Oxidation of 1-hydrazino-3,3-dimethyl-3,4-dihydroisoquinoline. X-Ray, spectroscopic, and quantum-chemical study of the structure of 3,3-dimethyl-3,4-dihydroisocarbostyryl azine

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3,3-Dimethyl-3,4-dihydroisocarbostyryl azine (**2**) has been synthesized by oxidation of 1-hydrazino-3,3-dimethyl-3,4-dihydroisoquinoline (**1**). The crystal and molecular structures of compound **2** were determined. It has been established that in the solid state, compound **2** exists as an azine tautomer. The IR, electronic, and NMR spectral data indicate that in solution the tautomeric form of **2** does not change. A possible mechanism of the oxidation of **1** to **2** is suggested.

Key words: dihydroisoquinoline derivatives; crystal structure; electronic, IR, and ^{1}H NMR spectra; quantum-chemical calculation.

Previously, we reported the synthesis of 1-hydrazino-3,3-dimethyl-3,4-dihydroisoquinoline (**1**),[1] which can be used as a synthon for obtaining heterocyclic diazo compounds,[2] various heterocyclic systems,[3] and their metallocomplexes. It was shown[1] that the reaction of hydrazine **1** with HNO_2 in the cold (0 °C) yields 5,5-dimethyl-5,6-dihydrotetrazolo[5,1-*a*]isoquinoline (Scheme 1).

Taking the oxidative properties of HNO_2 into account, it could be expected that this process would give other products at higher temperatures. In the present work we studied the reaction of compound **1** with

Scheme 1

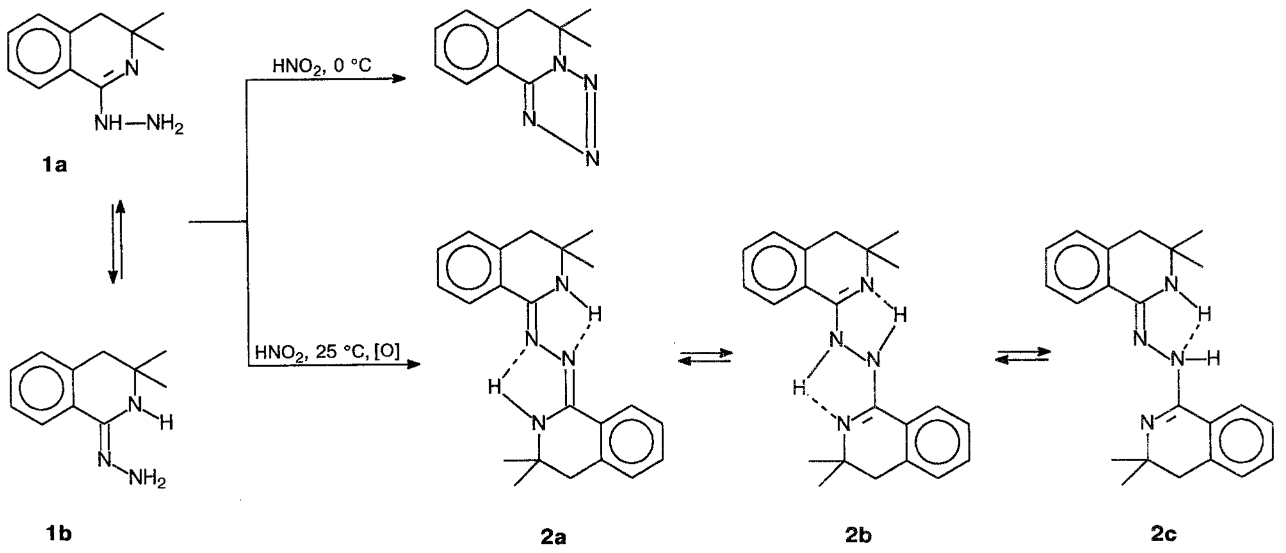

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Table 1. Atomic coordinates and thermal corrections for 3,3-dimethyl-3,4-dihydroisocarbostyryl azine structure

Atom	x	y	z	$B_{iso}^{eq}/Å^2$
N(1)	0.0418(1)	0.1999(3)	0.5782(1)	3.20(7)
N(2)	−0.0369(1)	0.4867(3)	0.5092(1)	3.31(7)
N(3)	−0.4283(1)	0.1908(3)	0.4658(1)	3.91(8)
N(4)	−0.5274(1)	0.4775(3)	0.4688(1)	3.52(7)
C(1)	−0.0279(1)	0.3285(3)	0.5541(1)	2.98(8)
C(2)	−0.0987(1)	0.2827(3)	0.5802(1)	2.99(8)
C(3)	−0.1664(1)	0.4334(4)	0.5675(1)	3.42(9)
C(4)	−0.2308(1)	0.3919(4)	0.5934(1)	3.9(1)
C(5)	−0.2283(1)	0.1980(4)	0.6321(1)	4.0(1)
C(6)	−0.1618(1)	0.0462(4)	0.6447(1)	4.2(1)
C(7)	−0.0960(1)	0.0867(4)	0.6193(1)	3.35(8)
C(8)	−0.0228(1)	−0.0763(4)	0.6317(1)	3.94(9)
C(9)	0.0577(1)	0.0537(4)	0.6364(1)	3.32(8)
C(10)	0.1271(1)	−0.1155(4)	0.6356(1)	3.8(1)
C(11)	0.0848(1)	0.2041(4)	0.6977(1)	4.9(1)
C(12)	−0.4994(1)	0.3128(3)	0.4390(1)	3.30(8)
C(13)	−0.5494(1)	0.2504(3)	0.3721(1)	3.15(8)
C(14)	−0.6151(1)	0.3911(4)	0.3376(1)	3.35(9)
C(15)	−0.6640(1)	0.3281(5)	0.2761(1)	4.0(1)
C(16)	−0.6463(2)	0.1250(5)	0.2480(1)	4.9(1)
C(17)	−0.5793(1)	−0.0112(4)	0.2810(1)	5.5(1)
C(18)	−0.5302(1)	0.0492(3)	0.3431(1)	4.13(9)
C(19)	−0.4576(1)	−0.0956(4)	0.3806(1)	5.3(1)
C(20)	−0.3889(1)	0.0485(4)	0.4264(1)	4.06(9)
C(21)	−0.3253(1)	−0.1090(4)	0.4721(1)	5.8(1)
C(22)	−0.3464(1)	0.2064(4)	0.3888(1)	4.6(1)
H[N(1)]	0.0884(1)	0.2395(3)	0.5560(1)	7.3367(0)
H[N(3)]	−0.3987(1)	0.2484(3)	0.5115(1)	5.2814(0)
H[C(3)]	−0.167	0.567	0.540	
H[C(4)]	−0.277	0.497	0.584	
H[C(5)]	−0.273	0.169	0.650	
H[C(6)]	−0.161	−0.089	0.671	
H(1)[C(8)]	−0.032	−0.187	0.596	
H(2)[C(8)]	−0.017	−0.160	0.671	
H(1)[C(10)]	0.109	−0.208	0.596	
H(2)[C(10)]	0.176	−0.030	0.636	
H(3)[C(10)]	0.138	−0.214	0.673	
H(1)[C(11)]	0.040	0.310	0.698	
H(2)[C(11)]	0.096	0.105	0.735	
H(3)[C(11)]	0.134	0.290	0.698	
H[C(14)]	−0.626	0.534	0.356	
H[C(15)]	−0.710	0.423	0.252	
H[C(16)]	−0.680	0.079	0.205	
H[C(17)]	−0.566	−0.150	0.260	
H(1)[C(19)]	−0.435	−0.176	0.350	
H(2)[C(19)]	−0.476	−0.210	0.405	
H(1)[C(21)]	−0.353	−0.207	0.495	
H(2)[C(21)]	−0.298	−0.203	0.447	
H(3)[C(21)]	−0.284	−0.016	0.502	
H(1)[C(22)]	−0.387	0.305	0.360	
H(2)[C(22)]	−0.305	0.301	0.418	
H(3)[C(22)]	−0.319	0.113	0.363	

HNO_2 at temperatures above 25 °C and the oxidation of **1** with yellow mercuric oxide and manganese dioxide. The structures of compounds obtained in these reactions were studied by X-ray diffraction and electron, IR, and ^1H NMR spectroscopy. In addition, quantum-chemical calculations of model compounds were carried out.

Results and Discussion

It was found that at temperatures above 25 °C, the reaction of hydrazine **1** with HNO_2 occurs by a different pathway than has been reported previously[1] and results in a yellow-green crystalline product **2**, m.p. 193—194 °C. Its elemental analysis and IR and ^1H NMR spectra could correspond both to 3,3-dimethyl-3,4-dihydroisocarbostyryl (**2a**) and to its isomers, namely, 1,2-bis(3,3-dimethyl-3,4-dihydroisoquinolyl-1)hydrazine (**2b**) and 3,3-dimethyl-3,4-dihydroisocarbostyryl 3,3-dimethyl-3,4-dihydroisoquinolyl-1-hydrazone (**2c**). Product **2** is also formed when yellow mercuric oxide or manganese dioxide is used instead of HNO_2.

An X-ray diffraction study of compound **2** (Tables 1—3) showed that its unit cell contains two independent centrosymmetric molecules located in different centers of symmetry (Fig. 1) (Figure 1 shows one of the independent molecules; the corresponding atoms in the second molecule are numbered as N(3), N(4), C(12)—C(22)). In the crystal, azine tautomer **2a** exists (see Scheme 1). This is suggested by the following data: the H atoms in compound **2** are located only at two intracyclic N atoms of the dihydroisoquinoline moieties, and they are absent at the exocyclic N atoms. This fact allows us to rule out tautomers **2b** and **2c**. In addition, the C(1)—N(2) exocyclic bonds, which are 1.301(3) Å long (hereinafter, the mean values over the two inde-

Table 2. Bond lengths in two crystallographically independent molecules of structure **2**

Molecule 1		Molecule 2	
Bond	d/Å	Bond	d/Å
N(2)—N(2A)	1.416(2)	N(4)—N(4A)	1.404(2)
N(1)—C(1)	1.349(3)	N(3)—C(12)	1.354(3)
N(1)—C(9)	1.462(3)	N(3)—C(20)	1.466(3)
N(2)—C(1)	1.298(3)	N(4)—C(12)	1.305(2)
C(1)—C(2)	1.480(3)	C(12)—C(13)	1.474(3)
C(2)—C(3)	1.388(3)	C(13)—C(14)	1.389(3)
C(2)—C(7)	1.395(3)	C(13)—C(18)	1.394(3)
C(3)—C(4)	1.376(3)	C(14)—C(15)	1.378(3)
C(4)—C(5)	1.381(3)	C(15)—C(16)	1.384(4)
C(5)—C(6)	1.378(3)	C(16)—C(17)	1.379(3)
C(6)—C(7)	1.387(3)	C(17)—C(18)	1.385(3)
C(7)—C(8)	1.504(3)	C(18)—C(19)	1.496(3)
C(8)—C(9)	1.518(3)	C(19)—C(20)	1.517(3)
C(9)—C(10)	1.520(3)	C(20)—C(21)	1.514(3)
C(9)—C(11)	1.524(3)	C(20)—C(22)	1.523(3)
N(1)—H[N(1)]	1.05	N(3)—H[N(3)]	1.01

Table 3. Bond angles in two crystallographically independent molecules of structure **2**

Molecule 1		Molecule 2	
Angle	φ/deg	Angle	φ/deg
N(2A)N(2)C(1)	111.3(2)	N(4A)N(4)C(12)	111.8(2)
C(1)N(1)C(9)	123.9(2)	C(12)N(3)C(20)	122.3(2)
H(N1)N(1)C(1)	113	H(N3)N(3)C(12)	111
H(N1)N(1)C(9)	123	H(N3)N(3)C(20)	124
N(1)C(1)N(2)	124.2(2)	N(3)C(12)N(4)	124.5(2)
N(1)C(1)C(2)	117.4(2)	N(3)C(12)C(13)	117.5(2)
N(2)C(1)C(2)	118.3(2)	N(4)C(12)C(13)	118.0(2)
C(1)C(2)C(3)	121.1(2)	C(12)C(13)C(14)	120.6(2)
C(1)C(2)C(7)	118.9(2)	C(12)C(13)C(18)	119.7(2)
C(3)C(2)C(7)	119.9(2)	C(14)C(13)C(18)	119.7(2)
C(2)C(3)C(4)	120.5(2)	C(13)C(14)C(15)	120.6(2)
C(3)C(4)C(5)	119.7(2)	C(14)C(15)C(16)	119.6(2)
C(4)C(5)C(6)	120.3(2)	C(15)C(16)C(17)	120.1(2)
C(5)C(6)C(7)	120.6(2)	C(16)C(17)C(18)	120.8(2)
C(2)C(7)C(6)	118.9(2)	C(13)C(18)C(17)	119.1(2)
C(2)C(7)C(8)	119.1(2)	C(13)C(18)C(19)	118.6(2)
C(6)C(7)C(8)	122.0(2)	C(17)C(18)C(19)	122.3(2)
C(7)C(8)C(9)	111.7(2)	C(18)C(19)C(20)	112.7(2)
N(1)C(9)C(8)	107.0(2)	N(3)C(20)C(19)	106.8(2)
N(1)C(9)C(10)	107.5(2)	N(3)C(20)C(21)	108.2(2)
N(1)C(9)C(11)	110.1(2)	N(3)C(20)C(22)	109.6(2)
C(8)C(9)C(10)	110.7(2)	C(19)C(20)C(21)	110.3(2)
C(8)C(9)C(11)	111.5(2)	C(19)C(20)C(22)	111.5(2)
C(10)C(9)C(11)	109.8(2)	C(21)C(20)C(22)	110.3(2)

pendent moieties are presented), are much shorter than the intracyclic bonds C(1)—N(1) (1.352(3) Å), which are, in turn, also shorter than the N(1)—C(9) bonds (1.464(3) Å) linking the N atom in the heterocycle and the C(9) atom bonded to methyl groups. These facts suggest that the π-electron density is somewhat delocalized over the C—N bonds and insignificantly delocalized over the N—N bond linking the two dihydroisoquinoline moieties (1.410(2) Å). The exocyclic nitrogen atoms, N(2) and N(2A), have an sp^2 configuration with a 111.5° angle at the N atom. Other geometric characteristics (bond lengths and bond angles) of the dihydroisoquinoline moieties are similar to those found previously for 1-(4,4-dimethyl-2,6-dioxocyclohexyl)-3,3-dimethyl-3,4-dihydroisoquinoline,[4,5] its 6,7-dimethoxy-derivative,[6] and 3,3-dimethyl-6,7-dimethoxy-3,4-dihydroisocarbostyryl.[7] For example, the heterocycles in molecule **2** have the same half-chair conformation as in the above compounds. The N(1) atom and the C(9) atom linked to the former are on the same side of the plane formed by four C atoms of the dihydropyridine part of the molecule coplanar with the atoms of the benzene ring to within 0.007 Å. It should, however, be noted that the N(1) atoms are out of the planes of the dihydroisoquinoline moieties in molecule **2** to a slightly smaller extent (0.184 Å), and the C(9) atoms to a greater extent (1.053 Å) than in the compounds studied,[4–6] in which the mean deviations of the N(1) and C(9) atoms are 0.411 and 0.828 Å, respectively. This difference probably results from the formation of intramolecular H-bonds N(1)—H...N, which close the five-membered rings N(1)C(1)N(2)N(2A)H(N(1)), in the molecules of azine **2**. The geometric parameters of these bonds are: N(1)...N(2A), 2.581 Å; N(1)—H(N(1)), 1.05 Å; and H(N(1))...N(2A), 2.125 Å. Due to the strain in five-membered H-rings, the angles at the H atoms are considerably reduced (to 106°) in comparison

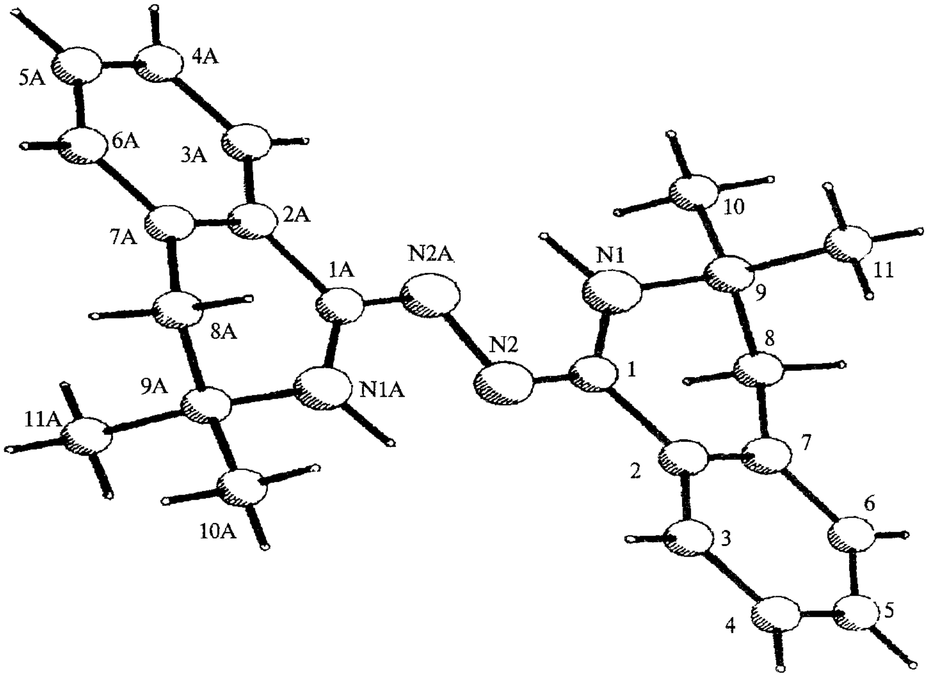


Fig. 1. Structure of 3,3-dimethyl-3,4-dihydrocarbostyryl azine (for one of the independent molecules).

Table 4. Electronic absorption spectra of 3,3-dimethyl-3,4-dihydroisocarbostyryl azine

Medium	λ_{max}/nm (logε)						
Ethanol	218 (4.32),	249 (4.40),	352 (sh),	369 (4.40),	383 (sh)	
Acetone			358 (sh),	376 (4.49),	396 (sh),	419 (sh)
Heptane			358 (sh),	376 (4.49),	396 (sh),	419 (sh)
DMF			360 (sh),	378 (4.43),	398 (sh),	421 (sh)
CCl_4			362 (sh),	376 (4.26),	398 (sh),	421 (sh)
Nujol*			364 (sh),	381,	399 (sh),	419 (sh)

* In the crystalline state, as a suspension in Nujol.

with the usual values. The five-membered H-rings, which are planar to within 0.075 Å, are inclined by 12° towards the medium planes of the dihydroisoquinoline moieties. The exocyclic N(2) atoms are, on average, by 0.282 Å out of the medium planes of the dihydroisoquinoline moieties and are directed to the sides opposite to those of the intracyclic N(1) atoms. The neighboring independent azine molecules in a crystal of compound **2** are almost perpendicular to each other: the angle between the medium planes of the nearest dihydroisoquinoline rings is 83°. All contacts between the molecules in a crystal of **2** are usual and do not differ from van der Waals contacts.

The IR spectrum of azine **2a** in the polycrystalline state (in KBr pellets) is characterized by an intense band with a maximum at 3360 cm^{-1} (N—H). The low-frequency shift of the maximum of this band relative to the maximum of the stretching vibrations of free NH groups in secondary amines (3450 cm^{-1})[8] is consistent with X-ray diffraction data concerning the presence of intramolecular H-bonds NH...N in compound **2a**. The estimation of the energy of hydrogen bonds by the Iohansen formula[9]

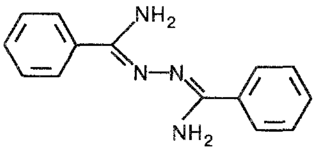
$$\Delta\nu = -720\Delta H/(18 + \Delta H)$$

gives $\Delta H = -2.0$ kcal mol^{-1}, which indicates that they have relatively low strength. The bands at 1610, 1600, 1563, 1486, and 1463 cm^{-1} in the spectrum of azine **2a** can be attributed to ν(C=N) and ν(C=C). The absence of a band at 1630—1628 cm^{-1} observed in the spectrum of 1,3,3-trimethyl-3,4-dihydroisoquinoline[10] can suggest in favor of decreasing the order of the endocyclic CN bond in the molecule of azine **2a** in comparison with that in 1,3,3-trimethyl-3,4-dihydroisoquinoline.

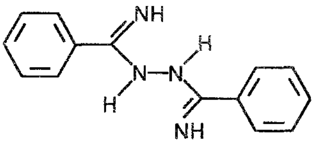
The electronic absorption spectrum of solid azine **2a** recorded for its suspension in Nujol (Table 4) is characterized by an intense band with a maximum at 381 nm, which is absent in the spectrum of 1,3,3-trimethyl-3,4-dihydroisoquinoline. The presence of this band in the spectrum results from the elongation of the conjugation chain due to linking of two dihydroisoquinoline moieties by an azine group.

The spectroscopic characteristics of azine **2a** found in this study were then used for considering its state in solution. In fact, generally speaking, the existence of compound **2** as an azine in the solid state does not exclude the possibility of tautomerism on passing into solution or into a gaseous phase.

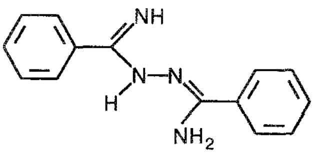
To estimate the relative stability of azine, hydrazine, and azine—hydrazine tautomers, we performed a quantum-chemical calculation (PPP) of the corresponding tautomers (**A**, **B**, and **C**) of a model compound that did not contain atoms not involved in π-bonds.



A



B



C

Table 5. Results of calculating the atomization energies (ΔH_{at}), solvation coefficients (*M*), π-bond energies (*E*(π)), wavelengths (λ), and oscillator strengths (*f*) of the longwave band in the calculated electronic absorption spectra of models **A**, **B**, and **C** of tautomers of compound **2**

Tautomer	ΔH_{at}	*M*	*E*(π)	λ/nm (*f*)
	/eV			
A	177.878	1.770	32.230	384 (1.14)
B	177.869	2.705	31.878	304 (0.66)
C	177.847	2.250	32.049	325 (0.77)

The calculated electronic absorption spectra of tautomer **A** (Table 5) are in satisfactory agreement with the experimental spectra of compound **2** (see Table 4), which suggests the validity of the results and makes it possible to use them for a semi-quantitative estimation of the relative stability of tautomers and their spectral characteristics. It is evident from Table 5 that the atomization energies, ΔH_{at}, of all three possible tautomers are similar. The azine tautomer **A** existing in crystalline compound **2** has somewhat higher stability. The gain in ΔH_{at} of tautomer **A** is obtained due to a higher energy of the π-bonds, $E(\pi)$, *i.e.*, due to more effective conjugation in the molecule. The solvation coefficient M of tautomer **A** is higher than those of tautomers **B** and **C**, which is in favor of tautomeric transformations in solutions. According to the calculations, the maxima of long-wave bands in the electronic absorption spectra of the tautomers differ significantly (see Table 5), which allows one to use them for determining which particular tautomeric form of a compound exists in solution.

The electronic absorption spectrum of compound **2** in ethanol is characterized by the presence of three intense bands at 218, 249, and 369 nm (see Table 4). The bands with maxima at 218 and 249 nm correspond to $\pi-\pi^*$ transitions of the benzene ring in the molecule and are typical of 3,4-dihydroisoquinoline derivatives.[11,12] The latter band, which characterizes the conjugation between the two dihydroisoquinoline moieties, has a vibrational structure with $\Delta\nu \approx 1360$ cm^{-1} that has the form of shoulders both on the short-wave and on the long-wave sides of the main band. The electronic absorption spectra of compound **2** in solvents incapable of forming hydrogen bonds (heptane, CCl_4) and in aprotic solvents forming hydrogen bonds (acetone, DMF) almost coincide with that in the crystalline state (as suspensions in Nujol). Both the position of the maximum of the long-wave band and its vibrational structure remain the same. This allows us to conclude that in these solutions, like in the crystal, compound **2** exists as azine **2a**. In the spectra of compound **2** in ethanol, which has both pronounced proton-donor and proton-acceptor properties, the maximum of the long-wave band is hypsochromically shifted by 7—12 nm relative to its position in the spectra in aprotic solvents. The shift is much lower than that calculated for the tautomeric transformation of azine **2a** (see Table 5). Therefore, it is most probably determined by a change in the molecular conformation of the azine due to the cleavage of the NH...O or N...HO intramolecular bonds with the solvent. A similar but greater (~30 nm) shift of the maximum of the long-wave band is observed upon the protonation of compound **2** in acid media.

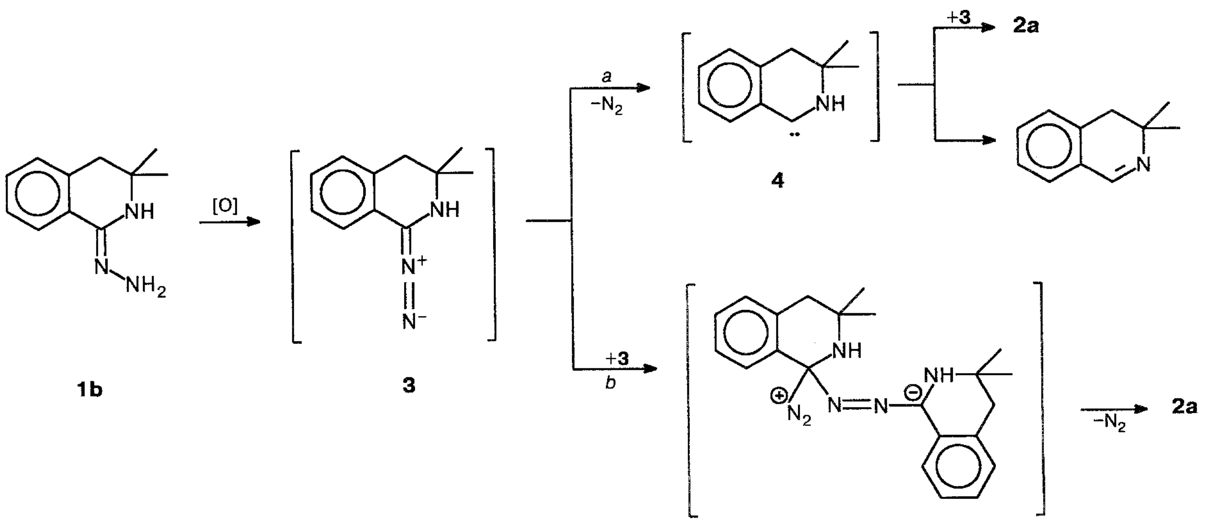
The IR spectrum of a solution of compound **2** in CCl_4, which almost coincides with the spectrum of the solid sample, also supports the retention of the tautomeric form and the intramolecular H-bond in compound **2** dissolved in inert solvents. In particular, the ν(NH) band in the spectrum of **2** in solution also has a maximum at 3360 cm^{-1}, and no new bands (bands of free NH groups) appear upon dilution of the solution.

The ^{1}H NMR spectra of a solution of azine **2** in CCl_4 display only one signal of "acid" protons, whose intensity corresponds to two protons. This agrees with the data of electron and IR spectra and unambiguously confirms the absence of tautomer **2c** of compound **2** in solution. It can thus be considered as proven that azine **2a** is a product of the oxidation of hydrazine **1** under the conditions specified above.

The ease of the oxidation of hydrazine **1** with yellow mercuric oxide forces us to assume that it is its hydrazone tautomer **1b** that undergoes oxidation to give the corresponding diazo compound **3** (Scheme 2).[13]

As has been noted previously,[14] substituted diazomethanes can form azines by two pathways: by decomposition to carbene **4** followed by the reaction of the carbene with a diazomethane molecule (pathway *a*) or

Scheme 2



by dimerization of the diazo compound followed by elimination of a nitrogen molecule (pathway *b*).

Diazo compounds with electron-donating substituents are extremely unstable and eliminate nitrogen at the instant of their formation. For this reason, pathway *a* seems more reasonable. In fact, the reaction of carbene **4** with diazo compound **3** that has not decomposed yet should result in azine **2a**. However, carbene **4**, once formed, can be stabilized by different pathways: by dimerization, by insertion into π-bonds of the solvent or unchanged **1**, or by 1,2-hydrogen shift. We did not detect products of dimerization or carbene insertion, but the reaction mixture was found to contain 3,3-dimethyl-3,4-dihydroisoquinoline (TLC, comparison with an authentic sample obtained by a known procedure[15]). Since this compound can be formed only by 1,2-hydrogen shift from the nitrogen atom, one might assume that the oxidation of **1b** occurs *via* formation of carbene **4** followed by attack at a yet undecomposed molecule of diazo compound **3**. However, the reaction in the presence of cyclohexene or butyl vinyl ether did not result in products of carbene insertion into the double bond. The same result was obtained when the reaction was carried out in the presence of 1,3,3-trimethyl-3,4-dihydroisoquinoline, whose azomethine bond is highly reactive toward carbenes.[16] This suggests that the 1,2-hydrogen shift occurs much faster than the carbene insertion into a multiple bond.

Based on the above results, it can be concluded that, although decomposition of molecule **3** to give carbene **4** is observed, azine **2a** is formed by dimerization of diazomethane **3** followed by elimination of a nitrogen molecule (pathway *b*).

Experimental

X-ray diffraction analysis. The single crystals used for the X-ray diffraction study were obtained by recrystallization of compound **2** from acetone. The experimental data for yellow-green crystals were obtained on an automatic four-circle Enraf Nonius CAD-4 diffractometer (Mo-Kα irradiation, graphite monochromator, ω/2θ-scanning). The crystallographic characteristics are presented in Table 6. The structure was solved by direct methods followed by difference syntheses, analysis of which revealed the position parameters of the H atoms at the cyclic N atoms. The positions of the remaining H atoms were calculated geometrically under the assumption that the C—H bond length is 0.96 Å and U_j = 0.08 Å^2. Anisotropic refinement taking into account fixed H atoms gave R = 0.037. All calculations were carried out using the SHELX-76 program on an IBM PC/386 computer.

Table 6. Crystallographic data

Characteristics	Value	Characteristics	Value
Crystal size /mm	0.5×0.4×0.4	Overall number of reflections	4889
Space group	$P\,2_1/c$	Number of reflections used for calculations by the least-squares method with $I \geq 3\sigma(I)$	2113
a/Å	16.776(3)		
b/Å	5.738(6)		
c/Å	21.440(7)		
β/deg	107.3(3)		
V/Å^3	1971(2)	Number of parameters	235
Z	4		
ρ_{calc}/g cm^{-3}	1.17	R	0.037
μ/cm^{-1}	0.5	R_w	0.040

The quantum-chemical calculation was carried out using the Pariser—Parr—Pople (PPP) method with optimization of interatomic distances by the minimum heat of atomization.[17]

IR spectra were recorded on a Specord 75-IR spectrophotometer (KBr pellets and $2 \cdot 10^{-2}$ mol L^{-1} solutions in CCl_4). **Electronic absorption spectra** were recorded on a Specord UV-VIS spectrophotometer, in solid state as suspensions in Nujol, and in solutions. **^{1}H NMR spectra** of compound **2** were obtained on a Bruker WP-200 SY spectrometer (CCl_4). The chemical shifts were determined relative to $SiMe_4$. ^{1}H NMR, δ: 1.28 (s, 12 H, CH_3); 2.82 (s, 4 H, CH_2); 6.45 (br.s, 2 H, NH); 6.92—7.25 (m, 6 H arom.); 8.07—8.20 (m, 2 H arom.).

Interaction of compound 1 with HNO_2 at 25 °C. A solution of $NaNO_2$ (0.69 g, 0.01 mol) in a minimum amount of water was added with stirring to a solution of compound **1** (1.89 g, 0.01 mol) in acetic acid (20 mL). The mixture was stirred for 0.5 h, poured into water (100 mL), and alkalized with a NH_4OH solution to pH 8. The product was extracted with chloroform (2×50 mL), the extract was dried with $MgSO_4$, and the solvent was distilled off on an water bath to give 1.32 g (76 %) of compound **2a**, m.p. 193—194 °C.

Oxidation of compound 1 with yellow mercuric oxide. A solution of compound **1** (0.38 g, 2 mmol) in hexane (30 mL) was refluxed for 0.5 h with yellow mercury(II) oxide (0.48 g, 2.2 mmol). The solution was decanted from metallic mercury, the precipitate in the flask was washed with hexane (20 mL), and the solvent was evaporated to 1/2 of the initial volume. On cooling, compound **2a** (0.23 g, 66 %) was obtained. The mother liquor was dried with $MgSO_4$. The solvent was distilled off to give 0.10 g (30 %) of 3,3-dimethyl-3,4-dihydroisoquinoline.[15]

Oxidation of compound 1 with manganese dioxide. A solution of compound **1** (0.38 g, 2 mmol) in hexane (30 mL) was refluxed with manganese dioxide (0.35 g, 4 mmol) and worked-up as described above to give 0.19 g (54 %) of compound **2a** and 0.14 g (40 %) of 3,3-dimethyl-3,4-dihydroisoquinoline.

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