SYNTHESIS AND INVESTIGATION OF N-PHENYL-SUBSTITUTED DIBENZIMIDAZOLES

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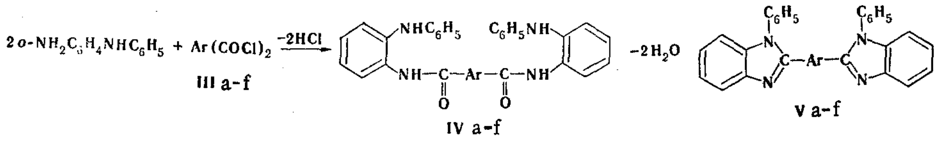
o-Phenylaminoamides with different structures were obtained by reaction of N-phenyl-substituted mono- or bis(o-phenylenediamines) with aromatic carboxylic acid chlorides. The corresponding N-phenylbenzimidazoles were obtained by cyclodehydration of the o-phenylaminoamides. The dependence between the structure and thermal characteristics of the synthesized compounds was studied.

It has been shown [1, 2] that poly(N-phenyl)benzimidazoles obtained under the conditions of the Marvel reaction by reaction of N,N'-diphenyl-substituted bis(o-phenylenediamines) with diphenyl esters of dicarboxylic acid in a melt are characterized by high thermal stability and satisfactory solubility in organic solvents. However, the polymers obtained by this method have molecular weights that are too low, and this hinders the manufacture of articles with high strength properties from them. To eliminate this deficiency of poly(N-phenyl)benzimidazoles, we undertook a study of the possibility of obtaining these polymers by two-step polycyclization, i.e., by carrying out low-temperature polycondensation in a solution of dicarboxylic acid dichlorides with N,N'-diphenyl-substituted bis(o-phenylenediamines) in the first step with subsequent cyclodehydration of the resulting polymers.

To determine the optimum conditions for the synthesis of the polymers and to establish their structure, we studied the conditions for the synthesis of model compounds and synthesized a number of previously undescribed bis(o-phenylaminoamides) and bis(N-phenylbenzimidazoles). In addition, we made a preliminary estimate of the dependence of the thermal stability of N-phenylbenzimidazoles on their structure.

A study of the conditions for the synthesis of o-phenylaminoamides demonstrated that it is most expedient to use low-temperature condensation in N,N-dimethylacetamide (DMA) or N-methylpyrrolidone to obtain these compounds. The o-phenylaminoamides were cyclized to N-phenylbenzimidazoles by thermal cyclodehydration in vacuo above 250° or by catalytic cyclization in the presence of HCl.

In contrast to the method described in the literature [3], the simplest model compounds – N-phenyl-N'-benzoyl-o-phenylenediamine (I) and 1,2-diphenylbenzimidazole (II) – were obtained in 90-95% yield by reaction of o-aminodiphenylamine with benzoyl chloride in DMA and subsequent thermal cyclization of the reaction product. An investigation of the thermodynamics of the cyclodehydration of I [4] demonstrated that reaction I → II is thermodynamically permissible even at 400.6°K but proceeds with an appreciable rate only above 500°K.



III–V a, Ar = $1,4\text{-}C_6H_4$; b Ar = $1,3\text{-}C_6H_4$; c Ar = $4,4'\text{-}(C_6H_4)_2$; d Ar = $2,6\text{-}C_{10}H_6$;
e Ar = $4,4'\text{-}C_6H_4OC_6H_4$; f Ar = $4,4'\text{-}C_6H_4SO_2C_6H_4$

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TABLE 1. Characteristics of Arylamides IV and VII and Benzimidazole Derivatives V and VIII

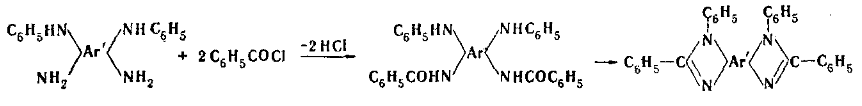
Comp.	mp, °C*	Empirical formula	Found, %			Calc., %			Thermal character.†		Yield, %
			C	H	N	C	H	N	T_1	T_2	
IVa	238—243	$C_{32}H_{26}N_4O_2$	77,3	5,4	11,1	77,0	5,2	11,2	—	—	90
IVb	230—235	$C_{32}H_{26}N_4O_2$	76,8	5,2	11,1	77,0	5,2	11,2	—	—	90
IVc	260—265	$C_{38}H_{30}N_4O_2$	79,3	5,2	9,9	79,4	5,2	9,7	—	—	92
IVd	253—258	$C_{36}H_{28}N_4O_2$	79,1	5,0	10,3	78,8	5,1	10,2	—	—	90
IVe	202—206	$C_{38}H_{30}N_4O_3$	77,1	5,0	9,5	77,2	5,0	9,4	—	—	85
IVf	240—244	$C_{38}H_{30}N_4SO_4$	71,6	4,6	8,6	71,4	4,7	8,7	—	—	70
VIIa	238—242	$C_{32}H_{26}N_4O_2$	77,2	5,2	11,4	77,0	5,2	11,2	—	—	80
VIIb	260—265	$C_{38}H_{30}N_4O_2$	79,5	5,2	9,9	79,4	5,2	9,7	—	—	85
VIIc	200—204	$C_{38}H_{30}N_4SO_4$	71,2	4,6	8,8	71,4	4,7	8,7	—	—	65
Va	291—292	$C_{32}H_{22}N_4$	83,3	4,6	12,1	83,0	4,7	12,1	355	470	80
Vb	247—248	$C_{32}H_{22}N_4$	83,2	4,9	12,4	83,0	4,7	12,1	350	460	80
Vc	308—309	$C_{38}H_{26}N_4$	84,4	4,7	10,2	84,7	4,8	10,4	340	510	75
Vd	290—291	$C_{36}H_{24}N_4$	83,3	4,6	10,8	84,3	4,7	10,9	340	480	75
Ve	235—237	$C_{38}H_{26}N_4O$	82,1	4,6	10,0	82,2	4,7	10,1	340	490	65
Vf	267—269	$C_{38}H_{26}N_4SO_2$	75,5	4,6	8,9	75,7	4,3	9,3	340	510	65
VIIIa	283—283	$C_{32}H_{22}N_4$	82,8	4,7	12,2	83,0	4,7	12,1	350	465	70
VIIIb	293—295	$C_{38}H_{26}N_4$	84,7	4,7	10,5	84,7	4,8	10,4	360	485	82
VIIIc	218—220	$C_{38}H_{26}N_4SO_2$	75,8	4,3	9,2	75,7	4,3	9,3	370	510	65

*Bis(o-phenylaminoamides) IV and VII do not have sharp melting points, since they cyclize with the production of water over the indicated temperature range.

† T_1 is the temperature of the onset of decomposition, and T_2 is the temperature of maximum rate of decomposition.

Like I and II, N,N'-arylenedicarbonylbis(2-aminodiphenylamines) (IVa-f) and 2,2'-arylenebis(1-phenylbenzimidazoles) (Va-f) were obtained from o-aminodiphenylamine and aromatic dicarboxylic acid dichlorides.

Bis(o-phenylaminoamides) (VIIa-c) and the products of their cyclization – 1,2,5,6-tetraphenylbenzo-[1,2-d;4,5-d']diimidazole (VIIIa) and 1,1',2,2'-tetraphenyldibenzimidazoles (VIIIb,c) – were obtained by benzoylation of N,N'-diphenylbis(o-phenylenediamines) (VIa-c) in DMA with subsequent thermal cyclodehydration of the reaction products in vacuo.

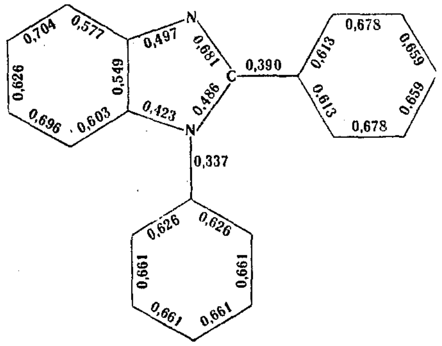


VI a-c VIIa-c VIII a-c

VI-VIII a $Ar' = 1,2,4,5\text{-}C_6H_2$; b $Ar' = 3,3',4,4'\text{-}(C_6H_3)_2$; c $Ar' = 3,3',4,4'\text{-}C_6H_3SO_2C_6H_3$

The structures of the synthesized compounds were proved by IR spectroscopy. Absorption maxima at 3200-3400 cm^{-1} (NH group) and at 1520-1540 and 1635-1660 cm^{-1} (NHCO group) are observed in the IR spectrum of all of the o-phenylaminoamides. Absorption bands at 1620, 1600-1605, 1500-1510, 1460, 1420, 960-980, and 760-770 cm^{-1}, which were assigned to benzimidazole rings [5], and at 1380 cm^{-1}, which is characteristic for the tertiary nitrogen atom, are observed in the IR spectra of all of the N-phenylbenzimidazoles.

The thermal characteristics of the compounds obtained were studied by differential thermal analysis and thermogravimetric analysis. The investigation demonstrated that all of the bis(N-phenylbenzimidazoles) begin to decompose at 340-370°; the maximum rate of the destruction processes of these compounds are observed at 460-510°. According to the data obtained, the destruction of bis(N-phenylbenzimidazoles) is an exothermic process. It probably commences with destruction of the N-phenyl bond, as evidenced by the composition of the products of destruction of poly-N-phenylbenzimidazoles [6], in which the major product in the initial stages of the destruction is benzene. The molecular diagram of 1,2-diphenylbenzimidazole, which was obtained as a result of calculation of this compound by the LCAO MO method with the Hückel π-electron approximation, according to which the lowest bond order is observed for the phenyl-N bond, also indicates the same thing. Similar data were obtained in a calculation of N-phenylimidazole [7]. The results are in agreement with the previously expressed assumption of the lower conjugation between the benzimidazole ring and the phenyl groups in the 1 position as compared with the phenyl groups in the 2 position [8] (the calculation was carried out with neglect of the coplanarity of the phenyl and benzimidazole rings). The principal properties of the synthesized o-phenylaminoamides and N-phenylbenzimidazoles are presented in Table 1.



EXPERIMENTAL

The aromatic dicarboxylic acid dichlorides (IIa-f) were obtained by treatment of the appropriate acids with thionyl chloride in the presence of catalytic amounts of pyridine. After the excess thionyl chloride was removed by distillation, the dichlorides were purified by recrystallization from inert anhydrous solvents or by distillation. The dichlorides had the melting points indicated in [9-14].

1,5-Diamino-2,4-dianilinobenzene. This compound was obtained in 70% yield by the method in [1] and had mp 215° (alcohol, mp 210-211° [1]).

3,3'-Diamino-4,4'-dianilinodiphenyl. This compound was obtained in 91% yield by the method in [14] and had mp 206-207° (alcohol, mp 203.5-204° [15]).

3,3'-Diamino-4,4'-dianilinodiphenyl Sulfone. This compound was obtained in 68% yield by the method in [16] and had mp 186° (alcohol).

o-Phenylaminoamides (I, IVa-f, and VIIa-c, Table 1). A 0.01-mole sample of the acid chloride was added gradually with stirring at −10° to a solution of 0.01 mole of amine in 30 ml of DMA. The mixture was then heated to room temperature, stirred for another 1 h, and poured into 200 ml of distilled water. The resulting powdery o-phenylaminoamides were removed by filtration, washed thoroughly with water, and recrystallized from DMF−water.

N-Phenylbenzylimidazoles (V and VIII, Table 1). These compounds were obtained by both thermal and chemical cyclodehydration of arylamides IV and VII. The thermal cyclodehydration was accomplished by heating IV and VII in condensation test tubes in vacuo (1 mm) at 260-270° for 6 h. The products were purified by vacuum sublimation (1 mm) at 280-300°. Chemical cyclodehydration was accomplished by refluxing IV and VII in alcohol in the presence of a catalytic amount of HCl until these compounds had dissolved completely. The resulting solution was neutralized with ammonium hydroxide, and the precipitated V or VIII was removed by filtration, washed thoroughly with hot distilled water until the washings gave a negative reaction for chlorine, and recrystallized from DMF−water. The thus-obtained N-phenylbenzimidazoles were identical to the thermal cyclodehydration products.

The thermal characteristics of the N-phenylbenzimidazoles were determined with a Derivatograph in air at a temperature-rise rate of 4.5°C/min.

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LITERATURE CITED

1. H. Vogel and C. S. Marvel, J. Polym. Sci., A-1, 1531 (1963).
2. V. V. Korshak, G. M. Tseitlin, G. M. Cherkasova, A. L. Rusanov, and N. A. Berezkina, Vysokomol. Soedin., A11, 35 (1969).
3. H. Wolff, Ann., 394, 66 (1912).
4. N. V. Karyakin, I. B. Rabinovich, V. V. Korshak, A. L. Rusanov, D. S. Tugushi, A. N. Mochalov, and V. N. Sapozhnikov, Summaries of Papers Presented at the Conference on the Thermal Chemistry of Heteroorganic Compounds and Polymers [in Russian], Gor'kii (1970), p. 53.
5. K. J. Morgan, J. Chem. Soc., 2343 (1961).
6. V. V. Rodé, N. M. Kotsoeva, G. M. Cherkasova, D. S. Tugushi, G. M. Tseitlin, A. L. Rusanov, and V. V. Korshak, Vysokomol. Soedin., A12, 1854 (1970).
7. V. I. Minkin, A. F. Pozharskii, and Yu. A. Ostroumov, Khim. Geterotsikl. Soedin., 551 (1966).

8. L. N. Pushkina, S. A. Mazalov, and I. Ya. Postovskii, Zh. Obshch. Khim., 32, 2624 (1962).
9. W. Profft, Chem. Techn., 5, 503 (1953).
10. W. Schneider and H. Goltz, Arch. Pharm., 294, 506 (1961).
11. T. S. Work, J. Chem. Soc., 1315 (1940).
12. J. Starr, J. Polym., Sci., A4, 3041 (1966).
13. V. M. Ivanova, S. A. Kemleva, Z. N. Seina, É. G. Kaminskaya, S. S. Gitis, and A. Ya. Kaminskii, Zh. Organ. Khim., 3, 146 (1967).
14. M. Adamek and J. Novak, Sbornik Vederckych Prei Lyscla, Skola Chem. Technol. Pardubice, No. 2, 87 (1960).
15. G. I. Braz, I. E. Kardash, V. V. Kopylov, A. F. Oleinik, G. G. Rozantsev, A. N. Prabednikov, and A. Ya. Yakubovich, Khim. Geterotsikl. Soedin., 339 (1968).
16. F. Ullmann and J. Korselt, Ber., 40, 645 (1907).