

Novel aromatic tetracarboxylic acid dianhydrides

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The Diels—Alder reactions of 4,4'-bis(2,4,5-triphenylcyclopentadienon-3-yl)benzophenone with carboxylic anhydrides containing multiple carbon—carbon bonds afforded novel tetracarboxylic dianhydrides.

Key words: 4,4'-bis(2,4,5-triphenylcyclopentadienon-3-yl)benzophenone, Fourier-IR spectroscopy, ¹H and ¹³C NMR spectra, Diels—Alder reaction, tetracarboxylic anhydrides.

Aromatic tetracarboxylic acid dianhydrides (ATD) are very important polyfunctional condensation monomers¹ used in the synthesis of polyimides,² polyarylenebenzoimidazoles,³ and other heterocyclic polymers. The main types of ATD are bis(phthalic anhydrides) (BPA)¹ and bis(naphthalic anhydrides) (BNA).^{1,4} Because the essential problem in the chemistry of polymers obtained from ATD is their processing, considerable attention is given to the elaboration of ATD having a particular structure that determines the enhanced solubility or thermoplasticity of ATD-based polymers. One of the most effective approaches to the solution of this problem is an increase in the number of phenyl substituents in ATD and, accordingly, in ATD-based polymers.^{5–8} Usually, this can be attained by the Diels—Alder reaction of bis(triphenylcyclopentadienonyl)arylenes with dicarboxylic anhydrides containing multiple carbon—carbon bonds.^{5–8}

In the present work, we synthesized novel BPA and BNA from 4,4'-bis(2,4,5-triphenylcyclopentadienon-3-yl)benzophenone (**1**) previously obtained by the reaction of 4,4'-bis(phenylglyoxalyl)benzophenone with 1,3-diphenylacetone⁹ (Scheme 1).

The reaction of compound **1** with a twofold molar amount of 4-phenylethynyl-1,8-naphthalic anhydride in boiling 1,2,4-trichlorobenzene results in 4,4'-bis[2,3,5,6-tetraphenyl-4-(4,5-dicarboxyphthal-1-yl)phenyl]benzophenone dianhydride (**2**) in 90% yield. The product obtained is a pale yellow amorphous substance, which is

well soluble in common organic solvents such as isopropyl alcohol, DMF, CHCl₃, THF, dioxane, etc. The reaction was monitored by following the disappearance of the IR signal at 1709 cm^{−1} corresponding to the cyclopentadienone C=O stretching vibrations (Fig. 1).

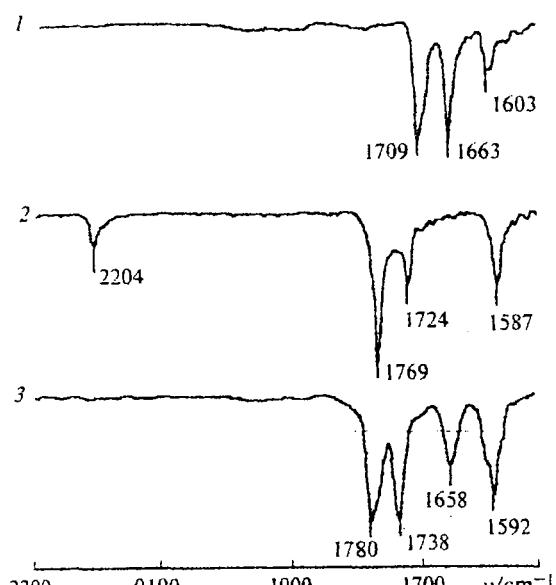
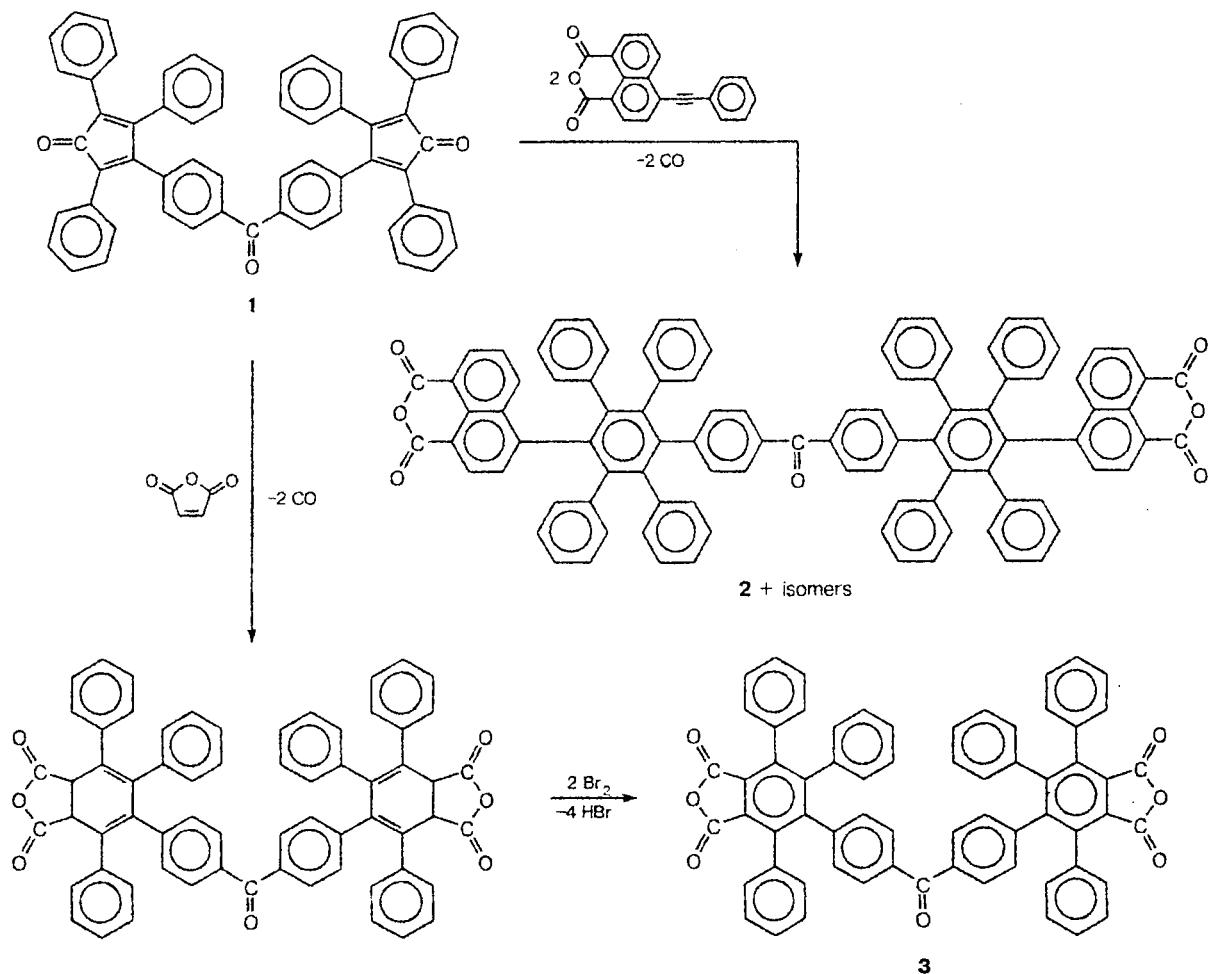


Fig. 1. IR spectra of (**1**) compound **1**, (**2**) 4-phenylethynyl-1,8-naphthalic anhydride, and (**3**) compound **2**.

Scheme 1



The composition and structure of the product were confirmed by data from elemental analysis and ^1H and ^{13}C NMR (see Experimental) and Fourier-IR spectroscopy (see Fig. 1). The IR spectrum of compound **2** exhibits an intense absorption band at 1658 cm^{-1} corresponding to the benzophenone $\text{C}=\text{O}$ stretching vibrations and intense bands at $1738\text{--}1780\text{ cm}^{-1}$ for the $\text{C}=\text{O}$ stretching vibrations of the naphthalic anhydride. The ^1H NMR spectrum of dianhydride **2** contains broad peaks at δ $6.5\text{--}8.5$. The broadening of the bands may be associated with the presence of different isomers. ^{13}C NMR spectroscopy gave stronger evidence of the structure of compound **2**. An important feature of the ^{13}C NMR spectra is the presence of low-field signals at δ 160.33 and 160.53 characteristic of two nonequivalent carbonyl groups of the anhydride. Signals at δ 196.19 , 196.14 , and 196.09 correspond to the carbonyl C atoms of the benzophenone fragment with an integral intensity ratio of $1:2:1$. Probably, the product obtained is a

mixture of three possible isomers of the types **A**— CO —**A**, **A**— CO —**B**, and **B**— CO —**B** (Scheme 2).

However, it should be noted that ^1H and ^{13}C NMR spectral data are insufficient to discriminate accurately among these isomers. We did not attempt to separate the isomers because their solubilities in organic solvents are close.

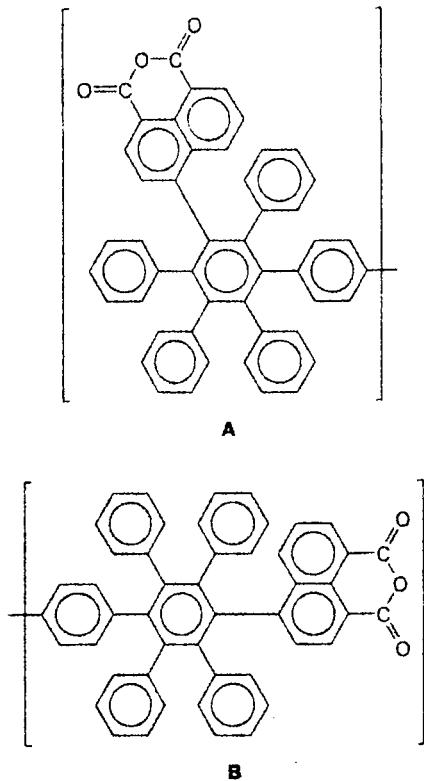
The reaction of compound **1** with a twofold molar amount of maleic anhydride in boiling bromobenzene with subsequent dehydrogenation under the action of bromine gave $4,4'$ -bis(2,3,6-triphenyl-4,5-dicarboxyphenyl)benzophenone dianhydride (**3**). This is a white crystalline substance, which is well soluble in common aprotic solvents such as benzene, toluene, DMF, CHCl_3 , etc.; compound **3** was characterized by data from elemental analysis and ^1H and ^{13}C NMR (see Experimental) and Fourier-IR spectroscopy (Fig. 2). The reaction was IR-monitored by following the disappearance of the intense band at 1709 cm^{-1} corresponding to the cyclo-

pentadienone CO group (see Fig. 2). The IR spectrum of **3** shows, along with an absorption band for the benzophenone C=O group at 1663 cm^{-1} , bands for the C=O group at $1743\text{--}1779\text{ cm}^{-1}$ characteristic of the CO stretching vibrations of phthalic anhydride. The ^1H NMR spectrum of compound **3** contains not only a doublet at δ 8.65 (*d*, $J = 8.1\text{ Hz}$) for the *meta*-protons of the benzophenone fragment but also four multiplets for the other aromatic protons.

In the ^{13}C NMR spectra, one can observe signals at δ 195.28 (the benzophenone CO group) and an intense signal at δ 161.21 corresponding to four virtually equivalent carbonyl C atoms. In addition, these spectra also exhibit 29 intense signals for 30 different types of C atoms in compound **3**.

The thermal behavior of dianhydrides **2** and **3** was studied by DSC in an atmosphere of argon (Fig. 3), the temperature increase being programmed with a rate of $20\text{ }^\circ\text{C min}^{-1}$. The DSC curves of dianhydride **3** (spectrum *1*) have two melting endotherms at 351.7 and $360.1\text{ }^\circ\text{C}$, which were not observed if the melting point was determined in a capillary (m.p. $361\text{--}362\text{ }^\circ\text{C}$). Finally, beginning at $\sim 420\text{ }^\circ\text{C}$, slow thermal destruction occurs, probably, because of decarboxylation. The DSC curves of dianhydride **2** (spectrum *2*) indicate no distinct melting point, and the product intensely decomposes near $450\text{ }^\circ\text{C}$.

Scheme 2



Experimental

The starting compounds and solvents were purified according to the known procedures.

^1H and ^{13}C NMR spectra were recorded on a Bruker-AMX 400 spectrometer (400.13 and 100.61 MHz, respectively) in CDCl_3 with Me_3Si as the internal standard. The purity of the individual compounds was checked by TLC on Silufol UV-245 plates in benzene with UV visualization. IR spectra were recorded on a Perkin-Elmer 1720 X Fourier-IR spectrophotometer (KBr). DSC was performed on a Perkin-Elmer DSC-4 instrument with a heating rate of $20\text{ }^\circ\text{C min}^{-1}$.

4,4'-Bis[2,3,5,6-tetraphenyl-4-(4,5-dicarboxynaphth-1-yl)phenyl]benzophenone dianhydride (2). A solution of compound **1** (0.79 g, 1 mmol) and 4-phenylethynyl-1,8-naphthalic anhydride (0.5966 g, 2 mmol) in 16 mL of 1,2,4-trichlorobenzene was refluxed with stirring in an atmosphere of argon for 10 h, cooled, and poured into a tenfold excess of MeOH. The precipitate that formed was filtered off, dried, and crystallized from isopropyl alcohol to give compound **2** in 91% yield. Found (%): C, 87.37; H, 4.60. $\text{C}_{97}\text{H}_{58}\text{O}_7$. Calculated (%): C, 87.24; H, 4.37. IR, ν/cm^{-1} : 1738, 1780 (C=O anhydride); 1658 (C=O benzophenone); 1592 (C=C_{arom}).

^1H NMR (CDCl_3), δ : 6.50–6.60 (*m*, 8 H); 6.60–6.70 (*m*, 4 H); 6.70–6.80 (*m*, 4 H); 6.80–6.98 (*m*, 28 H); 7.03–7.14 (*m*, 4 H); 7.40–7.48 (*m*, 2 H); 7.60–7.66 (*m*, 2 H); 8.22 (*d*, 2 H, $J = 8.1\text{ Hz}$); 8.32 (*d*, 2 H, $J = 8.1\text{ Hz}$); 8.42 (*d*, 2 H, $J = 8.1\text{ Hz}$). ^{13}C NMR (CDCl_3), δ : 116.59, 118.27, 125.56, 125.67, 125.94, 126.05, 126.26, 126.78, 127.78, 128.09, 128.34, 128.44, 128.53, 129.35, 129.76, 129.87, 130.49, 130.67, 130.68, 130.97, 131.58, 131.82, 132.26, 134.37, 134.38, 134.59, 135.58, 136.36, 138.87, 138.94, 139.01, 139.16, 139.45, 139.68, 140.24, 140.48, 140.71, 140.81, 140.95, 141.09, 141.62, 144.22, 144.51, 147.47, 147.54 (C_{arom}); 160.33 (–CO–, BNA); 160.53 (–CO–, BNA); 196.09, 196.14, 196.19 (–CO–, benzophenone).

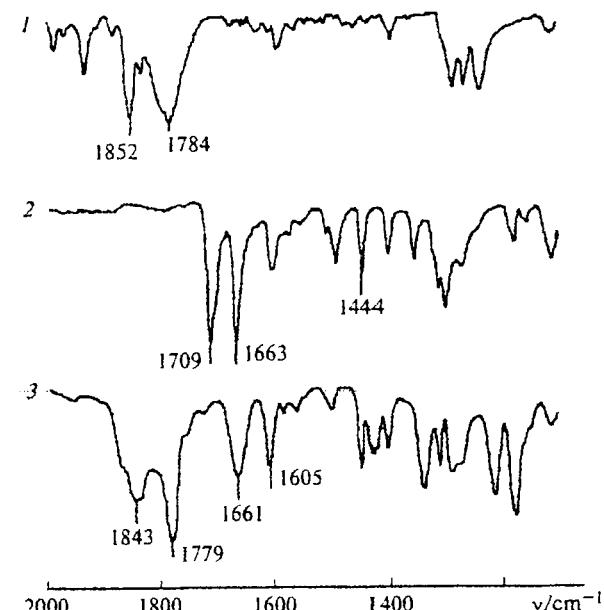


Fig. 2. IR spectra of (1) maleic anhydride, (2) compound **1**, and (3) compound **3**.

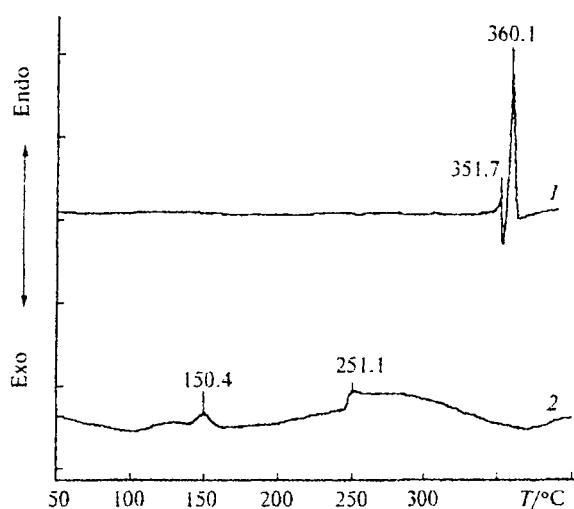


Fig. 3. DSC curves for dianhydrides (1) 3 and (2) 2.

4,4'-Bis(2,3,6-triphenyl-4,5-dicarboxyphenyl)-benzophenone dianhydride (3). A solution of compound 1 (2.46 g, 3.1 mmol) and maleic anhydride (0.61 g, 6.25 mmol) in 7.5 mL of bromobenzene was refluxed with stirring for 3 h and cooled, and Br_2 (0.55 mL) in 0.9 mL of bromobenzene was slowly added dropwise. The reaction mixture was refluxed for an additional 3 h, cooled, and poured into 150 mL of light petroleum. The precipitate that formed was filtered off and dried to give compound 3 in 87% yield, m.p. 361–362 °C (from BuOH). Found (%): C, 83.90; H, 4.15. $\text{C}_{65}\text{H}_{38}\text{O}_7$. Calculated (%): C, 83.85; H, 4.11. IR, ν/cm^{-1} : 1779, 1843 ($\text{C}=\text{O}$ anhydride); 1661 ($\text{C}=\text{O}$ benzophenone); 1605 ($\text{C}=\text{C}_{\text{arom}}$).

^1H NMR (CDCl_3), δ : 6.76–6.78 (m, 4 H); 6.85 (d, 4 H, J = 8.1 Hz); 6.90–7.00 (m, 6 H); 7.00–7.18 (m, 12 H); 7.18–7.30 (m, 12 H). ^{13}C NMR (CDCl_3), δ : 126.78 (2 C), 126.85 (2 C), 126.90 (2 C), 127.11 (2 C), 127.15 (2 C), 127.24 (2 C), 127.47 (2 C), 127.55 (2 C), 127.62 (2 C), 127.65 (2 C), 127.79 (2 C), 127.89 (2 C), 128.00 (2 C), 128.02 (2 C), 128.45 (2 C), 128.59 (2 C), 129.39 (2 C), 129.45 (2 C), 129.55 (2 C), 130.19 (2 C), 130.30 (2 C), 133.81 (2 C), 135.06 (2 C), 135.69 (2 C), 140.84 (2 C), 141.35 (2 C), 148.47 (2 C), 149.57 (2 C) (C_{arom}); 161.21 (–CO–, dianhydride, 4 C); 195.28 (–CO–, benzophenone, 1 C).

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