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HETEROCYCLIC ANALOGS OF PLEIADIENE. 63.* SYNTHESIS AND CRYSTAL STRUCTURE OF 1-AMINOPERIMIDINES

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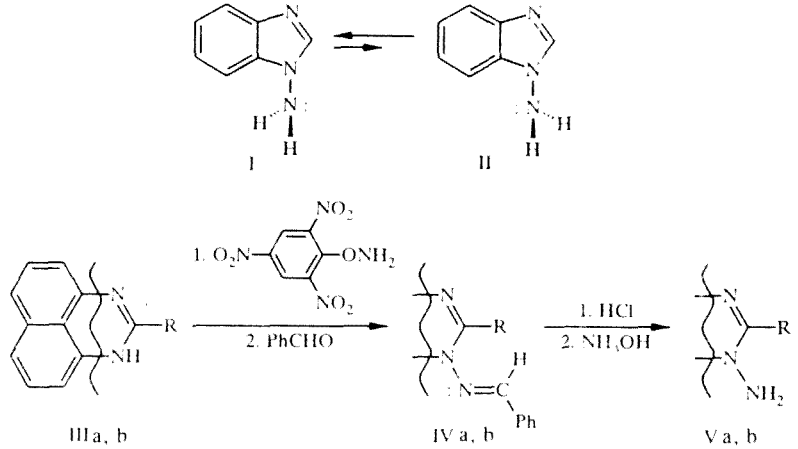
By action of O-picrylhydroxylamine on perimidine and 2-methylperimidine, we have synthesized their 1-amino derivatives. An x-ray diffraction investigated of 1-aminoperimidine showed that the amino group in them is found in a pyramidal configuration with the axis of the unshared electron pair lying in the plane of the heterocyclic ring, oriented toward the μ-carbon atom.

Recent investigations of different N-aminoazoles have shown that the amino group in them, both in solution and in the crystalline state, has a pyramidal configuration [2]. Moreover, the orientations of the unshared electron pair of the amino nitrogen relative to the plane of the heterocyclic ring may be different. Thus in 1-methyl-9-aminoxanthine [3], N-aminobenzimidazolium salts [4], and in 1-aminobenzimidazole itself [5], a conformation of type I is realized, in which the axis of the unshared electron pair is located in the plane of the aromatic ring and is oriented toward the μ-carbon atom. Stabilization of a conformation of type II proved to be possible in one case as a result of intramolecular hydrogen bonding with the substituent in the 2 position [6].



III–V a R=H, b R=Me

It is logical to assume that the major factor promoting realization of conformation I for 1-aminobenzimidazole and its salts is electrostatic attraction of the unshared electron pair of the amine nitrogen and the μ-carbon atom, bearing a significant positive charge. In this connection, we though it would be interesting to study the molecular structure of 1-aminoperimidine (Va), the six-membered analog of N-aminoazoles. On the other hand, in the molecule of this compound, the positive charge of $C_{(2)}$ atom is significantly higher than in benzimidazole [7], which should favor conformations of type I even more; on the other hand, in this conformation the hydrogen atoms of the amino group and the hydrogen atom in the 9 position prove to be somewhat closer than such atoms in the 1-aminobenzimidazole molecule. The latter circumstance might conversely destabilize conformation I and make conformation III preferred.

*For Communication 62, see [1].

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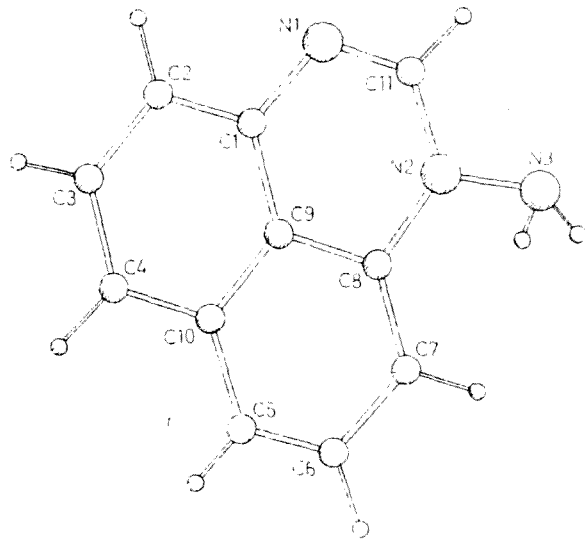

Fig. 1. Numbering of the atoms and the conformation of the N-amino group in the 1-aminoperimidine molecule (Va).

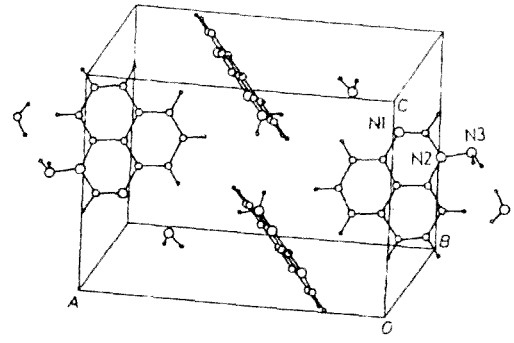

Fig. 2. Packing of 1-aminoperimidine (monohydrate) molecules in the crystal lattice.

N-Aminoperimidines were unknown until recently. Attempts to obtain them by electrophilic amination of perimidines by hydroxylamine-O-sulfonic acid in basic medium proved to be unsuccessful, predominantly due to them facile oxidizability of the N-anion and the related strong resinification [8]. Conversely, amination of 1-alkylperimidines under neutral conditions using O-mesitylsulfonylhydroxylamine led to formation of the corresponding N-aminoperimidinium salts in good yield [8, 9]. In this paper, we have attempted to use this method for amination of perimidine itself, in hopes that subsequent deprotonation of the salt formed would allow us to obtain 1-aminoperimidine as the base. As the aminating agent, we used O-picrylhydroxylamine, the use of which has given good results in a number of cases [4, 10].

The reaction between O-picrylhydroxylamine and a double equivalent of perimidine (IIIa) was carried out in ethanol at room temperature. The process was accompanied by strong resinification and led to formation of a mixture of perimidine picrate and 1-aminoperimidine, which could not be separated by conventional means. In order to isolate the amine Va, the reaction mixture was treated with benzaldehyde and the hydrazone IVa formed was separated using column chromatography. Its subsequent hydrolysis in hydrochloric acid led to the amine Va in 54% yield, calculated on the basis of the O-picrylhydroxylamine used. We synthesized 1-amino-2-methylperimidine (Vb) in 12% yield similarly from 2-methylperimidine (IIIb) through the hydrazone IVb.

TABLE 1. Atomic Coordinates (in fractions of the axes of the unit cell) and Thermal Corrections $U_{(iso)}/U_{(eq)}$ in the Molecule of Compound Va

Atom	x	y	z	$U_{(iso)}$, $U_{(eq)}$
N(1)	1,1413(3)	0,0547(9)	0,5106(4)	0,055(2)
N(2)	1,0178(3)	0,1821(8)	0,3691(4)	0,048(2)
N(3)	0,9480(4)	0,360(1)	0,3412(4)	0,060(2)
C(1)	1,1598(4)	-0,134(1)	0,4413(5)	0,050(2)
C(2)	1,2313(4)	-0,202(1)	0,4808(6)	0,065(3)
C(3)	1,2482(5)	-0,483(1)	0,4105(7)	0,075(3)
C(4)	1,1957(5)	-0,511(1)	0,3070(7)	0,071(3)
C(5)	1,0636(5)	-0,371(1)	0,1577(6)	0,076(3)
C(6)	0,9950(5)	-0,213(1)	0,1229(5)	0,080(3)
C(7)	0,9756(5)	-0,024(1)	0,1910(5)	0,066(3)
C(8)	1,0299(4)	-0,002(1)	0,2935(4)	0,052(2)
C(9)	1,1057(4)	-0,162(1)	0,3347(5)	0,048(2)
C(10)	1,1218(5)	-0,353(1)	0,2644(5)	0,059(3)
C(11)	1,0736(4)	0,197(1)	0,4700(5)	0,059(2)
W	0,7434(3)	-0,2192(9)	0,2889(4)	0,086(2)
H(N31)	0,900(3)	0,26(1)	0,320(5)	0,087(8)
H(N32)	0,952(4)	0,42(1)	0,274(4)	0,087(8)
H(2)	1,270(4)	-0,28(1)	0,557(4)	0,087(8)
H(3)	1,301(4)	-0,60(1)	0,435(5)	0,087(8)
H(4)	1,213(4)	-0,63(1)	0,253(5)	0,087(8)
H(5)	1,075(4)	-0,51(1)	0,113(5)	0,087(8)
H(6)	0,952(4)	-0,23(1)	0,049(4)	0,087(8)
H(7)	0,921(4)	0,08(1)	0,164(5)	0,087(8)
H(11)	1,057(4)	0,34(1)	0,514(5)	0,087(8)
H(1W)	0,781(3)	-0,182(8)	0,359(3)	0,08(1)
H(2W)	0,757(3)	-0,387(7)	0,294(3)	0,11(2)

TABLE 2. Bond Lengths in the Molecule of Compound Va

Bond	l (Å)	Bond	l (Å)
N(1)—C(1)	1,416(7)	N(1)—C(11)	1,287(8)
N(2)—N(3)	1,414(7)	N(2)—C(8)	1,419(7)
N(2)—C(11)	1,340(7)	N(3)—H(N31)	0,91(6)
N(3)—H(N32)	0,92(5)	C(1)—C(2)	1,376(9)
C(1)—C(9)	1,391(8)	C(2)—C(3)	1,42(1)
C(2)—H(2)	0,99(5)	C(3)—C(4)	1,35(1)
C(3)—H(3)	1,00(6)	C(4)—C(10)	1,41(1)
C(4)—H(4)	1,02(6)	C(5)—C(6)	1,34(1)
C(5)—C(10)	1,41(1)	C(5)—H(5)	0,97(6)
C(6)—C(7)	1,41(1)	C(6)—H(6)	1,00(5)
C(7)—C(8)	1,349(8)	C(7)—H(7)	0,99(6)
C(8)—C(9)	1,432(8)	C(9)—C(10)	1,418(8)
C(11)—H(11)	1,02(6)	W—H(1W)	0,95(4)
W—H(2W)	0,93(4)		

Like other 1-substituted perimidines, the amines Va,b are yellow-green crystalline materials whose V spectrum is quite identical to the spectrum of 1-methyl- or 1,2-dimethylperimidine. The latter circumstance indicates the absence of any conjugation between the amino group and the π system of the heterocycle, which is observed only or sp^3 hybridization of the amino nitrogen and realization of one of the two possible conformations corresponding to type I or II. In the hydrazones IVa,b, clear conjugation exists between the heterocycle and the azomethine group, evidence for which is their bright orange color and the presence of an absorption maximum at 430 nm.

TABLE 3. Bond Angles in the Molecule of Compound Va

Angle	ω (degrees)	Angle	ω (degrees)
$C_{(1)}N_{(1)}C_{(11)}$	117,0(5)	$N_{(3)}N_{(2)}C_{(8)}$	122,0(5)
$N_{(3)}N_{(2)}C_{(11)}$	117,1(5)	$C_{(8)}N_{(2)}C_{(11)}$	120,9(5)
$N_{(2)}N_{(3)}H_{(N31)}$	100(4)	$N_{(2)}N_{(3)}H_{(N32)}$	105(4)
$H_{(N31)}N_{(3)}H_{(N32)}$	101(5)	$N_{(1)}C_{(1)}C_{(2)}$	119,3(5)
$N_{(1)}C_{(1)}C_{(9)}$	120,2(5)	$C_{(2)}C_{(1)}C_{(9)}$	120,5(6)
$C_{(1)}C_{(2)}C_{(3)}$	118,5(6)	$C_{(3)}C_{(2)}H_{(2)}$	122(3)
$C_{(3)}C_{(2)}H_{(2)}$	119(3)	$C_{(2)}C_{(3)}C_{(4)}$	121,3(7)
$C_{(2)}C_{(3)}H_{(3)}$	121(4)	$C_{(4)}C_{(3)}H_{(3)}$	117(4)
$C_{(3)}C_{(4)}C_{(10)}$	121,4(7)	$C_{(3)}C_{(4)}H_{(4)}$	121(3)
$C_{(10)}C_{(4)}H_{(4)}$	117(3)	$C_{(6)}C_{(5)}C_{(10)}$	121,5(7)
$C_{(6)}C_{(5)}H_{(5)}$	123(4)	$C_{(10)}C_{(5)}H_{(5)}$	116(4)
$C_{(5)}C_{(6)}C_{(7)}$	122,1(7)	$C_{(5)}C_{(6)}H_{(6)}$	123(3)
$C_{(7)}C_{(6)}H_{(6)}$	115(3)	$C_{(6)}C_{(7)}C_{(8)}$	117,9(6)
$C_{(6)}C_{(7)}H_{(7)}$	119(3)	$C_{(8)}C_{(7)}H_{(7)}$	123(3)
$N_{(2)}C_{(8)}C_{(7)}$	123,0(5)	$N_{(2)}C_{(8)}C_{(9)}$	114,3(5)
$C_{(7)}C_{(8)}C_{(9)}$	122,7(6)	$C_{(1)}C_{(9)}C_{(8)}$	121,0(5)
$C_{(1)}C_{(9)}C_{(10)}$	121,3(5)	$C_{(8)}C_{(9)}C_{(10)}$	117,7(5)
$C_{(4)}C_{(10)}C_{(5)}$	124,9(7)	$C_{(4)}C_{(10)}C_{(9)}$	117,0(6)
$C_{(5)}C_{(10)}C_{(9)}$	118,2(6)	$N_{(1)}C_{(11)}N_{(2)}$	126,6(5)
$N_{(1)}C_{(11)}H_{(11)}$	121(3)	$N_{(2)}C_{(11)}H_{(11)}$	112(3)
$H_{(1W)}WH_{(2W)}$	100(4)		

TABLE 4. Deviations of Some Atoms from the Average Plane of the Va Molecule

Atom	Deviation (Å)	Atom	Deviation (Å)
$N_{(1)}$	-0,0034	$C_{(7)}$	-0,0079
$N_{(2)}$	-0,0031	$C_{(8)}$	-0,0055
$C_{(1)}$	0,0084	$C_{(9)}$	0,0155
$C_{(2)}$	-0,0017	$C_{(10)}$	0,0012
$C_{(3)}$	-0,0050	$C_{(11)}$	0,0011
$C_{(4)}$	-0,0039	$N_{(3)}$	0,0182
$C_{(5)}$	-0,0032	$H_{(1)}N$	0,700
$C_{(6)}$	0,0078	$H_{(2)}N$	-0,716

TABLE 5. Chemical Shifts of 4-H and 9-H Protons (in $CDCl_3$) and Position of Long-Wavelength Absorption Maximum (in CH_3OH) in Some 1-R-2-R^1-Perimidines

R	R^1	Chemical shift, ppm		λ_{max}, nm (lg ε)
		4-H	9-H	
CH_3	H	6,85	6,13	331 (4,16)
CH_3	CH_3	6,86	6,21	330 (4,10)
NH_2	H	6,86	6,24	331 (4,15)
NH_2	CH_3	6,84	6,29	330 (4,16)
$N{=}CHC_6H_5$	H	6,90	6,78	430 (3,92)
$N{=}CHC_6H_5$	CH_3	6,86	6,17	430 (3,22)

In the PMR spectra of amines Va,b, the signal from protons of the NH_2 group is found at 3.95 and 3.76 ppm respectively, which is a record upfield shift for all the known N-aminoazoles [2]. The most plausible explanation for this is that the amines Va,b exist in a conformation of type I, in which the hydrogen atoms of the amino group projecting over the naphthalene ring experience an effect from the paramagnetic component of the ring current. This effect, although to a somewhat lesser degree, probably also occurs in 1-aminobenzimidazole, in the PMR spectrum of which the signal from the NH_2 protons (4.84 ppm) also is found very much upfield compared with, for example, the N-aminopyrazoles and N-aminotriazoles [2]. Our x-ray diffraction investigation of 1-aminoperimidine confirmed that conformation I is realized also in the crystalline state (Figs. 1 and 2, Tables 1-4). This is probably the first crystallographic investigation of a simple derivative of perimidine, so let us first

mention a number of structural characteristics of the perimidine system itself. It is practically flat: the maximum deviation of the ring atoms from the average plane is no more than 0.015 Å (Table 4). Note the shortening of the $N_{(1)}-C_{(11)}$ bond in the heterocycle (1.28 Å), and also the marked alternation of the C–C bonds in the naphthalene system: the $C_{(1)}-C_{(2)}$, $C_{(3)}-C_{(4)}$, $C_{(5)}-C_{(6)}$, and $C_{(7)}-C_{(8)}$ bonds are somewhat shorter (1.34-1.38 Å) than the rest of the bonds, the lengths of which lie within the range 1.41-1.43 Å. The $N_{(3)}$ atom of the amino group insignificantly deviates from the plane (by only 0.02 Å). The amino group itself, as in 1-aminobenzimidazole, has a conformation of type I. Thus the hypothesis about the electrostatic nature of the stabilization of the given conformation has found further support. We note that we isolated 1-aminoperimidine in the form of a very stable monohydrate, for which we also performed a structural analysis. In the crystal lattice, each water molecule W participates in the formation of four hydrogen bonds, in which both unshared electron pairs of the oxygen atom and both hydrogen atoms are employed (Fig. 2). Two bonds connect the water with two different amino molecules $W-H...N_{(1)}$ (2 — x, y, 1 — z) and $W...H-N_{(3)}$ (3/2 — x, 1/2+y, 1/2 — z). In turn, each amine molecule is bonded through th $N_{(1)}$ atom and the $N_{(3)}-H$ bond with two different water molecules $W_{(1)}$ and $W_{(2)}$. The hydrogen bond $N_{(1)}...W_{(1)}$ is characterized by the following parameters: the $N_{(1)}...HW_{(1)}$ and $N_{(1)}...OW_{(1)}$ distances are 1.89(4) and 2.825(7) Å respectively, the $N_{(1)}...H-O$ angle is equal to 171(4)°. The hydrogen bond with participation of the N-amino group is looser and obviously less strong: $N_{(3)}H...OW_{(2)}$ is 2.28(6) Å and $N_{(3)}...OW_{(2)}$ is 3.011(7) Å, the angle $O...H-N_{(3)}$ is equal to 137(4)°. The second hydrogen atom of the water molecule participates in the conformation with the unshared electron pair of the adjacent water molecule W (3/2 — x, −1/2+y, 1/2 — z), the O–H...O and O...O distances are 2.00(4) and 2.882 Å respectively, the angle O–H...O is equal to 156(4)°. The described system of hydrogen bonds in this structure leads to formation of spirals of H-bonded water molecules, twisted about the 2_1 crystallographic axis and the Va molecules H-bonded with them. According to the classification in [11], this type of H-bonded water molecule in hydrates is assigned to type E.

Interesting conclusions concerning the conformations of the azomethine group in the compounds IVa,b can be drawn by analyzing the features of their PMR spectra and electronic absorption spectra (Table 5). We know that for the PMR spectra of 1-substituted perimidines, appreciable upfield separation of the signals from the 4-H protons and especially the 9-H protons is characteristic, where they appear as two doublets of doublets at 6.8-6.9 and 6.2-6.3 ppm respectively [12]. As we see from Table 5, this also pertains to the amines Va,b, and also to the hydrazone IVb. However, in the PMR spectrum of the hydrazone IVa, the signal from the 9-H proton is shifted by −0.5 ppm downfield compared with its usual position. An obvious reason for this may be the anisotropic effect on this proton of the unshared electron pair of the azomethine nitrogen, which is possible only or realization of a flat or almost flat conformation of IVa. However, in the PMR spectrum of the hydrazone IVb, we do not observe an anomalous shift of the 9-H proton signal. It is logical to assume that in this case, due to overlap of the 2-methyl group and the azomethine proton, the benzylidene amino group is turned about the N–N bond by a very significant angle, which completely removes its deshielding effect on the 9-H proton. The value of this angle (φ) may be estimated by comparing the intensity of the long-wavelength band of both hydrazones IVa,b using the familiar relation in [13] $\varepsilon/\varepsilon_0 = \cos^2\varphi$, where ε and ε_0 are the extinction coefficients of the nonplanar (IVb) and the planar (IVa) models. Taking into account the data presented in Table 5, the angle φ is found to be equal to 63°.

EXPERIMENTAL

The PMR spectra were recorded on the Unity-300 instrument in a $CDCl_3$ solution, internal standard TMS. The IR spectra were taken on the IKS-40 instrument in vaseline oil, the electronic spectra were taken on the Specord M-40 spectrophotometer in methanol. The course of the reactions and the purity of the compounds obtained were monitored by TLC on plates with Al_2O_3 (Brockmann activity III), chloroform as the eluent, visualization by iodine vapor. The melting points were measured on the PTP instrument in sealed glass capillaries and were uncorrected.

The elemental analysis data for the synthesized compounds for C and H correspond to the calculated values.

X-ray Diffraction Analysis of 1-Aminoperimidine (Va). The crystals of composition $C_{11}H_9N_3 \cdot H_2O$ were grown from aqueous ethanol (1:1), monoclinic, a = 15.422(1), b = 5.3694(6), c = 12.586(1) Å, γ = 105.05(1)°, V = 1006.5(2), Å^3, Z = 4, space group $P2_1/n$. The structure was deciphered by the direct method and refined by the least-squares method in the full-matrix anisotropic approximation (isotropic approximation for the hydrogen atoms) to R = 0.0696 (R_w = 0.073) for 886 reflections with $F^2 > 6\sigma$. Syntex-P1 diffractometer, λCuKα, graphite monochromator, $\theta/2\theta$ scanning, $3 < 2\theta < 120°$. The final coordinates of the atoms are presented in Table 1, the bond lengths and bond angles are presented in Tables 2 and 3.

1-Benzylideneaminoperimidine (IVa, $C_{18}H_{13}N_3$). **A.** O-Picrylhydroxylamine (1.71 g, 7.0 mmoles) was added to a solution of 2.3 g (13.7 mmoles) perimidine (IIIa) in 40 ml ethanol [14]. The mixture was stirred for 30 min at room temperature, after which the precipitate formed was filtered, washed with 10 ml ethanol, dissolved in 50 ml glacial acetic acid, and boiled for 1 h with 0.4 ml benzaldehyde. Then the acetic acid was completely driven off under reduced pressure 20 ml chloroform was added to the residue, and 2.46 g (44%, based on the perimidine) perimidine picrate was filtered off: yellow-green needles, mp 252-254 decomp., from water), identical in all characteristics to a known sample. The chloroform solution was passed through a column with Al_2O_3 (l = 30 cm, d = 2), chloroform as the eluent. The fraction with R_f = 0.7 was collected, which is the hydrazone IVa. Yield, 0.38 g (20%).

An additional amount of the amine Va is found in the alcoholic filtrate remaining after the first filtration of the reaction mixture. Benzaldehyde (0.7 ml) was added to it, and this was boiled for 4 h. Then 0.36 g (19%) of hydrazone IVa was isolated as described above. Overall yield, 0.72 g (38%, based on the perimidine). Fine orange crystals with mp 173-174°C (decomp., from ethanol). IR spectrum: 1631 (C=N), 1588 cm^{-1} (ring). UV spectrum, λ_{max} (lg ε): 234 (4.49), 250 shoulder (4.34), 320 shoulder (4.04), 334 (4.11), 345 shoulder (4.02), 364 shoulder (3.97), 430 nm (3.92). PMR spectrum: 6.78 (1H, m, 9-H), 6.90 (1H, d.d, 4-H), 7.20 (4H, m, 5-H-8-H), 7.48 (3H, m, 3'-H-5'-H), 7.58 (1H, s, 2-H), 7.84 (2H, m, 2'-H, 6'-H), 8.40 ppm (1H, s, N=CH), J_{45} = 6.45, J_{46} 1.90 Hz.

B. A mixture of 0.58 g (3.5 mmoles) perimidine and 0.37 g (1.5 mmoles) O-picrylhydroxylamine in 15 ml ethanol was stirred at room temperature for 30 min, then 0.15 ml benzaldehyde was added and this was boiled for 4 h. The solvent was evaporated to dryness, the residue was triturated with 10 ml chloroform, and 0.45 g (46%) perimidine was filtered off. The filtrate was passed through a column with Al_2O_3, collecting 0.13 g (4%) of compound IVa.

1-Benzylideneamino-2-methylperimidine (IVb, $C_{19}H_{15}N_3$). A mixture of 3.75 g (20.6 mmoles) 2-methylperimidine (IIIb) and 2.5 g (10.2 mmoles) O-picrylhydroxylamine in 35 ml ethanol was stirred at room temperature for 2 h, after which the solvent was driven off under vacuum. Acetic acid (35 ml) and 2 ml benzaldehyde were added to the residue and this was boiled for 1 h. Then the acetic acid was completely driven off, the residue was triturated with 40 ml chloroform, and 2.76 g (38%) 2-methylperimidine picrate was filtered off: brown platelets, darkening at > 170°C and melting with decomposition at 237-238°C (from DMF-water, 1:2). The chloroform mother liquor was passed through a column with Al_2O_3 (l = 30 cm, d = 2.5 cm), eluting with chloroform and collecting the fraction with R_f = 0.8, which is the hydrazone IVb. Yield, 0.57 g (10%). Fine orange crystals with mp 116-118°C (decomp., isooctane). IR spectrum: 1623 (C=N), 1610, 1578 cm^{-1} (ring). UV spectrum, λ_{max} (lg ε): 260 (4.32), 320 (4.08), 430 nm (3.22). PMR spectrum: 2.19 (3H, s, CH_3), 6.17 (1H, d.d, 9-H), 6.86 (1H, d.d, 4-H), 7.12 (4H, m, 5-H-8-H), 7.58 (3H, m, 3'-H-5'-H), 7.94 (2H, m, 2'-H, 6'-H), 8.56 ppm (1H, s, N=CH), J_{45} = J_{89} = 7.33, J_{46} = 0.88, J_{79} = 1.17 Hz.

1-Aminoperimidine (Va, $C_{11}H_9N_3 \cdot H_2O$). A suspension of 0.56 g 1-benzylidenaminoperimidine (IVa) in 30 ml 15% hydrochloric acid was boiled with simultaneous distillation of the benzaldehyde (Dean and Stark attachment) until complete disappearance of the hydrazone residue (~2 h). The solution formed was boiled for 5 min with activated charcoal and filtered hot, and then the mother liquor was evaporated to dryness. Obtained: 0.32 g (70%) of 1-aminoperimidine hydrochloride in the form of the monohydrate $C_{11}H_9N_2 \cdot HCl \cdot H_2O$. Yellow crystals with mp 223-225°C (decomp., from water), darken at > 170°C. IR spectrum: 3395 (broad H_2O), 3300, 3150, (NH_2), 1680 (H_2O), 1640 (C=N), 1613 cm^{-1} (ring). Upon neutralization of the aqueous solution of the hydrochloride with concentrated aqueous ammonia, we obtained grayish-green platelets of the base in the form of the monohydrate, mp 120-122°C (decomp., from an ethanol–water mixture, 1:1). IR spectrum: 3434 (H_2O), 3314, 3140, (NH_2), 1640, 1587 cm^{-1} (ring). UV spectrum, λ_{max} (lg ε): 233 (4.54), 331 nm (4.15) with ring absorption up to ≈ 420 nm. PMR spectrum: 3.95 (2H, s, NH_2), 6.24 (1H, d.d, 9-H), 6.86, (1H, d.d, 4-H), 7.19 (4H, m, 5-H-8-H), 7.46 ppm (1H, s, 2-H), J_{89} 5.86, J_{79} = 2.34, J_{45} = 7.33, J_{46} = 9.88 Hz.

1-Amino-2-methylperimidine (Vb, $C_{12}H_{11}N_3$). The amine Va was obtained similarly from the hydrazone IVb. Yield, 60%. Light green crystals, mp 153-157°C (decomp., from isooctane). IR spectrum: 3450 (broad, H_2O), 3325, 3158 (NH_2), 1626, 1584 cm^{-1} (ring). UV spectrum, λ_{max} (lg ε): 330 nm (4.16). PMR spectrum: 2.38 (3 H, s, CH_3), 3.76 (2H, s, NH_2), 6.29 (1 H, d.d, 9-H), 6.84 (1 H, d.d, 4-H), 7.20 (4H, m, 5-H-8-H), J_{45} = 7.32, J_{46} = 0.88, J_{89} = 6.44, J_{79} = 1.76 Hz. The hydrochloride was fine yellow crystals, mp 285-287°C (decomp., from water), darken at a temperature > 170°C. IR spectrum: 3290, 3193, 3149 (NH_2), 2635 cm^{-1} (NH).

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