# SYNTHESIS AND STUDY OF SOME BIS(1',8'-NAPHTHOYLENE-1,2-BENZIMIDAZOLES)

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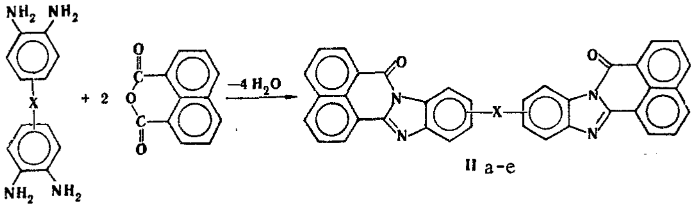
A number of previously undescribed bis(1',8'-naphthoylene-1,2-benzimidazoles) were obtained by reaction of bis(o-phenylenediamines) with various structures with naphthalic anhydride. Under the same conditions, the reaction of o-phenylenediamine with naphthalene-1,4,5,8-tetracarboxylic acid dianhydride leads to a mixture of cis and trans isomers of bisbenzimidazobenzophenanthrolinedione. The spectral and thermal characteristics of the synthesized compounds were studied.

Polynaphthoylenebenzimidazoles constitute a promising class of staircase polyheteroarylenes that have high-grade exploitational characteristics [1-3]. The successful development of this field of the chemistry of heat-resistant polymers suggest the necessity for the solution of a number of problems associated with the establishment of the structures of the systems obtained, the determination of their degree of cyclization, and the prediction of a number of properties characteristic of polymeric structures with a degree of cyclization of 100%.

Proceeding from the information stated above and taking into account the inadequate amount of data [4-9] pertaining to compounds that model poly(naphthoylenebenzimidazoles), we felt that it would be expedient to obtain these substances by the method in [10, 11], which we developed for the synthesis of poly(naphthoylenebenzimidazoles).

The bis(1',8'-naphthoylene-1,2-benzimidazoles) were synthesized via the scheme

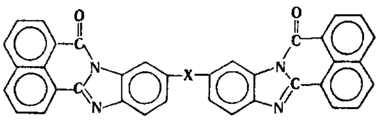


Ia-e    II a-e

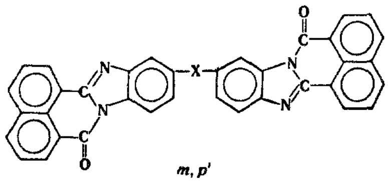
I–II a X = —; b X = O; c X = $CH_2$; d X = $SO_2$; e X = $C(CF_3)_2$

The IR spectra of all of the synthesized compounds contain absorption maxima at 1710-1715 $cm^{-1}$, which are characteristic for the CO groups of naphthoylenebenzimidazole [12, 13], but do not contain absorption maxima at 1680 $cm^{-1}$, which are characteristic for the carbonyl group of a six-membered imide ring; this constitutes evidence for the absence of incompletely cyclized fragments. The regions of the absorption maxima in the UV spectra of the synthesized compounds (e.g., IIIb) are in agreement with the literature data [8] (Table 1).

The broad ranges of the melting points of the compounds obtained are probably a consequence of the presence in them of three isomers:



*m, m'*



*m, p'*

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TABLE 1. Bis(1',8'-naphthoylene-1,2-benzimidazoles) and Bisbenzimidazobenzophenanthrolinediones

| Compound | mp, °C [a] (literature data) | UV Spectra[b] (conc. $H_2SO_4$) c·$10^4$ mole/l |  | Found, % |  |  | Empirical formula | Calc., % |  |  | Yield, % |
|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  | $\lambda_{max}$ | lg $\varepsilon_{max}$ | C | H | N |  | C | H | N |  |
| IIa | 432—436<br>(430)[5] | 245<br>312<br>428 | 4,83<br>4,52<br>4,08 | 80,3 | 3,3 | 10,2 | $C_{36}H_{18}N_4O_2$ | 80,3 | 3,4 | 10,4 | 95 |
| IIb | 317—325 | 231<br>305<br>416 | 4,86<br>4,49<br>4,74 | 78,0 | 3,4 | 9,7 | $C_{36}H_{18}N_4O_3$ | 78,0 | 3,3 | 10,2 | 96 |
| IIc | 282—288 | 305<br>420 | 4,44<br>4,56 | 80,4 | 3,7 | 9,9 | $C_{37}H_{18}N_4O_2$ | 80,4 | 3,6 | 10,1 | 93 |
| IId | 420—426 | 235<br>304<br>405 | 4,53<br>3,78<br>4,50 | 71,7 | 3,0 | 9,4 | $C_{36}H_{18}N_4O_4S$ [c] | 71,7 | 3,0 | 9,3 | 95 |
| IIe | 373—374 | 231<br>303<br>412 | 4,86<br>4,36<br>4,66 | 68,1 | 2,7 | 8,1 | $C_{39}H_{18}O_2F_6N_4$ [d] | 68,0 | 2,6 | 8,1 | 93 |
| IIIa + IIIb | >400 | 249<br>292<br>329<br>382<br>488 | 4,55<br>4,44<br>3,88<br>4,08<br>4,49 |  |  |  | $C_{26}H_{12}N_4O_2$ |  |  |  | 98 |
| IIIa | 490—492<br>(478—480)[5] | 246<br>328<br>382<br>492 | 4,53<br>4,19<br>4,03<br>4,45 |  |  |  | $C_{26}H_{12}N_4O_2$ |  |  |  | 45[e] |
| IIIb | 512—514<br>(>510)[5] | 250<br>291<br>382<br>474 | 4,49<br>4,57<br>4,03<br>4,47 |  |  |  | $C_{26}H_{12}N_4O_2$ |  |  |  | 55[e] |

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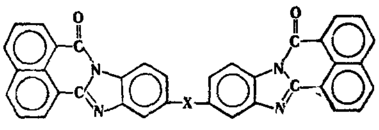
a) These are the melting points of the unsublimed substances. b) The results of elementary analysis and the UV-spectral characteristics are presented for the sublimed substances. c) Found: S 5.4%. Calculated S 5.3%. d) Found: 16.5%. Calculated: F 16.6%. The yield given is the yield with respect to the total amount of isomers.



p, p'

The ratio of these isomers is determined by the ratio of the rates of acylation of the m- and p-amino groups of the bis(o-phenylenediamines) with naphthalic anhydride; to a first approximation, the ratio of the m,m' and p,p' isomers can be described by an equation similar to the equation presented in [14]:

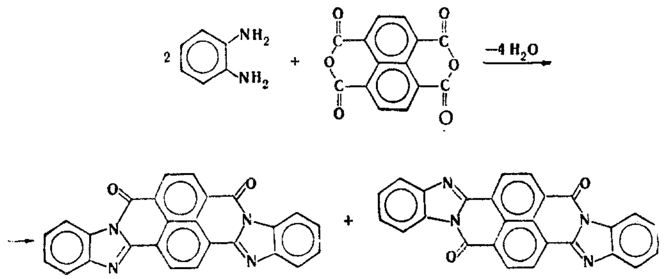
$$\lg\left(\frac{p}{m}\right) = -\rho(\sigma_p - \sigma_m) + \lg\alpha,$$

where p and m are the amounts of the resulting p,p' and m,m' isomers, $\sigma_m$ and $\sigma_p$ are the Hammett constants of the meta and para substituents, and $\alpha$ is a coefficient of proportionality that links the amounts of meta and para isomers formed with the rate constants for acylation of bis(o-phenylenediamine) at the m- and p-amino groups.

It follows from this equation that bis(1',8'-naphthoylene-1,2-benzimidazoles) based on bis(o-phenylenediamines) that contain electron-donor bridging groups (O and $CH_2$) should be enriched in the p,p' isomer. This is confirmed by the results of quantum-chemical calculations [15].

One's attention is directed to the extremely high yields of bis(1',8'-naphthoylene-1,2-benzimidazoles): The yield was close to quantitative even when the least basic [16] of all of the bis(o-phenylenediamines), viz., 3,3',4,4'-tetraaminodiphenyl sulfone, was used. It should be noted that attempts to purify II by high-vacuum sublimation [320-390°C ($10^{-3}$ mm)] were accompanied by significant losses of the substances. As a result of sublimation the melting points of the compounds were raised 4-10°C, and the compounds melted over narrower ranges (1-2°C); this is possibly associated with the preferred sublimation of one of the isomers.

Model compounds based on o-phenylenediamine and naphthalene-1,4,5,8-tetracarboxylic acid dianhydride were also obtained in close to quantitative yields (Table 1) under the conditions for the synthesis of the polymers [10, 11]:



IIIa IIIb

The resulting bisbenzimidazo[1,2-b:2',1'-h]benzo[k,*l*,m]-3,8-phenanthroline-6,9-dione (IIIa) and bisbenzimidazo[1,2-b:1',2'-i]benzo[k,*l*, m]-3,8-phenanthroline-6,14-dione (IIIb) were separated by the method in [17]. The mixture contained 45% of isomer IIIa and 55% of isomer IIIb (with respect to the total amount of isomers).

The IR spectra of isomers IIIa and IIIb differ only slightly, in agreement with the data in [18]: The intense absorption maxima at 1710-1715 $\text{cm}^{-1}$ that are characteristic for the carbonyl groups of naphthoylenebenzimidazole are observed in the spectra of both compounds. The UV spectra of the cis and trans isomers differ extremely substantially (Table 1). The ranges of the absorption maxima in the UV spectrum of a mixture of isomers IIIa and IIIb are in agreement with the data in [8], and, as expected [5] (Table 1), the melting point of the trans isomer is higher than that of the cis isomer.

It should be noted that monoaddition products similar to those previously observed during a study of the reaction of 1,2,4,5-tetraaminobenzene with naphthalic anhydride [19] and of naphthalene-1,4,5,8-tetracarboxylic acid with o-phenylenediamine [20] are not observed under the conditions for the synthesis of the polymers [10, 11]; the changes in the reactivities [21] of the bis(o-phenylenediamines) and naphthalene-1,4,5,8-tetracarboxylic acid that occur as a result of the reaction of the first of their functional groups are not so substantial as to prohibit the reaction of the second half of the molecule under the reaction conditions [10].

The characteristics of the synthesized model compounds are virtually the same as the properties of the same substances obtained in polyphosphoric acid [5].

## EXPERIMENTAL

The IR spectra were recorded with a UR-20 spectrometer, and the UV spectra were recorded with a Hitachi EPS-3T spectrophotometer.

Bis(o-phenylenediamines) Ia-d were obtained and purified by the methods in [22]. The 2,2-bis(3,4-diaminophenyl)hexafluoropropane (mp 223-224°C) was kindly furnished by B. R. Livshits and T. Kh. Dymshits (State Research and Planning Institute LKP, Moscow). The anhydrides of naphthalic acid and naphthalene-1,4,5,8-tetracarboxylic acid were kindly provided by N. I. Ternovskaya (VNIPIM, Tula) and were purified by high-vacuum sublimation; their melting points were in agreement with the literature data [22].

Bis(1',8'-naphthoylene-1,2-benzimidazoles) (II). A three-necked flask equipped with a stirrer and a bubbler for argon was charged with 0.04 mole of the tetraamine, 0.08 mole of naphthalic anhydride, and 0.026 mole of benzoic acid, and m-cresol was added until the concentration of the starting monomers was 15%. The mixture was then heated at 160-200°C for ~ 5 h, after which it was cooled and poured into methanol. The resulting precipitate was removed by filtration, extracted with ethanol, and dried at 150°C (2 mm).

Isomeric Bisbenzamidobenzophenanthrolinediones. A mixture of isomers IIa, b, which was separated by the method in [17], was similarly obtained from equimolar amounts of o-phenylenediamine and naphthalene-1,4,5,8-tetracarboxylic acid dianhydride.

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# HETEROCYCLIC COMPOUNDS BASED ON MALEIC ACID MONOUREIDE

## 1. STRUCTURE AND TRANSFORMATIONS OF THE PRODUCT OF BROMINATION OF MALEIC ACID MONOUREIDE

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and U. Ya. Mikstais

UDC 547.781'787'854.9'867.2:541.61

The products of the bromination in water of maleic acid monoureide and its methyl ester have the 2-imino-5-bromocarboxy(carbomethoxy)methyl-4-oxazolidone structure. 2-Imino-5-bromocarboxymethyl-4-oxazolidone undergoes dehydrobromination in aprotic polar solvents to give 2-imino-5-carboxymethylidene-4-oxazolidone. In the presence of dry hydrogen chloride in dimethylacetamide the oxazole ring undergoes dehydrobromination and isomerization to an imidazole ring with the formation of 5-carboxymethylidenehydantoin. Methyl α-bromofumarate monoureide is formed when the oxazole ring of 2-imino-5-bromocarbomethoxymethyl-4-oxazolidone is opened with alkali.

Promising methods for the synthesis of orotic acid (II) and its salts have been developed on the basis of the halogenation of maleic acid monoureide (I) [1-4].

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