric and molecular structures of compound IIIb, we investigated this compound by x-ray diffraction. In Fig. 1 we show a model of this molecule, along with the numbering of the atoms. The bond lengths, bond angles, and torsion angles are listed in Tables 4-6. The 1,4-dihydropyridine ring has the conformation of a shallow boat. The $N_{(1)}$ and $C_{(4)}$ atoms deviate on the same side of the strictly planar fragment $C_{(2)}C_{(3)}C_{(5)}C_{(6)}$ by 0.09(1) and 0.14(1) Å, respectively.

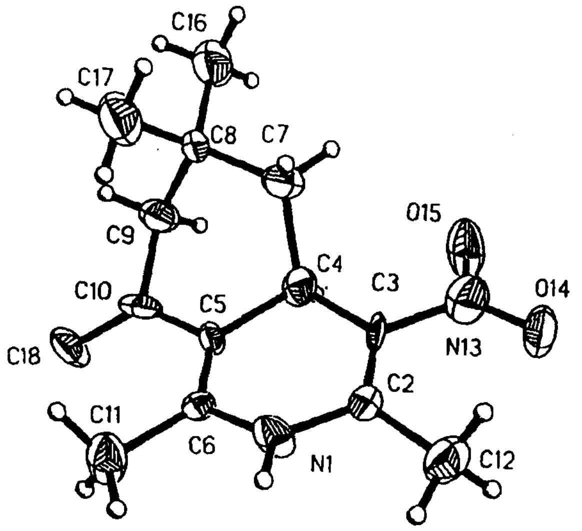

Fig. 1. Molecule of 1,3,6-tetramethyl-4-nitro-2,4a,5,6,7,8-hexahydro-8-isoquinolone (IIIb).

The second ring also has the boat conformation. The deviations of the $C_{(4)}$ and $C_{(9)}$ atoms from the plane of the other four atoms are 0.57(1) and 0.66(1) Å, respectively. The $C_{(3)}$ occupies an equatorial position relative to the second ring. The single bond $C_{(5)}-C_{(10)}$ is slightly shortened (1.44 Å) owing to the presence of conjugation in the chain $N_{(1)}-C_{(6)}-C_{(5)}-C_{(10)}-O_{(18)}$; however, full coplanarity is not observed in this group of five atoms; the torsion angle $C_{(6)}-C_{(5)}-C_{(10)}-O_{(18)}$ is $-21(2)°$ (Table 5), and the dihedral angle between the mean planes of the two rings is 38.6(4)°. The molecules in the crystal form intermolecular hydrogen bonds $N_{(1)}-H...O_{(18)}$ (N...O = 3.01, H...O = 2.17 Å, transformation of symmetry 1/2 − x, 1/2 + y, z).

EXPERIMENTAL

The IR spectra were obtained on a Perkin-Elmer 580B instrument in white mineral oil; the electronic spectra were obtained on a Spectra UV-Vis instrument in ethanol; the PMR spectra were obtained on a Bruker WH-90/DS spectrometer, with TMS internal standard. The mass spectra were taken in an AEI MS-50 instrument. The course of the reaction was monitored by TLC on Silufol UV-254 plates in a system of solvents consisting of chloroform, hexane, acetone, and ethanol in a 9:7:2:1 ratio, development in UV light.

The electrochemical oxidation potentials of compounds III-V ($c = 5 \cdot 10^{-4}$ M) were determined in anhydrous acetonitrile [15] (background electrolyte 0.1 M tetrabutylammonium hexafluorophosphate) on a rotating disk electrode with a ring (graphite/graphite) Bruker 350C (comparison electrode 0.1 M $Ag/AgNO_3$ in acetonitrile, auxiliary electrode platinum wire, rotation rate 2000 rpm). The number of electrons was determined by comparing the height of the polarographic waves of the test compounds with the height of the one-electron reduction wave of 4'-(m-nitrophenyl)-3,5-diethoxycarbonyl-1,2,6-trimethyl-1,4-dihydropyridine, recorded under identical conditions. The half-wave potentials were referred to $Ag/AgNO_3$.

Crystals of the compound IIIb, with the composition $C_{13}H_{18}N_2O_3$, grown from chloroform, were found to be rhombic, with the following crystallographic parameters: a = 11.391(4), b = 11.887(4), c = 19.316(7) Å, V = 2615(2)Å^3, M = 250.29, d_{calc} = 1.27 g/cm^3, Z = 8, sp. gp. Pbsa.

The intensities of 1178 reflections were measured in a Syntex $P2_1$ automatic diffractometer (MoKα radiation, graphite monochromator, $\theta/2\theta$ scanning, $2\theta_{max} = 43°$). In the calculations, we used 707 independent reflections with $I \geq 2\sigma_I$.

The structure was deciphered by the direct method on the basis of the SHELXS-86 program [16] and was refined by the full-matrix least-squares method in the anisotropic approximation for the nonhydrogen atoms, down to a final value R = 0.078. The coordinates of the nonhydrogen atoms are listed in Table 6.

Compounds IIId,e were synthesized by a procedure given in [2], IVb,c and VIa-g by procedures given in [5, 6], and VIj by a procedure given in [20].

1,6,6-Trimethyl-4-nitro-2,4a,5,6,7,8-hexahydro-8-isoquinolone (IIIa). A mixture of 1.76 g (20 mmoles) of 1-amino-2-nitroethylene [16, 17] and 3.3 g (20 mmoles) of the enedione II, which had been prepared by a procedure given in [1], was refluxed in 30 ml of methanol for 3 h, after which the solution was filtered and chromatographed in four batches on preparative glass plates, 220 × 280 mm, on a nonbonded layer of silica gel L 40/100, in a system consisting of chloroform, hexane, acetone, and ethanol in a 9:7:2:1 ratio. The orange-colored bands were collected from the plates, eluted with a mixture of 120 ml of ethanol and 60 ml of acetone, filtered, and vacuum-dried; the residue was treated with dry ether. Obtained an orange substance with mp 108-110°C (from ethanol). Yield 0.5 g (11%). Mass spectrum:* 236 (M^+). Found, %: C 60.7; H 7.1; N 11.9. $C_{12}H_{16}N_2O_3$. Calculated, %: C 61.0; H 6.8; N 11.8.

1,3,6,6-Tetramethyl-4-nitro-2,4a,5,6,7,8-hexahydro-8-isoquinolone (IIIb). Analogously, from 3.3 g (20 mmoles) of the enedione II and 2.05 g (20 mmoles) of 2-amino-1-nitropropylene [17, 18], obtained 0.8 g (16%) of compound IIIb with mp 175°C (from ethanol). Mass spectrum: 250 (M^+). Found, %: C 62.5; H 7.3; N 11.0. $C_{13}H_{18}N_2O_3$. Calculated, %: C 62.5; H 7.2; N 11.2.

2,4,7,7-Tetramethyl-3-nitro-1,4,5,6,7,8-hexahydro-5-isoquinolone (IVa). A solution of 1.4 g (10 mmoles) of 5,5-dimethylcyclohexane-1,3-dione, 1.49 g (10 mmoles) of the potassium salt of nitroacetone [18], 2.5 ml (45 mmoles) of acetaldehyde, and 2.5 g of ammonium acetate was refluxed 3 h in a mixture of 15 ml of ethanol and 10 ml of acetic acid. After cooling, a yellow substance separated out, mp 246-248°C (from ethanol–AcOH mixture). Yield 1.6 g (65%). Mass spectrum: 250 (M^+). Found, %: C 62.5; H 7.2; N 11.0. $C_{13}H_{18}N_2O_3$. Calculated, %: C 62.4; H 7.2; N 11.2.

4,7,7-Trimethyl-3-nitro-1,4,5,6,7,8-hexahydro-5-isoquinolone (IVd). Analogously, from 1.4 g (10 mmoles) of 5,5-dimethylcyclohexane-1,3-dione, 1.27 g (10 mmoles) of the potassium salt of nitroacetaldehyde [18], 2.5 ml (45 mmoles) of acetaldehyde, and 2.5 g of ammonium acetate, obtained the hexahydroquinolone IVd. The product was separated on preparative plates with silica gel and with a solvent system consisting of chloroform, hexane, acetone, and ethanol in a 9:7:2:1 ratio. Obtained 0.81 g (0.35%) of a yellow substance with mp 207-210°C (from ethanol-AcOH mixture). Mass spectrum: 236 (M^+). Found, %: C 60.8; H 6.9; N 11.7. $C_{12}H_{16}N_2O_3$. Calculated, %: C 61.0; H 6.8; N 11.9.

7,7-Dimethyl-4-phenyl-3-nitro-1,4,5,6,7,8-hexahydro-5-isoquinolone (IVe). A solution of 1.4 g (10 mmoles) of 5,5-dimethylcyclohexane-1,3-dione, 0.88 g (10 mmoles) of 1-amino-2-nitroethylene, and 1.06 g (10 mmoles) of benzaldehyde was refluxed 6 h in a mixture of 30 ml of ethanol and 3 ml of acetic acid. The solvents were removed under vacuum, and the residue was treated with methanol. Obtained 1.19 g (40%) of a yellow substance with mp 250°C (from methanol–AcOH mixture). Found, %: C 68.4; H 6.1; N 9.4. $C_{17}H_{18}N_2O_3$. Calculated, %: C 68.2; H 6.2; N 9.1.

2,4-Dimethyl-3-acetyl-5-nitro-1,4-dihydropyridine (VIh). A solution of 0.6 g (5 mmoles) of acetylacetone, 0.44 g (5 mmoles) of 1-amino-2-nitroethylene, and 0.84 ml (15 mmoles) of acetaldehyde in a mixture of 10 ml of ethanol and 1 ml of acetic acid was refluxed 1 h. The solvents were removed under vacuum, and the residue was separated in two batches on preparative plates with silica gel in a system consisting of chloroform, hexane, acetone, and ethanol in a 9:7:2:1 ratio. The orange band was collected from the plates. Obtained 0.4 g (41%) of compound VIh, mp 165-167°C (from methanol). Found, %: C 54.8; H 6.0; N 14.1. $C_9H_{12}N_2O_3$. Calculated, %: C 55.0; H 6.1; N 14.3.

2-Methyl-4-phenyl-3-acetyl-5-nitro-1,4-dihydropyridine (VIi). A solution of 0.99 g (10 mmoles) of 4-amino-3-penten-2-one, 1.27 g (10 mmoles) of the potassium salt of nitroacetaldehyde, and 1.06 g (10 mmoles) of benzaldehyde in 20 ml of a mixture of ethanol and 3 ml of acetic acid (1:1) was refluxed for 4 h. The solvents were removed under vacuum, and the residue was treated with methanol. Obtained 0.9 g (35%) of the red substance VIi with mp 152-156°C (from methanol). Mass spectrum: 258 (M^+). Found, %: C 65.0; H 5.4; N 10.8. $C_{14}H_{14}N_2O_3$. Calculated, %: C 65.1; H 5.5; N 10.9.

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*Here and subsequently, m/z values are given for the ion peaks.

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