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HETEROCYCLIC ANALOGS OF PLEIADIENE
76.* SYNTHESIS AND TAUTOMERIC CONVERSIONS OF MONO- AND DISUBSTITUTED PERIMIDINES WITH ELECTRON-WITHDRAWING SUBSTITUENTS IN THE NAPHTHALENE FRAGMENT**

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A series of new mono- and disubstituted perimidines with electron-withdrawing substituents in the naphthalene fragment has been synthesized. Their prototropic annular tautomerism has been investigated by ^{1}H NMR spectroscopy.

Keywords: perimidine, PPA (polyphosphoric acid), annular prototropy, arenesulfonation, acylation.

We reported previously on the extremely slow annular prototropic tautomerism of derivatives of 2-trifluoromethylperimidine containing a formyl, acetyl, or *p*-toluenesulfonyl group in position 6(7) [2, 3]. This phenomenon is expressed in the ^{1}H and ^{19}F NMR spectra of these compounds by the simultaneous observation of signals of both tautomers in low polarity solvents at room temperature and even on heating to 120-130°C. It is assumed that the reason for this is the low basicity of these compounds in combination with spatial screening of both heteroatoms not only from the side of the 2-CF_3 substituent but also from the hydrogen atoms in positions 4 and 9.

In the light of this it seemed of interest to investigate the prototropic tautomerism of 2-*tert*-butylperimidine (**1**) and also of the product of its 6(7)-acylation. It was expected that, not being an acceptor but being large, the *tert*-butyl group may hinder transfer of proton.

We obtained compound **1** by the action of pivaloyl chloride on 1,8-naphthalenediamine. On acylation with acetic acid in PPA at 70-75°C the isomeric 6(7)- and 4(9)-diacetyl derivatives of 2-*tert*-butylperimidine **2** and **3** were synthesized in 66 and 11% yield respectively.

The ^{1}H NMR spectrum of 2-*tert*-butylperimidine (**1**) in $CDCl_3$ was unresolved. A strongly broadened peak of the *ortho* protons (H-4 and H-9) and a multiplet signal of the remaining aromatic protons indicated a somewhat slow prototropy. However, unlike other perimidines, the picture of the spectrum is practically

* For Communication 75 see [1].

** Dedicated to Professor M. A. Yurovskaya on her birthday.

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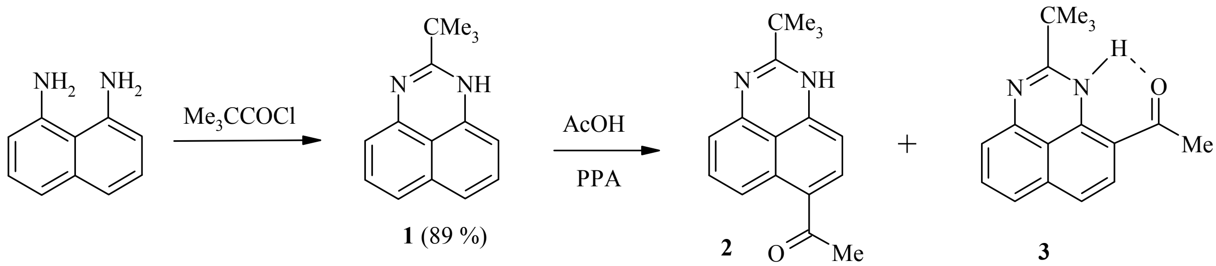
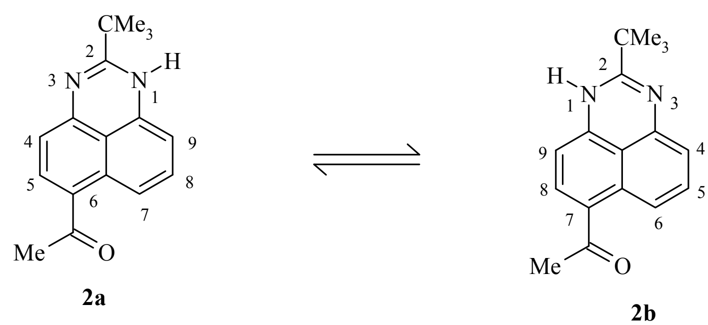


unchanged on transferring to DMSO-d_6. Only on heating to 50°C was the signal of the *ortho* protons converted into a broadened doublet and the fine structure of the signals of the other aromatic protons displayed (see Table 1). This means that the nonpolar *tert*-butyl group hinders substantially the formation of a hydrogen bond with the NH group proton and a solvent molecule.

The ^{1}H NMR spectrum of 6(7)-acetyl-2-*tert*-butylperimidine (**2**) in $CDCl_3$ in the region of 6-9 ppm is a set of 11 strongly broadened singlets. Only the most low-field of them was double the remainder in intensity (Table 1 and Fig. 1, *a*). Judging by the chemical shift this combined signal of the *peri* protons of tautomers **2a** and **2b** is deshielded by the carbonyl group.



It follows from the relative intensities of the remaining singlets that in tautomeric equilibrium **2a** and **2b** are in a ~1:1 ratio. Consequently, for 6(7)-acetyl-2-*tert*-butylperimidine in low-polarity $CDCl_3$ the rate of tautomeric conversion is somewhat greater than in the case of the trifluoromethyl analogs. But unlike the latter the addition of a drop of D_2O to a solution of ketone **2** in $CDCl_3$ does not lead to acceleration of prototropy (Fig. 1, *b*). Only two singlets at 8.0 and 8.1 ppm disappear from the spectrum, which permits their assignment to the NH proton of the two tautomers.

It was somewhat unexpected that on changing from $CDCl_3$ to DMSO-d_6 the rate of proton transfer was not increased but fell (Fig. 1, *c*), in difference to their 2-CF_3 analogs [3], and also other derivatives of perimidine [4]. In this case the ratio of tautomers **2a** and **2b** in the equilibrium mixture was 38:62, i.e. the more basic 7-tautomer **2b** predominates. In our view this is scarcely whether this is not the first stage of slow prototropy in so polar a proton-withdrawing solvent. The relatively high basicity and low NH-acidity of 6(7)-acetyl-2-*tert*-butylperimidine explains its insensitivity in the scheme of tautomerism to the presence of water and, on the other hand, its sensitivity to the known contaminant HCl in $CDCl_3$, which also leads, in our opinion, to some acceleration of proton exchange (in comparison with DMSO-d_6).

Since 4(9)-isomeric aldehydes, ketones, and sulfones are formed together with 6(7) derivatives on acylation, formylation, and arene sulfonation [5-7], it seemed of interest to investigate the possibility of their prototropic conversions, and also the degenerate tautomerism of 4,9-disubstituted analogs.

TABLE 1. ^{1}H NMR Spectra of Compounds Synthesized for the First Time

Compound*	Solvent	T °C	Chemical shifts, δ, ppm (*J*, Hz)							
			H-2	H-4	H-5	H-6	H-7	H-8	H-9	Other protons
1	$CDCl_3$	25	—	6.5 (br. s)	7.1 (m)	7.1 (m)	7.1 (m)	7.1 (m)	6.5 (br. s)	1.31 (9H, s, $C(CH_3)_3$)
	DMSO-d_6	15	—	6.5 (br. s)	7.1 (br. s)	7.0 (br. s)	7.0 (br. s)	7.1 (br. s)	6.5 (br. s)	1.25 (9H, s, $C(CH_3)_3$); 9.88 (1H, br. s, NH)
	DMSO-d_6	50	—	6.5 (br. d, ^3J = 6.2)	7.1 (br. t)	7.0 (d, ^3J = 8.1)	7.0 (d, ^3J = 8.1)	7.1(br. t)	6.5 (br. d, ^3J = 6.2)	1.27 (9H, s, 2-$C(CH_3)_3$); 9.72 (1H, br. s, NH)
2a	$CDCl_3$	25	—	6.3 (br. s)	7.9 (br. s)	—	8.6 (br. s)	7.3 (br. s)	6.8 (br. s)	1.36 (9H, s, $C(CH_3)_3$); 2.60 (3H, s, CH_3CO); 8.02 (1H, br. s, NH)
2b	$CDCl_3$	25	—	7.1 (br. s)	7.5 (br. s)	8.6 (br. s)	—	7.8 (br. s)	6.5 (br. s)	1.36 (9H, s, $C(CH_3)_3$); 2.60 (3H, s, CH_3CO); 8.12 (1H, br. s, NH)
2a	DMSO-d_6	25	—	6.6 (br. d, ^3J = 8.2)	8.0 (br. d, ^3J = 8.2)	—	8.5 (br. d, ^3J = 8.6)	7.3 (br. t)	6.8 (br. d, ^3J = 7.6)	1.30 (9H, s, $C(CH_3)_3$); 2.51 (3H, s, CH_3CO); 10.05 (1H, br. s, NH)
2b*	DMSO-d_6	25	—	6.9 (br. d, ^3J = 7.5)	7.4 (br. t)	8.6 (br. d, ^3J = 8.7)	—	8.0 (br. d, ^3J = 8.2)	6.6 (br. d, ^3J = 8.2)	1.30 (9H, s, $C(CH_3)_3$); 2.51 (3H, s, CH_3CO); 10.1 (1H, br. s, NH)
3	DMSO-d_6	25	—	7.1 (d, ^3J = 8.2)	7.6 (dd, ^3J = 8.2, ^3J = 7.7)	7.3 (d, ^3J = 7.7)	7.0 (d, ^3J = 8.8)	7.65 (d, ^3J = 8.8)	—	1.37 (9H, s, $(CH_3)_3C$); 2.58 (3H, s, CH_3CO); 12.97 (1H, br. s, NH···O=)
12	$CDCl_3$	25	7.88 (d, $^3J_{2H\text{–}NH}$ = 2.2)	—	7.98 (d, ^3J = 8.6)	7.26 (d, ^3J = 8.6)	7.10 (d, ^3J = 8.9	7.66 (d, ^3J = 8.9)	—	2.63 (3H, s, 9-$COCH_3$); 2.80 (3H, s, 4-$COCH_3$); 12.67 (1H, br. s, NH)
	DMSO-d_6	20	8.12 (d, $^3J_{2H\text{–}NH}$ = 2.75)	—	7.89 (d, ^3J = 8.8)	7.22 (d, ^3J = 8.8)	7.34 (d, ^3J = 8.8)	7.80 (d, ^3J = 8.8)	—	2.61 (3H, s, 9-$COCH_3$); 2.72 (3H, s, 4-$COCH_3$); 12.79 (1H, s, NH)
	DMSO-d_6	100	8.12 (s)	—	7.83 (d, ^3J = 8.6)	7.28 (br. s)	7.28 (br. s)	7.83 (d, ^3J = 8.6	—	2.65 (6H, br. s, $2CH_3$); 12.67 (1H, br. s, NH)
13	$CDCl_3$	25	7.75 (d, $^3J_{2H\text{–}NH}$ = 3.4)	—	8.22 (d, ^3J = 8.8)	7.25 (d, ^3J = 8.8)	7.13 (d, ^3J = 9.0)	7.51 (d, ^3J = 9.0)	—	2.38 (6H, s, $2CH_3$); 7.23 (2H, d, J = 8.3, H-*m* 9-$SO_2C_6H_4CH_3$); 7.27 (2H, d, ^3J = 8.3, H-*m* 4-$SO_2C_6H_4CH_3$); 7.72 (2H, d, ^3J = 8.3, H-*o*, 9-$SO_2C_6H_4CH_3$); 7.95 (2H, d, J = 8.3, H-*o* 4-$SO_2C_6H_4CH_3$); 10.8 (1H, br. s, NH)
	DMSO-d_6	20	7.94 (s)	—	8.10 (d, ^3J ~ 8.5)	7.37 (m)	7.37 (m)	7.72(br. d, ^3J ~ 9)	—	2.34 (6H, s, $2CH_3$); 7.37 (6H, m, H-6,7, H-*m* 4- and 9-$SO_2C_6H_4CH_3$); 7.85 (2H, br. d, ^3J ~ 8.4, H-*o* 9-$SO_2C_6H_4CH_3$); 7.90 (2H, br. d, ^3J ~ 8.4, H-*o* 4-$SO_2C_6H_4CH_3$); 11.35 (1H, br. s, NH)

*A spectrum averaged for tautomers **a** and **b** is given for compounds **2a,b**.

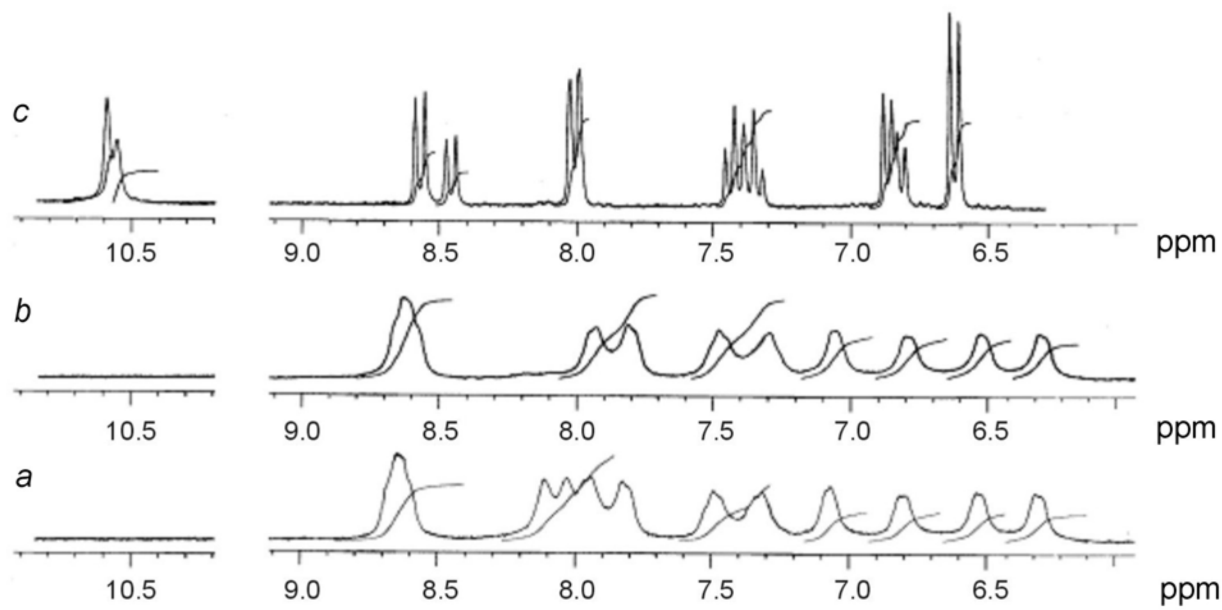
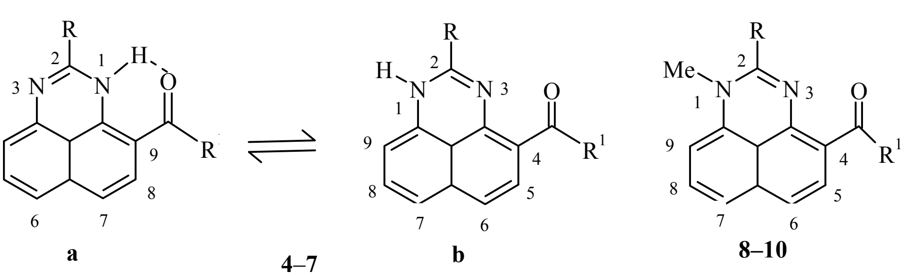


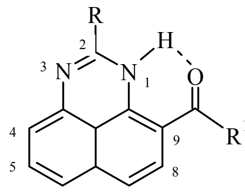
Fig. 1. ^{1}H NMR spectra of 6(7)-acetyl-2-*tert*-butylperimidine (**2**) in the aromatic proton region: *a* – in $CDCl_3$, 25°C; *b* – in $CDCl_3 + D_2O$, 25°C; *c* – in DMSO-d_6, 25°C.

Due to the formation of an extremely stable intramolecular hydrogen bond between the NH proton and the oxygen of the carbonyl group, the 4(9)-formyl- (**4**, **6**) and 4(9)-acetylperimidines (**5**, **7**) in nonpolar solvents, and judging overall, in the solid state exist exclusively in the chelated 9-CO form. This indicates that the tautomerism in them is frozen under these conditions. A characteristic feature of such compounds is the presence in their ^{1}H NMR spectra in nonpolar solvents of a low-field signal of the chelated NH proton at 12-13 ppm. For example, in the spectrum of 9-formyl-2-trifluoromethylperimidine (**6**) in $CDCl_3$ it is found at 12.34 against 8.23 ppm for the peak of the nonchelated NH proton in the 6(7) isomeric analog [6].



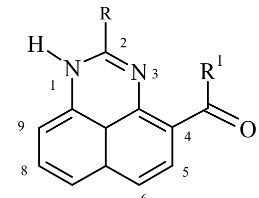
4, **8** R = R^1 = H; **5**, **9** R = H, R^1 = Me; **6**, **10** R = CF_3, R^1 = H; **7** R = CF_3, R^1 = Me

The fixed (N-methylated) 4-CO forms of the same aldehydes and ketones **8-10** have a series of characteristic special features. Firstly, the 4-CHO group proton of aldehydes **8** and **10** in $CDCl_3$, in comparison with the 9-tautomers **4** and **6** with fixed intramolecular hydrogen bonds, is found at far weaker field (~10.75 ppm). This indicates that in their stable conformation the aldehydic proton is oriented to the side of the pyridine nitrogen atom, by which it is also deshielded. In other words, if the 9-tautomer exists in the (*Z*)-configuration then for the 4-tautomers the (*E*)-isomer, in which repulsion between the unshared electron pairs of the oxygen atom and the nitrogen atom is absent, is more beneficial.



a

(Z)-configuration



b

(E)-configuration

Secondly, the furthest low field of the aromatic protons is not the proton in the electron-deficient position 2, but proton H-5. Finally, thirdly, the distinguishing special feature of compounds **8-10** is the high field signal of the proton in position 9 (see EXPERIMENTAL). All this enables the 4- and 9-tautomeric forms of compounds **4-7** to be identified reliably.

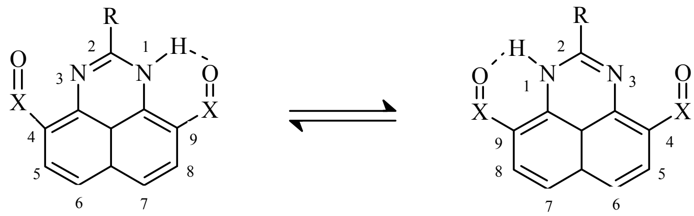
Since the proton-accepting properties of DMSO are extremely significant (p*K*a 0 [8]), and allowing for the fact that it is in a large excess, this solvent may successfully compete with the carbonyl group for the NH group proton. The truth of ruptures of the IHB assumes a preliminary bifurcational interaction of the solvent with this proton with the formation of a three-center hydrogen bond [9, 10]. It is also known that conjugation between the substituents in one benzene ring of the naphthalene is more efficient in comparison with substituents located in different nuclei [11], since the 9-tautomer, even without allowing for the IHB, must possess a high thermodynamic stability. All these factors, it might seem, do not assist the display of prototropy for the given compounds.

In reality, a comparative analysis of the spectral data of compounds **4, 5**, and **7** and their fixed 4-CO forms **8-10** shows that if a rapid equilibrium also exists, and the absence of a *meta* constant of the spin-spin interaction, then in DMSO-d_6 it is strongly displaced towards the 9-tautomer (see EXPERIMENTAL). It is interesting that even heating 4(9)-acetylperimidine (**5**) in DMSO-d_6 to 110°C does not change the picture of the spectrum significantly. Attention is drawn by the fact that on going from $CDCl_3$ to DMSO-d_6 the chemical shift of the NH···O signal is changed insignificantly, but the proton in position 2 is split into a doublet in both solvents ($J_{2H\text{-}NH}$ = 3.1 and 3.3 Hz respectively). The signs of annular prototropy are also absent from the spectrum of 4(9)-acetyl-2-*tert*-butylperimidine (compound **3**, see Table 1).

The sole exception, indicating the presence of a tautomeric equilibrium, proved to be 4(9)-formyl-2-trifluoromethylperimidine (**6**), the ^{1}H NMR spectrum of which on going from $CDCl_3$ to DMSO-d_6 became averaged for two tautomers and unresolved due to strong broadening of all signals. Two signals were observed for the CHO group protons at 9.90 and 10.45 ppm. If the first of them to all appearances belongs to the chelated 9-CHO group and the second to the 4-CHO group in tautomer **6b**, then the ratio of tautomers **6a:6b** estimated by integral intensity is 1:3. This unexpected result may be partially explained by steric hindrance of the reverse conversion of tautomer **6b** into tautomer **6a**, both from the side of CF_3 and from the side of the hydrogen atom of the CHO group in the (*E*)-configuration. On heating to 95°C both signals of the CHO group protons melted into one at 10.20 ppm and the signal of the NH proton disappeared, which indicates the rapid conversion of the tautomers into one another. It is interesting that even for the closest analog of aldehyde **6** – ketone **7** – similar conversions were not a characteristic (see EXPERIMENTAL).

Previously [2] we reported that on going from $CDCl_3$ to DMSO-d_6 the ^{1}H NMR spectrum of 4,9-di-formyl-2-trifluoromethylperimidine (**11**) becomes symmetrical even at 25°C, which indicates the facile cleavage of the IHB between the NH proton and the CHO group under the action of the polar solvent and to a rapid equilibrium between the degenerate forms of aldehyde **11**.

However the ease of fission of the IHB in dialdehyde **11** might have been predicted from an estimate of the enhanced NH-acidity of this compound in comparison with aldehyde **6**. It seemed of interest to compare the prototropy of dialdehyde **11** and of 4,9-diformyl-, 4,9-diacetyl-, and 4,9-di(*p*-toluenesulfonyl)perimidines.



11 R = CF_3, X = CH; **12** R = H, X = CMe; **13** R = H, X = SOC_6H_4Me-*p*

We were unable to obtain the first compound under the conditions of the Vilsmeier reaction [1]. The synthesis of the second and third was effected on interacting perimidine with an excess of acetic acid or *p*-toluenesulfonic acid respectively, at 125-135°C in PPA. In the course of the acetylation a complex mixture of substances was formed from which, by dry flash chromatography [12] on silica gel, only diketone **12** possessing the greatest mobility was isolated in a pure state in 5% yield. 4,9-Di(*p*-toluenesulfonyl)perimidine (**13**) was obtained analogously in the same yield together with the previously described 4(9)- and 6(7)-monosulfones [7].

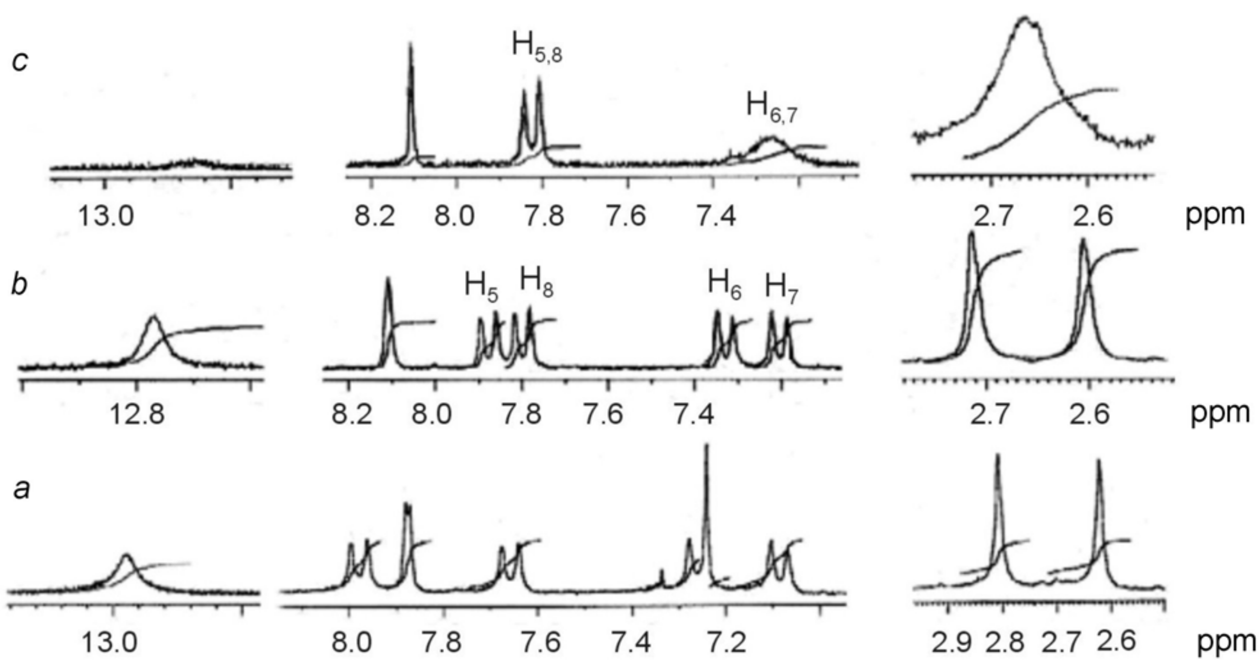


Fig. 2. ^{1}H NMR spectrum of 4,9-diacetylperimidine (**12**), *a* – in $CDCl_3$; *b* – in DMSO-d_6 at 25°C; *c* – in DMSO-d_6 at 100°C.

As is seen from Fig. 2 the ^{1}H NMR spectrum of the diacetyl derivative **12** is not symmetrized on going from $CDCl_3$ to DMSO-d_6, i.e. the IHB in this case is significantly more stable than in dialdehyde **11**. The signal of the H-2 proton is displayed as a doublet with $J_{2H\text{-}NH}$ = 2.75 Hz, which indicates the slow chemical NH exchange. The signals of the H-5 and H-8 protons coalesce at 70°C, and of the methyl groups at 80°C, but even at 100°C the signal of the IHB NH···O is displayed, but the H-6 and H-7 protons give only a broadened singlet.

Since sulfones form less stable hydrogen bonds than sulfoxides [13], we expected symmetrization of the spectrum of 4,9-di-*p*-toluenesulfonylperimidine (**13**) on going from $CDCl_3$ to DMSO-d_6. It was made clear however that it was also asymmetric in both solvents at room temperature which indicates a slow degenerate tautomerism in the scale of NMR time (Fig. 3). On heating a solution in DMSO-d_6 the signal of the NH proton disappeared and the spectrum mainly was simplified. However even at 110°C complete symmetrization was not established, and two of the aromatic protons seemed to disappear (the initial spectrum was restored on cooling).

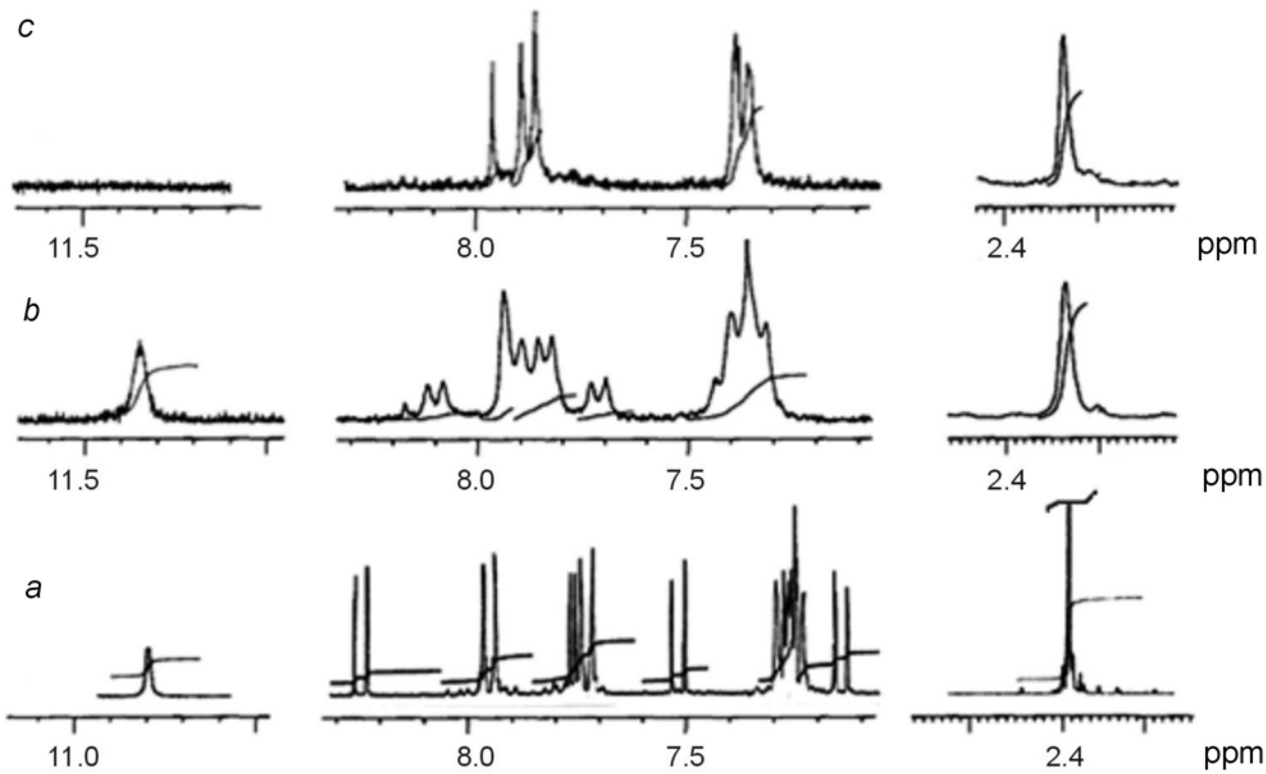


Fig. 3. [1]H NMR spectrum of 4,9-di-*p*-toluenesulfonylperimidine **13,** *a* – in $CDCl_3$; *b* – in DMSO-d_6 at 25°C; *c* – in DMSO-d_6 at 110°C.

Such a phenomenon is usually observed at intermediate rates of chemical exchange of proton in the NMR time scale.

In the absence of the 2-CF_3 group fission of the IHB in the molecules of 4(9)-mono- and 4,9-dicarbonyl or 4,9-di-*p*-toluenesulfonyl derivatives of perimidine requires significant energy consumption, consequently in both polar and nonpolar solvents their degenerate prototropy becomes noticeable only at enhanced temperature.

EXPERIMENTAL

The [1]H NMR spectra were described on a Bruker-250 instrument (250 MHz), internal standard was TMS. The IR spectra were recorded on a UR-20 instrument. A check on the progress of reactions and the homogeneity of the synthesized compounds was effected on Silufol UV-254 plates, column chromatography was carried out on Chemapol L 40/100 silica gel, and flash chromatography on Chemapol L 5/40 silica gel.

PPA with 86% P_2O_5 content was obtained by the standard procedure of [14] (we reported previously [15] on its relatively special features in comparison with standard PPA).

2-*tert*-Butylperimidine (1). Pivaloyl chloride (6.03 g, 50 mmol) was added with stirring to a solution of 1,8-naphthalenediamine (1.58 g, 10 mmol) in benzene (30 ml) and the mixture was stirred at room temperature for 1 h. The solvent was evaporated in vacuum, the residue was treated with cold water (100 ml), and made alkaline with ammonia to pH ~8-9. The precipitated oil was extracted with ethyl acetate (3×10 ml), the solution was boiled with a mixture of silica gel and anhydrous Na_2SO_4, filtered, and the solvent evaporated. The yellow oil slowly crystallized on extended trituration and cooling. Yield of compound **1** was 2.0 g (89%). Yellow-green crystals, mp 65-66°C (petroleum ether). Found, %: C 80.66; H 7.50; N 12.21. $C_{15}H_{16}N_2$. Calculated, %: C 80.32; H 7.19; N 12.49.

Acetylation of 2-*tert*-Butylperimidine (1). A mixture of 2–*tert*-butylperimidine (0.45 g, 2 mmol), glacial acetic acid (0.18 ml, 3 mmol), and PPA (5 g) was stirred at 75-80°C for 3 h, then poured into cold water (50 ml) with vigorous stirring, and made alkaline with ammonia to pH ~8-9. A semicrystalline solid separated. The mixture was extracted with ethyl acetate (3×10 ml), and the solvent evaporated. The residue was treated with benzene (10 ml) and chromatographed on a column of silica gel, eluting the first and second fractions with benzene, and then a third with ethyl acetate (all fractions were yellow in color). After distilling off the solvent 4(9)-acetyl-2-*tert*-butylperimidine (**3**) (0.6 g, 11%) was obtained from the first fraction. Yellow crystals of mp 98-99°C (petroleum ether). Found, %: C 76.36; H 6.98; N 10.16. $C_{17}H_{18}N_2O$. Calculated, %: C 76.66; H 6.81; N 10.52.

The initial 2-*tert*-butylperimidine (0.04 g, 9%) was isolated from the second fraction.

6(7)-Acetyl-2-*tert*-butylperimidine (2) (0.35 g, 66%) was isolated from the third fraction. Yellow-orange crystals of mp 204-205°C (benzene). IR spectrum (nujol mull), ν, cm^{-1}: 3313 (NH); 1633 (C=O). Found, %: C 76.28; H 6.52; N 10.36. $C_{17}H_{18}N_2O$. Calculated, %: C 76.66; H 6.81; N 10.52.

4,9-Diacetylperimidine (12). Glacial acetic acid (0.5 ml, 8 mmol) was added with vigorous stirring to a mixture of perimidine (0.34 g, 2 mmol) and 86% PPA (8 g) heated to 100°C. The temperature was increased to 130-135°C and the mixture was stirred at this temperature for 3 h. The mixture was cooled to 85°C, poured into water (~70 ml), and made alkaline with ammonia to pH ~8. The solution together with the resinous solid was then extracted with ethyl acetate (3×25 ml), the extract was dried over Na_2SO_4, and the solvent evaporated. The residue was dissolved in the minimum volume of benzene–ethyl acetate, 4:1, and separated by dry flash chromatography on silica gel [12] by washing with portions (about 4-5 ml) of the same mixture to give the first fraction (check by TLC). Yield of compound **12** was 0.025 g (5%). Light-yellow crystals, mp 241-242°C (benzene). Found, %: C 71.33; H 4.53; N 11.06. $C_{15}H_{12}N_2O_2$. Calculated, %: C 71.42; H 4.79; N 11.10.

4,9-Di(*p*-toluenesulfonyl)perimidine (13). A mixture of perimidine (0.34 g, 2 mmol), *p*-toluenesulfonic acid monohydrate (0.57 g, 3 mmol), and 86% PPA (7 g) was stirred at 140-150°C for 1.5 h, cooled to 85°C, and poured into water. The solution was made alkaline with ammonia to pH~8, the solid was filtered off, washed with water, and dried. Separation was made by dry flash chromatography on silica gel 5/40 [12]. The first fraction was washed off with benzene–ethyl acetate, 4:1, the second with benzene–ethyl acetate, 1:1, and the third with ethyl acetate–alcohol, 10:1. Compound **13** (0.046 g, 5%) was obtained from the first fraction, 4(9)-*p*-toluenesulfonylperimidine (0.3 g, 46%) from the second, and 6(7)-*p*-toluenesulfonylperimidine (0.2 g, 31%) from the third. The compounds from the second and third fractions were identical with samples obtained previously [7].

Compound **13** formed pale-yellow crystals, mp 163-164°C (benzene with petroleum ether). Found, %: C 63.18; H 4.35; N 5.70. $C_{25}H_{20}N_2O_4S_2$. Calculated, %: C 63.01; H 4.23; N 5.88.

The ^{1}H NMR spectra of compounds **1-3** and **12, 13** are given in Table 1, and of compounds **4** [1], **5** [5], **6** [6], **7** [3], **8** [1], **9** [16], and **10** [6] in the corresponding publications. New spectral data of compounds discussed in the present work are given below.

4(9)-Acetylperimidine (tautomer 5a). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.56 (3H, s, CH_3CO); 6.99, 7.44 (2H, two d, AB system, ^3J = 9.1, H-7,8); 7.11, 7.26, 7.51 (3H, three dd, ABC system, $^3J_{4,5}$ = 7.6, $^3J_{6,5}$ = 8.1, ^4J = 1.1, H-4,6,5); 7.68 (1H, d, $J_{2\text{-NH}}$ = 3.1, H-2); 12.60 (1H, br. s, NH···O). ^{1}H NMR spectrum (DMSO-d_6, 20°C), δ, ppm (*J*, Hz): 2.55 (3H, s, CH_3CO); 6.98 (1H, br. d, $3J_{4,5}$ = 7.6, H-4); 7.08, 7.65 (2H, two d, AB system, ^3J = 9.1, H-7,8); 7.33 (1H, br. d, $^3J_{6,5}$ = 7.2, H-6); 7.52 (1H, br. t, H-5); 7.86 (1H, d, $J_{2\text{-NH}}$ = 3.3, H-2); 12.40 (1H, br. s, NH···O). ^{1}H NMR spectrum (DMSO-d_6, 50°C), δ, ppm (*J*, Hz): 2.55 (3H, s, CH_3CO); 7.0 (1H, m, H-4); 7.08, 7.62 (2H, two d, AB system, ^3J = 9.1, H-7,8); 7.33 (1H, m, H-6); 7.55 (1H, br. t, H-5); 7.87 (1H, s, H-2); 12.37 (1H, br. s, N···O).

4-Acetyl-1-methylperimidine (9). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.74 (3H, s, CH_3CO); 3.26 (3H, s, N–CH_3); 6.29 (1H, d, $^3J_{9,8}$ = 7.7, H-9); 7.11, 7.72 (2H, two d, AB system, ^3J = 8.8, H-6,5); 7.18 (1H, d, $^3J_{7,8}$ = 8.3, H-7); 7.30 (1H, dd, $^3J_{8,7}$ = 8.3, $^3J_{8,9}$ = 7.7, H-8); 7.46 (1H, s, H-2).

4(9)-Formyl-2-trifluoromethylperimidine (tautomer **6a**). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.17, 7.38 (2H, d, AB system, ^3J = 8.8, H-7,8); 7.27, 7.42, 7.62 (3H, three dd, ABC system, $^3J_{4,5}$ = 7.2, $^3J_{6,5}$ = 8.0, ^4J <1, H-4,6,5); 9.83 (1H, s, 9-CHO); 2.32 (1H, br. s, NH).

4(9)-Formyl-2-trifluoromethylperimidine (tautomers **6a** and **6b**). ^1H NMR spectrum (DMSO-d_6, 25°C), δ, ppm (*J*, Hz); 6.80 (1H, br. s, H-4a,9b); 7.24 (2H, m, H-6a,b,7a,b); 7.49 (2H, m, 5a,b,8a,b); 9.90 (1H, br. s, 9-CHO); 12.45 (1H, br. s, 4-CHO). ^1H NMR spectrum (DMSO-d_6, 95°C), δ, ppm (*J*, Hz): 7.00 (1H, br. s, H-4a,9b); 7.22 (2H, br d, ^3J = 8.8, H-7a,6b); 7.38 (2H, br. s, H-6a,7b); 7.52 (2H, m, H-5a,b,8a,b); 10.2 (1H, br. s, 4,9-CHO).

(9)-Acetyl-2-trifluoromethylperimidine (7). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.61 (3H, s, CH_3); 7.10, 7.52 (2H, two d, AB system, ^3J = 9.1, H-7,8); 7.24, 7.38, 7.57 (3H, three dd, $^3J_{4,5}$ = 7.6, $^3J_{6,5}$ = 8.2, ^4J = 0.8, H-4,6,5); 13.2 (1H, br. s, NH). ^1H NMR spectrum (DMSO-d_6, 20°C), δ, ppm (*J,* Hz); 2.62 (3H, s, CH_3); 7.20 (1H, br. d, $^3J_{4,5}$ = 7.3, H-4); 7.27, 7.77 (2H, two d, AB system, ^3J = 9.1, H-7,8); 7.55 (H, br. d, $^3J_{6,5}$ = 8.0, H-6); 7.66 (1H, dd, $^3J_{5,6}$ = 8.0, $^3J_{5,4}$ = 7.3, H-5); 13.2 (1H, br. s, NH).

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