3. The stereospecificity of the reaction is evidently greatly influenced by the formation of associates between the ground states of the enone and alkyne.

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SYNTHESIS OF TETRACARBOXYLIC ACID DIANHYDRIDES BY AROMATIZATION OF ADDUCTS OF BIS-FURAN COMPOUNDS WITH MALEIC ANHYDRIDE

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Aromatic tetracarboxylic acid dianhydrides are used in the synthesis of thermostable polyimides and poly(aroylene-bis-benzimidazoles) and dyes, and as hardeners for epoxy resins. Hitherto, they have been prepared mainly by oxidation of alkyl-substituted aromatic compounds. The disadvantage of this method is that the synthesis and purification of the starting materials is complicated [1].

In the present communication we will discuss a new general method for synthesizing aromatic tetracarboxylic acid dianhydrides by dehydrating the adducts of bis-furan compounds with maleic anhydride (MA) according to the reaction scheme [2] shown on the following page.

The availability of bis-furans with different groupings between the furan rings (R) [3] makes it possible to vary widely the structure of the dianhydride molecule.

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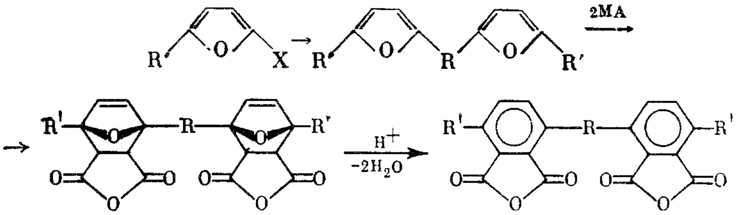
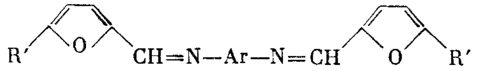


R' = H or aryl; X = functional group

Since the dianhydrides were intended for the synthesis of thermostable polymers, we selected the following bis-furans as starting materials in accordance with known relationships between the structure and properties of such polymers [4, 5]: N, N'-bis(5-R'-furfurylidene)-diaminoarylenes, bis(α-furyl)arylenes, bisfurfuryl esters of aromatic dicarboxylic acids, and cyclic acetals of furfural and tetramethylol derivatives.

The N,N'-bis(5-R'-furfurylidene)diaminoarylenes (bis-azomethines) were prepared by condensing furfural or 5-phenylfurfural with aromatic diamines. The reactions were carried out either by mixing the reactants in vacuo [6] (the water formed being removed due to the heat of reaction), or in benzene with azeotropic distillation of the water. The latter method is suitable for synthesizing large batches of product (> 20 g) and for synthesizing bis-azomethines derived from phenylfurfural [7]. These methods gave (Ia-i) and (IIa-c) in yields of up to 85% (Table 1).



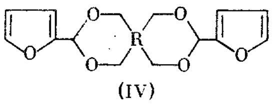
(Ia — i), (IIa — c)

(Ia-i): R' = H, Ar = p- and m-phenyl (a,b), 4,4'-diphenyl (c), 3,3'-dimethyl-4,4'-diphenylene (d), 1,4-naphthylene (e), 4,4'-$C_6H_4XC_6H_4$, where X = O (f), SO_2 (g), CH_2 (h), and CH_2CH_2 (i); (IIa-c): R' = C_6H_5, Ar = p-phenylene (a), 4,4'-diphenylene (b), 4,4'-oxydiphenylene (c)

The main complication in the synthesis of the bis-azomethines is their purification to remove resinous impurities. According to TLC data, pure (I) and (II) are obtained by vacuum filtration of saturated solutions of (I) and (II) in benzene or cyclohexane through a bed of Al_2O_3 in an inert atmosphere. Pure (I) and (II) are comparatively stable substances and can be stored in the dark even in the presence of atmospheric oxygen. Proton magnetic resonance shows that the azomethine system of (Ia) is destroyed in ∿20 min by CF_3COOH, but is stable to the action of CD_3COOD and is also stable under the reaction conditions indicated below. The preparation of 5-phenylfurfural was carried out under modified Meerwein reaction conditions [7] and by formylation of α-phenylfuran [11].

Several methods were tested for the synthesis of p-bis(α-furyl)benzene (IIIa) and 4,4'-bis(α-furyl)biphenyl (IIIb). Arylation of furan by decomposition of aqueous bis-diazonium chlorides in excess furan in the presence of NaOH or by decomposition of solid diazo salts (stabilized by naphthalenesulfonic acids) in excess furan in the presence of AcONa/Ac_2O [12] leads mainly to polymeric products. Compounds (IIIa, b) were prepared in 6-12% yield by decomposing solid bis-diazonium acetates in furan containing AcONa [13], and also using N-nitroso-N-acetylaryldiamines. Nitrosation of N,N'-diacetylbenzidine at 0° with excess molten nitrosylsulfuric acid gives the N,N'-bisnitroso derivative in a yield of ∿100%. Decomposition of the latter in boiling furan gives (III) in a yield of 50-60%. Analysis of the reaction mixture by TLC showed five other products in amounts of 0.1-4% and ∿20% of a polymeric fraction.

The bis-spirans (IVa, b) were prepared by condensing furfural with pentaerythritol [9] or 2,2,5,5-tetramethylolcyclopentanone in the presence of $ZnCl_2$



(IV)

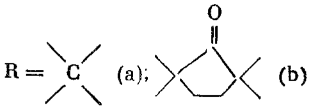


TABLE 1. Bis-furan Compounds

Bis-furan	Yield, %	mp, °C (from benzene)	Empirical formula	Found/Calculated, %			IR spectrum, cm^{-1}					UV spectrum (in DMF), λ_{max}, nm (log ε)
							furan		$\nu_{C=N}$	other bands		
				C	H	N	γ_{CH}	δ_{CH}				
(Ia)	74	164–165 cf. [8]	–	–	–	–	883	1070	1635	–		290 (4,35) 360 (4,17)
(Ib)	70	144,5–145	$C_{16}H_{12}N_2O_2$	72,4/72,1	4,71/4,58	10,4/10,6	887	1070	1637	–		–
(Ic)	84	232–233 cf. [6]	–	–	–	–	883	1070	1630	–		295 (4,48) 365 (4,72)
(Id)	78	191–192 cf. [6]	–	–	–	–	887	1075	1635	δ_{CH_3}	1380	295 (4,41) 370 (4,77)
(Ie)	62	136–138	$C_{20}H_{14}N_2O_2$	76,8/76,5	4,72/4,46	8,17/8,93	884	1080	1617	–		295 (4,30) 400 (4,50)
(If)	81	137–138 (cyclohexane)	$C_{22}H_{16}N_2O_3$	74,1/74,1	4,67/4,53	7,9/7,86	887	1080	1632	ν_{ArOAr}	1252	290 (4,46) 345 (4,46)
(Ig)	67	177–178,5	$C_{22}H_{16}N_2O_4S$	65,8/65,3	4,25/3,99	6,75/6,93	885	1090	1640	ν_{SO_2}	1310 1160	300H (4,35) 320 (4,42)
(Ih)	74	163–164	$C_{23}H_{18}N_2O_2$	77,9/77,9	5,16/5,08	7,45/7,90	885	1080	1635	ν_{CH_2}	2940 2865	–
(Ii)	78	159,5–160,0	$C_{24}H_{20}N_2O_2$	78,2/78,3	5,61/5,46	7,73/7,60	884	1075	1635	–		290 (4,57) 333 (4,42)
(IIa)	82	148–149	$C_{28}H_{20}N_2O_2$	80,2/80,7	5,02/4,84	6,60/6,75	930 962		1612	–		–
(IIb)	74	201,5–202,0	$C_{34}H_{24}N_2O_2$	83,2/83,1	4,88/4,80	5,79/5,65	930 975		1605	–		305 (4,61) 365 (4,76)
(IIc)	78,5	153–153,5	$C_{34}H_{24}N_2O_3$	81,0/81,4	4,62/4,76	5,63/5,52	925 960		1617	ν_{ArOAr}	1250	–
(IIIa)	12	87–89	$C_{14}H_{10}O_2$	79,3/80,0	4,31/4,76	–	886	1070	–	ν_{CH}	3106 3035	–
(IIIb)	62	106,5–107,5	$C_{20}H_{14}O_2$	83,6/83,9	5,44/4,90	–	890	1085	–	–		320 (4,69)
(IVa)	75	164,5–165,0 cf. [9]	–	–	–	–	885	1075	–	–		–
(IVb)	28	184–187 (acetone)	$C_{19}H_{20}O_7$	63,0/63,3	5,78/5,58	–	883	1082	–	Acetal	1178 1143	–
(Va)	73	77–78 cf. [10]	–	–	–	–	885	1067	–	ν_{CO}	1725	–
(Vb)	63	70–70,5 (pet. ether)	$C_{18}H_{14}O_6$	66,5/66,2	4,41/4,32	–	887	1075	–	ν_{CO}	1725	–

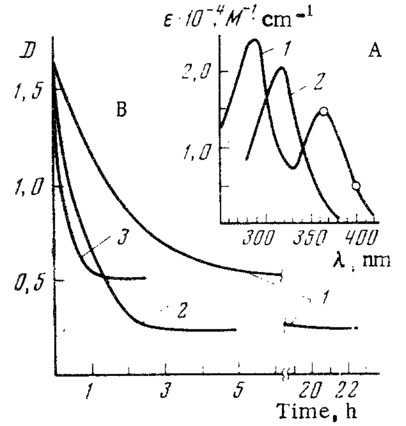


Fig. 1

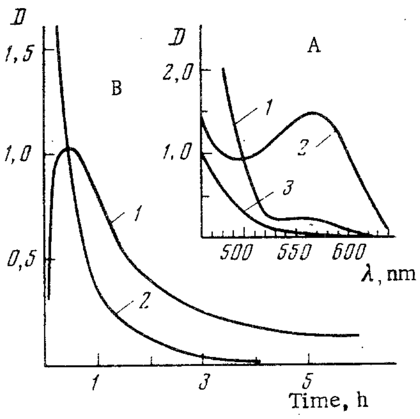


Fig. 2

Fig. 1. A) Electronic spectra of bisfurfurylidenebenzidine (Ic) (1) and its bis-adduct with MA (2). B) Variation in optical density during reaction of (Ic) with MA at a (Ic) concentration of $1 \cdot 10^{-4}$ M and $[MA] = 3 \cdot 10^{-4}$ M: 1) 365 nm, THF, 30°; 2) 365 nm, THF, 50°; 3) 400 nm, DMF, 52.26°.

Fig. 2. A) Charge-transfer band in the reaction of bis(5-phenylfurfurylidene)benzidine (IIb) with MA at the start of reaction (1), at the point of maximum intensity (2), and at the end of reaction (3) (DMF, ∿25°, (IIb) concentration $5 \cdot 10^{-2}$ M, $[MA] = 0.1$ M). B) Variation in optical density of charge-transfer band (570 nm, DMF, 52.26°) during reaction of (IIb) with MA in a ratio of 1:10 (1) and 1:100 (2).

Compounds (IVa) and the previously unknown (IVb) were obtained in yields of up to 75%.

The bisfurfuryl esters of terephthalic and isophthalic acid (Va, b) are formed by transesterification of the corresponding dimethyl esters with sodium furfurylate while azeotropically distilling off the lower alcohol [10]. The structure of the bis-furan products was confirmed by analysis of their UV, IR, and PMR spectra (see Table 1)

The cycloaddition of MA to furans is a classic example of the Diels—Alder reaction, but the synthesis of bis-adducts has not been described hitherto. The reaction itself and the structure of the bis-adducts was studied mainly for bis-azomethines (I) and (II).

Since the addition of MA to furans is an equilibrium process giving mixtures containing 85-92% adduct [14], we increased the yield of the bis-adducts by using a solvent which readily dissolves the bis-azomethine but is a poor solvent for the bis-adduct. In most cases the most suitable solvent was THF, which dissolves up to 30% of the bis-azomethine and ∿0.5% of the bis-adduct (UV spectra); this was necessary to prevent the mono-adduct from separating out of the solution. In THF the reaction goes at a fairly high rate at ∿20° and is completed in 1-2 h at ∿60°. The yield of adduct in all cases was close to 90-95%.

The course of the cycloaddition reaction was studied on the basis of the variation in the concentration of the bis-diene by following the variation in the optical density of the long-wave band of the azomethine system in (I) and (II) ($\lambda = 320$–370 nm). Figure 1 shows the UV spectra of (Ic) and the corresponding bis-adduct, and also the variation in optical density at $\lambda = 365$ and 400 nm. Analysis of the curves shows that the bis-diene is converted practically quantitatively into the bis-adduct in THF (the residual absorption is due to the adduct), while the reaction reaches an equilibrium state with a 35-40% content of the bis-diene in DMF, which readily dissolves both components of the mixture. In benzene, the bis-adduct is insoluble and the mono-adduct is precipitated in a yield of ∿50%. When solutions of the bis-azomethine and MA in THF or DMF are mixed, the mixture rapidly becomes colored bright crimson due to a π complex formed by the addends. Complex formation accompanied by partial or complete charge transfer has also been observed in other Diels—Alder reactions [15]. The absorption band of the charge-transfer complex between MA and (I) appears in the

530-540 nm region, and that of the complex between MA and (II) appears at 540-570 nm. Figure 2 shows the UV spectra of the reaction mixture formed by (IIb) and MA in the 450-650 nm region at different times during the reaction, and also the variation in the intensity of the charge-transfer band in the course of reactions with different diene: dienophile ratios. Obviously, increases in the dienophile concentration increase the rate of cycloaddition, but not in proportion to the increase in concentration; this is additional evidence for the formation of a charge-transfer complex in this reaction. At the same time, it is not necessary to use a large excess of dienophile to obtain a high yield of the bis-adduct. In the case of (Ic), the maximum yield of bis-adduct is obtained at a MA:(Ic) ratio of 2.1:1.

Maleic anhydride can add on to bis-azomethines in several ways, viz., by normal cycloaddition across the 2,5 positions of the furan rings, by [4 + 2] cycloaddition with the participation of the exocyclic C = N bond, by "indirect substitutive addition," or transacylation of the bis-azomethine to form HOOCCH = CHCONHRNHCOCH = CHCOOH. We have shown by UV, IR and PMR spectroscopy and by chemical methods that (I) and (II) form [4 + 2] bis-adducts only via the furan rings (data on the structure of the adducts will be reported in a subsequent article).

The bis-adducts derived from (I) and (II) are stable compounds. When kept in 0.1 N HCl, the acid numbers of the adducts remain unchanged for 480 h, as they do after repeated reprecipitation from dilute solution in KOH in 0.1 N HCl.* The adducts quantitatively split off two molecules of MA in vacuo at ∿110°, but in air the retrodiene reaction is complicated by oxidation of the bis-azomethine.

The cyclic acetals (IVa, b) dissolve slowly and to a small extent (5-7%) in THF, but the addition of MA to a suspension of (IV) in THF leads, after 4-5 h at 25°, to the formation of a transparent solution containing 15-20% of the diene, from which the bis-adduct is precipitated in a yield of up to 70% after 20-30 h at 25°. Obviously, the complex of the addends in more soluble in THF than the diene of the product. The adducts derived from (IVa, b) are unstable in the solid state, but are stable even to the action of AcOH at 60-80° in solution or suspension.

The furan rings in the bisfurfuryl esters (Va, b) display less diene activity than those in (I), (II) or (IV): the adduct yield is not more than 40% in THF at 25°, but the corresponding bis-adducts are formed in 60-65% yield after 6-8 h at 60°, although the adducts are readily soluble in THF. The bis-adducts derived from (IV) and (V) have similar stabilities.

As would be expected, the bis(α-furyl)arylenes (III) are the least active dienes of the bis-furans studied. Treatment of the low-molecular fraction formed by decomposition of the bis-diazo salt in furan with MA, or heating (III) with MA in an autoclave (THF, 100-120°), gives a 15-20% yield of the bis-adducts.

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*As in Russian original.

TABLE 2. Adducts of Bis-furans with Maleic Anhydride

Diene	Adduct yield, %	Acid No. found/calculated, mg KOH/g	Empirical formula	Found/Calculated*, %		
				C	H	N
(Ia)	92	453/452	$C_{24}H_{20}N_2O_{10}$	57,8/58,1	4.24/4,06	5.84/5.64
(Ib)	82	450/452	$C_{24}H_{20}N_2O_{10}$	57,6/58.1	4,12/4.06	5.81/5.64
(Ic)	88	375/374	$C_{30}H_{24}N_2O_{10}$	62,6/62.9	4.45/4,23	5,30/4,99
(Id)	92	370/368	$C_{32}H_{28}N_2O_{10}$	63,8/64,0	4.87/4,70	5,31/4,66
(Ie	84	408/410	$C_{28}H_{22}N_2O_{10}$	62,0/61.6	4,65/4,43	5,02/5.13
(If)	94	381/381	$C_{30}H_{24}N_2O_{11}$	65,5/65,2	3,48/3,65	5,32/5,07
(Ig)	67	346/350	$C_{30}H_{24}N_2O_{12}S$	56,5/56,6	3,78/3,80	4,11/4.40
(Ih)	90	362/365	$C_{31}H_{26}N_2O_{10}$	63.5/63,8	4,68/4,47	4,42/4.78
(Ii)	94	356/357	$C_{32}H_{28}N_2O_{10}$	63.8/64.2	4,55/4.69	4,80/4.67
(IIa)	84	346/346	$C_{36}H_{28}N_2O_{10}$	66,1/66.8	4,56/4.35	4,52/4.33
(IIb)	88	313/310	$C_{42}H_{32}N_2O_{10}$	70,4/69,7	4,61/4,46	3,72/3,87
(IIc)	89	300/303	$C_{42}H_{32}N_2O_{11}$	68,2/68.4	4.71/4.33	3,60/3,78
(IIIb)	16	410/414	$C_{28}H_{22}O_{10}$	65,4/64,9	4,01/4,25	–
(IVa)	68	430/428	$C_{23}H_{24}O_{14}$	52,6/52,8	4,44/4.61	–
(IVb)	74	380/384	$C_{27}H_{28}O_{15}$	54,7/54.8	4,92/4,76	–
(Va)	67	402/402	$C_{26}H_{22}O_{14}$	56,1/56.0	3.62/3.96	–
(Vb)	63	402/402	$C_{26}H_{22}O_{14}$	56,3/56,0	4,26/3,96	–

*Data quoted for tetra-acids.

TABLE 3. Aromatic Tetracarboxylic Acid Dianhydrides

Bis-furan	Product yield, %	Acid No. found/calculated, mg KOH/g	mp, °C (from AcOH)	Empirical formula	Found/Calculated, %		
					C	H	N
(Ia)	82	530/528	>360	$C_{24}H_{12}N_2O_6$	67.8/67.8	2.99/2.83	6,73/6.60
(Ic)	73	448/448	>360	$C_{30}H_{16}N_2O_6$	71.8/72.0	3,24/3.20	5,71/5,60
(Id)	89	427/424	>360	$C_{32}H_{20}N_2O_6$	72.4/72.7	3,83/3.79	5,18/5.28
(Ie)	64	469/473	>360	$C_{28}H_{14}N_2O_6$	70.7/70.9	3.20/2.91	–
(If)	85	428/434	337.5–338.5	$C_{30}H_{16}N_2O_7$	70.3/69.9	3,27/3.10	5,26/5.42
(Ii)	88	425/424	327–328	$C_{32}H_{20}N_2O_6$	73.0/72.6	3,74/3,85	5,15/5.30
(IIa)	93	388/388	247.5–249.5	$C_{36}H_{20}N_2O_6$	74.6/75.0	3,52/3,48	5,03/4.86
(IIb)	90	348/344	300 (decomp.)	$C_{42}H_{24}N_2O_6$	77.7/77.4	3.24/3.69	4,12/4.30
(IIc)	74	332/335	258–260	$C_{42}H_{24}N_2O_7$	76.0/75,5	3.42/3,61	3,98/4.18
(IIIa)	79	605/605	230 (subl.)	$C_{22}H_{10}O_6$	71.6/71.4	3,03/2,71	–
(IVa)	51	490/495	284 (decomp.)	$C_{23}H_{16}O_{10}$	61.3/61.0	3,51/3,40	–
(IVb)	64	443/443	242 (decomp.)	$C_{27}H_{20}O_{11}$	63.0/62.1	4,40/4.25	–
(Va)	56	457/460	316–317	$C_{26}H_{14}O_{10}$	64.2/64.1	3,18/2,98	–
(Vb)	59	458/460	288–289	$C_{26}H_{14}O_{10}$	64,6/64.1	2,74/2.98	–

It should be noted that their spectral data, acid numbers, and elementary analyses indicate the presence of free COOH groups in the bis-adducts, even when freshly sublimed MA and dry solvents are used. In view of this, the analysis of the adducts was carried out after converting them into the corresponding tetra-acids (Table 2).

The oxygen endo bridge in the furan adducts is thermodynamically stable, and thermolysis leads only to a retrodiene reaction with regeneration of the addends. In most cases, dehydration of the adducts to phthalic acids requires acid catalysis [14]. The catalysts used were orthophosphoric acid, sulfuric acid, hydrochloric and nitric acids (in admixture), P_2O_5, gaseous HCl and HBr, and other reagents.

The most suitable method for aromatizing the bis-adducts derived from (I), (II), and (III) is dehydration in conc. H_2SO_4 at temperatures between −30 and −10° followed by raising the temperature to 0-5°. The yield of the aromatic dianhydrides is 65-80%. The phenyl-substituted adducts derived from (II) are particularly easy to dehydrate. In this case the dianhydride yield reaches 90%. These bis-adducts can be aromatized by other methods, but with considerably reduced yields. The adducts containing acetal and ester groups [from (IV) and (V)] form aromatic dianhydrides only when treated gaseous HCl or HBr in glacial AcOH solution, the yield being up to 60%. Treatment with concentrated mineral acids gives only resinous substances. The characteristics of the aromatic dianhydrides obtained are given in Table 3.

One of the steps in the sysnthesis of polyheteroarylenes [16] is intramolecular dehydration, which proceeds most completely in polyphosphoric acid (PPA). The fact that the cyclization of prepolymers and the aromatization of bis-adducts are processes of the same type suggested that the bis-adducts could be used directly, instead of the aromatic dianhydrides, for the synthesis of polymers in PPA. Indeed, the bis-adducts derived from (I), (II), and (III) dehydrate smoothly in PPA at 25-50° to give 60-95% yields of the aromatic dianhydrides, and the polymers obtained from the bis-adducts in PPA have similar structures and properties to the polymers obtained from the aromatized bis-adducts. This method of dehydration makes it possible to simplify the general scheme for synthesizing the polymers by the method describe in [17].

The IR spectra of all of the aromatization products contain the doublet of bands characteristic of anhydrides at 1845 ± 5 and 1780 ± 15 cm^{-1} (C = O) and 1300 ± 20 cm^{-1} (anhydride C—O—C). The position of ν_{CO} is practically independent of the nature of R and, in accordance with the data in [18], the low-frequency band has the greater intensity. The number of anhydride groups in the aromatization products was determined from their acid numbers (100 ± 5% based on dianhydride) and by elementary analysis. The azomethine and ester groupings in the bis-adducts derived from (I), (II), and (V) are completely stable under the aromatization conditions, and the reaction mixture contains no carboxyl-containing compounds other than the aromatic dianhydrides. All of the characteristic bands for R in the IR spectra of the dianhydrides appear at approximately the same frequencies as in the corresponding bis-furan. In the case of the conversion of (I) or (II) to the bis-adduct and then to the dianhydride, valuable information about the structure of the products was obtained from their UV spectra. Thus, the azomethine system of (Ic) is characterized by two transitions with $\lambda = 295$ and 365 nm ($\varepsilon = 4.48$ and 4.72). This system is disrupted in the bis-adduct, the spectrum of which contains a single band with $\lambda = 328$ nm ($\varepsilon = 4.67$). Aromatization restores the azomethine chromophore, and the spectrum of the dianhydride shows two transitions with $\lambda = 300$ and 370 nm ($\varepsilon = 4.63$ and 4.2), the position and intensity of which correspond to the spectrum of the known dibenzalbenzidine [19].

Aromatization of the bis-adducts derived from (IV) is accompanied by partial cleavage of the acetal bonds, and, as well as the corresponding dianhydrides, lower-molecular anhydrides of indeterminate structure are detected in the reaction mixture.

EXPERIMENTAL

The IR spectra were recorded with a UR-20 instrument using KBr pellets. The UV spectra were recorded with a Specord UV-VIS instrument in THF or DMF solution. The PMR spectra were recorded with a Varian HA-100 instrument in DMSO-d_6 or hexachloroacetone. The acid numbers were determined by back titration using a Radiometer instrument with automatic recording of the titration curve, and melting points were determined on a Beotus stand.

N,N'-Bis(5-phenylfurfurylidene)-p-phenylenediamine (IIa). A mixture of 10.8 g (0.1 mole) of p-phenylenediamine, 56.4 g (0.3 mole) of 5-phenylfurfural, and 1.8 liters of benzene was boiled in an argon atmosphere until water ceased to separate in a Dean–Stark trap (∿2 h). The hot solution was filtered through a bed of Al_2O_3 in a stream of argon, half of the benzene was distilled off in vacuo, and the product was filtered off after cooling. The other compounds (I) and (II) were prepared similarly (see Table 1).

4,4'-Bis(α-furyl)biphenyl (IIIb). A solution of 3.26 g (0.01 mole) of N,N'-bisnitroso-N,N'-diacetylbenzidine in 125 ml (2 moles) of furan was boiled for 5 h. The unreacted furan was distilled off and the solid residue (2.5 g) applied to a column of neutral Al_2O_3 in THF solution. After eluting with a mixture of benzene and THF (20:1), the solvent was removed to give (IIIb).

3,11-Bis(α-furyl)-2,4,10,12-tetraoxadispiro[5,1,5,1]pentadecan-7-one (IVb). A mixture of 28.8 g (0.3 mole) of furfural and 20.4 g (0.1 mole) of 2,2,5,5-tetramethylolcyclopentanone was heated at 100-110° for 1.5 h in the presence of 2.7 g of anhydrous $ZnCl_2$. The mass solidifying after cooling was recrystallized from acetone.

N,N'-Bis(2,3-dicarboxy-1,4-oxo-1,2,3,4-tetrahydrobenzylidene)-p-phenylenediamine 2,3-Dianhydride. A solution of 26.43 g (0.1 mole) of (Ia) in 0.7 liter of boiling THF was treated with 20.6 g (0.21 mole) of MA. The solution rapidly became colored bright crimson, and the bis-adduct precipitated after 20 min. After 2 h, the solution became colorless and the bis-adduct was filtered off from the cooled solution in an argon atmosphere. The bis-adduct was washed with THF on the filter and dried at 25-40° in vacuo (see Table 2).

N,N'-Bis(2,3-dicarboxybenzylidene)-p-phenylenediamine 2,3-Dianhydride. While stirring intensively, 4.6 g (10 mmoles) of N,N'-bis(2,3-dicarboxy-1,4-oxo-1,2,3,4-tetrahydrobenzylidene)-p-phenylenediamine 2,3-dianhydride was added portionwise to conc. H_2SO_4 cooled to −20°. When dissolution of the bis-adduct was complete, the cooling was stopped. On reaching 0°, the mixture was poured onto ice, and the precipitate filtered off, washed with water, and dried. Recrystallization from AcOH and treatment (1 h) with boiling Ac_2O gave the aromatic dianhydride (see Table 3).

3,9-Bis(2,3-dicarboxyphenyl)-2,4,8,10-tetraoxaspiro[5,5]undecane 2,3-Dianhydride. A solution of 9.6 g (20 mmoles) of 3,9-bis(2,3-dicarboxy-1,4-oxo-5-cyclohexenyl)-2,4,8,10-tetraoxaspiro[5,5]undecane 2,3-dianhydride in 0.7 liter of AcOH saturated with HBr was slowly heated at 80-100° for 6 h in a continuous stream of HBr. The solvent was removed in vacuo. Recrystallization from Ac_2O gave the aromatic dianhydride.

N,N'-Bis(4-phenyl-2,3-dicarboxybenzylidene)benzidine 2,3-Dianhydride. A solution of 6.97 g (13 mmoles) of N,N'-bis(4-phenyl-1,4-oxo-2,3-dicarboxy-1,2,3,4-tetrahydrobenzylidene)-benzidine 2,3-dianhydride in 100 ml of PPA was stirred at 40°. After 6-8 h, the solution was poured into 1.5 liters of ice-water, and the precipitate washed with water and acetone, dried, and recrystallized from Ac_2O.

CONCLUSIONS

1. Dehydration (aromatization) of bis-adducts formed by Diels—Alder reaction between maleic anhydride and bisfuran compounds gives dianhydrides of aromatic tetracarboxylic acids with different structures, which are suitable for the preparation of thermostable polymers.

2. The nonaromatized bis-adducts can be used for the one-step preparation of polyimides and polyimidazopyrrolones in polyphosphoric acid, since they are aromatized under the polymer-synthesis conditions.

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