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Branched Polyphenylenes by Repetitive Diels−Alder Cycloaddition

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ABSTRACT: Diels−Alder reactions between 1,4-bis(2,4,5-triphenylcyclopentadienone-3-yl)benzene and either phenylacetylene (model reaction) or 1,4-diethynylbenzene (polymer formation) were studied. NMR spectra suggest that the main product in the model reaction is the *m*,*m*-isomer (up to 83% yield). X-ray crystal structure analysis convincingly proved the structure of the above isomer. The polymer-forming reaction was carried out using different concentrations of the monomeric building block and different reaction times. As a result, branched polyphenylenes with M_w in the range of 1.2×10^4−12×10^4 g mol^{-1} were obtained. Both the model compound and the polymers were subjected to intramolecular oxidative cyclodehydrogenation with copper(II) trifluoromethanesulfonate and aluminum chloride. According to LD-TOF mass spectrometry, the cyclodehydrogenation of the model compound afforded the planarized polycyclic aromatic hydrocarbon $C_{66}H_{26}$. This polycyclic aromatic compound was isolated in 91% yield. The extended π-conjugation and ordering of cyclodehydrogenated products were demonstrated by Raman spectroscopy.

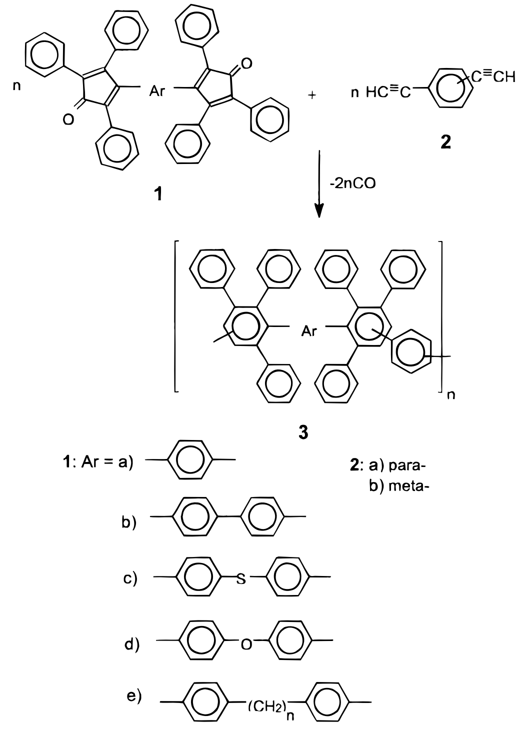
Introduction

The Diels−Alder reaction has proven of outmost importance in synthetic organic chemistry. This method was also employed as a step-growth reaction in the formation of linear, ladder, and stepladder polyphenylenes.[1,2] Branched, high molecular weight polyphenylenes were successfully synthesized by Stille and coworkers and other authors[3−11] using Diels−Alder cycloadditions of different bis(tetraphenylcyclopentadienone-yl)arenes (**1**) and diethynylarenes (**2**) (Scheme 1).

The surprisingly high solubility of these polymers in common organic solvents was ascribed by Stille to the occurrence of both meta and para couplings in the above Diels−Alder reactions which feature increased disorder along polymer chains. In our recent synthesis of dendritic and hyperbranched polyphenylenes we used the repetitive Diels−Alder reaction of A_2B- and A_4B-type tetraphenylcyclopentadienone building blocks which carry additional ethynyl substituents and thus possess both diene and dienophile functions.[12] The resulting 3D polyphenylenes are structurally well-defined and possess a high solubility in organic solvents which, in the case of the dendrimers, increases upon going to higher generations. This finding leaves little doubt that the structural requirement for the high solubility of branched and hyperbranched polyphenylenes is the significant torsion about inter-ring bonds.

We have recently shown that oligophenylenes can readily be transformed into polycyclic aromatic hydrocarbons (PAHs) by intramolecular cyclodehydrogenation. The reaction conditions closely correspond to those used by Kovacic for the oxidative coupling of benzenoid monomers.[13] The resulting giant PAHs self-organize into unique supramolecular architectures which appear as useful components of molecular electronics.[14,15]

Scheme 1. Synthesis of Branched Polyphenylenes by Diels−Alder Reaction



We report here our results concerning the formation of meta or para coupling of the Diels−Alder reactions of 1,4-bis(2,4,5-triphenylcyclopentadienone-3-yl)benzene (**1a**) and ethynylbenzene (**4**) (Scheme 2). Earlier, Stille and Noren showed[16] that the ratio of para to meta isomers in the model reaction of 3-(4-biphenylyl)-2,3,4-triphenylcyclopentadienone with 4-ethynylbiphenyl varied from 0.55 at 100 °C to 1.0 at 255 °C. The isomer ratios of the crude reaction mixture were determined by UV analysis, and data were kinetically analyzed by application of the Arrhenius equation. However, in our opinion, the question regarding the ratio of para and

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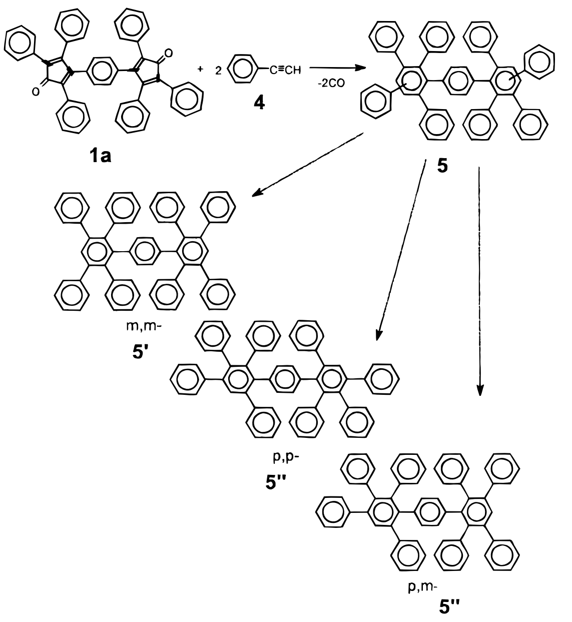
Scheme 2. Possible Isomers (5′, 5″, 5‴) Obtained upon Diels−Alder Reaction of Phenylacetylene (4) with 1,4-Bis(2,4,5,-triphenylcyclopentadienone-3-yl)benzene (1a)



meta coupling needs further consideration because an unequivocal assignment of isomer structures has not been achieved. Accordingly, to evaluate the relative amount of each type of regioisomer in the Diels−Alder reaction and to reliably assign isomer structures, we studied the model reaction of 1,4-bis(2,4,5-triphenylcyclopentadienone-3-yl)benzene (**1a**) with ethynylbenzene (**4**). We choose this model reaction because it most closely simulates the polymer-forming, repetitive Diels−Alder reaction of 1,4-bis(2,4,5-triphenylcyclopentadienone-3-yl)benzene (**1a**) and 1,4-diethynylbenzene (**2a**) reported in this paper as well.

This paper is also concerned with the synthesis of extended PAH structures by planarization of the high molecular weight soluble polyphenylene precursors through intramolecular cyclodehydrogenation reactions.

Results and Discussion

Model Reaction. The Diels−Alder reaction of 1,4-bis(2,4,5-triphenylcyclopentadienone-3-yl)benzene (**1a**), prepared according to the literature,[17] and 2 equiv of phenylacetylene (**4**) can, in principle, produce the *m,m*-, *p,p*-, and *m,p*-linked isomers according to Scheme 2.

The reaction was carried out at 240 °C in α-methylnaphthalene, for 24 h, in a Schlenk tube under argon atmosphere. A change of the color of the reaction mixture from magenta to yellow suggested the end of the reaction. The crude product **5** obtained in 92% yield clearly consisted of an isomeric mixture (Scheme 2). Separation of isomers by crystallization gave a 83% yield of a single product with a melting point of ca. 350 °C. The structure of the product was studied by high-resolution NMR (including C−H correlation in 2D-NMR spectra and NOE measurements), IR spectroscopy, and single-crystal X-ray analysis. The signal of a cyclopentadienone carbonyl group was absent in both the FTIR spectrum and the ^{13}C NMR spectrum.

The NMR analysis strongly suggests that the main product obtained in the Diels−Alder reaction of 1,4-bis(2,4,5-triphenylcyclopentadienone-3-yl)benzene (**1a**) and ethynylbenzene (**4**) is the *m,m*-isomer (**5′**) (Figure 1).

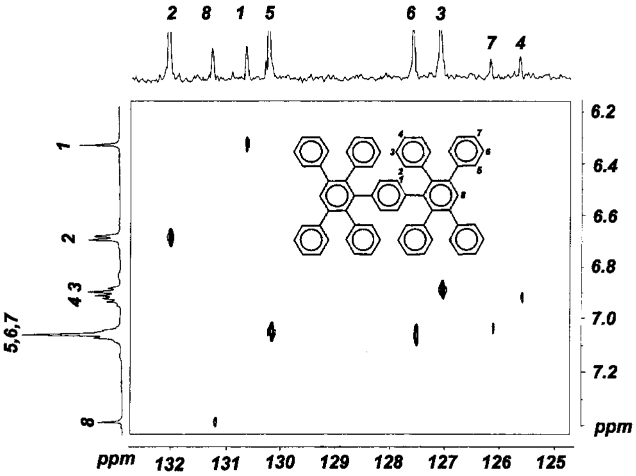


Figure 1. C−H correlation in 2D-NMR spectra of **5′**.

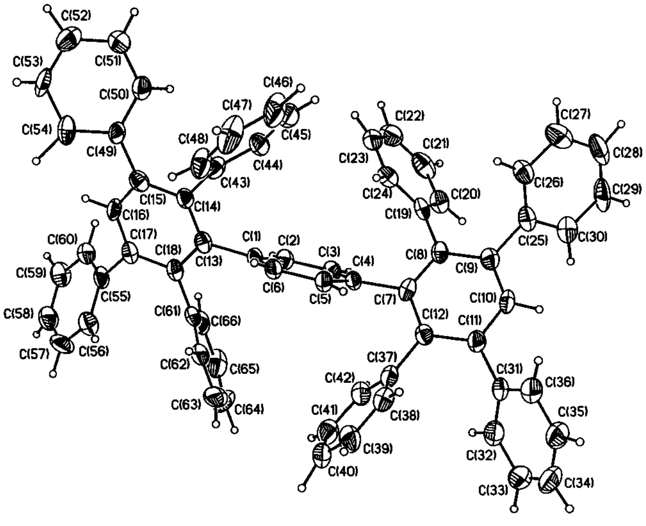


Figure 2. Crystal structure of **5′**.

This structure was further confirmed by use an X-ray analysis of a single crystal prepared from a solution of **5′** in chloroform (Figure 2). Details of the X-ray analysis are presented in the Experimental Section.

The identification of the *m,m*-isomer **5′** as major product differs from that of Stille and Noren, who concluded that no more than 50% of the *meta*-isomers were produced in the Diels−Alder reaction of 1 equiv of 3-(4-biphenylyl)-2,3,4-triphenylcyclopentadienone with 1 equiv of 4-ethynylbiphenyl under similar reaction conditions.

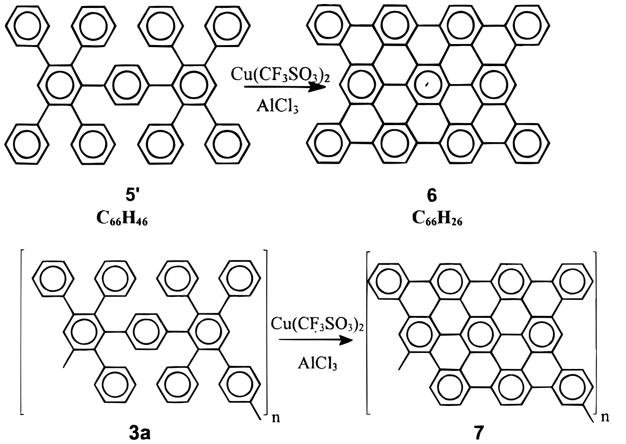
Polymer Synthesis. Earlier, Stille and Harris[5] reported the repetitive Diels−Alder cycloaddition of bis(tetraphenylcyclopentadienone-yl)arylenes (**1**) with diethynylarenes (**2a**,**b**) in a Parr reactor at 200 °C and at a pressure of 200 psi (Scheme 1). In our experiment we performed the polycondensation of 1,4-bis(2,4,5-triphenylcyclopentadienone-3-yl)benzene (**1a**) and 1,4-diethynylbenzene (**2a**) in a Schlenk tube under argon in a mixture of diphenyl ether/α-methylnaphthalene (1:1) at 240 °C. The change of the color from magenta, first, to brown and then to yellow was observed after 5 h. Experiments were performed at different concentrations of the starting compounds and for different reaction times. The characterization of the polymers was performed by size-exclusion chromatography (SEC), ^{1}H and ^{13}C NMR spectroscopy, and mass spectrometry. The latter gives very precise information on the low molec-

Table 1. Reaction Conditions and Characterization of the Polymers (3a) Prepared by the Diels–Alder Polycondensation between 1,4-Bis(2,4,5-triphenylcyclopentadienone-3yl)benzene (1a) and 1,4-Diethynylbenzene (2a)

runs	concn of **1a** and **2a** [mol/L]	time of reaction [h]	yield [%]	$M_w \times 10^{-3\,a}$ [g mol^{-1}] (SEC)	$M_n \times 10^{-3\,a}$ [g mol^{-1}] (SEC)	M_w/M_n	MALDI-TOF (detected species)
a	0.3	18	92	12.3	6.2	1.9	16mer
b	0.3	30	94	17.4	8.6	2.0	18mer
c	0.5	18	91	32.2	14.1	2.3	18mer
d	0.5	30	92	40.6	16.8	2.5	*b*
e	0.5	48	94	51.5	19.7	2.7	*b*
f	0.7	48	93	101.4	26.6	3.9	*b*
g	0.7	72	94	121.6	30.1	4.0	*b*

[a] Determined with polystyrene as standard. [b] Measurements were not performed.

Scheme 3. Transformation of Oglio- and Polyphenylene into PAHs



ular weight fraction of the polymer distribution (see Table 1). According to SEC, the molecular weights of the polymers vary from 12 000 to 120 000 g/mol (M_w). As expected, an increase of the concentration of both monomers by a factor of 2.3 and of the reaction time from 18 to 72 h leads to a significant increase of the molecular weight. The polydispersity of the polymers changes moderately with increasing molecular weight. The polymers proved to be soluble in standard organic solvents (toluene, methylene chloride, chloroform, etc.). The ^{13}C NMR spectra of the polymers were rather complex in the aromatic region and did not significantly depend on the reaction conditions. Signals of the cyclopentadienone carbonyl groups or of terminal acetylene groups could not be detected.

UV/vis spectra of both the model **5′** and the branched polyphenylene **3a** fail to contain absorptions above 310 nm because an extended π-conjugation is prevented due to the lack of resonance beyond three phenylene units. This finding is in agreement with the literature[18,19] where the *m*-phenylene units are considered as conjugation barriers in conjugated polymers. Further, the strong twist of the phenylene rings excludes any π-conjugation.

Oxidative Cyclodehydrogenation. Both the model compound **5′** and polymer **3a** were subjected to intramolecular oxidative cyclodehydrogenation (Scheme 3). Thereby, the reaction of **5′** proceeds in the same manner as shown by us for various hexaarylbenzenes[20,21] for which treatment with copper(II) trifluoromethanesulfonate and aluminum(III) chloride gave the desired PAH structure. According to laser desorption time-of-flight (LD TOF) mass spectroscopy, the cyclodehydrogenation of **5′** resulted in the formation of 10 new carbon–carbon bonds giving the $C_{66}H_{26}$ hydrocarbon **6**. The extremely low solubility of **6** in standard solvents did not allow to characterize the compound by NMR and also excluded further purification. We did not succeed in obtaining a soluble product by partial cyclodehydrogenation of $C_{66}H_{46}$. An alternative synthesis of **6** will be published by us elsewhere.[22]

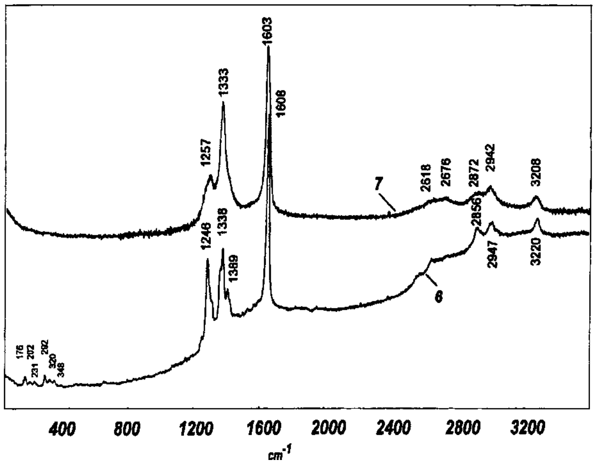


Figure 3. Raman spectra of **6** and **7** (λ_{excit} = 514.5 nm).

We also performed preliminary studies on the cyclodehydrogenation reaction of polymer **3a**. **3a** (run b, Table 1) was subjected to oxidative cyclodehydrogenation with copper (II) trifluoromethanesulfonate and aluminum chloride in carbon disulfide at room temperature according to Scheme 3. A dark brown, insoluble product **7** was formed which escaped NMR characterization because of its insolubility, and like model compound **6** was studied by IR and Raman spectroscopy. In the IR spectrum of **7** the band at 700 cm^{-1} which can be attributed to the out-of-plane δ(CH) vibration of monosubstituted benzene as well as bands that are typical for the in-plane δ(CH) vibration of differently substituted benzenes in the region 900–1160 cm^{-1} and that of three peaks at 3020, 3050, and 3080 cm^{-1} (aromatic ν(=C–H)) are absent. In the Raman spectra of polymer **7** and model compound **6** only very intense lines of aryl ring stretching vibration are observed (Figure 3), which can be rationalized in terms of preresonance enhancement of the lines corresponding to the modes of strongly conjugated structures.[23] It is worthy to note that no ν_{CH} lines are registered; the overtones and combinations of the above-mentioned modes in the region 1300–1600 cm^{-1} are observed instead, which is typically for resonance-enhanced spectra. Further, the bands at 994 cm^{-1} characteristic of monosubstituted benzene rings are entirely absent in the Raman spectra of polymer and model compounds. Accordingly, while at least partial dehydrogenation is obvious, a full structure proof for the desired polymer **7** is not possible.

Conclusion

It appears that the Diels–Alder reaction of bis(cyclopentadienone)s **1** and ethynylbenzene results in the predominant formation of the *m*,*m*-isomer **5′.** In principle, in each [4 + 2]-cycloaddition, two different regioisomers can be formed. In the case of a polymer-forming reaction, this leads to *para*- or *meta*-coupling within the main polymer chain, and a structurally perfect, phenyl-substituted poly(*p*-phenylene) is not to be expected.

The branched polyphenylenes obtained have molecular weights in the range 12 000–120 000 g mol^{-1}, and their polydispersity changes insignificantly with increasing molecular weight. Intramolecular cyclodehydrogenation of 3D-oligophenylene model compound **5′** provides polycyclic aromatic hydrocarbon **6.** The same reaction transforms polyphenylene **3a** into an insoluble product whose detailed structural elucidation is in progress.

Experimental Section

1,4-Bis(2,4,5-triphenylcyclopentadienone-3-yl)benzene (**1a**) was prepared according to the literature.[17] 1,4-Diethynylbenzene (**2a**) was used after sublimation. Phenylacetylene (**4**) was used as purchased. Solvents were dried and stored under N_2.

^{1}H and ^{13}C NMR chemical shifts were obtained using a Bruker AMX 500 spectrometer (deuterated solvents as the internal standard) and expressed in parts per million (ppm). Mass spectra were obtained using a VG Trio 2000 (EI,70 eV) and a VG Instruments ZAB2-SE-FPD (FD). Size-exclusion chromatography analyses were performed with PPS gel columns using polystyrene standard. IR spectra were recorded using a Nicolet FT-IR 320. Raman spectra were taken using Jobin-Yvon T 64000. The UV–vis absorption spectra were measured with a Perkin-Elmer Lambda 9.

Synthesis of Model Compound 5′. The Diels–Alder reaction between 1,4-bis(2,4,5-triphenylcyclopentadienone-3-yl)benzene (**1a**) (1.3816 g, 2 mmol) and phenylacetylene (**4**) (0.4086 g, 4 mmol) was carried out at 240 °C in α-methylnaphthalene (6 mL) with stirring, for 24 h, in a Schlenk tube, under argon. The tube was degassed by a series of freeze–pump–thaw cycles to remove O_2. A color change from magenta to yellow served as an indication of the end of the reaction. After the reaction was finished the mixture was precipitated into acetone, filtered off, washed, and dried, giving almost colorless product in 92% yield. One recrystallization of the above product from a mixture of chloroform/methanol (1:1) gave a 83% yield of colorless crystals (**5′**) with mp of 350 °C.

^{13}C NMR (125 MHz, tetrachloroethane-d_2, 130 °C): δ = 142.45, 141.19, 140.93, 140.47, 139.65, 137.21, 131.96, 131.17, 130.56, 130.14, 127.50, 127.02, 126.11, 125.57. ^{1}H NMR (500 MHz, tetrachloroethane-d_2, 130 °C): δ = 7.37 (s, 2H); 7.06–7.03 (m, 20H); 6.94–6.87 (m, 12H); 6.68–6.62 (m, 8H); 6.31 (s, 4H). FD-MS for **5′**: *m*/*z*: 838.2 [M$^+$]. UV/vis ($CHCl_3$): λ_{max} = 265, 287 nm.

General Procedure for the Synthesis of Polyphenylene 3a (See Table 1). A 50 cm^3 Schlenk tube was charged with a suspension of the 1,4-bis(2,4,5-triphenylcyclopentadienone-3-yl)benzene (**1a**) (1.338 16 g, 2 mmol), 1,4-diethynylbenzene (**2a**) (0.2524 g, 2 mmol), and a mixture of diphenyl ether/α-methylnaphthalene (1:1) (5 mL) and then degassed by a series of freeze–pump–thaw cycles to remove O_2. The reaction was carried out for the desired time (see Table 1) at 240 °C, with stirring, under argon atmosphere. After the reaction was complete, the clear viscous yellow liquid was precipitated into methanol, filtered off, washed with an excess of methanol, and dried in vacuo at 80 °C for 24 h. Conditions of synthesis, yield, and molecular weights of polymer prepared **3a** are shown in Table 1.

Intramolecular Cyclodehydrogenation. (a) Model Compound. Model compound $C_{66}H_{46}$ (**5′**) was subjected to oxidative cyclodehydrogenation with copper(II) trifluoromethanesulfonate ($Cu(CF_3SO_3)_2$) and aluminum chloride. Thereby, a degassed solution of **5′** (150 mg, 0.18 mmol) in CS_2 (5 mL) was added to a degassed mixture of $Cu(CF_3SO_3)_2$ (3.86 g, 10.7 mmol) and sublimed aluminum chloride (1.43 g, 10.7 mmol) in 25 mL of CS_2 via a syringe. The deep gray mixture was stirred at room temperature under argon for 5 h. After precipitation into methanol, the reaction mixture was filtered off and the residue washed with dilute HCl and methanol to produce a dark brown solid **6** in 91% yield (133.2 mg, 0.163 mmol).

MS (LD-TOF), calibrated with [60]fullerene and [70]fullerene: *m*/*z* = 819 [M$^+$], calcd for C_{66} H_{26} = 818.93. Raman spectrum for **6**: ν (cm^{-1}) 1246, 1338, 1369, 1608, 2856, 2947, 3220 (see Figure 3).

(b) Polymer. Polymer **3a** was treated with $Cu(CF_3SO_3)_2$ and aluminum chloride in carbon disulfide as described above for model compound. Raman spectrum for **7**: ν (cm^{-1}) 1257,-1333,1603, 2676, 2872, 2942, 3208 (see Figure 3).

Determination of the Crystal Structure of 5′. Crystals of the 1:3 solvate of $C_{66}H_{46}\cdot 3CHCl_3$ (M = 1197.13) are triclinic, space group $P1$, at −120 °C, a = 11.782(4) Å, b = 16.326(5) Å, c = 18.099(7) Å, α = 114.90(3)°, β = 107.57(3)°, γ = 90.76(3)°, V = 2970 Å^3, d_{calc} = 1.339 g cm^{-3} for Z = 2, μ(Mo Kα) = 4.66 cm^{-1}. Unit cell parameters and intensities of 9219 reflections were measured at −120 °C with a Siemens P3/PC diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å, $\theta/2\theta$ scan technique, θ_{max} = 24°, the transparent crystals had a needlelike habit of 0.5 × 0.3 × 0.2 mm dimensions, no absorption correction was applied). The structure was solved by direct methods and refined by full-matrix least-squares technique in the anisotropic approximation. The hydrogen atoms were located in a series of difference Fourier syntheses and included in the refinement with isotropic thermal parameters. Two of the three solvate $CHCl_3$ molecules are disordered over two positions; the positions of disordered chlorine and carbon atoms were refined with the site occupation factors equal to 0.5. Final discrepancy factors are R_1 = 0.0633 (on F_{hkl} for 4535 reflections with $I > 2\sigma(I)$), wR_2 = 0.1833 (on F^2_{hkl} for all 8475 reflections used in the refinement of 945 parameters). All calculations were carried out on an IBM PC with the help of the SHELXTL PLUS 5 (gamma version) program.

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