REACTION OF AROYLENEBENZIMIDAZOLES WITH NUCLEOPHILIC REAGENTS

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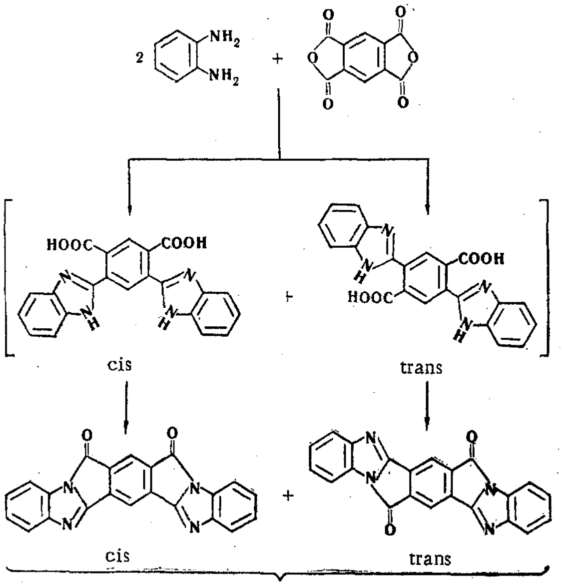
The reaction of aromatic mono- and bis(o-phenylenediamines), -(aminophenols), and -(o-aminothiophenols) with mono- and diaroylenebenzimidazoles in polyphosphoric acid was studied. The interrelationship between the structures and properties of the resulting compounds, which contain benzimidazole and other rings in the ortho position relative to one another, was investigated.

We have previously demonstrated [1] that the well-known cleavage of the benzoylenebenzimidazole ring by o-phenylenediamine can be readily extended to other aromatic nucleophilic compounds; moreover, it was established that it is expedient to accomplish this reaction in polyphosphoric acid. Extending this reaction to aroylene benzimidazoles of various structures and to aromatic tetrafunctional nucleophilic reagents, we obtained both high-molecular-weight polybenzazoles that contain benzimidazole side groups [1, 2] and copolymers of unsymmetrical structure that contain other benzazole rings in addition to the benzimidazole ring in the main chains of the macromolecules [1, 3].



V

To establish the optimum conditions for the synthesis of these polymers and also for a more thorough identification of them, we undertook a detailed study of the synthetic conditions and properties of compounds that model the structure of the synthesized polybenzazoles.

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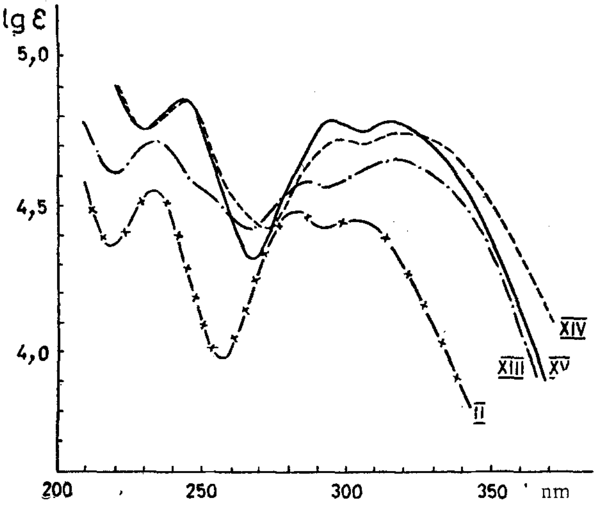
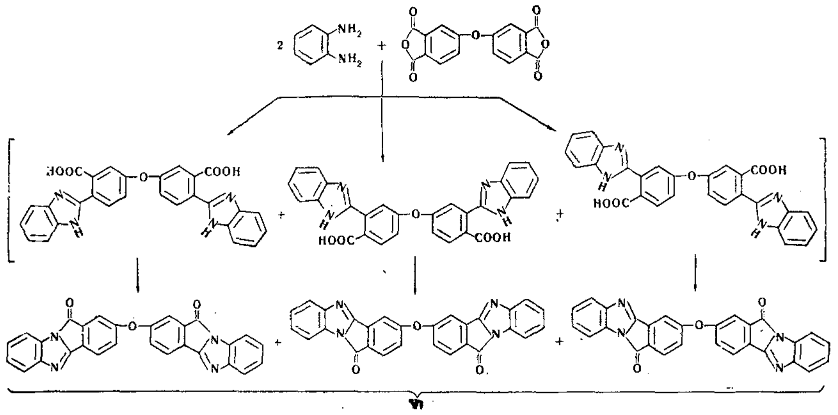


Fig. 1. UV spectra of benzimidazoles II, XIII, XIV, and XV.

The reaction of 1,2-benzoylenebenzimidazole [4] (I) with o-phenylenediamine, o-aminophenol, and o-aminothiophenol in polyphosphoric acid gave the simplest model compounds – 1,2-bis(2-benzimidazolyl)-benzene (II), 1-(2-benzoxazolyl)-2-(2-benzimidazolyl)benzene (III), and 1-(2-benzothiazolyl)-2-(2-benzimidazolyl)benzene (IV) [1].

Model compounds with more complex structures were obtained by the reaction of aroylenedibenzimidazoles with o-phenylenediamine, o-aminophenol. The starting aroylenedibenzimidazoles were obtained by the reaction of o-phenylenediamine with the dianhydrides of tetracarboxylic acids. The product of the reaction of o-phenylenediamine with the dianhydride of pyromellitic acid (V) is probably a mixture of cis and trans isomers.

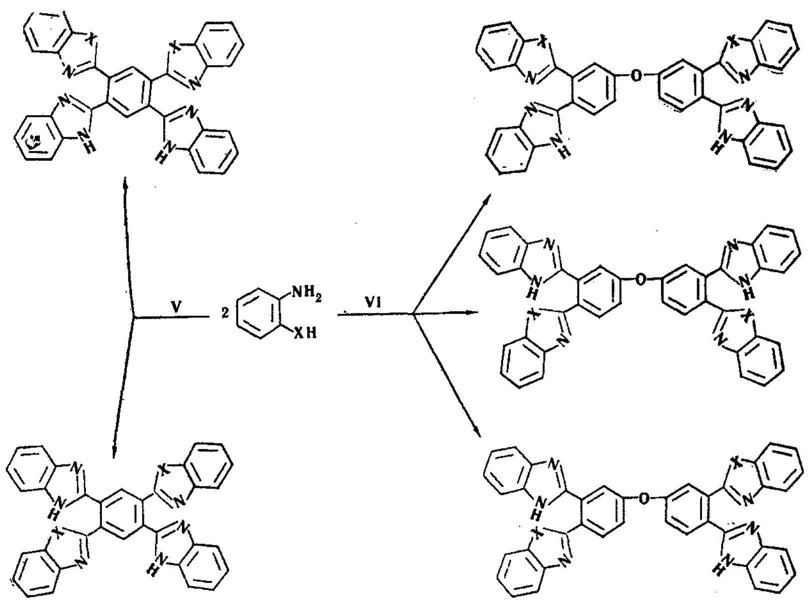
A mixture of isomeric aroylenedibenzimidazoles with the following structures (VI) is also formed by the reaction of o-phenylenediamine with the dianhydride of diphenyl ether 3,3',4,4'-tetracarboxylic acid:



The isomeric 1,2,4,5-(2-tetrabenzazolyl) benzenes and 3,3',4,4'-(2-tetrabenzazolyl)diphenyl ethers, respectively, were obtained in high yields as a result of the reaction of V and VI with o-phenylenediamine, o-aminophenol, and o-aminothiophenol in polyphosphoric acid at 140-200°C.

It should be noted that, although the formation of a mixture of stereoisomers is also possible for VIII, IX, XI, and XII, judging from the rather sharp melting point, it can be assumed that one isomer predominates in the mixture. Compounds XIII-XIX were obtained by the reaction of I with tetrafunctional reagents – bis(o-phenylenediamine), bis(o-aminophenols), and bis(o-aminothiophenols).

Compounds II-IV and VII-XIX are crystalline substances with high melting points and are soluble in amide solvents, tetrachloroethane, and nitrobenzene. When R = CH_2 (XV, XVIII) and R = O (XIV, XVII, XIX) bridging groups are present, the compounds are also soluble in ethanol.



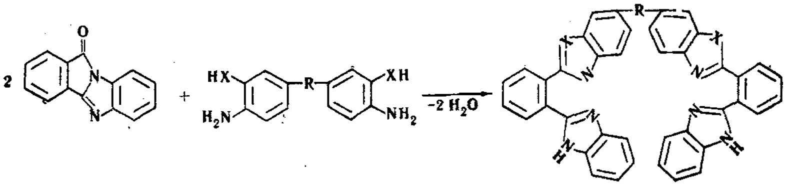
VII-IX

X-XII

VII X=NH; VIII X=S; IX X=O; X X=NH; XI X=S; XII X=O

Solutions of II-IV and VII-XIX in concentrated sulfuric acid and amide solvents have intense fluorescence (from blue to yellow-green) in UV light. The IR spectra of all of the compounds contain an absorption band at 1620-1630 cm^{-1}, which characterizes the vibrations of the benzazole ring [5]; this band appears as a shoulder for X, XI, and XII. The IR spectra of compounds that contain benzoxazole rings have distinct absorption at 1040 cm^{-1}, which can be ascribed to vibrations of these rings [6].

The electronic spectra of a number of heteroaromatic compounds have recently been investigated, and various authors have drawn contradictory conclusions regarding the nature of the conjugation in these compounds on the basis of these spectra.



XIII R=—, X=NH; XIV R=O, X=NH; XV R=CH_2, X=NH; XVI R=—, X=S*;
XVII R=O, X=S*; XVIII R=CH_2, X=O*; XIX R=O, X=O*

While Shopov and Popov assumed that the ether oxygen in the indoloquinoxaline molecule does not disrupt the conjugation system, Hergenrother and Kiyohara [8] offer proof to the contrary in the case of quinoxalines.

Our study of the electronic spectra of a number of benzazoles and dibenzazoles that do not contain bridging groups between the benzazole rings but do contain an ether oxygen and a methylene group between them demonstrated that the spectral data are absolutely inadequate for unambiguous conclusions regarding the presence or absence of conjugation in the system, especially with respect to its nature.

On the basis of the identical character of the spectra obtained (Fig. 1), one can only conclude that the interaction between the benzimidazole rings in XIII-XV is approximately the same, i.e., that the presence of bridging groups (O or CH_2) in the molecule does not have a substantial effect on this interaction. It is possible that the conjugation in XIII is weakened as a result of the noncoplanarity of the ring in the benzidine system, while conjugation in XIV and XV is disrupted by the bridging groups.

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* 3,3'-Diamino-4,4'-dihydroxydiphenyl ether and 3,3'-diamino-4,4'-diphenylmethane were used in the synthesis of XIX and XVIII, while 3,3'-dimercapto-4,4'-diaminodiphenyl ether and 3,3'-dimercapto-4,4'-diaminodiphenyl were used in the synthesis of XVII and XVI.

TABLE 1. Chief Characteristics of the Synthesized Benzazoles

Compound	Mp, °C	Empirical formula	Found, %				Calc., %				UV spectra,[a] λ_{max}, nm (log ε)
			C	H	N	S	C	H	N	S	
I	212—214[4]	$C_{14}H_8N_2O$	—	—	—	—	—	—	—	—	210 пл. (4,39); 245 (4,46); 265 (2,25); 346 (3,66)
II	440(dec.)[4]	$C_{20}H_{14}N_4$	—	—	—	—	—	—	—	—	233 (4,44); 282 (4,38); 303 (4,35)
III	240—241	$C_{20}H_{13}N_3O$	77,25	4,36	13,85	—	77,15	4,21	13,50	—	229 (4,41); 249 sh (4,17); 281 (4,32); 318 (4,45)
IV	216—217	$C_{20}H_{13}N_3S$	73,06	4,08	12,73	9,88	73,37	4,00	12,83	9,80	243 (4,54); 298 (4,46); 322 (4,50)
V	368—375	$C_{22}H_{10}N_4O_2$	72,84	2,82	15,22	—	72,92	2,78	15,46	—	209 sh (4,74); 237 (4,44); 270 (4,27); 277 (4,26); 326 (4,30)
VI	265—274	$C_{28}H_{14}N_4O_3$	73,83	3,01	12,31	—	74,00	3,11	12,33	—	223 (4,61); 254 (4,67); 273 (4,72); 295 (4,56); 352 (4,16)
VII	>450[9]	$C_{34}H_{22}N_8$	—	—	—	—	—	—	—	—	208 (4,81); 245 (4,41); 261 (4,23); 317 (4,62); 357 (4,64)
VIII	402—404	$C_{34}H_{20}N_6S_2$	70,46	3,50	14,40	10,98	70,81	3,50	14,57	11,12	212 (7,74); 247 (4,35); 321 (4,50); 359 (4,56)
IX	405—407	$C_{34}H_{20}N_6O_2$	74,55	3,68	15,33	—	74,99	3,70	15,43	—	212 (2,56); 243 (4,27); 270 (4,19); 320 (4,35); 380 (4,50)
X	392—394	$C_{40}H_{26}N_8O$	75,48	4,20	17,47	—	75,69	4,13	17,66	—	235 (4,62); 290 (4,72); 316 (4,63)
XI	285—292	$C_{40}H_{24}N_6OS_2$	71,72	3,70	12,37	9,51	71,83	3,62	12,57	9,59	245 (4,65); 296 (4,79); 338 (4,82)
XII	271—276	$C_{40}H_{24}N_6O_3$	75,45	3,82	13,17	—	75,46	3,80	13,20	—	240 (4,30); 296 (4,42); 340 (4,47)
XIII	402—404	$C_{40}H_{26}N_8$	77,70	4,30	18,19	—	77,65	4,24	18,11	—	233 (4,61); 285 (4,47); 316 (4,55)
XIV	404—405	$C_{40}H_{26}N_8O$	75,65	4,08	17,37	—	75,69	4,13	17,66	—	243 (4,75); 298 (4,61); 320 (4,64)
XV	382—384	$C_{41}H_{28}N_8$	78,09	4,41	17,71	—	77,83	4,46	17,71	—	243 (4,75); 293 (4,67); 325 (4,67)
XVI	400—402	$C_{40}H_{24}N_6S_2$	73,55	3,45	12,92	9,59	73,59	3,71	12,88	9,82	216 (4,90); 272 (4,65); 355 (4,63)
XVII	377—380	$C_{40}H_{24}N_6OS_2$	71,73	3,68	12,61	9,58	71,83	3,62	12,57	9,59	225 (4,77); 280 (4,47); 298 (4,46); 337 (4,49)
XVIII	277,5—280,5	$C_{41}H_{26}N_6O_2$	77,07	4,10	13,24	—	77,59	4,13	13,24	—	231 (4,59); 255 (4,34); 282 (4,49); 323 (4,61)
XIX	279—281	$C_{40}H_{24}N_6O_3$	75,72	3,91	13,42	—	75,46	3,80	13,20	—	226 (4,75); 278 (4,60); 326 (4,66)

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[a] Recorded from solutions in concentrated H_2SO_4.

In any case, one can state that, if there is an interaction between the rings in the benzidine structure, the ether bond and the methylene group do not disrupt it, and their contribution to this interaction is approximately the same (compare with the spectrum of II). A bathochromic shift in the electronic spectra of various benzazoles of similar structure is observed for benzoxazoles and benzothiazoles as compared with benzimidazoles, which is apparently associated with the nature of the heterorings themselves.

EXPERIMENTAL

Terephthaloylene-2,5-dibenzimidazole (V). A mixture of 2.7 g (25 mmole) of o-phenylenediamine and 2.7 g (12.4 mmole) of pyromellitic dianhydride in hydrochloric acid solution (25 ml of deoxygenated water and 4.5 ml of concentrated hydrochloric acid) was refluxed with stirring under argon for 3 h. Water was added to the resulting yellow suspension, and the solid was removed by filtration and washed with water until chloride ions were no longer present in the solid. The residue was dried at 100-110°C and cyclized at 325-350° (1-2 mm). Compound V was obtained in 25% yield as a yellow-orange solid with mp 368-375° (mp 373-378° [9]) (see Table 1).

Bis(1,2-benzoylenebenzimidazole) Ether (VI). A 31 g (0.1 mole) sample of diphenyl ether 3,3',4,4'-tetracarboxylic acid dianhydride (recrystallized from anisole) and 21.6 g (0.2 mole) of o-phenylenediamine were suspended in 130 ml of nitrobenzene, and the suspension was heated under argon at 170 and 220° for 5 h at each temperature. The water liberated during the reaction was vented through a glass tube. The reaction mass was cooled, and the resulting solid was removed by filtration, washed with ether, and combined with the precipitate obtained when the nitrobenzene filtrate was poured into ether. The product was heated gradually in vacuo (15-20 mm) to 220° and then for 3 h at the same temperature at 1-2 mm, after which it was crystallized from dimethylformamide (DMF). Sublimation at 230-250° (10^{-3} mm) gave 25% of bright-yellow crystals of VI with mp 265-274°.

Known methods were used to synthesize 3,3',4,4'-tetraaminodiphenylmethane [10] with mp 140-141° (after three recrystallizations from ethanol and activated charcoal) and 3,3'-diamino-4,4'-dihydroxydiphenylmethane [11].

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Cleavage of Aroylenebenzimidazoles in Polyphosphoric Acid. Stoichiometric amounts of the starting substances in polyphosphoric acid (10-fold quantity by weight) were stirred thoroughly under argon at room temperature until a homogeneous mixture was obtained. The mixture was then also heated under argon at 140-200° for 5-10 h. It was then cooled to room temperature and poured into ice water. The mixture was then neutralized with 5% $NaHCO_3$ solution and allowed to stand overnight. The precipitate was removed by filtration, washed with water, and reprecipitated from DMF solution by the addition of water, after which it was crystallized twice from DMF-water. The product was then vacuum sublimed at 10^{-2}-10^{-3} mm at a temperature close to the melting point of the sample.

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