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Synthesis and Spectral Characteristics of Novel Bis(tetraarylcyclopentadienones)

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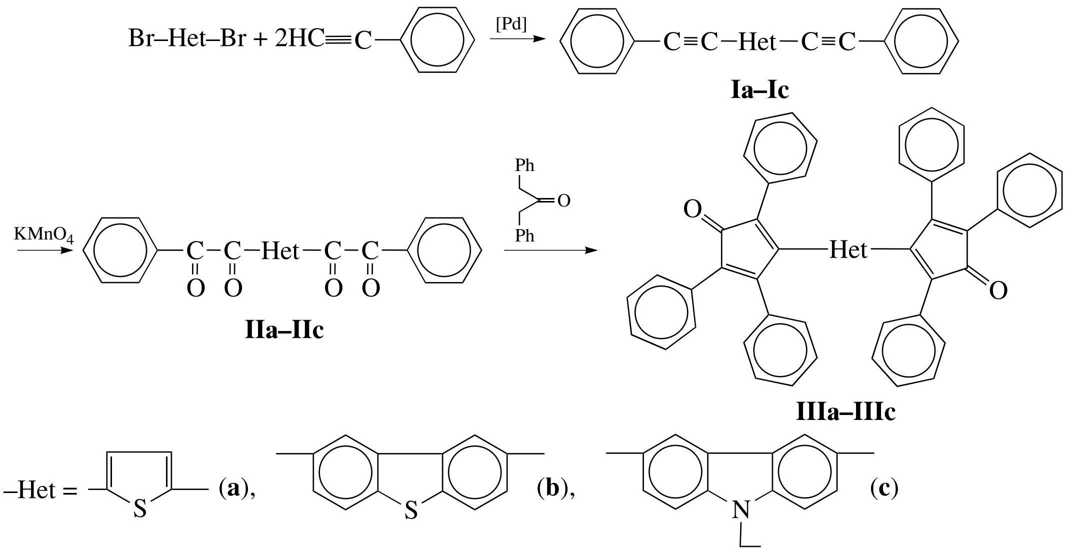
Bis(tetraarylcyclopentadienones) (BTACPDs) are key monomers used for preparing aromatic polymers and, in particular, aryl-substituted polyphenylenes (ASPPs) via the Diels–Alder reaction [1]. ASPPs are unique polymers that combine the aromaticity of macromolecules with a high molecular weight and high solubility in organic solvents. Most ASPPs contain only carbocyclic fragments, whereas the introduction of heterocycles, such as thiophene, benzothiophene, dibenzothiophene, and carbazole, would impart a number of new properties to these polymers, in particular, the possibility of their use in light-emitting devices since the presence of the above heterocycles in polymer macromolecules determines their electron transport properties [2, 3].

In continuing our studies in the field of novel BTACPDs [4] and ASPPs on their basis [5], we carried out the synthesis and studied the spectral characteristics of previously unknown BTACPDs containing thiophene, benzothiophene, dibenzothiophene, and carbazole rings as core groups or substituents.

The synthesis of BTACPDs was performed similarly to [1, 2, 4–6] according to Schemes 1 and 2.

Scheme 1.



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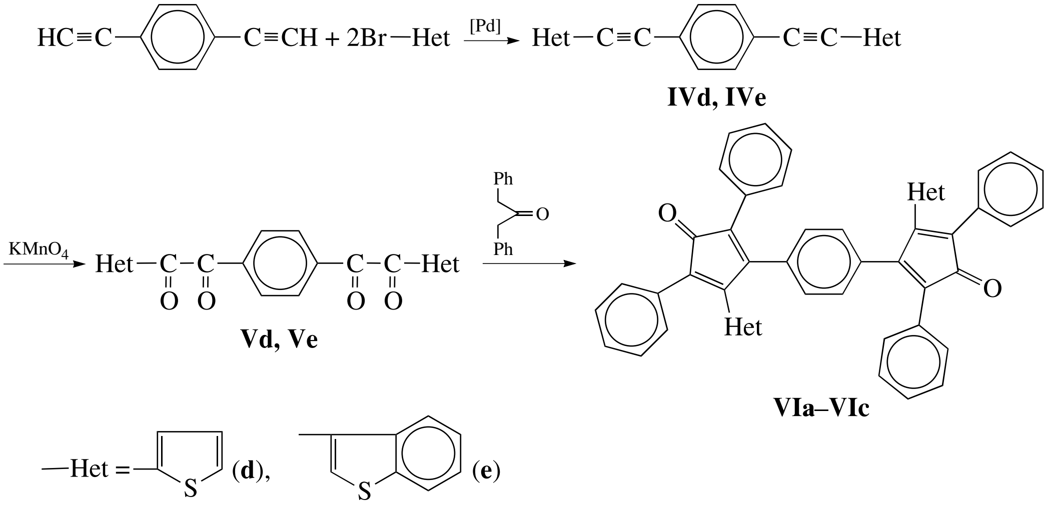
Scheme 2.



The synthesis involves the following:

(1) The palladium-catalyzed cross coupling [7–9] of 2,5-dibromothiophene, 2,8-dibromodibenzothiophene, and 3,6-dibromo(9-ethyl)carbazole with twofold molar amounts of phenylacetylene; the oxidation of resulting bis(phenylethynyl)hetarylenes (BPEHAs) **Ia**–**Ic** with $KMnO_4$ to give bis(phenylglyoxalyl)hetarylenes (BPGHAs) **IIa**–**IIc** [11]; and the treatment of BPGHAs with a twofold molar amount of diphenylacetone to produce BTACPDs **IIIa**–**IIIc** [1, 2, 4, 6].

(2) The palladium-catalyzed cross coupling [8] of 1,4-diethynylbenzene with twofold molar amounts of 2-bromothiophene and 3-bromobenzothiophene, the oxidation of resulting 1,4-bis(hetarylethynyl)phenylenes (BHEPs) **IVd** and **IVe** with $KMnO_4$ to yield

Table 1. Selected characteristics of intermediate and final compounds

Compound no.	T_m, °C	Elemental analysis, calculated/found, %				Yield, %	Compound no.	T_m, °C	Elemental analysis, calculated/found, %				Yield, %
		C	H	S	N				C	H	S	N	
Ia	88	84.47/84.52	4.25/4.28	11.17/11.41	–	90	**IIIc**	275–277	89.19/89.31	5.10/5.01	–	1.73/1.87	91
Ib	171–172	87.47/87.52	4.20/4.23	8.00/8.23	–	94	**IVd**	187–189	74.45/74.28	3.47/3.46	22.10/22.20	–	95
Ic	159–160	91.11/91.11	5.35/5.51	–	3.54/3.56	95	**IVe**	197–199	79.97/80.01	3.61/3.66	16.42/16.81	–	95
IIa	95–97	68.95/69.03	3.47/3.41	9.20/9.39	–	93	**Vd**	171–173	61.00/60.97	2.84/2.84	18.09/17.79	–	90
IIb	238–240	75.00/75.03	3.57/3.70	7.14/7.20	–	88	**Ve**	238–240	68.71/68.71	3.10/3.24	14.11/13.83	–	89
IIc	219–220	78.41/78.32	4.61/5.31	–	3.05/3.03	96	**VId**	343–345	82.02/81.91	4.30/4.38	9.12/9.24	–	70
IIIa	230–232	86.18/87.31	4.63/4.51	4.60/4.27	–	72	**VIe**	271–273	83.76/83.78	4.27/4.27	7.99/7.93	–	72
IIIb	220–222	87.41/87.31	4.55/4.52	4.02/4.58	–	82							

Table 2. Spectral characteristics of intermediate and final compounds

Compound no.	Raman spectra, ν, cm^{-1}	^{1}H NMR spectra, δ, ppm	^{13}C NMR spectra, δ, ppm
Ia	2202 (C≡C)	7.20 (s, 2H), 7.38 (m, 6H), 7.56 (m, 4H)	82.17 (C≡C), 93.95 (C≡C), 122.42 (C), 124.48 (C), 128.27 (CH), 128.53 (CH), 131.34 (CH), 131.71 (CH)
Ib	2202 (C≡C)	7.43 (m, 6H), 7.58 (m, 4H), 7.65 (d, 2H), 8.03 (d, 2H), 8.63 (s, 2H)	89.79 (C≡C), 119.21 (C), 122.61 (C), 123.76 (CH), 125.62 (CH), 129.10 (CH), 130.36 (CH), 131.63 (CH), 134.95 (C), 139.67 (C)
Ic	2210 (C≡C)	7.38 (m, 8H), 7.62 (d, 4H), 7.68 (d, 2H), 8.31 (s, 2H,), 4.33 (m, 2H, $C\underline{H}_2$), 1.45 (t, 3H, $C\underline{H}_3$)	87.5 (C≡C), 90.9 (C≡C), 108.4 (CH), 113.6 (C), 122.3 (C), 123.5 (CH), 123.9 (CH), 127.6 (CH), 128.1 (CH), 129.4 (CH), 131.2 (CH), 139.6 (C), 37.5 ($\underline{C}H_2$), 13.5 ($\underline{C}H_3$)
IIa	1681 (C=O)	7.54 (t, 4H), 7.69 (t, 2H), 7.84 (s, 2H), 8.05 (d, 4H)	128.94 (CH), 130.25 (CH), 131.93 (C), 135.18 (CH), 135.76 (CH), 146.11 (C), 184.97 (C=O), 190.57 (C=O)
IIb	1675 (C=O)	7.63 (t, 4H),7.76 (t, 2H), 7.98 (d, 4H), 8.04 (d, 2H), 8.29 (d, 2H), 9.05 (s, 2H)	126.40 (CH), 125.61 (CH), 126.70 (C), 129.020 (CH), 129.89 (CH), 130.71 (CH), 132.36 (C), 134.29 (CH), 148.04 (C), 148.38 (C), 194.27 (CO), 194.57 (CO)
IIc	1661 (C=O)	7.53 (t, 6H), 7.67 (t, 2H), 8.04 (d, 4H), 8.21 (d, 2H), 8.66 (s, 2H), 4.44 (m, 2H, $C\underline{H}_2$), 1.48 (m, 3H $C\underline{H}_3$)	109.4 (CH), 122.9 (C), 124.1 (CH), 125.5 (C), 128.1 (CH), 129.01 (CH), 129.7 (CH), 132.9 (C), 134.5 (CH), 144.1 (C), 193.6 (C), 194.7 (Cé), 38.1 ($\underline{C}H_2$), 13.5 ($\underline{C}H_3$)
IIIa	1711 (C=O)	7.25–7.38 (m, 20H), 7.43 (s, 2H), 7.58–7.77 (m, 8H)	200.14 (CO), 164.05 (C), 157.04 (C), 145.27 (C), 139.12 (C), 137.07 (C), 134.84 (C), 133.14 (C), 122.26 (C), 132.48 (CH), 131.93 (CH), 127.57 (CH), 126.78 (CH), 126.38 (CH), 126.13 (CH), 126.08 (CH), 125.85 (CH), 124.85 (CH)
IIIb	1711 (C=O)	6.90 (d, 6H), 7.05 (d, 4H), 7.13 (d, 8H), 7.15–7.30 (m, 16H), 7.60 (d, 2H)	200.16 (CO), 154.34 (C), 153.75 (C), 139.74 (C), 134.84 (C), 132.98 (C), 130.51 (C), 129.61 (C), 125.29 (C), 125.21 (C), 130.02 (CH), 129.97 (CH), 129.09 (CH), 128.42 (CH), 127.99 (CH), 127.53 (CH), 127.42 (CH), 122.34 (CH), 122.11 (CH)
IIIc	1710 (C=O)	6.9–7.26 (m, 36H, Ar), 1.45 (m, 3H, $C\underline{H}_3$), 4.25 (m, 2H, $C\underline{H}_2$)	200.29 (CO), 155.07 (C), 154.34 (C), 140.08 (C), 133.31 (C), 131.20 (C), 130.79 (C), 125.52 (C), 124.21 (C), 123.77 (C), 122.21 (C), 130.07 (CH), 129.27 (CH), 128.29 (CH), 127.87 (CH), 127.76 (CH), 127.26 (CH), 127.11 (CH), 121.70 (CH), 108.03 (CH), 37.76 ($\underline{C}H_2$), 13.81 ($\underline{C}H_3$)
IVd	2191 (C≡C)	7.16 (m, 2H), 7.46 (m, 2H), 7.61 (s, 4H), 7.72 (m, 2H)	85.42 (C≡C), 93.10 (C≡C), 122.76 (C), 123.41 (C), 128.57 (CH), 129.87 (CH), 132.27 (CH), 133.81 (CH)
IVe	2191 (C≡C)	7.50 (t, 2H), 7.58 (t, 2H), 7.68 (s, 4H), 7.78 (s, 2H), 7.95 (d, 2H), 8.13 (d, 2H)	85.07 (C≡C), 91.62 (C≡C), 118.18 (C), 122.69 (C), 123.07 (C), 123.11 (CH), 124.83 (CH), 125.18 (CH), 130.21 (CH), 131.67 (CH), 131.73 (CH), 138.88 (CH), 139.09 (CH)
Vd	1681 (CO)	7.39 (m, 2H), 8.06 (m, 2H), 8.25 (s, 4H), 8.38 (m, 2H)	131.29 (CH), 137.67 (C), 139.00 (CH), 139.59 (CH), 139.72, 185.69 (CO), 192.27 (CO)
Ve	1680 (C=O)	7.65 (t, 2H), 7.72 (t, 2H), 8.28 (d, 2H), 8.36 (s, 4H), 8.82 (d, 2H), 9.14 (s, 2H)	124.54 (C), 124.70 (C), 128.32 (C), 129.65 (C), 129.87 (C), 130.08 (C), 132.69 (CH), 135.12 (CH), 135.69 (C), 146.59 (CH), 194.46 (CO), 194.54 (CO)
VId	1709 (C=O)	7.10–7.70 (m, 26H), 7.72 (s, 4H)	122.26 (C), 124.86 (CH), 125.70 (CH), 125.85 (CH), 126.13 (CH), 126.25 (CH), 126.38 (CH), 129.17 (CH), 131.80 (CH), 131.93 (CH), 132.48 (CH), 133.50 (C), 134.84 (C), 137.06 (C), 139.11 (C), 143.84 (C), 155.30 (C), 156.86 (C), 200.14 (CO)
VIe	1709 (C=O)	6.73 (s, 4H), 7.00–7.29 (m, 28H, Ar), 7.83 (d, 2H)	199.98 (CO), 153.39 (C), 148.03 (C), 139.63 (C), 136.32 (C), 133.35 (C), 130.66 (C), 130.22 (C), 128.93 (C), 126.03 (C), 125.28 (C), 129.93 (CH), 129.30 (CH), 128.70 (CH), 127.99 (CH), 127.93 (CH), 127.63 (CH), 127.39 (CH), 124.45 (CH), 123.95 (CH), 123.77 (CH), 122.45 (CH)

1,4-bis(hetarylglyoxalyl)phenylenes (BHGPs) **Vd** and **Ve**, and the treatment of BHGPs with a twofold molar amount of 1,3-diphenylacetone to give BTACPDs **VId** and **VIe** [1, 2, 4, 6].

It is worth noting that the intermediate compounds formed in the course of the synthesis of BTACPDs (Schemes 1, 2), namely, BPEHAs **Ia**–**Ic**, BPGHAs **IIa**–**IIc**, BHEPs **IVd** and **IVe**, and BHGPs **Vd** and **Ve**, are of intrinsic interest as monomers for the synthesis of different polymers. Thus, BPEHAs **Ia**–**Ic** and BHEPs **IVd** and **IVe** can be used for preparing cross-linked polyphenylenes and as the comonomers of BTACPDs in the synthesis of ASPPs containing an increased number of aryl substituents [9], while BPGHAs **IIa**–**IIc** and BHGPs **Vd** and **Ve** can be used in the synthesis of polyquinoxalines and poly(asym-triazines) containing phenyl and hetaryl substituents.

All syntheses of BPEHAs **Ia**–**Ic** and BHEPs **IVd** and **IVe** were carried out in triethylamine using $PdCl_2(PPh_3)_2$, PPh_3, and CuI as catalysts and promoters. The reaction mixtures were boiled under reflux for 10 h.

The oxidation of BPEHAs **Ia**–**Ic** to BPGHAs **IIa**–**IIc** and the oxidation of BHEPs **IVd** and **IVe** to BHGPs **Vd** and **Ve** were accomplished using $KMnO_4$ in acetone with glacial CH_3COOH under reflux for 2–3 h until the crimson color disappeared.

BTACPDs **IIIa**–**IIIc**, **VId**, and **VIe** were synthesized in boiling absolute ethanol during 1 h using a KOH solution in ethanol.

All the intermediate and target compounds were obtained in high yields, and elemental analysis data agree well with calculated values (Table 1).

The structure of the intermediate and target compounds was also confirmed by Raman and NMR (^{1}H, ^{13}C) spectroscopy (Table 2). In particular, the Raman spectra of compounds **I** and **IV** show strong absorption bands in the range 2191–2210 cm^{-1} typical for the acetylene moiety, whereas the spectra of compounds **II** and **V** exhibit weak bands at 1661–1681 cm^{-1} from the stretching vibrations of CO groups in the α-diketone moieties.

All aromatic protons in the ^{1}H NMR spectra of compounds **I**–**V** show resonances in the range 7.1–8.82 ppm except compounds **Ic** and **IIc**, exhibiting two upfield multiplets at $\delta = 1.43$ ppm (m, 3H) and $\delta = 4.44$ ppm (m, 2H) from the CH_3 and CH_2 groups, respectively. The ^{13}C NMR spectra of compounds **I** and **IV**, as well as **II** and **V**, are characterized by the presence of upfield signals at $\delta = 80$–90 ppm from the acetylene moieties and downfield signals at 190–200 ppm from the two different carbonyl groups of the α-diketone moiety. The ^{1}H NMR spectra of bis-cyclones **III** and **VI** are rather complex. The aromatic protons appear as downfield multiplets at 7.25–7.77 and 6.80–7.50 ppm, respectively. The spectrum of compound **IIIc** shows two upfield multiplets at $\delta = 1.45$ ppm and $\delta = 4.25$ ppm from the CH_3 and CH_2 groups, respectively, and the ratio of the integrated intensities of the aliphatic and aromatic portions agrees well with the proposed structure. The ^{13}C NMR spectra are more informative. The ^{13}C NMR spectra of compounds **III** and **VI** show a signal at ~200 ppm due to the CO group of the cyclopentadienone moiety, whereas the signals between 110 and 160 ppm belong to the quaternary carbon atoms.

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