# INVESTIGATION OF PERINONE COMPOUNDS

## III.* EFFECT OF THE ELECTRONIC NATURE OF THE SUBSTITUENTS IN NAPHTHALIC ANHYDRIDE ON THE FORMATION OF ISOMERIC NAPHTHALOPERINONES

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The electronic nature of the substituent in naphthalic anhydride has a substantial effect on the isomeric composition of the naphthaloperinones formed in reactions with 1,8-naphthylenediamine. An electron-accepting substituent in the 4 position of naphthalic anhydride promotes predominant retention of the carbonyl group in the 1 position, while an electron-donating substituent promotes retention of the carbonyl group in the 8 position of the naphthalene ring. 10-Amino- and 11-amino-14H-benzo[4,5]isoquinolino[2,1-a]perimidin-14-ones were synthesized.

Having accomplished the directed synthesis of 11-nitro- and 10-nitro-14H-benzo[4,5]isoquinolino-[2,1-a]perimidin-14-ones (Va and VIa) [1], and having reduced them to the corresponding amines (Vb and VIb), we set out to study the effect of the electronic nature of the substituents in naphthalic anhydride on the isomeric composition of the substituted naphthaloperinones formed on reaction with 1,8 naphthylenediamine. The nitro and amino groups were selected as model substituents because of their distinctly expressed electron-accepting and electron-donating properties. The proposed problem was solved by a detailed study of the properties of the products formed by reaction of 1,8-naphthylenediamine with 4-nitro- and 4-aminonaphthalic anhydride in comparison with the properties of the substituted naphthaloperinones obtained by directed synthesis. The percentage of each isomer in the mixture was calculated from the absorption spectra of the mixture obtained and of the individual substances. Calculation at 410 and 450 nm by the well-known method [2] indicated that the mixture contains 78.1% of 11-nitronaphthaloperinone (Va) and 21.9% of 10-nitronaphthaloperinone (VIa); in the second case, the mixture contains 75.4% of 10-amino-naphthaloperinone (Vb) and 24.6% of 11-aminonaphthaloperinone (VIb). The ratio of the isomeric naphthaloperinones did not change when the reaction was carried out in acetic acid or chlorobenzene.

If it is assumed that the interaction of substances I and II begins with nucleophilic attack of the amino group on the carbon atom of one of the carbonyl groups of the substituted naphthalic anhydride, the results obtained are unexpected. It is not possible to identify the probable intermediate compounds, as was previously done in the case of phthaloperinones [3], since here the reaction proceeds so rapidly that the intermediate products cannot be detected; only the starting and final substances are visible on the chromatogram.

To explain these results we proposed the following possible mechanism for the formation of the substituted naphthaloperinones. Cleavage of the first water molecule from compounds I and II does not affect the ratio of isomeric naphthaloperinones and leads to compounds IIIa and b. Cleavage of the second water molecule can be accomplished in two directions: at the expense of the oxygen of the carbonyl group in the ring with a substituent or in the other naphthalene ring; this determines the ratio of the nitro and amino-naphthaloperinone isomers.

*For Communication II see [1].

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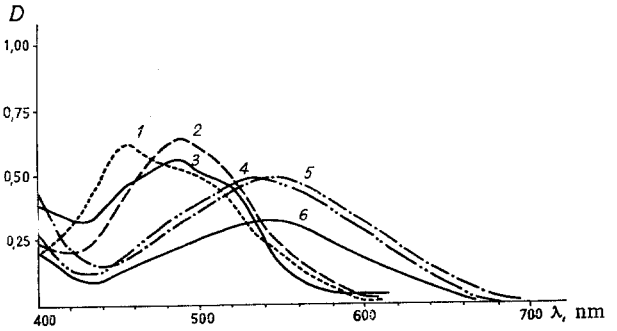
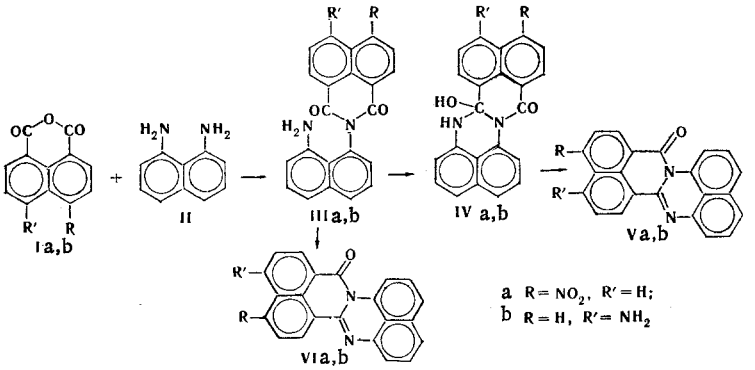



Fig. 1. Absorption spectra of isomeric naphthaloperinones in chlorobenzene: 1) Vb (c $1.2 \cdot 10^{-5}$ M); 2) VIb (c $1.08 \cdot 10^{-5}$ M); 3) mixture of VIb and Vb (c $0.98 \cdot 10^{-5}$ M); 4) VIa (c $1.12 \cdot 10^{-5}$ M); 5) Va (c $1.01 \cdot 10^{-5}$ M); 6) mixture of Va and VIa (c $1.10 \cdot 10^{-5}$ M).




## EXPERIMENTAL

11-Amino-14H-benzo[4,5]isoquinolino[2,1-a]perimidin-14-one (VIb). A suspension of 0.45 g of 5% palladium on carbon in 25 ml of dimethylformamide was saturated with hydrogen at 50° for 10 min and 0.73 g (0.002 mole) of 11-nitronaphthaloperinone (Va) was added and hydrogenated up to absorption of the theoretically required amount of hydrogen. The bright-red suspension was filtered from the catalyst and poured into 150 ml of water. The precipitate was filtered, washed with water, dried, dissolved in 300 ml of benzene–ethyl acetate (1 : 2), and passed through a column with aluminum oxide [benzene–ethyl acetate eluent (1 : 2)]. Evaporation of the solvent yielded 0.64 g (96%) of VIb with mp 319-319.5°; $\lambda_{max}$ 493 nm, ε $0.75 \cdot 10^3$ (chlorobenzene). Found %: C 78.2; H 4.2. $C_{22}H_{13}N_3O$. Calculated %: C 78.8; H 3.9.

10-Amino-14H-benzo[4,5]isoquinolino[2,1-a]perimidin-14-one (Vb). Compound Vb [0.52 g (97.2%)] was obtained in the form of brown needles with mp 306-307° from 0.6 g (0.0016 mole) of VIa and 0.4 g of 5% palladium on charcoal in 20 ml of dimethylformamide, as described above; $\lambda_{max}$ 456 nm, ε $0.73 \cdot 10^3$ (chlorobenzene). Found %: C 78.8; H 3.8. $C_{22}H_{13}N_3O$. Calculated %: C 78.8; H 3.9.

Reaction of 1,8-Naphthylenediamine (II) with 4-Nitronaphthalic Anhydride (Ia). A suspension of 0.54 g (0.0034 mole) of II and 0.83 g (0.0034 mole) of Ia in 30 ml of glacial acetic acid was refluxed with stirring for 5 h. The solution was cooled and poured into 100 ml of water. The resulting precipitate was filtered, washed with water, dried, dissolved in chlorobenzene–acetone (3 : 1), and passed through a column filled with aluminum oxide. The solvent was removed with steam to give 1.03 g of a dark-blue substance. The absorption spectrum is shown in Fig. 1.

Reaction of II with 4-Aminonaphthalic Anhydride (Ib). Reaction of 0.81 g (0.0051 mole) of II and 0.46 g (0.0051 mole) of Ib in 30 ml of glacial acetic acid, as described above, yielded 0.39 g of substance [benzene–ethyl acetate eluent and solvent (1 : 2)]. The absorption spectrum is shown in Fig. 1.

## LITERATURE CITED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