and the residue was treated with ice water (40 ml). The resulting precipitate was removed by filtration and dried in a vacuum desiccator over P_2O_5 and KOH to give colorless plates (Vd) or needles (Vf).

N-Phenyl-N'-(4,6-dichloro-2-substituted 5-pyrimidinyl)oxamide (VId, f, Table 1). A mixture of 7 mmole of IIId, f and 14 mmole of freshly distilled aniline in 50 ml of absolute benzene was allowed to stand overnight. The resulting precipitate was removed by filtration and washed with benzene. The aniline hydrochloride was removed from the solid material with water. Workup gave VId (colorless prisms) or VIf (needles).

Reaction of Acid Chloride IIId with Aminopyrimidine Id. N,N'-Di-(4,6-dichloro-5-pyrimidinyl)oxamide (IId). A mixture of 1.27 g (5 mmole) of IIId and 0.82 g (5 mmole) of Id in 50 ml of chloroform was refluxed for 20-30 min, during which a precipitate formed. The mixture was cooled, and the precipitate was removed by filtration and washed with chloroform and water to give 1.73 g (91%) of IId with mp 260-261° (dec.). The product was identical to the IId obtained from Id and oxalyl chloride.

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HETEROCYCLIC ANALOGS OF PLEIADIENE

XXII.* SYNTHESIS AND SOME PHYSICAL PROPERTIES OF THE ACEPERIMIDYLENE HETEROAROMATIC SYSTEM

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and V. G. Zaletov

UDC 547.856.7.07:543.422.25.4.6

Derivatives of a new heteroaromatic system – aceperimidylene – were obtained by dehydrogenation of aceperimidine and its substituted derivatives. The physical properties of the aceperimidylenes provide evidence that they have greater aromatic character than perimidines.

It has been established that the π-electron density of the perimidine (I) and aceperimidine (IIa) molecules is distributed nonuniformly, and this brings about a decrease in the aromatic character and an increase in the reactivities of these compounds with respect to both nucleophilic and electrophilic reagents [2]. One of the possible reasons for this is the presence in perimidines of only 13 peripheral π electrons, which, according to Platt, is of decisive significance in the manifestation of aromatic properties by polynuclear systems [3].

The aim of the present research was the synthesis and study of the electronic properties of a new heteroaromatic system – acenaphtho-[5,6-d,e]pyrimidine (III) – which we have called aceperimidylene. System III has 14 peripheral π electrons, and it should therefore, in conformity with Hückel's rule, differ substantially from molecules I and II with respect to its physical and chemical properties.

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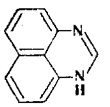
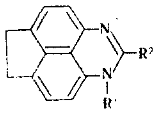
*See [1] for communication XXI.

Rostov State University, Rostov-on-Don. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 539-544, April, 1976. Original article submitted April 29, 1975.



I



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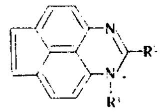


III

II—III a $R^1=R^2=H$; b $R^1=CH_3$, $R^2=H$; c $R^1=C_2H_5$, $R^2=H$;
d $R^1=R^2=CH_3$; e $R^1=CH_3$, $R^2=C_6H_5$

Synthesis of Aceperimidylenes. An attempt to obtain 1-methylaceperimidylene (IIIb) by dehydrogenation of 1-methylaceperimidine (IIb) with chloranil was described in [4]. A small amount of a substance, for which, however, Flowerday and co-workers [4] were unable to obtain a satisfactory elementary analysis and measurements of many physical constants, including the melting point, was isolated.

We have found that IIIa-d are actually formed in 56-77% yields in the dehydrogenation of aceperimidines (IIa-d) with chloranil in refluxing benzene (Table 1).

The dehydrogenation of 1-methyl-2-phenylaceperimidine (IIe) is a more complex reaction – the yield of IIIe under these conditions is only 10%. The chief reaction product is a dark-brown substance that is only slightly soluble in the ordinary organic solvents, acids, and alkalis. We did not establish the structure of this compound. We were able to raise the yield of 1-methyl-2-phenylaceperimidylene (IIIe) to 33% when the reaction was carried out under milder conditions (40°).

The structure of the compound was established on the basis of the results of elementary analysis and the UV, IR, and PMR spectra. Thus the PMR spectra of aceperimidylene and 1-methylaceperimidylene do not contain the singlet at 3.2 ppm characteristic for the CH_2CH_2 bridge in aceperimidines [5]. Instead, a singlet at 7.5 ppm corresponding to two protons attached to the C_6 and C_7 atoms appears. The singlet of the H_2 proton is found at weakest field. The protons bonded to the naphthalene ring appear in the form of doublets (Fig. 1).

It is known that treatment of acenaphthene with potassium amide in liquid ammonia converts it to a dicarbanion, which can be oxidized by azobenzene to acenaphthylene [6]. We attempted to use this reaction for the conversion of 1-methylaceperimidine to 1-methylaceperimidylene. However, the yield of the latter in this case was only 9%. The aliphatic C–H bonds in 1-methylaceperimidine are evidently considerably more acidic than those in acenaphthene because of the electron-donor effect of the heteroring.

Quantum-Chemical Calculations and Electronic Absorption Spectra

Quantum-chemical calculations by the Hückel MO method show that there is the same, if not more, alternation of the positive and negative charges in the aceperimidylene molecule (IV) as in the perimidine mole-

TABLE 1. Aceperimidylene Derivatives

Compound	mp, °C (solvent)	Empirical formula	Found, %			Calculated, %			Yield, %
			C	H	N	C	H	N	
IIIa	>350 (benzene)	$C_{13}H_8N_2$	80,3	5,2	14,3	80,4	5,2	14,4	57
IIIb	179—180 (CCl_4)	$C_{14}H_{10}N_2$	81,2	5,1	13,7	81,5	4,9	13,6	77
IIIc	118—119 (isooctane)	$C_{15}H_{12}N_2$	81,6	5,5	12,2	81,8	5,5	12,7	62
IIId	183—184 (petroleum ether + CCl_4)	$C_{15}H_{12}N_2$	82,6	5,8	13,0	81,8	5,5	12,7	56
IIIe	164—165 (petroleum ether + CCl_4)	$C_{20}H_{14}N_2$	85,0	5,2	9,6	85,1	5,0	9,9	33

TABLE 2. Position of the Longwave Absorption Band and Basicities of Perimidine and Aceperimidylenes

Compound	λ_{max}, nm		I_d, eV	pK_a
	base (in CH_3OH)	charge-transfer complex with trinitrobenzene in $CHCl_3$		
I	400	545	6,80	6,12
IIIa	418	—	—	4,09
IIIb	416	490	7,09	4,10
IIIc	420	485	7,12	3,98

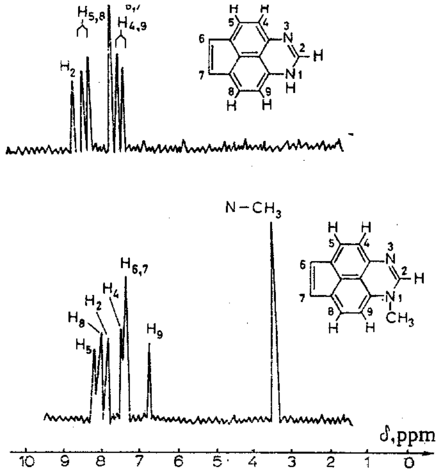


Fig. 1

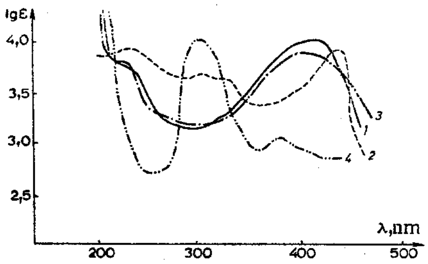
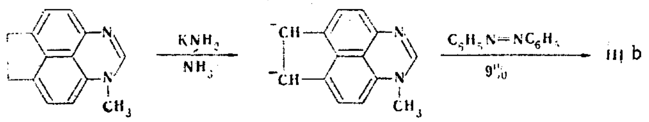


Fig. 2

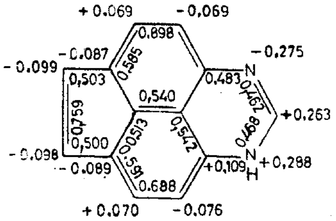
Fig. 1. PMR spectra of aceperimidylene (IIIa, in DMSO) and 1-methylaceperimidylene (IIIb, in $CDCl_3$).

Fig. 2. UV spectra (in methanol): 1) aceperimidylene (IIIa); 2) N-anion of aceperimidylene; 3) 1-methylaceperimidylene (IIIb); 4) perimidine (I).

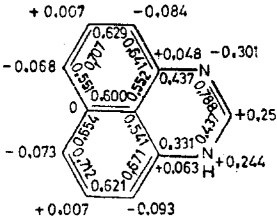
cule (V) [7]. Moreover, the positive charge is concentrated primarily in the heteroring, and the negative charge is concentrated in the ortho positions of the naphthalene ring and on the $-CH=CH-$ bridge. One's attention is drawn to the somewhat lower polarization of the C=N bond in the aceperimidylene molecule as compared with the perimidine molecule and also to the presence of considerable positive charge in the 5 and 8 positions.



The energy of the first π-π^* electron transition, $E^{\pi-\pi^*}$ (-0.969β), in the aceperimidylene molecule is lower than in the perimidine molecule (-1.002β). In conformity with this, the longwave absorption band of aceperimidylenes shifted somewhat to the red region of the spectrum (Fig. 2 and Table 2). Aceperimidylenes are bright-yellow substances, whereas perimidines are usually yellow or pale-green. In contrast to perimidines, aceperimidylenes luminesce intensely on irradiation with UV light. The λ_{max} value of the luminescence spectrum of III is 490 nm in methanol at 30°.

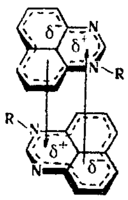


IV



V

However, the difference in the extinction coefficients of the longwave bands is more characteristic. In the case of perimidine the band at 400 nm has a very low ε value and sometimes appears as a barely noticeable shoulder. The origin of this band, which has given rise to differences of opinion [5, 8], is explained, in our opinion by the formation of intermolecular charge-transfer complexes between the dipolar fragments of two perimidine (VI) molecules. The dependence of the ε value on the concentration, in particular, constitutes evidence in favor of this. In aceperimidylenes the longwave band is indisputably associated with a π-π^* electron transition and has a normal extinction coefficient for this case. It is possible that a band associated with the formation of a charge-transfer complex (CTC) is also present in the spectra of aceperimidylenes, but it is masked by the stronger band of the $\pi-\pi^*$ transition.



VI

π-Donor Properties of Aceperimidylenes

Aceperimidylenes form 1:1 CTC with organic π acids, for example, with trinitrobenzene (TNB). The IIIb · TNB and IIIc · TNB complexes have less deep colors (dark-red and light-brown, respectively) than the CTC of I or 1-alkylperimidines with TNB (violet) [5]. Consequently, the charge-transfer band in the electronic spectra of the complexes is shifted to a lower wavelength region than in the case of perimidines (Table 2).

These data show that aceperimidylenes are weaker donors. In fact, the energy of the upper occupied molecular orbital (UOMO) of aceperimidylene ($E_{UOMO}^{\pi} = \alpha + 0.535\beta$), which is responsible for the π-donor properties, is substantially lower than the energy of the perimidine orbital ($E_{UOMO}^{\pi} = \alpha + 0.328\beta$). It should be noted that because of the low π-donor character of III, the charge-transfer band of their complexes with TNB is superimposed on the longwave absorption band of the donors themselves and appears on it in the form of a barely noticeable shoulder.

The ionization potentials of perimidine, 1-methylaceperimidylene, and 1-ethylaceperimidylene calculated from the following formula [9] are presented in Table 2:

$$I_d = 4.25 + 1.39 \times 10^{-4} \nu_{max},$$

where ν_{max} is the frequency of the charge-transfer band of the complex in chloroform solution.

It has previously been shown that the deeply colored N-anions of perimidine and aceperimidine undergo autoxidation extremely readily, and one can work with them only in an inert medium [10]. We have found that the N-anion of aceperimidylene is not oxidized to an appreciable extent by air oxygen. This is also a consequence of the lower π-donor character of the aceperimidylene system and the effective delocalization of the negative charge in it. The absorption spectrum of the aceperimidylene anion is presented in Fig. 2.

Basicities

The basicities of the aceperimidylenes lie in the range $pK_a \approx 4$ (Table 2), i.e., they are two orders of magnitude lower than the basicities of perimidines and aceperimidines [10] and considerably lower than the basicities of all of the other cyclic and acyclic amidines known to us. This can be explained by the very strong shift of the π-electron density from the heteroring of aceperimidylenes to the acenaphthylene fragment. Thus the total effective positive charges on the atoms of the $-N=C-N\langle$ amidine system of aceperimidylene and perimidine are, respectively, +0.276 and +0.199.

Magnetic Properties

Despite the considerable asymmetry of the π-electron cloud of the aceperimidylene molecule, the diamagnetic ring currents in it are expressed considerably more strongly than in the perimidine system. With respect to perimidines, the chemical shifts of the aromatic protons in the IIIa and IIIb molecules are shifted to weak field by, on the average, 0.6-1 ppm. This can be interpreted as an indication of the somewhat greater aromatic character of aceperimidylenes.

Like perimidines [5], aceperimidylenes give a single ESR signal with a width of 12 Oe. However, the number of paramagnetic centers in aceperimidylenes is appreciably smaller. Thus, for example, the number of paramagnetic centers in 1-methyl- and 1-ethylaceperimidylenes amounts to 13.2 and 21.3%, respectively, of the number in 1-methylaceperimidine. These data make it possible to assume that the nature of the ESR signal in the spectra of perimidines and aceperimidilenes is most likely associated with the formation of intermolecular CTC of the VI type. Inasmuch as the π-donor character of aceperimidylenes is lower, their tendency to form intermolecular CTC should also be lower.

EXPERIMENTAL METHOD

Quantum-mechanical calculations by the simple Hückel method were made by the method in [11]. The UV spectra were measured with an SF-4A spectrophotometer. The PMR spectra of solutions of the compounds (0.3 mole) were recorded with a Tesla-BS-487C spectrometer (80 MHz) with hexamethyldisiloxane as the internal standard. The ionization constants were measured by potentiometric titration of a 0.001 N solution of the substance in 10% aqueous alcohol (by volume) with a 0.01 N solution of HCl with a pH-340 meter at 20 ± 1°. The ESR spectra of crystalline samples were measured at room temperature.

Aceperimidylene (IIIa). A 5.0-g (0.026 mole) sample of IIa was refluxed with 6.1 g (0.026 mole) of chloranil in 100 ml of absolute chlorobenzene for 20 min, after which the solvent was evaporated, and the dry residue was treated with a mixture of formic acid and ethanol (1 : 1). The chloranil was removed by filtration, and the cooled solution was made alkaline carefully with concentrated ammonium hydroxide. The alkaline mixture was cooled with ice, and the resulting precipitate was removed by filtration and dried. The mixture of IIIa and tetrachlorohydroquinone was separated with a column filled with Al_2O_3 (elution with alcohol). The first fraction was collected and worked up to give 2.2 g (54%) of yellow crystals that were soluble in acids and alkalis and had mp > 350° (from toluene). PMR spectrum (in DMSO), δ, ppm: 8.52 (H_2, s), 7.40 ($H_{4,9}$, d), 7.47 ($H_{6,7}$, s), and 8.25 ($H_{5,8}$, d).

Aceperimidylenes IIIb-d. A mixture of 0.1 mole of IIa-d and 0.11 mole of chloranil was dissolved in 50 ml of absolute benzene, and the solution was refluxed for 10 min. The solvent was then removed by distillation, and the residue was treated with 10% sodium hydroxide solution, washed with water, and dried. The solid was dissolved in 30 ml of chloroform and chromatographed with a column filled with Al_2O_3. Compounds IIIb-d were eluted with chloroform–petroleum ether (1 : 1). The physical constants of the products are presented in Table 1. PMR spectrum of IIIb (in $CDCl_3$), δ, ppm: 7.62 (H_4, d), 7.57 ($H_{6,7}$, s), 7.87 (H_2, s), 8.05 (H_5, d), 8.25 (H_8, d), 6.65 (H_9, d), and 3.45 ($N\text{-}CH_3$).

1-Methyl-2-phenylaceperimidylene (IIIe). A 0.3-g (1.2 mmole) sample of chloranil was dissolved in 5 ml of absolute benzene, 0.2 (1.1 mmole) of IIe was dissolved in 4 ml of benzene, and the solutions were mixed. The color changed from orange to dark-green. The mixture was heated at 40° for 15 min, after which the solvent was evaporated, and the residue was refluxed with 10% sodium hydroxide solution. The mixture was filtered, and the solid material was washed with water until the wash waters were colorless. The solid was then dried, dissolved in 10 ml of chloroform, and chromatographed with a column filled with Al_2O_3. Petroleum ether eluted 0.1 g (33%) of IIIe.

Attempted Autoxidation of the N-Anion of Aceperimidylene. A mixture of 0.2 g (1 mmole) of IIIa and 0.07 g (1 mmole) of potassium hydroxide in 14 ml of ethanol was refluxed for 3 h, after which it was cooled, and 5 ml of formic acid was added to it. The resulting solution was made alkaline to pH 9 with ammonia and cooled with ice. The precipitate was removed by filtration and dried to give 0.16 g (80%) of a light-brown substance. No melting-point depression was observed for a mixture of this product with aceperimidylene.

Preparation of CTC of IIIb, c with Trinitrobenzene (TNB). A solution of 0.2 g (1 mmole) of IIIb, c and 0.2 g (1 mmole) of TNB in 5 ml of ethanol was refluxed for 5 min, after which the mixture was cooled, and the precipitated crystals were removed by filtration and washed with alcohol. The CTC of 1-methylaceperimidylene with trinitrobenzene was obtained as red-brown cyrstals with mp 181-182° (from alcohol). Found: N 17.0%. $C_{14}H_{10}N_2 \cdot C_6H_3N_3O_6$. Calculated: N 16.7%.

The CTC of 1-ethylaceperimidylene and TNB was obtained as brown needles with mp 137-138° (from alcohol). Found: N 15.7%. $C_{15}H_{12}N_2 \cdot C_6H_3N_3O_6$. Calculated: N 16.2%.

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HETEROCYCLIC ANALOGS OF PLEIADIENE

XXIII.* REDOX DISPROPORTIONATION OF N-SUBSTITUTED ACEPERIMIDONES. UNUSUALLY FACILE REDUCTION OF THE C=O GROUP

T. I. Vinokurova and A. F. Pozharskii

UDC 547.856.7:542.941.8:543.422.25.4

In the reaction of chloranil with N-monosubstituted aceperimidones, in addition to dehydrogenation of the CH_2CH_2 bridge, the C=O group is unexpectedly reduced, and 1-alkylaceperimidylenes are obtained. N,N'-Disubstituted aceperimidones form disubstituted aceperimidylenones under the same conditions.

Continuing our research on the synthesis of aceperimidylene derivatives, we subjected various aceperimidones to the action of chloranil. It was found that the corresponding aceperimidylenones (IIb-d) are formed in 57-70% yields on brief heating of N,N'-disubstituted aceperimidones with an equimolar amount of chloranil in benzene. Their structure was proved by their PMR spectra, in which a singlet related to the CH=CH bridge appears at 7.05 ppm in place of the signals of a CH_2CH_2 bridge at 3.16 ppm that are characteristic for the starting compounds. The UV spectra of the aceperimidylenones contain an intense longwave band at 380-385 nm, whereas this band is found at 320-330 nm in the spectra of aceperimidones. The aceperimidylenones are

TABLE 1. Synthesized Compounds

Compound	mp, °C (solvent)	$\nu_{C=O}$, cm^{-1} (mineral oil)	λ_{max}, nm (log ε)	Empirical formula	Found, %			Calc., %			Yield, %
					C	H	N	C	H	N	
Ia	313—314 (butanol)	1690		$C_{13}H_{10}N_2O$	74,4	5,2	13,1	74,3	4,8	13,3	70
Ic	219—220 (n-propanol)	1670	325	$C_{27}H_{22}N_2O$	83,0	5,3	6,8	83,0	5,7	7,2	60
Id	180—181 (butanol)	1670	333	$C_{21}H_{18}N_2O$	79,7	5,3	8,9	80,2	5,8	8,9	40
IIb	172—173 (heptane)	1660	385 (3,96)	$C_{15}H_{12}N_2O$	76,3	5,1	12,2	76,3	5,1	11,9	70
IIc	169—170 (aqueous acetone)	1660	385 (4.08)	$C_{27}H_{20}N_2O$	83,5	5,6	6,9	83,5	5,2	7,2	80
IId	148—149 (aqueous alcohol)	1660	380 (4,06)	$C_{21}H_{16}N_2O$	80,9	5,1	9,2	80,7	5,2	8,9	80
IIIb	261—262 (xylene)	1670		$C_{15}H_{14}N_2O$	75,8	6,2	12,3	75.6	6,0	11,8	65
IVa	275—276 (butanol)	1677		$C_{14}H_{10}N_2O$	75,4	5,0	12,7	75,7	4,6	12,6	15

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*See [1] for communication XXII.

Rostov State University, Rostov-on-Don. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 545-547, April, 1976. Original article submitted April 29, 1975.