New bis-tetraarylcyclopentadienones

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Reactions of new bis(α-diketones) with 1,3-diphenylacetone resulted in new bis(tetraarylcyclopentadienones).

Key words: bis(tetraarylcyclopentadienones), FT-IR spectra, ^{1}H and ^{13}C NMR spectra, polyarylphenylenes, synthesis.

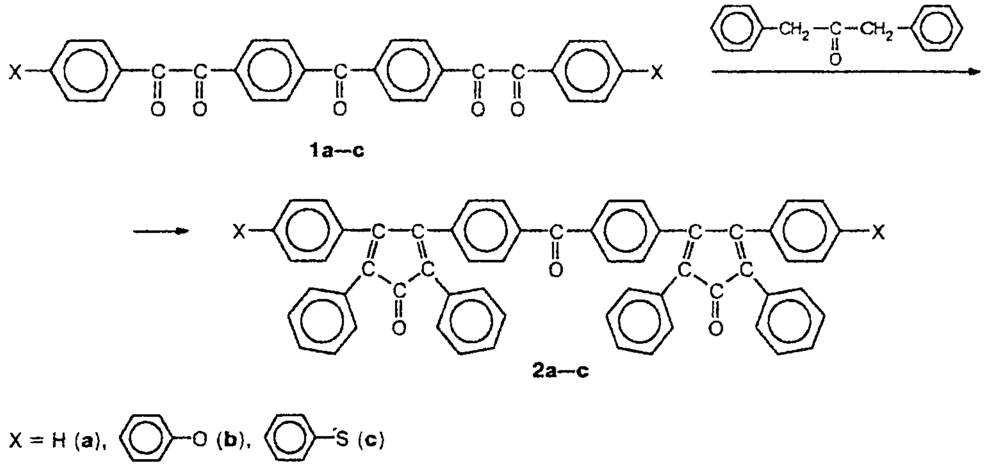
Bis(tetraarylcyclopentadienones) (BTACPD) are of considerable interest as monomers in the synthesis of phenyl-substituted polyphenylenes[1—3] and polyimides[4] by the Diels—Alder reaction.[5] They are usually obtained by base-catalyzed reactions of bis(arylglyoxalyl)arylenes with 1,3-diphenylacetone.[6,7]

In the present work, we describe the syntheses of new BTACPD from bis(arylglyoxalyl)benzophenones (**1a—c**) obtained previously[8,9] from 4,4′-diiodobenzophenone.[10,11]

The synthesis of BTACPD **2a—c** was performed according to Scheme 1.

The structures of compounds **2a—c** were confirmed by the data from elemental analyses and vibrational (FT-IR and Fourier-Raman) spectroscopy (Table 1) for all of the monomers synthesized.

Scheme 1



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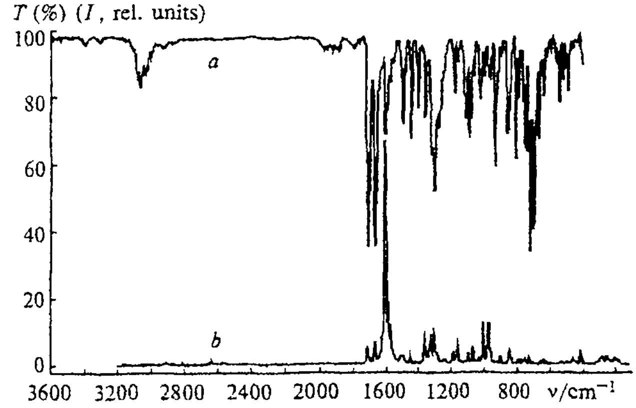

Fig. 1. Total vibrational spectra of monomer **2a**, FT-IR spectrum (*a*), Raman spectrum (*b*).

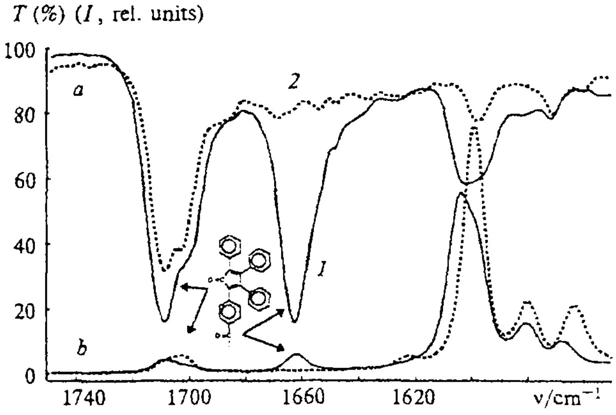

Fig. 2. Vibrational spectra of monomer **2a** (curve *1*) and 2,3,4,5-tetraphenylcyclopentadienone (curve *2*): *a*, FT-IR spectra; *b*, Raman spectra.

An example of total vibrational spectra is the spectrum of monomer **2a** presented in Fig. 1. Figure 2 shows a part of the total vibrational spectrum for monomer **2a** and the model 2,3,4,5-tetraphenylcyclopentadienone (TCPD), which allowed an unambiguous assignment of the IR and Raman bands near 1710 cm^{-1} to the stretching vibrations of the carbonyl group in the TCPD-moiety,[12,13] and the bands at 1660 cm^{-1} to the carbonyl of the benzophenone (BP) moiety of the monomer[14] (see Table 1). The IR spectrum of monomer **2b** contains a band at 1240 cm^{-1} (Ar—O—Ar), while the spectrum of monomer **2c** has a band at 1082 cm^{-1} (Ar—S—Ar).

The structures of compounds **2a—c** were also confirmed by ^{1}H and ^{13}C NMR spectroscopic data (Table 2). The ^{1}H NMR spectra of compound **2a** and the model TCPD contain multiplets in the regions of δ 7.60—7.58 (4 H); 7.28—7.21 (22 H); 7.21—7.17 (4 H); 7.06—7.04 (4 H); 6.95—6.93 (4 H), and 7.26—7.20 (12 H); 7.19—7.15 (4 H); 6.95—6.93 (4 H), respectively. A comparison of the chemical shifts of these compounds shows that the multiplets at δ 7.60—7.58 and at δ 7.06—7.04 can be assigned to the aromatic protons of the BP moiety, while those at δ 6.94—6.92 to *ortho-* and 7.21—

Table 1. Some characteristics of compounds **2a—c**

Compound	Yield (%)	M.p. /°C	$\frac{\text{IR}}{\text{Raman}}$ Fourier,	$\frac{\text{Found}}{\text{Calculated}}$ (%)			Molecular formula
			ν(C=O)/cm^{-1}	C	H	S	
2a	89.3	301	1709, 1663	89.06	4.80	—	$C_{59}H_{38}O_3$
			1709, 1663	89.14	4.81		
2b	88.4	450	1710, 1657	86.64	4.91	—	$C_{71}H_{46}O_5$
		(dec.)	1710, 1657	87.09	4.74		
2c	84.5	450	1709, 1658	84.31	4.63	6.09	$C_{71}H_{46}O_3S_2$
		(dec.)	1709, 1658	84.33	4.59	6.34	

Table 2. ^{1}H and ^{13}C NMR spectroscopic data for compounds **2a—c**

Compound	δ ^{1}H	δ ^{13}C
2a	7.59 (m, 4 H); 7.28—7.17 (m, 26 H); 7.01 (m, 4 H); 6.94 (m, 4 H)	199.73 (—CO— TCPD); 195.21 (—CO— BP); 154.03 (q); 152.80 (q); 137.57 (q); 136.62 (q); 132.66 (q); 130.32 (q); 130.11 (q); 130.03; 129.99; 129.57; 129.25; 129.05; 128.66; 128.10; 127.98; 127.77; 127.54; 126.32 (q); 125.32 (q, TCPD)
2b	7.74—7.00 (m, 38 H); 6.95—6.93 (d, 4 H); 6.85—6.83 (d, 4 H)	199.51 (—CO— TCPD); 195.01 (—CO— BP); 158.00 (q); 155.99 (q); 153.60 (q); 152.56 (q); 137.80 (q); 136.73 (q); 130.86 (q); 130.03 (q); 129.99; 129.76; 129.63; 129.60, 129.54; 129.29, 128.44; 128.38; 128.04; 127.99; 127.40 (q), 125.08 (q), 124.19 (q), 123.88; 117.39; 117.34
2c	7.67—7.00 (m, 42 H) 6.87—6.83 (d, 4 H);	199.45 (—CO— TCPD); 194.88 (—CO— BP); 153.36 (q); 152.26 (q); 138.29 (q); 137.70 (q); 133.09 (q); 131.61 (q); 130.84 (q); 130.71 (q), 130.54 (q), 130.09; 130.01; 129.83; 129.60; 129.30; 128.80; 128.46; 128.10; 128.04; 127.85; 127.65 (q); 125.47 (q)

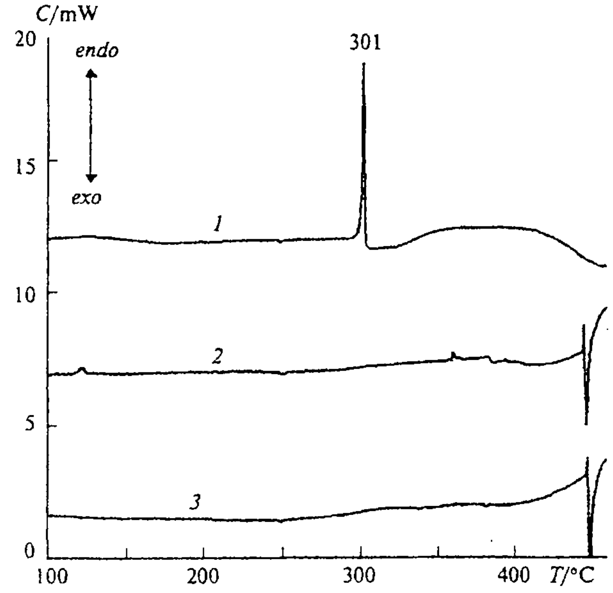

Fig. 3. Differential scanning calorimetry curves for monomers **2a**—**c**: *1*, **2a**; *2*, **2b**; *3*, **2c**.

7.17 to *meta*-protons of the lateral TCPD moieties in compound **2a**. Similar signal assignments can also be made for compounds **2b,c** (see Table 2).

The ^{13}C NMR spectra of BTACPD contain two peaks at $\delta \approx 200$ corresponding to the CO groups of the TCPD and BP moieties, and the number of characteristic signals between δ 160 and 110 conforms to that of quaternary carbon atoms (q).

The differential scanning calorimetry curves recorded in a dynamic mode with a temperature increase at a rate of 20 °C min^{-1} suggest that the monomer **2a** (Fig. 3) undergoes melting in a narrow temperature range (m.p. 301 °C) accompanied by exothermic transition into a state with a different heat capacity. The latter state, which is assumed to be liquid-crystalline, is detected up to 350 °C. Finally, above ~400 °C, the monomer **2a** undergoes slow thermodestruction, presumably due to decarbonylation. The differential scanning calorimetry curves for monomers **2b** and **2c** (see Fig. 3) recorded under identical conditions show that these monomers have no distinct melting point and undergo intense decomposition near 450 °C.

Experimental

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

Raman spectra were obtained on a U-1000 spectrometer with excitation by the 5145 Å line of a 100-MW ILA Ar$^+$-laser. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker-AMX 400 spectrometer with operating frequencies of 400.13 and 100.61 MHz, respectively.

IR spectra were obtained on a Perkin—Elmer-1720 X IR-Fourier spectrophotometer.

Synthesis of 4,4′-bis(3-oxo-2,4,5-triphenylcyclopentadienyl)benzophenone (2a). A solution of compound **1a** (11.6 g, 26 mmol) and 1,3-diphenylacetone (10.9 g, 52 mmol) in dry ethanol (700 mL) was heated to boiling, and a solution of KOH (1 g) in dry ethanol (20 mL) was added to the reaction mixture. The mixture was refluxed for 45 min and then cooled with ice water. The dark-violet precipitate that formed was filtered off, washed with cold methanol, and dried *in vacuo* at 100 °C. The product obtained was additionally purified by column chromatography on silica gel in toluene.

Compounds **2b,c** were obtained by a similar procedure; their characteristics are given in Table 1.

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