## BIS(1,8-NAPHTHYLIMIDES) AND BIS(1',8'-NAPHTHOYLENE-1,2-BENZIMIDAZOLES) BASED ON NEW BIS(NAPHTHALIC ANHYDRIDES)

A. L. Rusanov, E. G. Bulycheva, A. M. Berlin, and F. I. Adyrkhaeva

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The reaction of bis(naphthalic anhydrides) with aniline and o-phenylenediamine under conditions of hightemperature cyclocondensation in m-cresol in the presence of a catalyst (benzoic acid) gives bis(1,8naphthylimides) and bis(1',8'-naphthoylene-1,2-benzimidazoles) which model the elementary units of polyimides and polynaphthoylenebenzimidazoles, respectively.

Polyimides and polyaroylenebenzimidazoles are expected to meet every more rigorous specifications, and one route to the satisfaction of these requirements is the formulation of new polymers based on bis(naphthalic anhydrides) [1-4].

For this purpose, their reaction with aniline or o-phenylenediamine is expedient. The bis(1,8-naphthylimides) and bis(1',8'-naphthoylene-1,2-benzimidazoles) so obtained model the structure of the elementary units of polynaphthylimides and polynaphthoylenebenzimidazoles, respectively. In addition, they are of decided interest as luminophores and dyestuffs.

Reactions of bis(naphthalic anhydrides) with anilines were carried out under conditions of high-temperature cyclocondensation in m-cresol according to the following general scheme:



Even under such rigorous conditions, the reaction proceeds effectively only in the presence of a catalyst — benzoic acid; this is probably explained by the low reactivity of the six-membered anhydride ring. The reaction products are solid crystalline substances, varying in color from grav to greenish yellow.

The IR spectra of the bis(1,8-naphthylimides) so prepared show absorption bands at  $1355-1370 \text{ cm}^{-1}$  resulting from the presence of a tertiary nitrogen atom in the molecule and carbonyl bands from the imide ring at 1675-1680 and 1710-1720 cm<sup>-1</sup>, the 1675-1680 cm<sup>-1</sup> band being very strong, evidently connected with the absorption of the carbonyl "bridging" groups in this region; there were no absorption maxima above 3000 cm<sup>-1</sup> corresponding to carbonyl and amide group absorptions [5].

The high yields of the majority of the bis(1,8-naphthylimides) together with the spectral characteristics of the reaction products confirm that there are no impurities present containing peri-carboxyamide groups.

Reactions of bis(naphthalic anhydrides) with o-phenylenediamine take place under the same conditions:



A. N. Nesmeyanov Institute for Organometallic Compounds, Academy of Sciences of the USSR, Moscow 117813. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, pp. 649-652, May, 1991. Original article submitted August 14, 1989; revision submitted July 17, 1990.

Com-	Empirical formula	mp, °C (solvent)	UV spectrum (conc H <sub>2</sub> SO <sub>4</sub> , 10 mole/	Yield, %	
pound			(log $\varepsilon$ )	m-cresol	phenol
lla	C <sub>44</sub> H <sub>24</sub> N <sub>2</sub> O <sub>6</sub>	400	232 (5,88), 288 (5,40), 284 (5,60),	61	
Ilb	$C_{44}H_{24}N_2O_6$	321323	230 (5,96)	85	
IIc	$C_{50}H_{28}N_2O_7$	176177 3:1 toluene-pet.	229 (5,70), 368 (5,41)	86	—
IIq	$C_{51}H_{28}N_2O_7$	ether 217218 (DME)	230(5,78),	88	—
lle	C <sub>50</sub> H <sub>28</sub> N <sub>2</sub> O <sub>6</sub> S	247249 1:2 chloroform-ether	387 (5,48) 240 (5,94), 328 (5,40),	85	—
llt	$C_{53}H_{28}F_6N_2O_6$	<b>3</b> 34 <b>3</b> 35 2 <b>:</b> 1 DMF-water	400 (5,52)     228 (5,87),     260 (5,54),     261 (5,54), $ $	92	
IIIa	C44H22N4O4	390391 1:1 chloroform-	250 (5,70), 288 (5,49),	90	91
IIIb	C44H22N4O4	320322,5 (DMF)	248 (5,90), 280 (5,54),	97	98
IIIc	$C_{50}H_{26}N_4O_5$	204206 1:4 dioxane <del>-</del> ethanol	414 (5,37)	88	93
IIId	C <sub>51</sub> H <sub>26</sub> N4O <sub>5</sub>	215,218 (DMF)	248 (5,68), 298 (5,48), 350 (5,51),	96	96
Ille	$C_{50}H_{26}N_4O_6$	364372 1:2 chloroform ether	417 (5,66) 232 (5,58), 362 (5,24),	88	92
III f	C <sub>53</sub> H <sub>26</sub> F <sub>6</sub> N₄O₄	1:2) 319,5324 2:1 DMF-water	415 (5,44) 250 (5,88), 276 (5,71), 350 (5,53), 410 (5,69)	95	99

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

The bis(naphthoylenebenzimidazoles) so obtained are solid crystalline substances, brighter in color than the corresponding bis(1,8-naphthylimides), the colors ranging from bright yellow to bright orange. The IR spectra of compounds IIIa-f show bands for C=N stretching vibrations (1450-1460 and 1600-1610 cm<sup>-1</sup>) in the naphthoylbenzimidazole ring [6]; there were no bands above 3300 cm<sup>-1</sup>, characteristic for amino groups of o-aminoimide structures, which shows that the intermediate N-(o-aminophenyl)naphthylimides were not present as impurities in the products.

The reaction proceeds in a similar way, and even with a somewhat higher yields, when phenol is used as solvent and catalyst (Table 1) which is of interest from a technological standpoint.

The bis(1',8'-naphthoylenebenzimidazoles) show high resistance to hydrolysis: they are unchanged after heating at bp for 20 h in 10% aqueous sodium hydroxide. Scheme 1

The fairly narrow ranges of melting points of compounds IIIa-f would seem to indicate the preferential formation of compounds having one of the following isomeric structures (see Scheme 1).

Any conclusion about the preferred formation of one of these isomers must take account of the calculated positive charge on carbonyl carbon atoms [7]. This charge determines the reaction center undergoing first-order nucleophilic attack.

It can be assumed that the ratio of the positive charges on the carbonyl carbons in positions 4,4' and 5,5' to the "bridging" groups found by calculations of the electronic characteristics of the various bis(naphthalic anhydrides) which we used [7] are also retained for the bis[N-(o-aminophenyl)naphthylimides] formed in the course of their reaction with o-phenylenediamine. The most probable result in this case would be the formation, in the third (cyclization) stage of the process, of isomers having structure IV.

The high yields of the model compounds under conditions of high-temperature catalytic polyheterocyclization lead one to consider the possibility of preparing polynaphthylimides and polynaphthoylenebenzimidazoles under the same high-temperature conditions.

## EXPERIMENTAL

IR spectra were run on a UR 20 instrument as KBr disks and UV spectra on a Hitachi ESP 3T.

Aniline was purified by distillation in a current of argon (bp 184°C;  $n_D^{20}$  1.022) and o-phenylenediamine by distillation at 40°C/2 mm (mp 103.5-104°C); benzoic acid was recrystallized from distilled water (mp 122.5°C), m-cresol was twice redistilled, using a dephlegmator, in a current of argon at 93°C/5 mm, and phenol was redistilled in argon (mp 41°C).

Bis(naphthalic anhydrides) la-f were prepared by the method of [3].

Results for elemental analysis (C, H, N, F, S) of the compounds prepared were in agreement with the calculated figures.

**Bis(1,8-naphthylimides) IIa-f.** A mixture of 1 mmole bis(naphthalic anhydride) Ia-f, 2 mmoles aniline, 2 mmoles benzoic acid, and 10 ml m-cresol was heated with stirring in a current of argon for 7 h at 100°C and 10 h at 190°C. It was then cooled and poured into 100 ml methanol. The residue was filtered off washed with methanol, dried, and recrystallized.

Bis(1',8'-naphthoylene-1,2-benzimidazoles) IIIa-f were prepared in a similar manner, but heated for 7 h at 160°C.

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