HETEROCYCLIC ANALOGS OF PLEIADIENE.

# 46.* PHYSICOCHEMICAL PROPERTIES OF 4(9)- AND 6(7)-NITROPERIMIDINES

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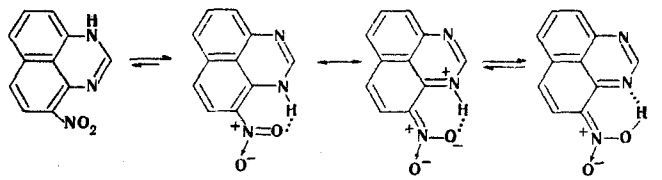
The IR spectra, basicities in acetonitrile, and electronic absorption spectra in neutral, acidic, and alkaline media of mono-, di-, tri-, and tetranitroperimidines were studied. Opinions regarding the reasons for the deep coloration of nitroperimidines, their fine structure in various media, and the form (cation or base) in which they undergo electrophilic substitution reactions are expressed.

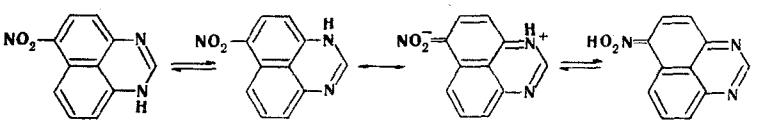
The recently synthesized [2,3] 4(9)-and 6(7)-nitroperimidines were found to be deeply colored substances; this distinguishes them markedly from the colorless or pale-yellow nitro derivatives of naphthimidazoles and other imidazole systems. To shed some light on the reasons for this difference, in the present research we studied the electronic absorption spectra and a number of other physicochemical properties of nitro derivatives of perimidine and aceperimidine.

## IR Spectra

The most interesting regions in the IR spectra of nitroperimidines are the regions of stretching vibrations of the NH and $NO_2$ groups. In the case of compounds with an o-nitro group the $\nu_{NH}$ band in the spectra of dilute solutions in chloroform is shifted markedly to low frequencies as compared with the unsubstituted compounds (Table 1 and Fig. 1). This shift ($\Delta\nu_{NH}$) is 105-120 $cm^{-1}$ for 4(9)-nitroaceperimidines and 140-160 $cm^{-1}$ for 4(9)-nitroperimidines. This constitutes evidence for the formation in these compounds of a strong intramolecular hydrogen bond (IHB) between the NH and $NO_2$ groups, which is favored not only by their convenient geometrical orientation, but also by the characteristic (for perimidines [4]) pronounced transfer of π-electron density from the heteroring to the naphthalene part of the system (the contribution of structures of the IIb type is significant).



I IIa IIb IIc



III IVa IVb IVc

The formation of an IHB evidently shifts the I ⇄ II tautomeric equilibrium completely to favor the chelated form, as evidenced by the absence in the IR spectra of 4(9)-nitroperimidines of the bands of an unassociated NH group, which should be found at 3400-3450 $cm^{-1}$ [compare the $\nu_{NH}$ values for 4(9)- and 6(7)-acylperimidines [5]]. If one judges from the $\Delta\nu_{NH}$ value, the IHB in 4(9)-nitroperimidines is one of the strongest in a series of chelates

*See [1] for Communication 45.

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TABLE 1. Frequencies of the Stretching Vibrations of the NH Groups in Nitroperimidines (in chloroform)

| Compound | $\nu_{NH}$, $cm^{-1}$ | $\Delta\nu_{NH}$, $cm^{-1}$ |
|---|---|---|
| Perimidine | 3440 | — |
| 9-Nitroperimidine | 3288 | −152 |
| 4,6,7,9-Tetranitroperimidine | (3245)* | (−195)* |
| 2-Methylperimidine | 3432 | — |
| 2-Methyl-9-nitroperimidine | 3290 (3250)* | −142 |
| 2-Methyl-6,9-dinitroperimidine | 3280 (3270)* | −152 |
| 2-Methyl-6,7,9-trinitroperimidine | 3275 | −157 |
| Aceperimidine | 3450 | — |
| 9-Nitroaceperimidine | 3335 | −115 |
| 4,9-Dinitroaceperimidine | 3328 | −122 |
| 2-Methylaceperimidine | 3436 | — |
| 2-Methyl-9-nitroaceperimidine | 3330 | −106 |

*In KBr pellets.

with chelated NH and $NO_2$ groups. Thus, $\Delta\nu_{NH}$ is only 20 $cm^{-1}$ in the spectra of o-nitroanilines [6] and 2-nitropyrroles [7]. The closest compounds to nitroperimidines in this respect are 1,3-dinitro-5,10-dihydrophenazines [8], for which $\Delta\nu_{NH}$ reaches 130 $cm^{-1}$.

The lower $\Delta\nu_{NH}$ values of 4(9)-nitroaceperimidines as compared with 4(9)-nitroperimidines can be explained by the electron-donor properties of the $CH_2CH_2$ bridge, as a consequence of which the acidity of the NH group and the strength of the IHB decrease. A similar principle was observed in the case of 4(9)-acyl derivatives of perimidine and aceperimidine [5]. On the other hand, the accumulation of nitro groups leads to an increase in the acidity of the NH bond and to a small but clearly expressed increase in the strength of the IHB (Table 1).

6(7)-Nitroperimidines (III) differ from 4(9)-nitroperimidines with respect to their low solubilities in nonpolar solvents, and we were therefore unable to measure their IR spectra in solution. Crystalline samples of 6(7)-nitroperimidines do not give bands of stretching vibrations of free NH groups (Fig. 1). In place of them, one observes a broad diffuse band at 2500-3300 $cm^{-1}$, which is characteristic for the vibrations of NH groups in intramolecular aggregates, which exist, in particular, in solid samples of perimidine and 2-substituted perimidines [9]. One's attention should be directed to the fact that the band of a chelated NH group in the spectra of 4(9)-nitroperimidines shows up in the form of an extremely narrow peak of medium intensity not only in solutions, but also in the solid state (Fig. 1); the $\nu_{NH}$ band of crystalline samples is shifted 30-40 $cm^{-1}$ to the low-frequency region as compared with solutions.

Considering the substantial contribution of dipolar structures of the IIb and IVb type to the resonance hybrid of nitroperimidine molecules, it is logical to expect shifts of the bands of the stretching vibrations of the nitro groups to the lower-frequency side for them. The data in Table 2 show that this actually occurs. The positions and intensities of the $\nu_{as}$ and $\nu_s$ bands for the compounds that we studied are almost independent of the aggregate state of the sample (the spectra of KBr pellets and chloroform solutions were recorded). The $\nu_{as}$ and $\nu_s$ values, respectively, are as follows: 1445 ± 5 and 1290 ± 10 $cm^{-1}$ for 9-nitroperimidines, 1470 and 1280 $cm^{-1}$ for 9-nitroaceperimidines, and 1475 ± 5 and 1285 $cm^{-1}$ for 6(7)-nitroperimidines. These values are considerably lower than the $\nu_{as}$ and $\nu_s$ values for nitroarenes (1535 and 1350 $cm^{-1}$, respectively) [10]. One's attention is directed to the somewhat smaller shift of the $\nu_{as}$ band in the case of 6(7)-nitroperimidines. This is evidently associated with the noncoplanarity of the naphthalene ring and the nitro group in such compounds as a consequence of interaction of the latter with the peri proton [11]. This noncoplanarity should be expressed particularly strongly in the case of 6,7-dinitroperimidines; it is not surprising that for them the shift of the $\nu_{as}$ band as compared with its normal position is especially small ($\nu_{as} \sim 1500$ $cm^{-1}$). However, steric factors do not have an appreciable effect on the position of the band of symmetrical stretching vibrations of the nitro group in 6(7)-nitroperimidines.

Among other peculiarities of the IR spectra we note the presence in the spectra of 4(9)-nitroperimidines of a strong absorption band at 1100-1150 $cm^{-1}$. The nature of this band is not completely clear.

Basicities

We measured the basicity constants of nitroperimidines in acetonitrile (Table 3). The pronounced difference in the basicities of 1-methyl-4-nitro derivatives of perimidine and

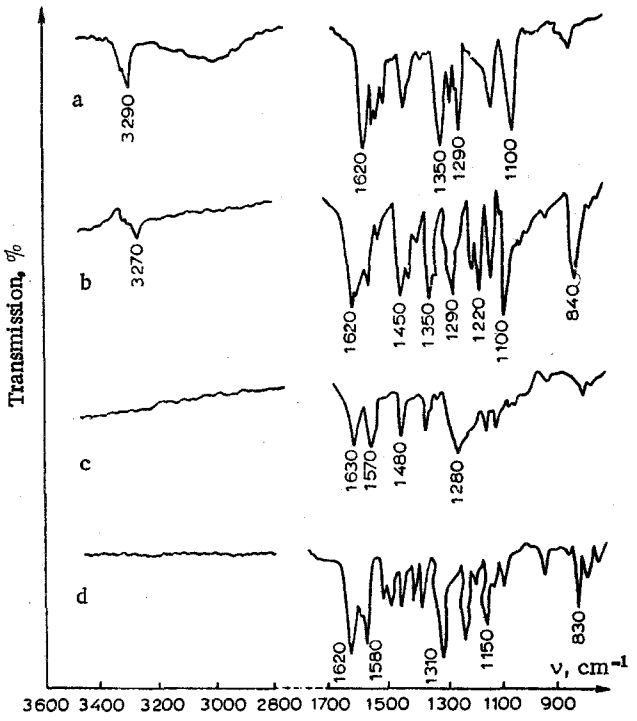


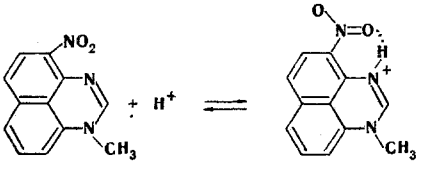

Fig. 1. IR spectra of nitroperimidines: a) 9-nitroperimidine (in $CHCl_3$); b) 9-nitroperimidine (in KBr); c) 6(7)-nitroperimidine (in KBr); d) 1-methyl-4-nitroperimidine (in KBr).

TABLE 2. Frequencies of the Stretching Vibrations of the Nitro Group in Nitroperimidines (in KBr pellets)

| Compound | $\nu_{as}$, cm$^{-1}$ | $\nu_s$, cm$^{-1}$ |
|---|---|---|
| 9-Nitroperimidine | 1450 (1450)* | 1285 (1290)* |
| 2-Methyl-9-nitroperimidine | 1440 | 1300 |
| 6(7)-Nitroperimidine | 1480 | 1280 |
| 2-Methyl-6(7)-nitroperimidine | 1470 | 1285 |
| 1-Methyl-4-nitroperimidine | 1450 | 1308 |
| 2-Methyl-6,7-dinitroperimidine | 1496 | 1285 |
| 9-Nitroaceperimidine | (1470)* | (1280)* |
| 2-Methyl-9-nitroaceperimidine | (1470)* | (1280)* |
| 1-Methyl-4-nitroaceperimidine | (1450)* | (1310)* |

*For solutions in chloroform.

aceperimidine, on the one hand, and the corresponding 9-nitroperimidines, on the other hand, is most interesting. The $pK_a$ value decreases an average of 4.1 units on passing from perimidine or aceperimidine to their 9-nitro derivatives. One might have expected that this decrease would be even more appreciable in the spectra of 1-methyl-4-nitroperimidines (V) because of the closeness of the nitro group and the pyridine nitrogen atom. However, it was found that the decrease in the $pK_a$ value does not exceed two units for these compounds. This difference cannot be ascribed to only the donor effect of the N-methyl group, which in the azole series increases the $pK_a$ value by no more than 0.3 [12]. There is little doubt that the high basicities of 1-methyl-4-nitroperimidines (V) are due to stabilization of the corresponding conjugate acid VI due to the formation of an intramolecular hydrogen bond (IHB) between the NH proton and the nitro group:




V VI

In the case of 9-nitroperimidines (I) the base itself is stabilized by a hydrogen bond, and protonation of the pyridine N atom does not lead to such additional stabilization. The

TABLE 3. Basicity Constants (in acetonitrole at 25°C)

| Perimidines | $pK_a$ | Aceperimidines | $pK_a$ |
|---|---|---|---|
| Perimidine | 13,58 | Aceperimidine | 13,9 |
| 9-Nitroperimidine | 9,40 | 9-Nitroaceperimidine | 9,89 |
| 1-Methyl-4-nitroperimidine | 11,98 | 1-Methyl-4-nitroaceperimidine | 12,92 |
| 6(7)-Nitroperimidine | 10,30 | 4,9-Dinitroaceperimidine | 8,62 |
| 1-Methyl-6-nitroperimidine | 10,75 | | |
| 1-Methyl-7-nitroperimidine | 10,47 | | |

sharp difference in the $pK_a$ values between compounds of the I and V type confirms the conclusion drawn from a study of the IR spectra that the former probably exist exclusively in the form of the 9-nitro isomer, i.e., chelate II. Unfortunately, a fixed model of this tautomer is not available, since it could not be synthesized because of steric hindrance [3].

The introduction of a nitro group in the para position of the perimidine molecule leads to a decrease of three $pK_a$ units in the basicity as compared with perimidine itself; the basicities of the fixed 6- and 7-nitro isomers differ by only 0.28 $pK_a$ (6-nitro-1-methylperimidine is more basic). This difference can be used to estimate (very approximately, of course) the tautomeric equilibrium constant of 6(7)-nitroperimidine in accordance with [13]. The $K_T$ value is 0.52 and corresponds to 35% of the 6-nitro form and 65% of the 7-nitro form in the tautomeric mixture.

The polynitroperimidines are only slightly soluble in acetonitrile, and only the basicity of 4,9-dinitroaceperimidine could therefore be measured. The value obtained (8.62) corresponds to the principles noted above.

## Electronic Absorption Spectra

The mononitroperimidines are bright-red substances that, depending on the position of the nitro group, have a long-wave absorption maximum at 445-490 nm (Fig. 2 and Table 4). With respect to the intensity of their color they are found to be on the same level as 1- and 3-nitro derivatives of phenoxazine [14] and dihydrophenazine [8] but surpass the mononitro derivatives of many other π-surplus heterocycles and aromatic amines (pyrrole, indole, carbazole, phenothiazine, aniline, diphenylamine, etc.). The deep color of 4(9)- and 6(7)-nitroperimidines is in agreement with all of the data on the chemistry of perimidine, which provide evidence for a pronounced shift of the electron density from the π-surplus heteroring to the naphthalene part of the molecule. This shift increases sharply under the influence of o- and p-nitro groups, which lead to an increase in the contribution of structures of the IIb and IVb type to the decrease in the energy of the first $\pi \rightarrow \pi^*$ electron transition, which is responsible for the long-wave absorption band. Thus, the energies of the first electron transition ($E^{\pi\rightarrow\pi^*}$) calculated by the Hückel MO method for 4-nitro- and 9-nitroperimidine molecules are $-0.308\beta$ and $-0.290\beta$ as compared with $-1.002\beta$ for perimidine itself. The lower $E^{\pi\rightarrow\pi^*}$ value for 9-nitroperimidine is in agreement with its deeper color. In fact, the difference in the $\lambda_{max}$ values for 1-methyl-4-nitroperimidine and 9-nitroperimidine is 15 nm, whereas it is 18 nm for 1-methyl-4-nitroaceperimidine and 9-nitroaceperimidine (Table 4).

p-Nitroperimidines are more deeply colored than the ortho isomers. Thus the long-wave absorption band of 6(7)-nitroperimidine is shifted 15 nm to the red region as compared with 9-nitroperimidine and 30 nm as compared with 1-methyl-4-nitroperimidine. The electronic spectra of 6(7)-nitroperimidines differ from the spectra of 4(9)-nitroperimidines also with respect to their appearance, and this can be used to identify the products of nitration of perimidine: the spectra of 6(7)-nitroperimidines contain a group of bands at 340-390 nm that is virtually absent in the spectra of 4(9)-nitroperimidines.

The maximum of the long-wave band of 6(7)-nitroperimidine (475 nm) lies between the maxima of the fixed tautomeric forms, viz., 1-methyl-7-nitro- (480 nm) and 1-methyl-6-nitroperimidine (470 nm). These data provide evidence that conjugation of the pyrrole N atom with the substituent in the 7 position is somewhat more effective than conjugation with the substituent in the 6 position.

An increase in the number of nitro groups in the perimidines leads to a hypsochromic shift of the long-wave absorption maximum. Correspondingly, the color of polynitroperimidines changes to orange or yellow, depending on the number of nitro groups and their positions. The smallest $\Delta\lambda_{max}$ value (from −7 to −8 nm) is observed on passing from 9-nitro- to 4,9-di-

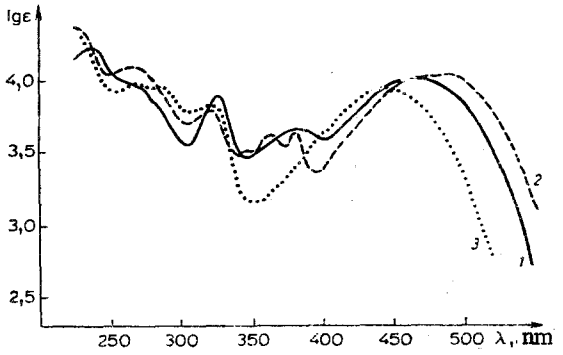



Fig. 2. Electronic absorption spectra of mononitroperimidines in methanol: 1) 1-methyl-6-nitroperimidine; 2) 1-methyl-7-nitroperimidine; 3) 1-methyl-4-nitroperimidine.

TABLE 4. Electronic Absorption Spectra of Nitro Derivatives of Perimidine and Aceperimidine (in methanol)

| Compound | $\lambda_{max}$, nm (lg ε) |
|---|---|
| **Perimidine derivatives** | |
| 9-Nitro | 460, 315*, 285 (3,99; 3,75; 4,11) |
| 9-Nitro-2-methyl | 465, 370*, 360*, 315*, 285 (4,10; 3,35; 3,43; 3,90; 4,27) |
| 6(7)-Nitro | 475, 382, 365, 350*, 325, 265 (3,93; 3,49; 3,44; 3,33; 3,65) |
| 6(7)-Nitro-2-methyl | 475, 377, 362, 350*, 325, 265 (4,03; 3,40; 3,35; 3,15; 3,57) |
| 6-Nitro-1-methyl | 470, 385, 365*, 325, 260*, 235 (4,02; 3,65; 3,61; 3,90; 3,99; 4,24) |
| 7-Nitro-1-methyl | 480, 380, 364, 345, 323, 265 (4,05; 3,66; 3,63; 3,52; 3,80; 4,10) |
| 4-Nitro-1-methyl | 445, 325, 315, 285, 270 (3,96; 3,82; 3,81; 3,96; 3,98) |
| 4,9-Dinitro | 454, 330, 275 (4,16; 3,71; 4,20) |
| 6,9-Dinitro | 440, 340*, 275, 245 (4,39; 3,70; 4,21; 4,27) |
| 6,9-Dinitro-2-methyl | 440, 350*, 325, 272, 250 (4,28; 3,56; 3,69; 4,22; 4,00) |
| 6,7-Dinitro-2-methyl | 425, 295*, 244 (4,19; 3,48; 4,27) |
| 4,6,9-Trinitro-2-methyl | 495, 370*, 355*, 315*, 285 (4,10; 3,35; 3,45; 3,90; 4,27) |
| 6,7,9-Trinitro-2-methyl | 425, 325, 260*, 235 (4,26; 3,60; 4,18; 4,40) |
| 6,7,9-Trinitro | 425, 260*, 235 (4,10; 4,05; 4,26) |
| 4,6,7,9-Tetranitro | 495, 410, 325, 280* (4,42; 4,19; 3,70; 3,90) |
| **Aceperimidine derivatives** | |
| 9-Nitro | 485, 325*, 290 (3,69; 3,48; 3,89) |
| 9-Nitro-2-methyl | 485, 385*, 328*, 290 (3,76; 3,27; 3,64; 3,98) |
| 4-Nitro-1-methyl | 470, 390*, 330, 315, 290 (4,05; 3,56; 3,98; 4,00; 4,14) |
| 4-Nitro-1,2-dimethyl | 470, 375*, 355*, 315*, 285 (3,98; 3,54; 3,50; 3,97; 4,10) |
| 4,9-Dinitro | 475, 280, 240 (4,23; 4,27; 4,20) |
| 4,9-Dinitro-2-methyl | 480, 390*, 330*, 280 (4,40; 3,80; 3,65; 4,40) |

*Inflection.

nitroperimidines. The latter are still somewhat more deeply colored than 1-methyl-4-nitroperimidines. The $\lambda_{max}$ value decreases considerably more markedly when a second nitro group is introduced in the para position: for example, for 6,9-dinitroperimidines $\lambda_{max}$ value decreases considerably more markedly when a second nitro group is introduced in the para position: for example, for 6,9-dinitroperimidines $\Delta\lambda_{max}$ ranges from −20 to −25 nm as compared with 9-nitroperimidines. The hypsochromic shift is particularly large when substitution takes place in the peri position relative to the nitro group already present in the ring [for example, compare 6(7)-nitro- and 6,7-dinitroperimidines or 6,9-dinitro- and 6,7,9-trinitroperimidines]. This is undoubtedly due to pronounced deviation of the two peri-nitro groups from the plane of the naphthalene ring. On the whole, 6,7-dinitro- and 6,7,9-trinitroperimidines ($\lambda_{max}$ 425 nm) proved to be the least colored of all of the nitro compounds of the perimidine series.

4,6,9-Trinitro- and 4,6,7,9-tetranitroperimidines, the $\lambda_{max}$ values of which in methanol are 495 nm, clearly deviate from the general pattern with respect to the principles noted above. We have established that the reason for this is the fact that, as a consequence of their high acidities, 4,6,9-trinitroperimidine exists primarily and 4,6,7,9-tetranitroperimidine exists exclusively in the anionic form in methanol. The coincidence of the $\lambda_{max}$ values of the tetranitro derivatives in methanol and in alkali and the closeness of these values for 4,6,9-trinitroperimidine constitute evidence in favor of this (Tables 4 and 5).

TABLE 5. Position of the Long-Wave Absorption Maximum of Nitroperimidines in Acidic and Alkaline Media and Shift of this Position as Compared with Solutions of Them in Methanol

| Compound | In acidic media | | In 0.1 N NaOH | |
|---|---|---|---|---|
| | $\lambda_{max}$, nm (lg ε) | $\Delta\lambda_{max}$, nm | $\lambda_{max}$, nm (lg ε) | $\Delta\lambda_{max}$, nm |
| 9-Nitroperimidine | 435 (3,86) | −25 (20% HCl) | 520 (4,26) | +60 |
| 9-Nitro-2-methylperimidine | 435 (3,49) | −30 (20% HCl) | | |
| | 452 (4,03) | −13 ($CH_3COOH$) | | |
| 9-Nitroaceperimidine | 460 (3,69) | −25 (20% HCl) | 530 (4,12) | +45 |
| 4-Nitro-1-methylperimidine | 430 (3,75) | −15 (20% HCl) | — | — |
| 4-Nitro-1-methylaceperimidine | 465 (3,81) | −5 (20% HCl) | — | — |
| 6(7)-Nitroperimidine | 440 (3,88) | −25 ($CH_3COOH$) | 525 (4,27) | +50 |
| 6(7)-Nitro-2-methylperimidine | 425 (3,79) | −40 ($CH_3COOH$) | 525 (4,23) | +50 |
| 4,9-Dinitroperimidine | 454 (4,03) | 0 ($CH_3COOH$) | 550 (4,39) | +96 |
| 4,9-Dinitroaceperimidine | 455 (4,13) | −20 (conc. HCl) | 563 (4,35) | +88 |
| 6,9-Dinitroperimidine | 440 (4,28) | 0 ($CH_3COOH$) | | |
| | 400 (4,05) | −40 ($CF_3COOH$) | 543 (3,47) | +103 |
| | 410 (3,90) | −30 (conc. HCl) | | |
| 6,7-Dinitro-2-methylperimidine | 395 (3,77) | −35 (20% HCl) | 563 (4,05)* | +138 |
| 6,7,9-Trinitro-2-methylperimidine | 380 (4,20) | −45 (20% HCl) | 495 (4,12) | +70 |
| 4,6,9-Trinitro-2-methylperimidine | 440 (4,33) | −55 ($CH_3COOH$) | 512 (4,35) | +17 |
| 4,6,7,9-Tetranitroperimidine | 440 (4,33) | −55 ($CH_3COOH$) | 495 (4,25) | 0 |

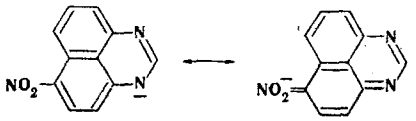
*An intense band at 463 nm (log ε 4.53) is also present.

The acidity of tetranitroperimidine is so high that it is converted to an anion even when it is chromatographed on aluminum oxide.

The $\Delta\lambda_{max}$ values, which characterize the change in the position of the $\lambda_{max}$ bands in the spectra of solutions in acids and alkalis as compared with solutions in methanol, are presented in Table 5 along with data on the position of the long-wave absorption band of nitroperimidines in acidic and alkaline media. Protonation of the heteroring should weaken its π-donor character with respect to the nitro group, and it is therefore natural that the conversion to the cations is accompanied by a hypsochromic shift of the long-wave maximum. From the $\Delta\lambda_{max}$ value one can to some extent form a judgment regarding the structure of the cation and the degree of protonation of the nitroperimidine molecules. Thus, for example, the small $\Delta\lambda_{max}$ value (only −5 nm) for the 1-methyl-4-nitroaceperimidine cation evidently indicates that the proton in it is located primarily at the nitro group. The $\Delta\lambda_{max}$ value for the 1-methyl-4-nitroperimidine cation is −15 nm, which constitutes evidence for a high degree of localization of the proton on the pyridine N atom. The difference in the absorption of these two cations may be the result of the usual (for aceperimidines) +I effect of the $CH_2CH_2$ bridge, which also leads to a certain increase in the basicity of the 4-nitro group.

The cations of 9-nitro-, 6(7)-nitro-, and dinitroperimidines have $\Delta\lambda_{max}$ values ranging from −25 to −40 nm. The $\Delta\lambda_{max}$ values of 9-nitroperimidines in acetic acid are appreciably lower than in hydrochloric acid. On the basis of this, it may be concluded that they are only partially protonated by acetic acid, while dinitroperimidines are not protonated at all by acetic acid ($\Delta\lambda_{max}$ 0). Thus the electronic spectra of 4,6,9-trinitro- and 4,6,7,9-tetranitroperimidines in acetic acid most likely belong to the neutral molecules. In fact, the $\lambda_{max}$ values of these compounds in $CH_3COOH$ (440 nm) are appreciably lower than in the case of their anions, although they are 15 nm higher than in the case of the neutral 6,7-dinitro- and 6,7,9-trinitroperimidine molecules. The latter difference does not correspond to the general tendency for a decrease in the color as the number of nitro groups increases. This can hardly be due only to the effect of the medium, since the spectra of the neutral molecules, just as in the case of the cations, in methanol and acetic acid were usually similar. It is possible that the reason for the certain increase in the $\lambda_{max}$ values for 4,6,9-trinitro- and 4,6,7,9-tetranitroperimidines is the fact that they exist partially in the aci form because of a pronounced shift of the π-electron density.

Nitroperimidines with a free NH group dissolve readily in alkali to give crimson-red or violet-red solutions. The deepening of the color of the anions is undoubtedly due to an increase in the contribution of quinoid structures of the VIIa type to the ground state of the anion:



VII VII a

The anions of dinitroperimidines, among which the anion of 6,7-dinitroperimidine occupies the leading position, followed by the anions of 6,9- and 4,9-dinitroperimidines, are most deeply colored. The maximum $\Delta\lambda_{max}$ values (90-140 nm) are observed for the same anions. The anions of mononitroperimidines, which have $\lambda_{max}$ values ranging from 520 to 530 nm and $\Delta\lambda_{max}$ values ranging from 45 to 60 nm, constitute a second group. The anions of tri- and tetranitroperimidines ($\lambda_{max}$ 495-512 nm) are the least deeply colored. Thus the principles of the change in the color as a function of the number and position of the nitro groups in the anions and neutral nitroperimidine molecules differ.

## Effect of Nitro Groups on the Reactivities of Perimidines

The introduction of nitro groups decreases the exceptionally high activity in electrophilic substitution reactions that is characteristic for perimidines [2-5]. Thus, for example, in contrast to the anions of mononitroperimidines, which can be subjected to N-methylation [3], the anions of dinitroperimidines are not alkylated under ordinary conditions. We obtained the 1-methyl derivative of 2-methyl-6,7-dinitroperimidine only by methylation of the silver salt of the latter, and the product was obtained in only 15% yield.

Electrophilic substitution in the naphthalene ring also is similarly hindered. Thus, whereas the 1,3-dimethylperimidinium cation is nitrated extremely readily in acetic acid to give the 6(7)-nitro derivative [15], the 6(7)-nitro-1,3-dimethylperimidinium cation, as we have now established, forms only traces of the dinitration product under the influence of nitric acid (sp. gr. 1.52) at 100°C for 5 h. This observation means that the second, third, and fourth nitrationsof perimidines most likely proceed through the neutral form, the concentration of which becomes significant as a consequence of a decrease in the basicities of the nitroperimidines.

## EXPERIMENTAL

The IR spectra were recorded with a UR-20 spectrometer. The UV spectra of $\sim 10^{-5}$ mole/liter solutions of the compounds were recorded with an SF-4A spectrophotometer. The $pK_a$ values in acetonitrile were measured by the method in [16]. The parameters in [17] for the heteroatoms and the parameters in [18] for the nitro group were used in the quantum-mechanical calculations of the nitroperimidine molecules.

1,2-Dimethyl-6,7-dinitroperimidine. A 1.1-g (4 mmole) sample of 2-methyl-6,7-dinitroperimidine was dissolved in 60 ml of ethanol containing 1 ml of concentrated ammonium hydroxide, and a saturated aqueous solution of 0.8 g (4.7 mmole) of silver nitrate was added. The dark-red precipitate of the silver salt of 2-methyl-6,7-dinitroperimidine was removed by filtration after 2-3 h and washed with water, alcohol, and acetone. The yield was 1.5 g (98%). The silver salt was suspended in 60 ml of absolute xylene, 0.5 ml (8 mmole) of methyl iodide was added, and the mixture was stirred initially at room temperature for 1 h and then at 100°C for 2 h. The precipitate was removed by filtration and extracted with acetone in a Soxhlet apparatus to give 0.17 g (15%) of 1,2-dimethyl-6,7-dinitroperimidine in the form of an orange powder with mp 283°C (from butanol). Found: C 55.0; H 3.2; N 19.3%. $C_{13}H_{10}N_4O_4$. Calculated: C 54.5; H 3.5; N 19.6%.

## LITERATURE CITED


1. V. S. Korytnyi, G. G. Yurchuk, A. F. Pozharskii, and N. M. Starshikov, Khim.-Farm. Zh., (1979, in press).
2. V. N. Koroleva and A. F. Pozharskii, Khim. Geterotsikl. Soedin., No. 5, 702 (1974).
3. A. F. Pozharskii and V. N. Koroleva, Khim. Geterotsikl. Soedin., No. 4, 550 (1975).
4. A. F. Pozharskii, I. S. Kashparov, V. N. Koroleva, V. I. Sokolov, and I. V. Borovlev, Summaries of the Papers Presented at the First All-Union Conference on the Chemistry of Heterocyclic Compounds (Nitrogen Heterocycles) [in Russian], Chernogolovka (1973), p. 101.

5. A. F. Pozharskii, I. V. Borovlev, and I. S. Kashparov, Khim. Geterotsikl. Soedin., No. 4, 543 (1975).
6. L. K. Dyall and A. N. Hambly, Chem. Ind., 262 (1958).
7. P. E. Sonnet, J. Heterocycl. Chem., 7, 399 (1970).
8. I. N. Borukhova, Dissertation Abstract (Master's Degree) [in Russian], Ural Polytechnic Institute, Sverdlovsk (1977).
9. K. J. Morgan, J. Chem. Soc., No. 6, 2243 (1961).
10. L. Bellamy, Infrared Spectra of Complex Molecules, Methuen, London (1958).
11. V. Balasubramanian, Chem. Rev., 66, 578 (1966).
12. A. R. Katritzky (ed.), Physical Methods in the Chemistry of Heterocyclic Compounds, Academic Press (1963).
13. A. R. Katritzky and J. M. Lagowsky, Advances in Heterocyclic Chemistry, Vol. 1, Academic Press, New York (1963), p. 403.
14. Z. Stransky and I. Gruz, Coll. Czech. Chem. Commun., 34, 3732 (1969).
15. I. V. Borovlev, A. F. Pozharskii, and V. N. Koroleva, Khim. Geterotsikl. Soedin., No. 12, 1692 (1975).
16. V. I. Minkin and V. A. Bren', Reakts. Sposobn. Org. Soedin., 4, 112 (1967).
17. A. Streitwieser, Molecular Orbital Theory for Organic Chemists, Wiley (1961).
18. A. I. Owen, Tetrahedron, 23, 1857 (1967).

# HETEROCYCLIC ANALOGS OF PLEIADIENE.

## 47.* N-AMINATION OF PERIMIDINES

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N-Aminoperimidinium salts were obtained by the action of O-mesitylsulfonylhydroxylamine on perimidine and its 1- and 2-substituted derivatives, and some transformations of the salts (reaction with p-nitrobenzaldehyde, reduction with sodium borohydride, and the synthesis of 2,4-dimethylpyrazolo[1,5-a]perimidine) were realized.

Of the amines of the perimidine series, most study has been devoted to 2-aminoperimidines, which are readily obtained via the Chichibabin reaction [2]. The available data on perimidines that contain an amino group in the naphthalene ring are meager [3], and N-aminoperimidines were unknown up until now. We have established that the N-amination of perimidines can be easily accomplished by means of O-mesitylsulfonylhydroxylamine (MSHA), which is an electrophilic aminating agent that has recently found extensive application [4]. The reaction of perimidine and its 1- and 2-substituted derivatives (Ia-e) with MSHA in methylene chloride at room temperature is complete in a few minutes, and salts IIIb-e are obtained in 72-100% yields. The amination of perimidine itself is somewhat less successful (the product is obtained in 42% yield).

The structure of N-aminoperimidinium salts II is confirmed by the results of elementary analysis from them of derivatives of a new heteroaromatic system, viz., pyrazolo[1,5-a]perimidine. Thus, 2,4-dimethyl-3-acetylpyrazolo[1,5-a]perimidine (III) is formed in quantitative yield by the action of acetic anhydride in the presence of potassium hydroxide on the 1,2-dimethyl-3-aminoperimidinium salt (IIc). Compound III is readily deacetylated to give 2,4-dimethylpyrazolo[1,5-a]perimidine (IV) by refluxing with concentrated HCl. Compound IV in turn can be reconverted to III by heating with acetic anhydride in the presence of potassium carbonate.

*See [1] for Communication 46.

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