Structures of branched oligophenylenes studied by NMR spectroscopy

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A series of model cyclotrimers was studied by NMR spectroscopy using 2D COSY, HSQC, and HMBC correlations to establish the structures of branched oligophenylenes, whose branching center is the 1,3,5-triphenyl-substituted benzene ring.

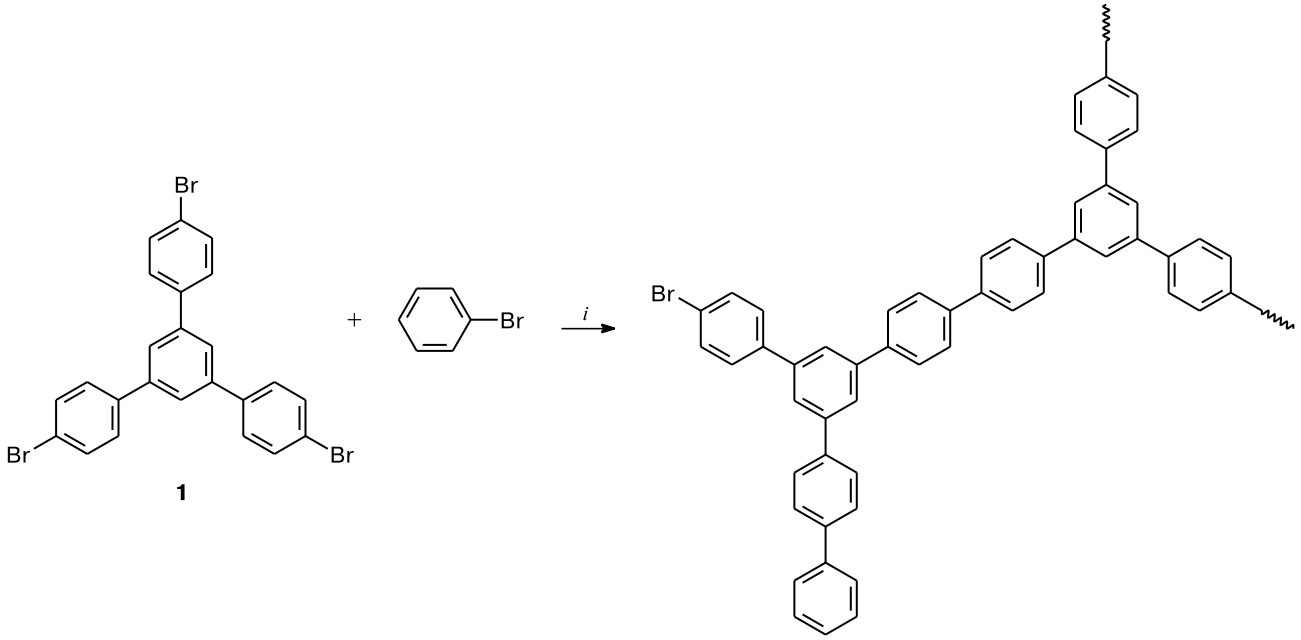
Key words: branched oligophenylenes, cyclotrimers, Suzuki reaction, NMR spectroscopy, 2D correlations.

One of the most intensely developed areas of practical use of conjugated polymers is the preparation of organic light-emitting diodes (OLED).[1—3] At present, considerable progress was achieved in using red[4—6] and green[7] displays based on both low-molecular-weight organic compounds and polymers. Rapt attention has recently been given to the synthesis of polymers luminescing in the blue region of the visible spectrum.[8—15] However, obtaining of efficient blue luminescence still remains to be a narrow unit in the production of a polymer-based full-color diode. Branched oligophenylenes having bright fluorescence in the blue region, being both in solution and in the solid state, can serve as an alternative for the development of such photodiodes.[16] However, problems on structure determination of chromophoric fragments and identification of the general structure of complicated aromatic systems restrain the development of this promising trend.

This work is devoted to the NMR studies of the structures of branched oligophenylenes, whose branching center is the 1,3,5-triphenyl-substituted benzene ring.

The synthesis of branched oligophenylenes based on 1,3,5-tris(*p*-bromophenyl)benzene (**1**) obtained by the cross-coupling in the presence of the nickel complexes (Scheme 1) has earlier been described.[17—19]

Scheme 1



i. Ni^0, Zn, DMF, 70 °C, 6 h.

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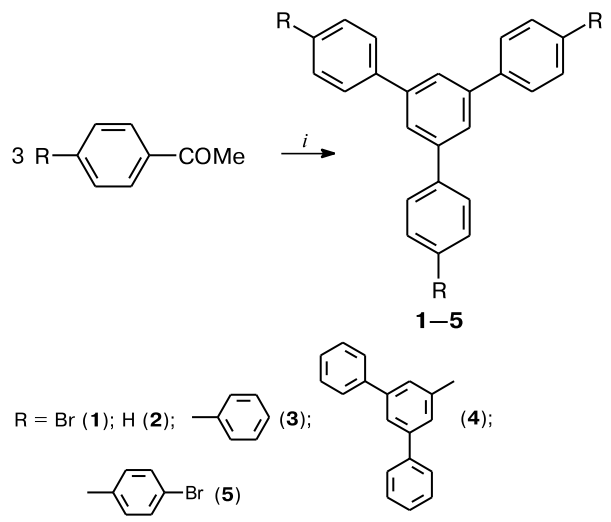
The formed macromolecules contain biphenyl bridges connecting the nodal trisubstituted benzene rings, terminal biphenyl groups, and unreacted bromophenyl groups. In addition, the trisubstituted benzene rings can have different environments.

The use of ^{1}H NMR spectroscopy in studying oligophenylenes is restrained because of overlapping of multiplet signals.

The ^{1}H and ^{13}C NMR spectra of monomer **1** and model compounds **2**—**6** were examined to assign the signals of protons in the aromatic region of branched oligophenylenes.

The following compounds were chosen as models of the main fragments of oligophenylenes: 1,3,5-tris(*p*-bromophenyl)benzene (**1**),[20] 1,3,5-triphenylbenzene (**2**),[21] 1,3,5-tris(*p*-diphenyl-4′-yl)benzene (**3**),[22] 1,3,5-tris(1,3,5-triphenylbenzen-4′-yl)benzene (**4**),[23] and 1,3,5-tris-(4-bromo-1,1′-diphenyl-4′-yl)benzene (**5**)[24] (Scheme 2).

Scheme 2



i. $HC(OEt)_3$, HCl, C_6H_6, 20 °C, 4 h.

Compound **5** was used for the synthesis of model compound **6**: 1,3,5-[tris(*p*-terphenyl-4-yl)]benzene[21] with terphenyl branches. The latter was synthesized using a standard procedure by the Suzuki reaction of compound **5** with phenylboronic acid.[25,26]

The corresponding signals in the NMR spectra for compounds **1**, **2**, and **4** (and oligophenyl **P-1**) are presented in Table 1. The assignment of chemical shifts for compounds **1** and **2** (see Table 1) is consistent with the published one.[27]

In the ^{1}H NMR spectrum of compound **2** (see Table 1), the protons of the central benzene ring can be assigned as a singlet at 7.81 ppm (H(1)), a doublet at 7.72 ppm (H(4)), a triplet at 7.50 ppm (H(5)), and a triplet at 7.40 ppm (H(6)).

In the ^{13}C NMR spectrum of compound **2** (see Table 1), the signal at 125.08 ppm (C(1)) corresponds to the tertiary carbon atoms of the central benzene ring. The signals at 142.26 (C(2)) and 141.07 ppm (C(3)) can be assigned to the quaternary carbon atoms of the central and peripheral benzene rings, respectively. The C atoms of the external benzene ring exhibit signals at 127.26 (C(4)), 129.75 (C(5)), and 127.44 ppm (C(6)).

In the ^{1}H NMR spectrum of compound **1** (see Table 1), the signals from protons of the central benzene ring can unambiguously be assigned as a singlet at 7.70 ppm (H(1)) and the signals from the 1,4-substituted benzene ring can be assigned as a doublet at 7.62 ppm (H(5)) and a doublet at 7.54 ppm (H(4)). In the spectrum of compound **1**, the signals from the H(5) protons are downfield shifted (see Table 1) compared to similar signals in the spectrum of compound **2** and the signals of the H(1) and H(4) protons are upfield shifted.

The ^{13}C NMR spectrum of compound **1** (see Table 1) exhibits signals at 125.19 ppm that can be assigned to the tertiary carbon atom of the central 1,3,5-trisubstituted benzene ring.

The signal assignment in the ^{13}C NMR spectrum on the basis of HSQC and HMBC experiments is unambiguous (Fig. 1).

The signal at 125.19 ppm (in HSQC) gives the correlation peak with a singlet at 7.70 ppm and corresponds to C(1). The signal at 122.32 ppm (in HSQC) unambiguously belongs to the C(6) atoms directly bound to the bromine atoms (calculated data: δ 122.32). However, signal assignment in the HSQC spectrum for the C(4) and C(5) carbon atoms is ambiguous. The calculations by the ACD/CNMR DB additive scheme (solvent $CDCl_3$) showed that the ^{13}C signals from the C(4) atoms (δ 129.10) are in a stronger field than the signals of the C(5) atom (δ 132.26). Since the difference in the calculated and experimental data for these atoms is low (1 and 2 ppm, respectively), HMBC data were required for the more exact assignment of these signals (see Fig. 2). The signal at 139.82 ppm (see Fig. 2) gives correlation peaks with a signal at 7.70 ppm, which is a downfield part of the AA′BB′ system and, thus, this signal is assigned to C(3). Therefore, the signals at 7.62 and 7.54 ppm correspond to H(5) and H(4), respectively. According to these assignments, the signal at 129.10 ppm is assigned to the C(4) atom, whereas the signal at 139.82 ppm is attributed to the C(3) atom. The signal at 141.73 ppm gives the correlation peak with the upfield AA′BB′ system of H(4) and is attributed to the C(2) atom.

Thus, the C atoms of the *p*-substituted benzene rings of molecule **1** are characterized by signals at 129.10 (C(4)), 132.26 (C(5)), and 122.32 ppm (C(6)), and the latter signal is assigned to the C atoms directly bound to the bromine atoms, whereas the signals at 141.73 and 139.82 ppm correspond to two quaternary carbon atoms of the benzene rings.

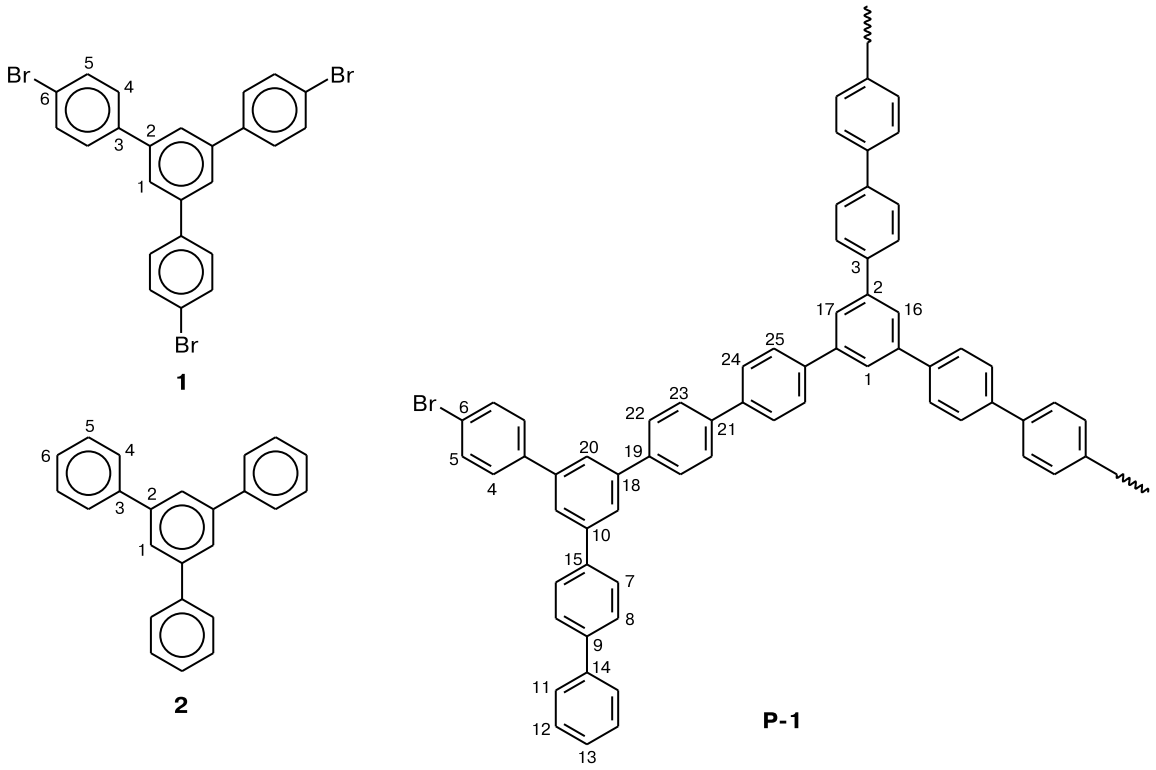


Table 1. Signal assignment in the ^{1}H and ^{13}C NMR spectra of compounds **1**—**3** and **P-1**

Compound	δ	
	^{1}H	^{13}C
1	7.70 (H(1)); 7.54 (d, H(4)); 7.62 (d, H(5))	125.19 (C(1)); 141.73 (C(2)); 139.82 (C(3)); 129.10 (C(4)); 132.26 (C(5)); 122.32 (C(6))
2	7.81 (H(1)); 7.72 (d, H(4)); 7.50 (t, H(5)); 7.41 (t, H(6))	125.08 (C(1)); 142.26 (C(2)); 141.07 (C(3)); 127.26 (C(4)); 129.75 (C(5)); 127.44 (C(6))
3	7.88 (H(8)); 7.84 (H(10)); 7.75 (H(11)); 7.52 (H(12)); 7.43 (H(13))	125.0—125.4 (C(1), C(8), C(10)); 140.66 (C(2)); 142.50 (C(9)); 140.52 (C(3)); 141.15 (C(14))
P-1	7.89 (H(1), H(16)), H(17)); 7.78 (H(20)); 7.56—7.62 (H(4)); 7.63—7.66 (H(5))	125.0 (C(1)); 141.4 (C(2)); 140.0 (C(3)); 128.9 (C(4)); 132.0 (C(5)); 122.0 (C(6))

The representative of the second generation of phenylene dendrimers, *viz.*, tridecaphenyl (**4**) (cyclotrimer with 13 benzene rings), was synthesized by the acetylation of 1,3,5-triphenylbenzene (**2**) *via* the Friedel—Crafts reaction to form [1-(4-acetylphenyl)-3,5-diphenyl]benzene followed by cyclocondensation. In this model compound, the protons of two different types of 1,3,5-trisubstituted benzene rings have different environments and, hence, several signals from these protons should appear in the spectrum. Differences in the ^{13}C NMR spectrum should also be expected.

The NMR spectra of compound **4** are shown in Figs 2 and 3.

In the ^{1}H NMR spectrum of compound **4** (see Fig. 2, *a*), the signals from the protons and carbon atoms of the aromatic AA´BB´X system can easily be assigned. The protons of the external benzene rings are characterized by a doublet at 7.75 ppm (H(11)) and triplets at 7.52 (H(12)) and 7.43 ppm (H(13)).

The HSQC and HMBC correlations (see Fig. 3) make it possible to assign all signals in the ^{1}H (see Fig. 2, *a*) and ^{13}C (see Fig. 2, *b*) NMR spectra of compound **4**.

Based on the HMBC spectrum (see Fig. 3, *b*), the signal at 142.71 ppm can be assigned to C(9) due to the single correlation with H(11). The signal at 141.35 ppm corresponds to the C(14) atom because of its correlation

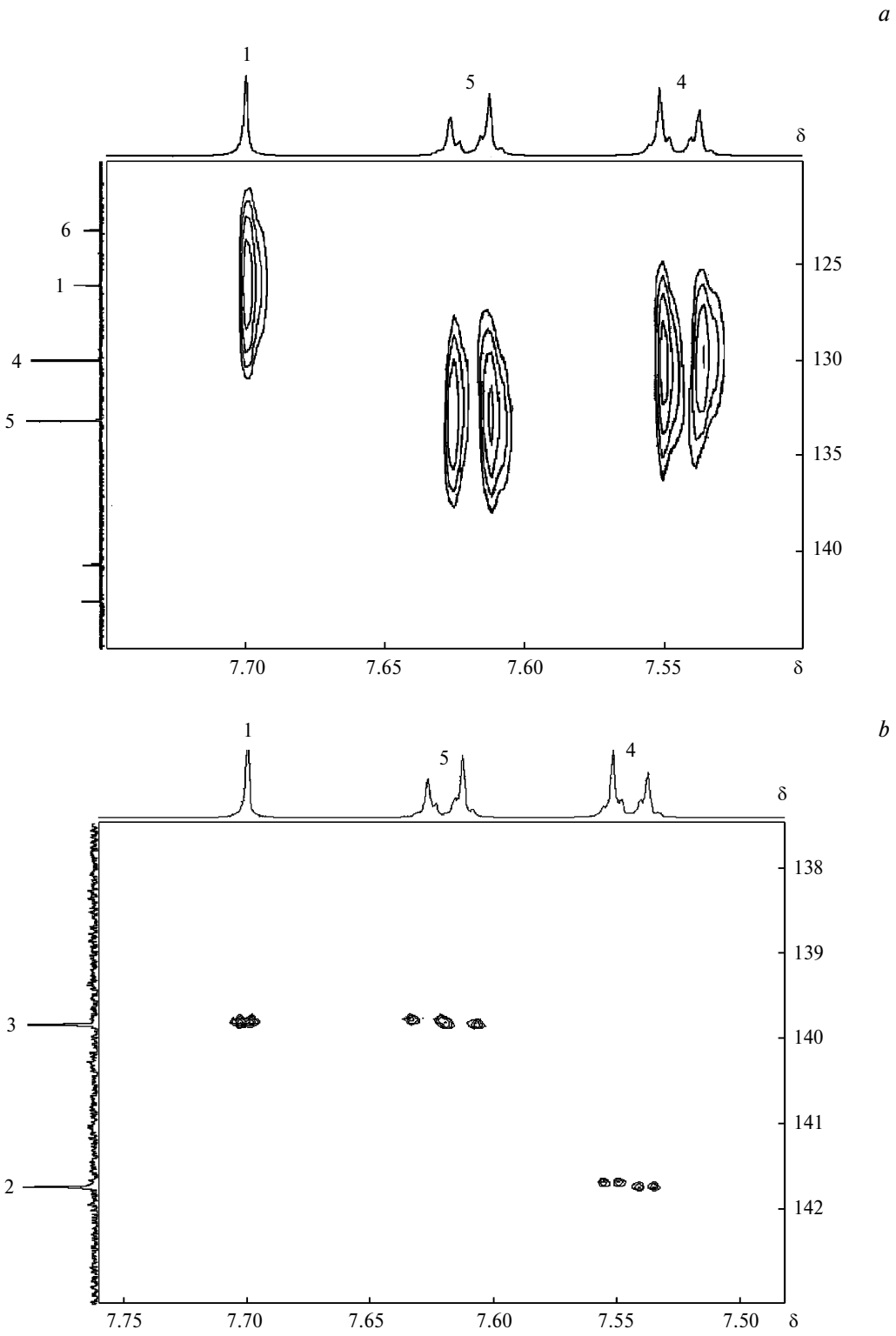


Fig. 1. Part of the HSQC spectrum (*a*) and the part of the HMBC spectrum (*b*) for compound **1**.

with H(12) and with two other aromatic protons at 7.88 and 7.84 ppm attributed to H(8) and H(10), respectively. Thus, among unassigned signals from the H(1), H(4), and H(5) protons, the singlet signal at 7.96 ppm can be for H(1) only.

Two other signals of non-quaternary carbon atoms merge into one signal at 128.09 ppm (see Fig. 3, *a*), and the signals from the corresponding protons are in the range δ 7.80—7.90, *i.e.*, they belong to C(4) and C(5). As for the

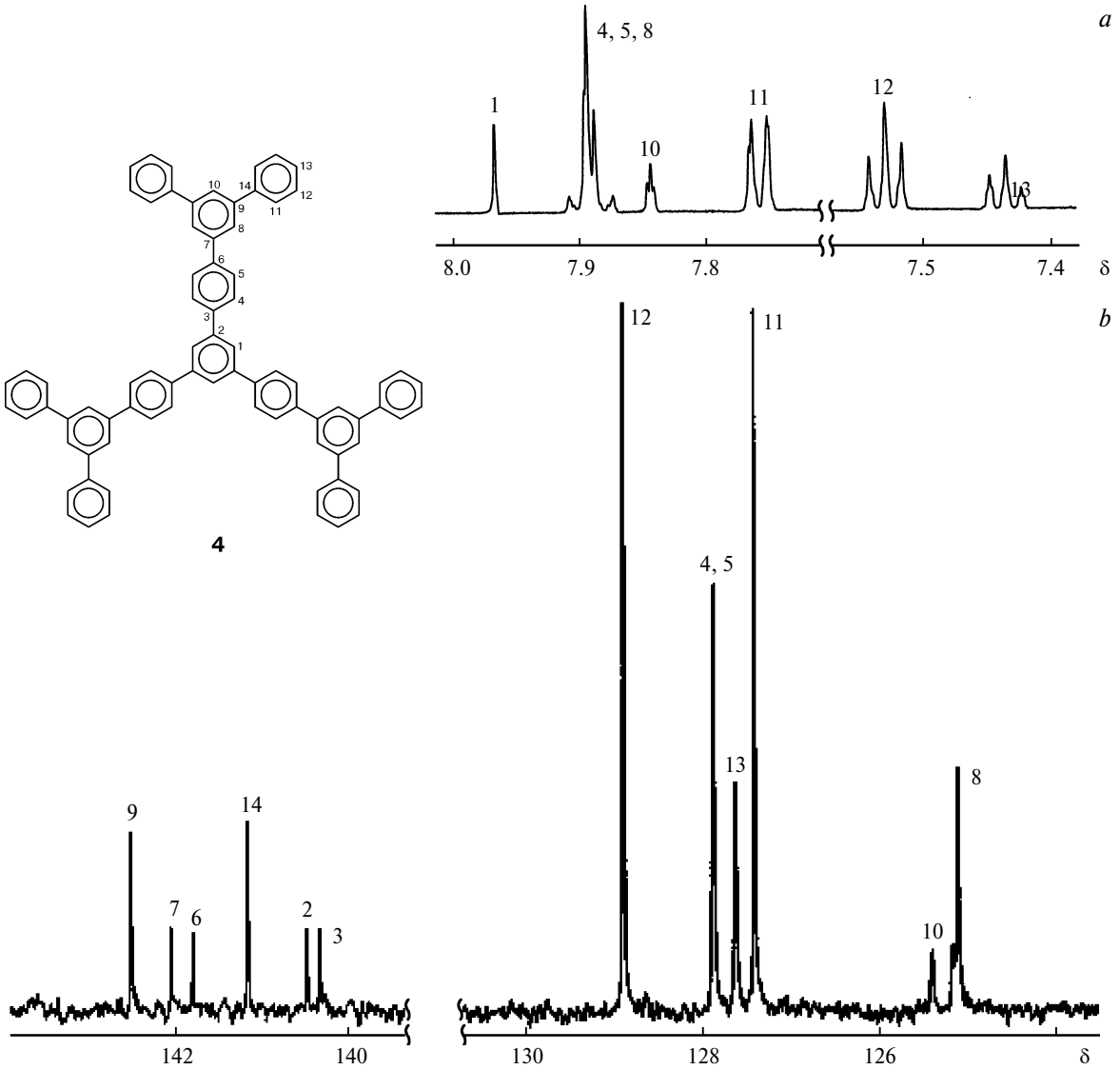


Fig. 2. ^{1}H (*a*) and ^{13}C (*b*) NMR spectra for compound **4**.

signals for the quaternary carbon atoms at 140.52 and 140.66 ppm, they can be assigned to C(3) and C(2), respectively, on the basis of their HMBC correlations (see Fig. 3, *b*).

The signal from C(3) correlates with the signal from H(1) at 7.96 ppm and with the H(5) signal at 7.88 ppm. The signal of the quaternary carbon atom at 42.25 ppm (C(7)) correlates with the H(4) and H(8) signals (δ ~7.89), and the signal at 142.00 ppm (C(6)) correlates with the H(5) signal (see Fig. 2, *b*).

The signal at 140.52 ppm (C(2)) shows the correlation with the signal from the H(4) proton only. Finally, these correlations make it possible to assign the signal at 7.84 ppm to H(10).

The ^{1}H NMR spectra of compounds **3** and **6** were also analyzed. The signal assignment is shown in Fig. 4. In the ^{1}H NMR spectrum of compound **6**, compared to the spectrum of compound **3** (see Fig. 4), two AB quadruplets at 7.75, 7.79 and 7.83, 7.87 ppm assigned to the H(25), H(24), H(23), and H(22) protons are observed instead of one AB quadruplet at 7.77 and 7.84 ppm corresponding to the H(7) and H(8) protons. In addition, the singlet signal of protons of the phentriyl fragment exhibits the downfield shift.

Branched model oligophenylene was synthesized by the polycondensation of 1,3,5-tris(4-bromophenyl)benzene (**1**) together with bromobenzene at the molar ratio 1 : 2.5 in a DMF solution in the presence of the zerovalent Ni complex. It was expected that the synthesis at this ratio of components would give low-molecular-weight oligophenylene, in the NMR spectra of which the signals of protons and carbon atoms would be resolved.

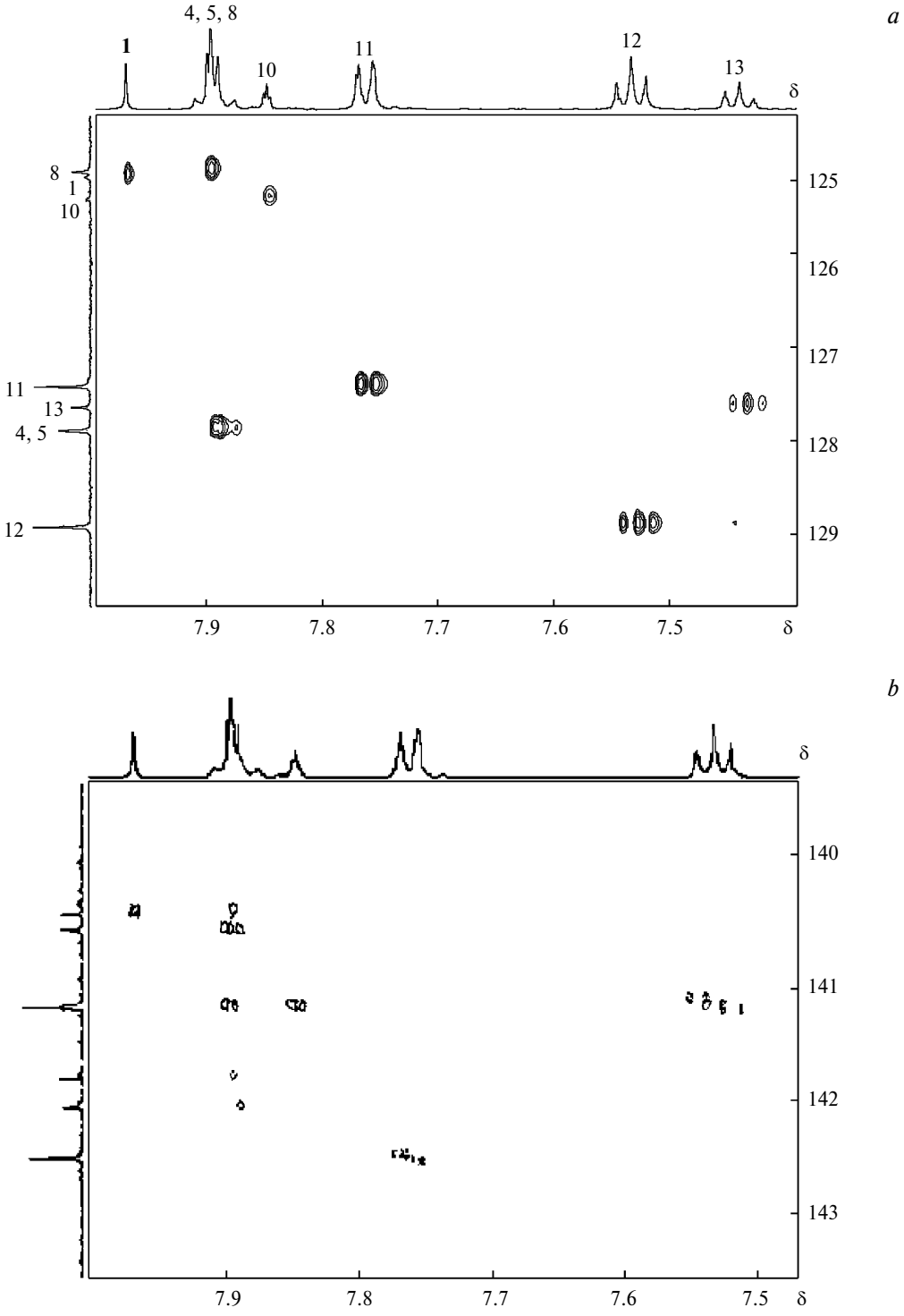


Fig. 3. Part of the HSQC spectrum (*a*) and the part of the HMBC spectrum (*b*) for compound **4**.

The ^{1}H and ^{13}C NMR spectra of branched oligophenylene are presented in Figs 5 and 6, respectively. The signals from protons in the NMR spectra of oligophenylene **P-1** were assigned due to a comparison with the spectra of monomer **1** and model compounds **2—6**.

In the complicated ^{1}H NMR spectrum of oligophenylene **P-1** (see Fig. 5), the characteristic triplet signals of the *m*-, *o*-, and *p*-protons H(11) (δ 7.67), H(12) (δ 7.48), and H(13) (δ 7.38) of the terminal phenyl groups can be assigned with high reliability. The ratio of integral intensi-

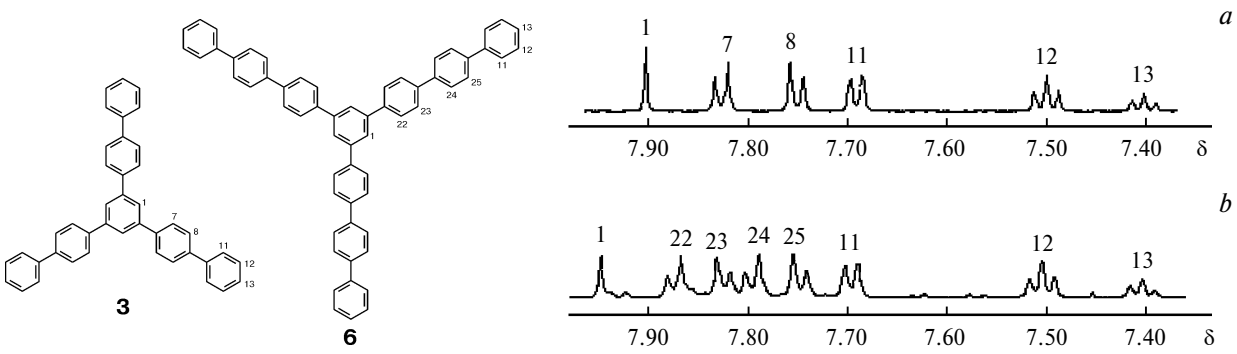


Fig. 4. ^{1}H NMR spectra for model compounds **3** (*a*) and **6** (*b*).

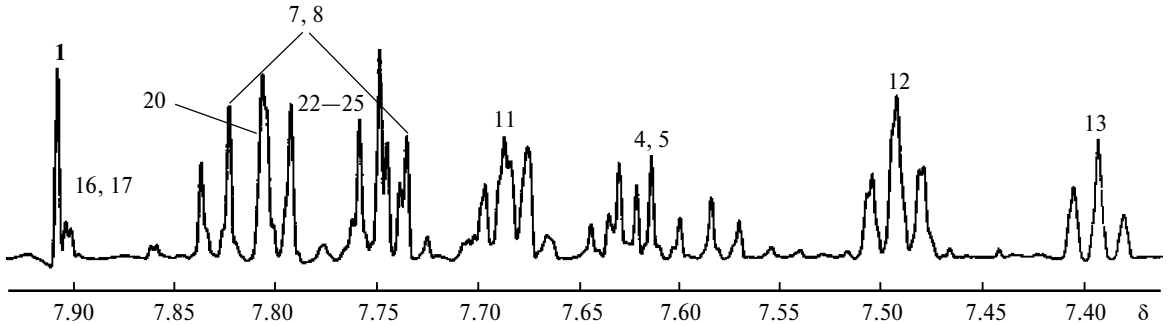


Fig. 5. ^{1}H NMR spectrum of oligophenylene **P-1**.

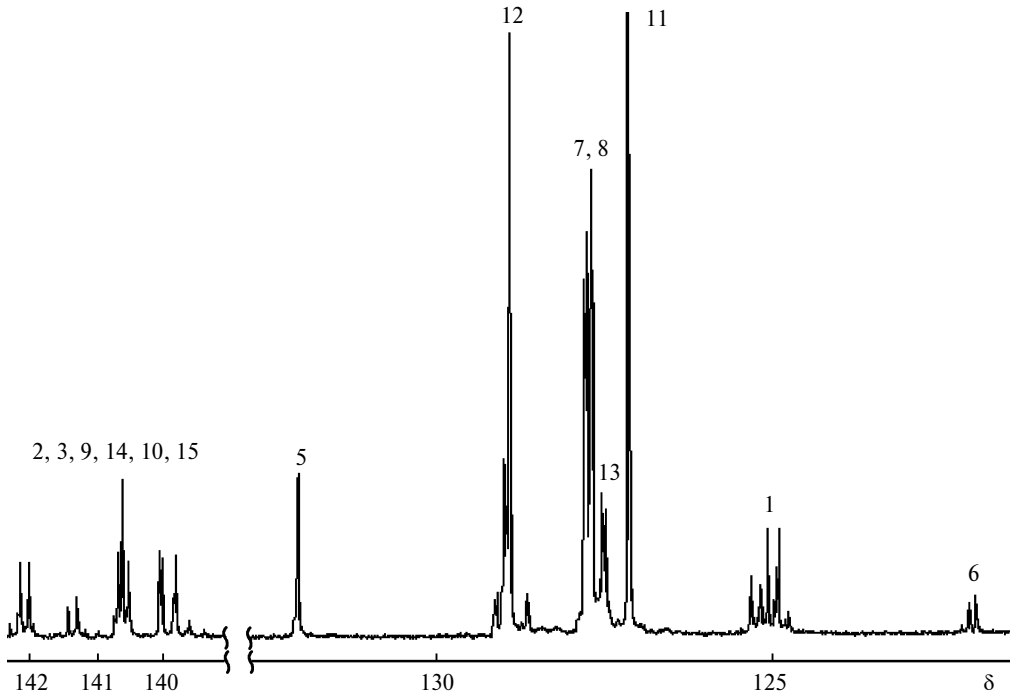


Fig. 6. ^{13}C NMR spectrum of oligophenylene **P-1**.

ties is 2 : 2 : 1. These signals almost coincide with signals of the same groups of model compounds **3**, **4**, and **6**. The COSY spectrum of **P-1** (Fig. 7) confirms that the assignment of signals from the H(11)—H(13) protons is valid.

The ^{1}H NMR spectrum (see Fig. 5) exhibits three singlets at 7.89 ppm, which characterize the protons of the 1,3,5-substituted benzene ring, namely, H(1), H(16), and H(17), differed by the environment of the ring. The COSY

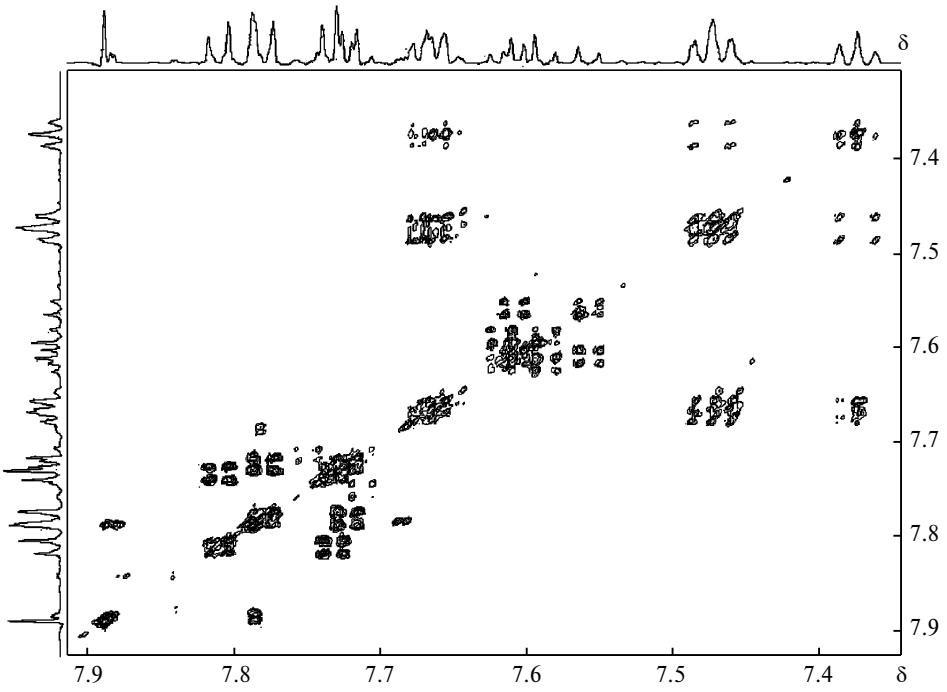


Fig. 7. COSY spectrum of oligophenylene **P-1**.

spectrum (see Fig. 7) clearly shows that the protons of the trisubstituted benzene ring also characterize the singlet at 7.78 ppm (cross-peak). A comparison shows that the signal from the H(1) proton in the spectrum of compound **2** is detected at 7.8 ppm, whereas the signal of the same H(1) proton in the spectrum of compound **1** (tribromo-substituted monomer) is observed at 7.7 ppm. It can be assumed that in the spectrum of the polymer the signal from the phentriyl proton H(20) is localized in the closest vicinity to the bromine atoms and appears at 7.78 ppm, unlike the signals at 7.89 ppm that belong to other phentriyl protons.

The COSY spectrum exhibits spin systems of the same type for oligophenylene **P-1** and for the monomer **1** with the terminal bromine atoms. For example, the components of the AA´BB´ system at 7.65/7.64 and 7.62/7.61 ppm are clearly seen. The both components have spin-spin coupling constants J = 8.5 Hz. The second system is at 7.65/7.63 and 7.59/7.58 ppm with J = 8.4 Hz. The chemical shifts and spin-spin coupling constants are consistent with similar values for compound **1**. Thus, the part of the spectrum in the region δ 7.55—7.65 is assigned to signals from the H(4) and H(5) protons localized in the nearest vicinity of the terminal bromine groups.

The COSY experiment also shows that the part of the ^{1}H NMR spectrum at 7.75 and 7.85 ppm characterizes the protons of the *p*-substituted benzene rings.

The HSQC spectrum (Fig. 8) clearly shows correlations of signals from the C(13), C(12), and C(11) carbon atoms at 127.67, 129.08, and 127.30 ppm with the corresponding protons. Another, more intense ^{13}C signal is observed at 127.89 ppm and correlates with multiplet signals at 7.81 and 7.74 ppm. A comparison with the spectra of compounds **1** and **3** indicates that the signals at 7.81 ppm belongs to the protons of the phenylene groups, namely, H(5) and H(4), as in compound **3**. Thus, the signals from the C(7) and C(8) atoms can be considered assigned. Based on the similarity of the chemical environment of these protons in positions 22—25, we can conclude that the corresponding signals from carbon C(22)—C(25) can overlap with the C(7) and C(8) signals in the ^{13}C NMR spectrum. The signals centered at 7.66 ppm are assigned to the protons of the bromosubstituted phenylene groups (protons H(4) and H(5) in compound **1** and oligophenylene **P-1**) and correlate with the C(5) signal at 132.02 ppm in the ^{13}C NMR spectrum. Thus, some signals at 7.55—7.65 ppm are assigned to the H(4) and H(5) protons situated in the nearest vicinity to the terminal bromine atoms (see Table 1).

The HSQC spectrum includes other correlations as well: the signals centered at 125.22 ppm correlate with those at 7.92/7.81 ppm assigned, most probably, to the protons H(1), H(16), and H(17) of the trisubstituted benzene rings.

The HMBC spectrum (Fig. 9) of oligophenylene **P-1** resembles similar spectra of the model compounds. The signal at 140.60 ppm correlates with the signals of triplets of the phenyl groups and can be assigned to C(14). The same multiplet signal from the carbon atom also correlates with the signals of protons at 7.69 (H(11)), 7.75 (H(22), H(23)) and 7.82 ppm (H(7), H(8)). The signals

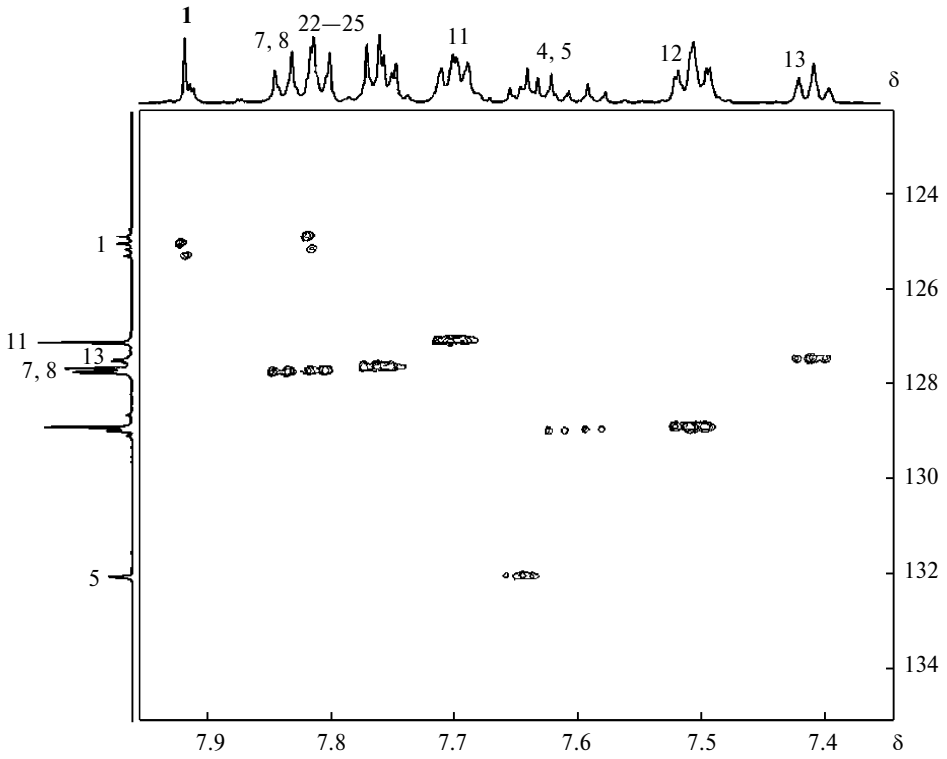


Fig. 8. HSQC spectrum of oligophenylene **P-1**.

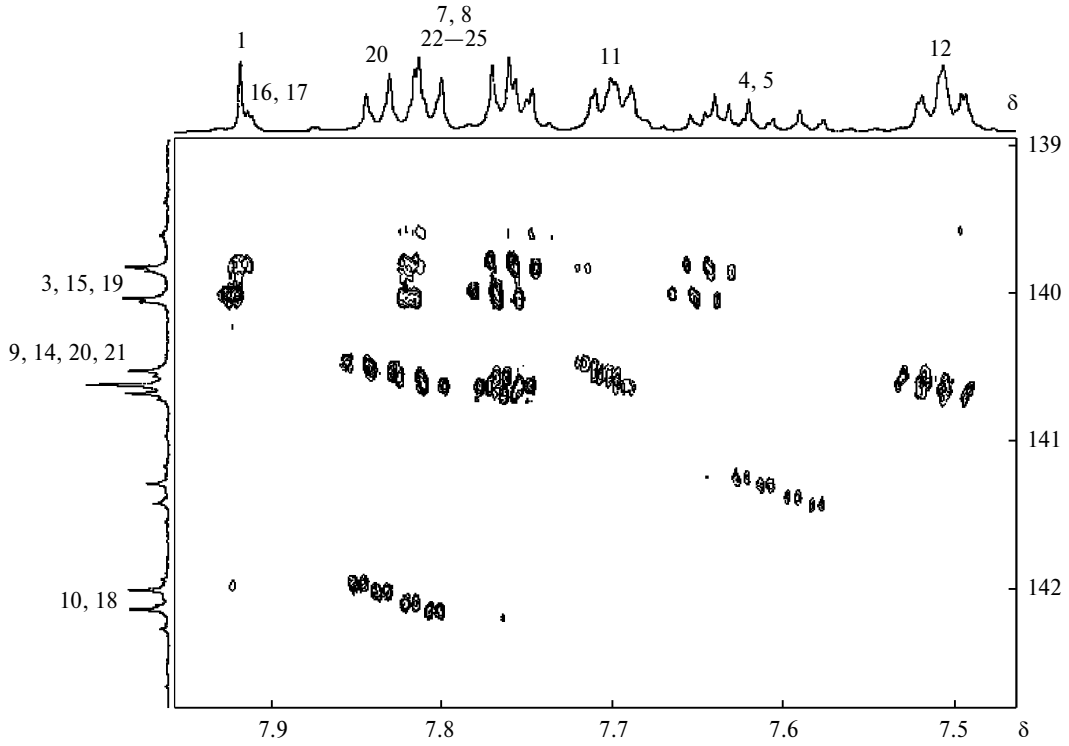


Fig. 9. HMBC spectrum of oligophenylene **P-1**.

from the C(20) and C(21) atoms are partially overlapped with the signals of C(14) and C(9). The signals from the C(10) and C(15) atoms at 142.26 ppm are similar to the signals from C(6) and C(7) of compound **5** and correlate with the signals of the H(7) and H(8) protons. The signals from the C(19) and C(18) atoms are, most likely, at 139.90

and 140.10 ppm and correlate with the signals from the protons H(16), H(17), and H(22) (C(19)) and H(23) (C(18)).

Based on the signal assignment of protons of model compound **6**, we can say more exactly that the signals in the ^{1}H NMR spectrum at 7.75—7.82 ppm characterize the H(22)—H(25) protons.

The ratio of the major fragment of **P-1** was calculated by the integration of the ^{1}H NMR spectrum. The integral intensity of protons of the bromosubstituted rings towards the sum of integral intensities of signals from all protons is ~1.2 : 10, *i.e.*, oligophenylene **P-1** contains a significant part of phenyl groups.

Since the biphenyl bridging group includes eight protons of the H(22)—H(25) type and each terminal biphenyl group contains four protons of the H(7) and H(8) type, the ratio of these groups can be calculated from the integral intensities as ~1 : 2.

Thus, we succeeded to determine signals from the bridging groups appeared due to the polymer formation reaction and to distinguish signals from the biphenyl groups in the NMR spectrum of oligophenylene **P-1**. These results provide the possibility of further studying the structures of branched oligo- and polyphenylenes containing various substituents.

Experimental

p-Bromoacetophenone, *p*-iodoacetophenone (Aldrich, 98%), aluminum(III) chloride (Aldrich, 99.9%), phenylboronic acid (Merck), 2,2′-bipyridyl (bpy) (Aldrich, 99%), and zinc dust (Aldrich, 98%, <10 μm) were used without additional purification. Nickel(II) chloride was dried for 8 h in a dry HCl flow at 600 °C. Triphenylphosphine (Aldrich, 99%) was purified by recrystallization from hexane and dried for 12 h *in vacuo* (0.133 Pa).

Solvents were dried under the corresponding reagents and distilled under argon prior to use. The Ni-catalyzed polycondensation was carried out in Schlenk tubes in a dry argon atmosphere. The catalysts were added in an argon flow. TLC on Silufol UV-254 plates were used to monitor the reaction course and purity of isolated products. Column chromatography was carried out using silica gel (Aldrich, 70—230 mesh).

To obtain dry deoxygenated argon, it was passed through three consequently connected columns packed with Al_2O_3, catalyst, and molecular sieves (pore size ~4Å).

The ^{1}H and ^{13}C NMR spectra and 2D COSY, HSQC, and HMBC correlations were recorded on a Bruker AM-600 pulse spectrometer (working frequency 600.12 MHz) with the Fourier transform and broad-band spin-spin proton decoupling. Solutions of the samples in deuterated chloroform were used. Chemical shifts were measured relatively to hexamethyldisiloxane (HMDS, δ 1.94) with an accuracy of 0.01 ppm, and spin-spin coupling constants (*J*) were measured with an accuracy of 0.1 Hz.

According to published data,[19] cyclotrimers **1—5** were synthesized by the cyclocondensation of the corresponding acetylaromatic compounds in a solution of dry benzene at 20 °C at the molar concentration of the starting monoacetyl compound in the presence of triethyl orthoformate (1.2 mol) passing the HCl current for 2 h. The formed precipitate was filtered off, washed with acetone and alcohol, and recrystallized from chloroform.

1,3,5-Tris(*p*-bromophen-4′-yl)benzene (1).[21] A round-bottom flask (200 mL) was charged with 4-bromoacetophenone (12.18 g, 60 mmol), benzene (60 mL), and ethyl orthoformate ester (13.47 mL, 79.5 mmol) at ~20 °C. Gaseous HCl was passed through the reaction mixture for 2 h with vigorous stirring. The solution gained a brown-red color within the first hour, and a precipitate began to form. After the end of the reaction, the precipitate was filtered off, washed with acetone and alcohol, and dried for 12 h *in vacuo* (0.133 Pa) at ~20 °C and purified using column chromatography on silica gel (chloroform as an eluent). The yield was 5.11 g (47%), pale yellow crystals, m.p. 267—270 °C. Found (%): C, 53.48; H, 3.08; Br, 43.48. $C_{24}H_{15}Br_3$. Calculated (%): C, 53.03; H, 2.76; Br, 44.19. ^{1}H NMR (600 MHz, $CDCl_3$), δ: 7.72 (s, 1 H); 7.63 (d, 2 H, J = 8.5 Hz); 7.56 (d, 2 H, J = 8.5 Hz). MS (EI), m/z: 542.2 $[M]^+$.

Compounds **2—5** were obtained similarly.

1,3,5-Triphenylbenzene (2).[20] The yield was 62%, m.p. 175 °C. Found (%): C, 94.21; H, 5.76. $C_{24}H_{18}$. Calculated (%): C, 94.12; H, 5.88.

1,3,5-Tris(*p*-diphenyl-4′-yl)benzene (3) was purified using column chromatography (silica gel, chloroform, R_f = 0.8). The yield was 52%, white powder, m.p. 240—242 °C. Found (%): C, 94.43; H, 5.57. $C_{42}H_{30}$. Calculated (%): C, 94.38; H, 5.62. ^{1}H NMR (600 MHz, $CDCl_3$), δ: 7.92 (s, 3 H); 7.84 (d, 6 H, J = 8.3 Hz); 7.76 (d, 6 H, J = 8.3 Hz); 7.70 (d, 6 H, J = 7.2 Hz); 7.51 (t, 6 H, J = 7.7 Hz); 7.40 (t, 3 H, J = 7.4 Hz). MS (EI), m/z: 534.7 $[M]^+$.

1,3,5-Tris(1,3,5-triphenylbenzene-4′-yl)benzene (4). The yield was 21.7%, m.p. 118 °C. Found (%): C, 94.73; H, 5.22. $C_{78}H_{54}$. Calculated (%): C, 94.55; H, 5.45.

1,3,5-Tris(4′′-bromodiphenyl-4′-yl)benzene (5) was purified using column chromatography (silica gel, benzene—ethanol (12 : 1), R_f = 0.9) followed by recrystallization from a dioxane—ethanol (20 : 1) mixture. The yield was 42%, white powder, m.p. 279 °C. Found (%): C, 65.48; H, 3.16; Br, 31.36. $C_{42}H_{27}Br_3$. Calculated (%): C, 65.34; H, 3.50; Br, 31.11. ^{1}H NMR (600 MHz, $CDCl_3$), δ: 7.90 (s, 3 H); 7.83 (d, 6 H, J = 8.2 Hz); 7.72 (d, 6 H, J = 8.2 Hz); 7.63 (d, 6 H, J = 8.4 Hz); 7.56 (d, 6 H, J = 8.4 Hz). MS (EI), m/z: 773.5 $[M]^+$.

1,3,5-Tris[(*p*-terphenyl)-4′′′-yl]benzene (6).[20] A Schlenk tube was evacuated several times and filled with argon. Then, compound **5** (0.463 g, 0.6 mmol), phenylboronic acid (0.366 g, 3.0 mmol), freshly distilled THF and DMSO (8 and 0.8 mL, respectively), and 2 *M* aqueous K_2CO_3 (0.8 mL) were placed into the tube. The Schlenk tube was evacuated several times, and $Pd[PPh_3]_4$ (0.029 g, 0.025 mmol) was added. The synthesis was performed in an argon atmosphere at 60 °C for 48 h. After the end of the reaction, the solution was extracted with chloroform and washed with 2 *M* HCl and water, dried over calcium chloride, and evaporated on a rotary evaporator. The product was purified using column chromatography (silica gel, chloroform, R_f = 0.9). The yield was 0.052 g (11%), white powder, m.p. 282 °C. Found (%): C, 94.05; H, 5.95. $C_{60}H_{42}$. Calculated (%): C, 94.36; H, 5.64. ^{1}H NMR (600 MHz, $CDCl_3$), δ: 7.95 (s, 3 H); 7.88 (d, 6 H, J = 8.2 Hz); 7.83 (d, 6 H, J = 8.2 Hz); 7.80 (d, 6 H, J = 8.2 Hz); 7.75 (d, 6 H, J = 8.2 Hz); 7.70 (d, 6 H, J = 7.7 Hz); 7.51 (t, 6 H, J = 7.6 Hz); 7.40 (t, 3 H, J = 7.4 Hz). MS (EI), m/z: 762.6 $[M]^+$.

Oligophenylene P-1. A Schlenk tube was preliminarily alternately evacuated five times and filled with argon. Then 1,3,5-tri-

(*p*-bromophenyl)benzene (**2**) (1.086 g, 2 mmol) and the catalytic system containing $NiCl_2$ (0.012 g, 0.1 mmol), Ph_3P (0.052 g, 0.2 mmol), bpy (0.015 g, 0.1 mmol), and Zn (0.392 g, 6.0 mmol) were loaded. The Schlenk tube was evacuated once more and filled with argon, and freshly distilled DMF (5 mL) was added in an argon countercurrent. The reaction was carried out in argon at 70 °C with vigorous stirring. In 10 min, the reaction mixture gained a red-brown color, indicating the *in situ* formation of the catalytic Ni^0 complex. In 30 min after the beginning of the reaction, freshly distilled bromobenzene (0.63 mL, 0.06 mmol) was added to the reaction solution, and the reaction was continued for 2 h more. After the end of the reaction, the solution was extracted with chloroform, the catalyst was filtered off, and the filtrate was evaporated on a rotary evaporator (before precipitation). The product was precipitated to methanol, filtered off, washed with 2 *M* HCl and methanol, and dried for 13 h *in vacuo* (0.133 Pa) at ~20 °C. A light beige powder was obtained. Found (%): Br, 21.98.

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