

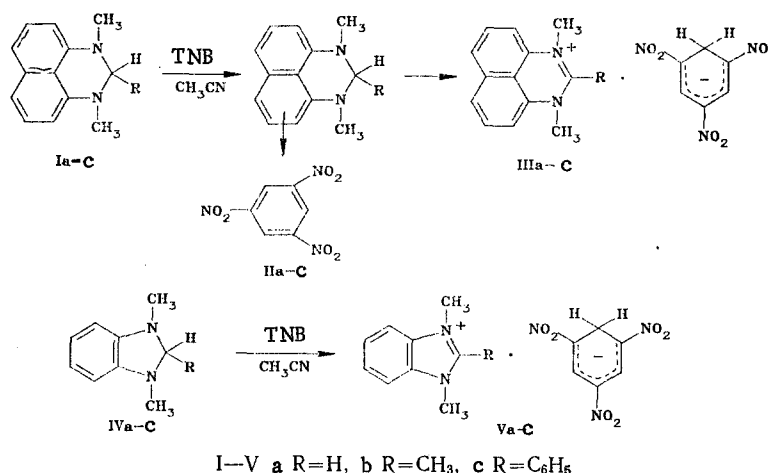
EFFECT OF GEMINAL SUBSTITUENTS ON DEHYDROGENATION
 OF DIHYDRO DERIVATIVES OF NITROGEN HETEROCYCLES.
 2,3-DIHYDROPERIMIDINES AND BENZIMIDAZOLINES

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A study was carried out on the rate of hydride ion displacement from 1,3-dimethyl-2-R-2,3-dihydroperimidines and 1,3-dimethyl-2-R-benzimidazolines to 1,3,5-trinitrobenzene. In all cases, inhibition by the substituents at C(2) is observed but this effect is much more pronounced in 2,3-dihydroperimidines than in benzimidazolines. An x-ray diffraction structural analysis of 1,3-dimethyl-2-phenyl-2,3-dihydroperimidine showed that the geometry of 2,3-dihydroperimidines causes steric blocking of the hydrogen atom at C(2) by the geminal substituent and substituents at the nitrogen atom.

In our previous work [1], we reported the dehydrogenation of dihydro derivatives of nitrogen heterocycles using 1,3,5-trinitrobenzene (TNB). A highly colored saltlike compound is formed during this transformation which consists of a heteroaromatic cation and 1,1-dihydro-2,4,6-trinitrocyclohexadienone anion. Thus, in the case of 1,3-dimethyl-2,3-dihydroperimidine (Ia) and 1,3-dimethylbenzimidazoline (IVa), the salts formed have structures IIIa and Va. In our subsequent work [2], we very unexpectedly found that, in contrast to Ia, its 2-methyl (Ib) and 2-phenyl derivatives (Ic) are not preparatively dehydrogenated by TNB but rather form π -complexes with this reagent (IIb) and (IIc), which were isolated in crystalline form and differ sharply in their physical and chemical properties from salts such as IIIa and V. The formation constants for IIb and IIc in acetonitrile at 25°C were found in the present work to be 3.3 and 3.2 liters/mole, respectively.



Since the geometrical and electronic characteristics of the methyl and phenyl groups differ significantly, we undertook to discover the reason for such a strong inhibition by these groups for hydride transfer in Ib and Ic. In the present work, we studied the effect of these substituents on the ease of hydride transfer in 2-substituted benzimidazolines IVb and IVc and the kinetics of this reaction for I and IV. We also undertook an x-ray diffraction structural investigation of I and IV in order to determine the possible role of steric factors.

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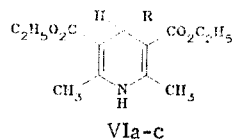
TABLE 1. Second-Order Rate Constants for the Dehydrogenation of I and IV by TNB

Compound	k_{25° , liter/mole · sec	Compound	k_{25° , liter/mole · sec
Ia	$(8,27 \pm 0,07) \cdot 10^{-3}$	IVa	$3,55 \pm 0,11$
Ib	$\sim 10^{-6}$	IVb	$1,85 \pm 0,05$
Ic	$\sim 10^{-6}$	IVc	$0,597 \pm 0,004$

TABLE 2. Coordinates of the Nonhydrogen Atoms ($\times 10^4$) and Their Isotropic Equivalent Temperature Factors $B_{iso}^{eq} = 1/3 \sum \sum B_{ij} a_i^* a_j^* (a_i a_j)$ in Ic

Atom	x	y	z	$B_{iso}^{eq}, \text{\AA}^2$
N ₍₁₎	826 (3)	4380 (2)	6590 (1)	5,77 (7)
N ₍₂₎	3676 (3)	3934 (2)	7295 (1)	6,16 (7)
C ₍₁₎	991 (4)	3429 (2)	6134 (1)	5,37 (8)
C ₍₂₎	-405 (5)	3110 (3)	5589 (2)	7,24 (11)
C ₍₃₎	-231 (7)	2123 (4)	5164 (2)	8,64 (14)
C ₍₄₎	1290 (7)	1441 (4)	5247 (2)	7,99 (14)
C ₍₅₎	4408 (7)	1066 (4)	5899 (3)	8,84 (15)
C ₍₆₎	5775 (8)	1375 (4)	6411 (3)	9,22 (16)
C ₍₇₎	5657 (5)	2368 (4)	6885 (2)	8,14 (13)
C ₍₈₎	4039 (4)	3043 (2)	6814 (2)	5,87 (9)
C ₍₉₎	2627 (4)	2744 (2)	6244 (1)	5,21 (8)
C ₍₁₀₎	2793 (5)	1724 (2)	5791 (2)	6,49 (10)
C ₍₁₁₎	2445 (4)	4888 (3)	7012 (2)	5,65 (8)
C ₍₁₂₎	3426 (3)	5840 (2)	6620 (1)	4,88 (7)
C ₍₁₃₎	3886 (4)	5695 (3)	5918 (2)	6,19 (9)
C ₍₁₄₎	4854 (4)	6569 (3)	5597 (2)	6,48 (9)
C ₍₁₅₎	5334 (4)	7600 (3)	5967 (2)	6,40 (10)
C ₍₁₆₎	4877 (4)	7760 (3)	6656 (2)	6,99 (11)
C ₍₁₇₎	3936 (4)	6890 (2)	6981 (2)	6,23 (9)
C ₍₁₈₎	-697 (6)	5212 (4)	6425 (3)	8,19 (14)
C ₍₁₉₎	5065 (8)	4256 (5)	7903 (3)	9,46 (16)

We should note that there is very little information, especially quantitative data, on the effect of geminal substituents on the hydride lability of dihydro derivatives of heterocyclic compounds. For example, any substituent at C₍₄₎ in the 1,4-dihydropyridine ring of the NADH coenzyme fully inhibits its enzymatic activity [3]. Dubur et al. [4] studied the kinetics of the dehydrogenation of 1,4-dihydropyridines VI using chloranil. Methyl and phenyl groups inhibit this reaction by factors of 215 and 250, respectively, relative to VIa. A study of the structure of VIc [5] showed that the 1,4-dihydropyridine ring has boat form, while the plane of the phenyl substituent is almost perpendicular to the plane containing C₍₂₎, C₍₃₎, C₍₅₎, and C₍₆₎ of the heterocycle. As a result, the hydrogen atom is sterically blocked by the ortho-hydrogen atoms of the phenyl group and the two ethoxycarbonyl groups, while it leads to a decrease in hydride lability.



VI a R=H, b R=CH₃, c R=C₆H₅

The kinetics of the hydride transfer between I and IV and TNB was studied in our laboratory at 25°C in acetonitrile. This reaction involves overall second-order kinetics and it is first-order relative to TNB and first-order relative to the dihydro derivative. The reaction rate was followed spectrophotometrically relative to the increase in absorption at 477 nm characteristic for the 1,1-dihydro-2,4,6-trinitrocyclohexadienate anion. The second-order rate constants obtained are given in Table 1.

TABLE 3. Coordinates of the Hydrogen Atoms ($\times 10^3$) and Their Isotropic Temperature Factors B_{iso} (Å^2) in Ic

Atom	x	y	z	B_{iso}	Atom	x	y	z	B_{iso}
H ₍₂₎	157 (5)	635 (3)	445 (2)	12 (1)	H ₍₁₅₎	602 (4)	821 (3)	574 (2)	8.8 (8)
H ₍₃₎	-125 (5)	193 (3)	476 (2)	11 (1)	H ₍₁₆₎	517 (4)	850 (3)	692 (2)	8.4 (8)
H ₍₄₎	142 (4)	78 (3)	496 (2)	7.4 (8)	H ₍₁₇₎	369 (3)	696 (2)	751 (2)	7.7 (7)
H ₍₅₎	457 (6)	25 (4)	556 (3)	16 (1)	H _(18,1)	-67 (5)	583 (3)	681 (2)	12 (1)
H ₍₆₎	701 (6)	107 (3)	652 (2)	12 (1)	H _(18,2)	-62 (5)	558 (3)	595 (2)	11 (1)
H ₍₇₎	648 (4)	266 (2)	726 (2)	6.4 (7)	H _(18,3)	-185 (5)	480 (3)	645 (2)	9.7 (9)
H ₍₁₁₎	202 (3)	525 (2)	744 (1)	5.9 (6)	H _(19,1)	443 (5)	479 (4)	821 (2)	11 (1)
H ₍₁₃₎	356 (4)	497 (3)	566 (2)	7.3 (2)	H _(19,2)	543 (5)	363 (3)	817 (2)	11 (1)
H ₍₁₄₎	516 (4)	642 (2)	508 (2)	8.4 (7)	H _(19,3)	629 (7)	466 (4)	767 (3)	15 (2)

As in the case of 1,3-dimethylbenzimidazoline studied in our previous work [1], 1,2,3-trimethylbenzimidazoline (IVb) and 1,3-dimethyl-2-phenylbenzimidazoline (IVc) react readily with TNB to form crystalline salts Vb and Vc. These salts have extremely limited solubility in ordinary organic solvents but are moderately soluble in dimethylsulfoxide. The PMR spectra of these compounds in DMSO and other data confirm their structure. Table 1 shows that the dehydrogenation of IVb and IVc proceeds more slowly than that for benzimidazoline IVa by factors of 1.9 and 5.9, respectively. These results indicate the absence of marked steric interference from the geminal substituents in the dehydrogenation of IVb and IVc. This conclusion is based on the following considerations. The effect of the geminal substituents should be the sum of four factors:

1) a statistical factor (the decrease in the number of hydride-labile hydrogen atoms by 2 should decrease the reaction rate by the same factor);

2) a steric factor (any substituent which is larger in bulk than the hydrogen atom may hinder the approach of the acceptor and decrease the angle for its attack on the remaining hydrogen atom);

3) a solvation factor (the introduction of hydrocarbon groups should hinder the solvation of the polar transition state and thereby increase the activation barrier).

In the case of IVb, the decrease in the reaction rate almost exactly corresponds to manifestation only of the statistical factor. This may be fortuitous since the electron-donor effect of the methyl group which increases the hydride lability is compensated by the steric and solvation effects. However, since the methyl group is a weak electron-donor, the role of the solvation and steric factors is also small. In the case of a phenyl group (IVc), all four factors act in the same direction, i.e., decrease hydride lability. Since a third of the decrease in reactivity of 5.9 is due to the steric factor, the effect of steric interference is also relatively small.

The kinetic data showed that 2,3-dihydroperimidines are dehydrogenated much more slowly than the benzimidazolines. Thus, the dehydrogenation rate of Ia is 438 times slower than for IVa, while the difference in dehydrogenation rates for Ib and Ic vs. IVb and IVc is almost six orders of magnitude. We should note that despite the conclusion of the completely inert nature of Ib and Ic in the hydride transfer reaction based on preparative data [2], kinetic measurements nevertheless showed a very slow change in the light absorption of the initially-formed π -complexes IIb and IIc. The nature of these changes indicates the generation of the 1,1-dihydro-2,4,6-trinitrocyclohexadienate anion in solution, i.e., a dehydrogenation reaction. As a consequence of the slowness of the process (about 0.5% over 3 h), the rate constant was determined only approximately and found to be about 10^{-6} liter/mole \cdot sec.

The data obtained for the benzimidazolines clearly indicate a sharp drop in hydride lability due to the effect of the geminal groups in Ib and Ic due to exclusively steric factors. Hence, we carried out an x-ray diffraction structural study of Ic. The data obtained are presented in Tables 2-5 and Figs. 1-4.

The naphthalene system in Ic shows a slight departure from planarity, which markedly exceeds the experimental error, reaching 0.032(5) Å [deviation of the atoms from the mean-square plane through C₍₂₎-C₍₁₀₎ (Plane 1) shown in Fig. 2]. The maximum departure from planarity in the naphthalene molecules is 0.004(2) Å [6]. The distortions in the naphthalene system

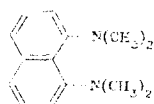
TABLE 4. Bond Angles ω (deg) in Ic

Angle	ω	Angle	ω
C ₍₁₎ N ₍₁₎ C ₍₁₁₎	120,3 (2)	C ₍₁₎ C ₍₉₎ C ₍₁₀₎	119,1 (2)
C ₍₁₎ N ₍₁₎ C ₍₁₈₎	119,8 (3)	C ₍₈₎ C ₍₉₎ C ₍₁₀₎	120,8 (2)
C _{(11)N₍₁₎C₍₁₈₎}	114,3 (3)	C ₍₄₎ C ₍₁₀₎ C ₍₅₎	123,3 (3)
C _{(8)N₍₂₎C₍₁₁₎}	117,9 (2)	C ₍₄₎ C ₍₁₀₎ C ₍₉₎	118,1 (3)
C _{(8)N₍₂₎C₍₁₉₎}	119,8 (3)	C ₍₅₎ C ₍₁₀₎ C ₍₉₎	118,6 (3)
C _{(11)N₍₂₎C₍₁₉₎}	115,5 (3)	N ₍₁₎ C ₍₁₁₎ N ₍₂₎	109,2 (2)
N ₍₁₎ C ₍₁₎ C ₍₂₎	121,9 (3)	N ₍₁₎ C ₍₁₁₎ C ₍₁₂₎	115,3 (2)
N ₍₁₎ C ₍₁₎ C ₍₉₎	118,4 (2)	N ₍₂₎ C ₍₁₁₎ C ₍₁₂₎	112,3 (2)
C _{(2)C₍₁₎C₍₉₎}	119,7 (3)	N ₍₁₎ C ₍₁₁₎ H ₍₁₁₎	106 (1)
C _{(1)C₍₂₎C₍₃₎}	120,5 (3)	N ₍₂₎ C ₍₁₁₎ H ₍₁₁₎	106 (1)
C _{(2)C₍₃₎C₍₄₎}	122,1 (4)	C _{(12)C₍₁₁₎H₍₁₁₎}	108 (1)
C _{(3)C₍₄₎C₍₁₀₎}	120,4 (4)	C _{(11)C₍₁₂₎C₍₁₃₎}	123,0 (2)
C _{(6)C₍₅₎C₍₁₀₎}	120,9 (4)	C _{(11)C₍₁₂₎C₍₁₇₎}	119,3 (2)
C _{(5)C₍₆₎C₍₇₎}	122,6 (5)	C _{(13)C₍₁₂₎C₍₁₇₎}	117,7 (2)
C _{(6)C₍₇₎C₍₈₎}	119,0 (4)	C _{(12)C₍₁₃₎C₍₁₄₎}	120,8 (3)
N _{(2)C₍₈₎C₍₇₎}	124,2 (3)	C _{(13)C₍₁₄₎C₍₁₅₎}	120,1 (3)
N _{(2)C₍₈₎C₍₉₎}	117,6 (2)	C _{(14)C₍₁₅₎C₍₁₆₎}	119,8 (3)
C _{(7)C₍₈₎C₍₉₎}	118,0 (3)	C _{(15)C₍₁₆₎C₍₁₇₎}	120,3 (3)
C _{(1)C₍₉₎C₍₈₎}	120,0 (2)	C _{(12)C₍₁₇₎C₍₁₆₎}	121,3 (3)

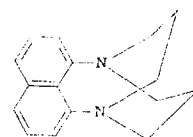
TABLE 5. Some Torsion Angles τ (deg) in Ic

Angle	τ	Angle	τ
N ₍₁₎ -C ₍₁₎ -C ₍₉₎ -C ₍₈₎	0,2 (3)	C ₍₁₁₎ -N ₍₁₎ -C ₍₁₁₎ -C ₍₁₂₎	87,1 (3)
C ₍₁₎ -C ₍₉₎ -C ₍₈₎ -N ₍₂₎	6,5 (3)	C ₍₈₎ -N ₍₂₎ -C ₍₁₁₎ -C ₍₁₂₎	-82,2 (3)
C ₍₉₎ -C ₍₈₎ -N ₍₂₎ -C ₍₁₁₎	-31,7 (3)	C ₍₁₎ -N ₍₁₎ -C ₍₁₁₎ -H ₍₁₁₎	-153 (3)
C ₍₈₎ -N ₍₂₎ -C ₍₁₁₎ -N ₍₁₎	47,0 (3)	C ₍₈₎ -N ₍₂₎ -C ₍₁₁₎ -H ₍₁₁₎	160 (3)
N ₍₂₎ -C ₍₁₁₎ -N ₍₁₎ -C ₍₁₎	-40,4 (3)	C ₍₉₎ -C ₍₁₁₎ -N ₍₁₎ -C ₍₁₈₎	170,4 (5)
C ₍₁₁₎ -N ₍₁₎ -C ₍₁₎ -C ₍₉₎	18,5 (3)	C ₍₉₎ -C ₍₈₎ -N ₍₂₎ -C ₍₁₉₎	178,4 (5)

in Ic result not only from closure of the heterocycle in peri-positions C₍₁₎ and C₍₈₎ (here and subsequently, the number of the atoms corresponds to Fig. 1), but also from the repulsion of the unshared electron pairs of the nitrogen atoms. Indeed, in a molecule such as dimethylnaphthalene [7], the steric difficulties are overcome by expansion of the C₍₁₎C₍₉₎C₍₈₎ bond angle to 125,2° without violation of the ring planarity. On the other hand, in 1,8-bis-(dimethylamino)naphthalene (VII), in which this angle is also expanded to 125.8°, there is also a significant extrusion of the nitrogen atoms in different directions from the mean plane of the naphthalene system (0.41 Å). This system is clearly nonplanar with marked twisting about the C₍₉₎-C₍₁₀₎ bond [8]. In Ic, the C₍₁₎C₍₉₎C₍₈₎ bond angle is not deformed [120,0(2)°] and, hence, the C_{(1)...C₍₈₎ distance [2,451(4) Å] is less than in VII (2.562 Å) due specifically to closure of the heterocycle. Indeed, the N_{(1)...N₍₂₎ distance in Ic is 2.363(3) Å, while the N...N distances in VII and VIII are 2.792 and 2.89 Å, respectively [9]}}



VII



VIII

The N₍₁₎ atom is virtually in Plane 1 [the deviation is only -0.025(2) Å], while N₍₂₎ and C₍₁₁₎ extrude by -0.208(2) and 0.337(3) Å, respectively, i.e., the dihydropyrimidine ring unexpectedly has an asymmetrical compressed half-chair conformation (the torsion angles in Ic are given in Table 5). N₍₂₎ and C₍₁₁₎ extrude by -0.143(2) and 0.401(3) Å from the N₍₁₎C₍₁₎-C₍₉₎C₍₈₎ plane (Plane 2), in which the component atoms do not deviate by more than 0.001(3) Å. The C₍₁₈₎H₃ and C₍₁₉₎H₃ methyl groups attached to the heterocycle occupy pseudoequatorial and equatorial positions, respectively. The H₍₁₁₎ atom occupies an equatorial position, while the phenyl group occupies an axial position. The N₍₁₎-C₍₁₈₎, N₍₂₎-C₍₁₉₎, C₍₁₁₎-H₍₁₁₎, and C₍₁₁₎-C₍₁₂₎ bonds form angles of 8.2°, -1.7°, -28.2°, and 78.9°, respectively, with Plane 2. The plane of the phenyl ring is twisted about the C₍₁₁₎-C₍₁₂₎ bond by 14(3)° relative to

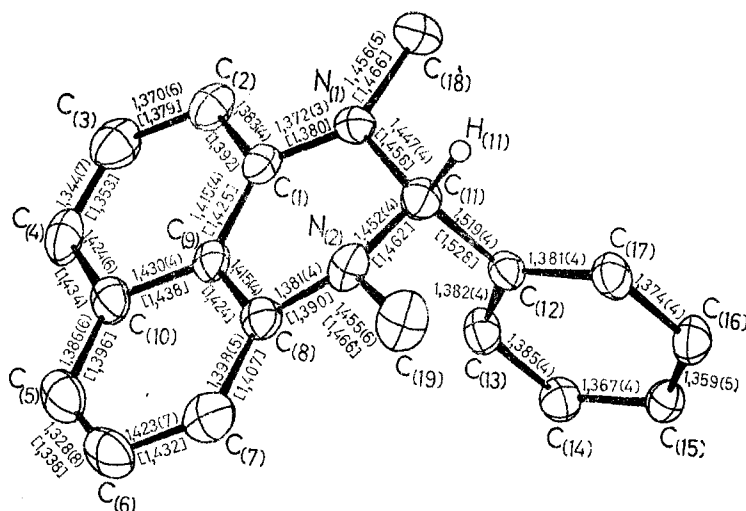


Fig. 1

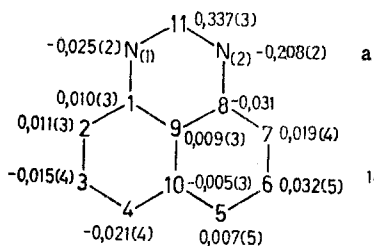


Fig. 2

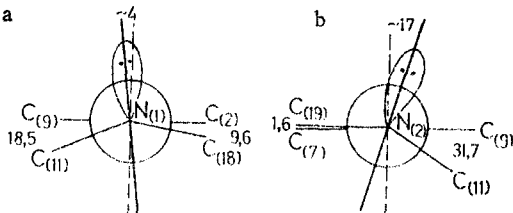


Fig. 3

Fig. 1. Molecular structure of Ic (of the hydrogen atoms, only H₍₁₁₎ is shown) with bond lengths (the bond lengths corrected for thermal oscillation are given in brackets).

Fig. 2. Deviation of atoms in Ic from the C₍₁₎-C₍₁₀₎ mean-square plane.

Fig. 3. Newman projection of Ic along the N₍₁₎-C₍₁₎ bond (a) and N₍₂₎-C₍₈₎ bond (b).

the C₍₁₁₎H₍₁₁₎C₍₁₂₎ plane [the H₍₁₁₎C₍₁₁₎C₍₁₂₎C₍₁₃₎ and H₍₁₁₎C₍₁₁₎C₍₁₂₎C₍₁₇₎ torsion angles are $-167(3)^\circ$ and $15(3)^\circ$, relatively, which is attributed to steric repulsion of H₍₁₁₎ and H₍₁₇₎, the distance between which [2.27(6) Å] is somewhat less than twice the van der Waals hydrogen radius (2.4 Å) [10]].

The bond length distribution of Ic is interesting. The N₍₁₎-C₍₁₎ [1.372(3) Å] and N₍₂₎-C₍₈₎ [1.381(4) Å] bond lengths indicate significant conjugation of the nitrogen unshared electron pairs and the naphthalene system π -electrons, which is in accord with our previous conclusion [2]. These bonds are shorter than the N-C_{ar} bonds in VII (mean 1.397 Å), in which the conjugation is less and to an even greater extent in VIII (mean 1.425 Å), in which there is virtually no conjugation. In addition, we should note the breakdown in the symmetry of the bond length distribution in the naphthalene system. Thus, the bonds involving C₍₁₎ and C₍₈₎ [C₍₁₎-C₍₂₎ (1.383(4) Å), C₍₁₎-C₍₉₎ [1.415(4) Å], C₍₇₎-C₍₈₎ [1.398(5) Å], and C₍₈₎-C₍₉₎ [1.415(4) Å] are longer than the bonds involving the other peri atoms C₍₄₎ and C₍₅₎, with the exception that the C₍₄₎-C₍₁₀₎ bond [1.424(6) Å] C₍₃₎-C₍₄₎ [1.344(7) Å], C₍₅₎-C₍₆₎ [1.328(8) Å], and C₍₅₎-C₍₁₀₎ [1.386(6) Å]], which is attributed, first, to the partial π -character of the N₍₁₎-C₍₁₎ and N₍₂₎-C₍₈₎ bonds and, second, to "overloading" [8] of the segment of the naphthalene system, which is connected to the heterocycle. This bond length distribution is typical for 1,8-disubstituted naphthalenes [7, 8]. The differences in the lengths of chemically equivalent bonds, specifically C₍₂₎-C₍₃₎ [1.370(6) Å] vs. C₍₆₎-C₍₇₎ [1.423(7) Å], C₍₄₎-C₍₁₀₎ [1.424(6) Å] vs. C₍₅₎-C₍₁₀₎ [1.386(6) Å], and C₍₃₎-C₍₄₎ [1.344(7) Å] vs. C₍₅₎-C₍₆₎ [1.328(8) Å] may be attributed to the greater participation of N₍₁₎ in conjugation; this

nitrogen atom, in contrast to N(2), is located in the plane of the naphthalene system. A representation of this arrangement is given by the Newman projections along the N(1)-C(1) and N(2)-C(8) bonds (Fig. 3), which indicate that the angle of about 4° in projection between the normal to the naphthalene system and the axis of the unshared electron pair (which is assumed to coincide with the external bisector of the CNC bond angle) is less than the corresponding angle in projection b (about 17°).

The C(4)C(10)C(5) bond angle [123.3(3)°] and the C(4)...C(5) nonbonded distance [2.473(7) Å] are somewhat greater than the corresponding values in 1,8-dimethylnaphthalene and VII (mean 119.5° and 2.444 Å) [7, 8]. The remaining bond lengths and bond angles in Ic have the ordinary values [11].

These differences in the bond lengths objectively reflect the somewhat unusual molecular geometry of Ic and are not a consequence of the atomic temperature oscillations. The corrections for the thermal oscillations of the dihydroperimidine fragment (without the phenyl substituent) do not lead to a change in the bond length distribution (the bond lengths are given in brackets in Fig. 1) [12].

The molecular geometry of Ic implies that the difficulty in the removal of a hydride ion from C(11) by the action of TNB is a consequence of shielding of H(11) by the two methyl groups. Indeed, H(17), H(18.1), and H(19.1) have contacts with H(11) of 2.27(6), 2.25(6), and 2.17(6) Å, which are less than twice the van der Waals hydrogen radius and form a "shielding" plane relative to which C(11) and H(11) are on the same side and 1.151(3) and 0.18(3) Å from the plane surface. The shielding of H(11) is a result of the rather rigid fixation of the positions of the hydrogen atoms of the methyl groups, which prevents the rotation both of these groups and the phenyl group. This hindrance to rotation results from the circumstance that H(18.2) and H(18.3) have short contacts with H(2) of 2.36(5) and 2.13(5) Å, respectively, and extrude from the C(1)C(2)H(2) plane in different directions by -1.10(3) and 0.49(3) Å. H(19.2) and H(19.3) contact H(7) at 2.21(5) and 2.38(5) Å and extrude from the corresponding plane by -0.86(3) and 0.77(3) Å. According to Fig. 4, in which the projection of H(11) on the H(17)H(18.1)H(19.1) shielding plane is shown, the minimal radius of the cavity between these three hydrogen atoms, through which the H(11)-hydride ions should pass is about 1 Å, while the radius of the hydride ion is 1.36 Å [13]. We shall not discuss the mechanism for loss of the hydride ion, but there is no doubt that it is not lost by itself, but rather is accepted by the TNB molecule. Thus, the transition complex of this reaction must be subject to even greater steric strain.

We should note that electric field forces also may affect the observed molecular geometry of Ic, specifically the breakdown of the apparently natural plane of symmetry through C(10), C(9), C(11), and C(12). However, the conformational changes when the molecule emerges changes when the molecule emerges from the crystal state should not have a significant effect on the shielding of H(11). This atom in Ib is apparently similarly shielded. On the other hand, the heterocycle geometry in benzimidazolines IVb and IVc, in which there is virtually no steric hindrance to dehydrogenation, should be considerably different. Unfortunately, it has not yet been possible to obtain sufficiently large crystals of 2-substituted benzimidazolines in order to study this question by x-ray diffraction structural analysis.

EXPERIMENTAL

X-ray Diffraction Structural Analysis. The unit cell parameters of monoclinic crystals of 1,3-dimethyl-2-phenyl-2,3-dihydroperimidine (Ic) at 20°C are as follows: $a = 7.3136(5)$, $b = 11.2316(8)$, $c = 18.352(2)$ Å, $\beta = 97.308(8)^\circ$, $Z = 4$, $d_{\text{calc}} = 1.219 \text{ g/cm}^3$, space group $P2_1/n$. The unit cell parameters and intensities of 1319 reflections with $F^2 \geq 2$ were measured on a Hilger-Watts automatic four-circle diffractometer using $\lambda\text{CuK}\alpha$ radiation, graphite monochromator, $\theta/2\theta$ scanning, $\theta \leq 66^\circ$.

The structure was solved by the direct method using the MULTAN programs. The positional parameters of the nonhydrogen atoms were refined by the method of least squares initially in the isotropic approximation and then in the anisotropic approximation. All the hydrogen atoms were revealed in the difference map and refined in the isotropic approximation. The final R factor was 0.0446 ($R_w = 0.0462$). All the calculations were carried out on an Eclipse S/200 computer using the modified EXTL programs.* The coordinates of the nonhydrogen atoms

*The programs were modified by A. I. Yanovskii and R. G. Gerr at the X-Ray Diffraction Structural Analysis Laboratory of the A. N. Nesmeyanov Institute of Heteroorganic Compounds of the Academy of Sciences of the USSR.

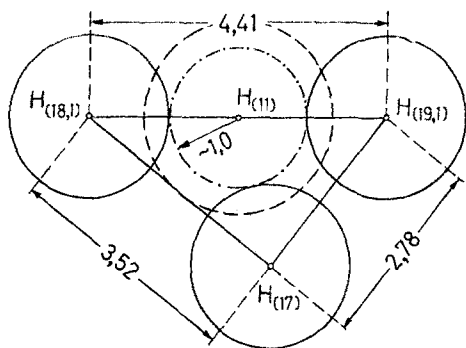


Fig. 4. Projection of the $H_{(11)}$ atom on the plane composed of $H_{(17)}$, $H_{(18,1)}$, and $H_{(19,1)}$ in Ic. The van der Waals radii (1.2 Å) are given by solid lines, the radius of the hydride ion (1.36 Å) is given by a dashed line, and the minimal radius of the cavity (1.0 Å) is given by a dot-dash line.

and their equivalent isotropic temperature factors, the coordinates of the hydrogen atoms and their isotropic temperature factors, and the bond angles not involving hydrogen atoms are given in Tables 2-4.

The rates of the reaction of I and IV with TNB were measured in acetonitrile at $25.0 \pm 0.1^\circ\text{C}$ spectrophotometrically at the absorption maximum of the 1,1-dihydro-2,4,6-trinitrocyclohexadienate anion at 477 nm. The detailed technique for the kinetic measurements will be published in a separate communication. The formation constants for π -complexes II were measured by our previous method [2].

The IR spectra of Vb and Vc were taken on a UR-20 spectrometer for Vaseline mulls. The UV spectra were taken on an SF-4A spectrophotometer in acetonitrile. The PMR spectra were taken on a Tesla BS-487C spectrometer in $\text{DMSO}-d_6$ at 60 MHz with HMDS as the internal standard. The acetonitrile sample was purified by heating at reflux over fresh portions of P_2O_5 until the liquid remained colorless and then distilled over potassium carbonate, selecting the fraction with bp 81.5°C . The sample of 1,3,5-trinitrobenzene was recrystallized from glacial acetic acid and twice from ethanol, mp 122°C .

The methods for the preparation and purification of the 2,3-dihydroperimidines and benzimidazolines have already been described: Ia [13], Ib,c [14], IVb,c [16]. The products of the reaction of IVb and IVc with TNB were obtained by the general method described in our previous work [1].

1,2,3-Trimethylbenzimidazolium 1,1-Dihydro-2,4,6-trinitrocyclohexadienate (Vb). This salt was obtained in 80% yield as black crystals with mp $127-128^\circ\text{C}$ (dec.). IR spectrum, ν_{NO_2} : 1220 cm^{-1} . UV spectrum, λ_{max} (ϵ): 477 (28,600), 586 nm (12,600). PMR spectrum: 2.80 (3H, s, 2- CH_3), 3.93 (6H, s, NCH_3), 7.74 (4H, m, H-4-7), 3.72 (2H, s, anion CH_2), 8.12 ppm (2H, s, anion H- β). Found, %: C 50.8, H 4.7, N 18.3. $\text{C}_{16}\text{H}_{17}\text{N}_5\text{O}_6$. Calculated, %: C 51.2, H 4.6, N 18.7.

1,3-Dimethyl-2-phenylbenzimidazolium 1,1-Dihydro-2,4,6-trinitrocyclohexadienate (Vc). This salt was obtained in 60% yield as black crystals with mp $128-129^\circ\text{C}$ (dec.). IR spectrum, ν_{NO_2} : 1205 cm^{-1} . UV spectrum, λ_{max} (ϵ): 477 (30,700), 586 nm (16,000). PMR spectrum: 3.94 (6H, s, NCH_3), 7.92 (4H, m, H-4-7), 7.82 (5H, singlet on the background of a multiplet, C_6H_5), 3.72 (2H, s, anion CH_2), 8.10 (2H, s, anion H- β). Found, %: C 58.0, H 4.4, N 16.3. $\text{C}_{21}\text{H}_{19}\text{N}_5\text{O}_6$. Calculated, %: C 57.7, H 4.4, N 16.0.

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ADDITIVITY OF $^{13}\text{C}-^1\text{H}$ AND $^1\text{H}-^1\text{H}$ SPIN-SPIN COUPLING CONSTANTS
IN SIX-MEMBERED AROMATIC NITROGEN-CONTAINING HETEROCYCLES

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UDC 543.422.25:547.852'853'861,873,491:
541.67

We have analyzed proton-coupled ^{13}C NMR and PMR spectra of pyridazine, pyrimidine, pyrazine, 1,3,5-triazine, and 1,2,4-triazine for one-molar solutions of the compounds in $\text{DMSO}-d_6$. Comparison of the values obtained for the $^{13}\text{C}-^1\text{H}$ and $^1\text{H}-^1\text{H}$ spin-spin coupling constants with the values calculated on the basis of the spin-spin coupling constants in pyridine and benzene has shown that it is possible to predict the constants using linear additive equations. Substantial nonlinear deviations (5-6 Hz) are observed for $^1J_{\text{CH}}$ when the carbon atom is located between two adjacent nitrogen atoms.

The investigation of the $^{13}\text{C}-^1\text{H}$ and $^1\text{H}-^1\text{H}$ spin-spin coupling constants in six-membered aromatic nitrogen-containing heterocycles is of great interest for the study of the structure of the compounds [1, 2] and electronic substitution effects [3-5]. Prediction of these values is especially important, since it substantially facilitates analysis of the NMR spectra.

In contrast to the chemical shifts for protons and ^{13}C nuclei, which on the whole are satisfactorily amenable to theoretical calculation [6, 7], the $^{13}\text{C}-^1\text{H}$ spin-spin coupling constants calculated by modern quantum-mechanical methods (for example by the INDO method in the Fermi-contact nuclear interaction approximation [8]) agree poorly with their experimental values. In most cases, this forces us to use empirical rules based on additive computational equations to determine the constants. Previously, for the case of poly-substituted benzenes [9-11] and monosubstituted pyridines [12, 13], it has been established that there is an additive substituent effect on the $^{13}\text{C}-^1\text{H}$ and $^1\text{H}-^1\text{H}$ spin-spin coupling constants.

$${}^nJ_{\text{bz}}(\text{XYZ}) = {}^nJ_{\text{bz}}(\text{H}) + \sum_{i=\text{X,Y,Z}} ({}^nJ_{\text{bz}}(i) - {}^nJ_{\text{bz}}(\text{H})); \quad (1)$$

$${}^nJ_{\text{pyr}}(\text{X}) = {}^nJ_{\text{pyr}}(\text{H}) + A \times ({}^nJ_{\text{bz}}(\text{X}) - {}^nJ_{\text{bz}}(\text{H})), \quad (2)$$

where ${}^nJ_{\text{bz}}$ and ${}^nJ_{\text{pyr}}$ are the constants in benzene and the pyridine ring; X, Y, and Z are substituents; A is a set of constants depending on the type of constant and the position of the substituent on the ring (range of values, 0.7-1.4).

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