g (92%) of pure **18** was recovered by flash chromatography[24] (ethyl acetate/petroleum ether, 1/4).

Preparation of 19a and 19b. Procedure A. 1-Hexyne (13 mmol) in hexane (10 mL) was added to a cooled (-15 °C) hexane solution (10 mL) of butyllithium (13 mmol). The formed white suspension was stirred at room temperature (30 min) and cooled to 0 °C. Then a hexane solution (15 mL) of diethylaluminum chloride (13 mmol) was added, and the resulting mixture was stirred for an additional 2 h before use.

Procedure B. Via the reported procedure,[16] the alkyne (15 mmol) was added to 13 mmol of triethylaluminum cooled at 0 °C. The mixture was stirred 48 h at room temperature, and additional alkyne (4 mmol) was added; the resulting solution was heated at 50 °C (15 h) and then diluted with 30 mL of hexane.

Reaction of 4 or 7 with 19. General Procedure. A benzene solution (15 mL) of the nitro olefin (10 mmol) was added dropwise to a cooled (-15 °C) hexane solution of the diethylalkynylalane **19** (13 mmol). The mixture was stirred at room temperature (30 min) and then hydrolyzed according to procedure A. The crude products obtained were purified by flash chromatography[24] (ethyl ether/petroleum ether, 4/96).

Hydrolysis. Procedure A. The cooled (0 °C) reaction mixture was poured into a flask containing 250 mL of a cooled (-10 °C) and vigorously stirred 0.2 N HCl solution saturated with NaCl and ether (50 mL). Sometimes a precipitate is formed from the reaction of the nitro olefins with **15** or **19**. In this case, the solid was triturated, suspended in ether, and added to the acid mixture. The organic product was extracted into ether (3 × 50 mL) and dried over Na_2SO_4. The solvent was evaporated (20 mmHg) to give crude products **16** and **20**, which were in turn purified by flash chromatography.[24]

Procedure B. The reaction mixture was poured into 200 mL of 3.0 N HCl solution and vigorously stirred for 2 h; the organic product was extracted into ether (3 × 50 mL) and dried over Na_2SO_4. The solvent was removed at reduced pressure, and crude products **17a** and **17b** were purified by flash chromatography.[24]

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Registry No. **4**, 2562-37-0; **5**, 22987-82-2; **6**, 2783-14-4; **7**, 705-60-2; **8**, 113810-80-3; **10**, 118921-40-7; **11a**, 74221-87-7; **11b**, 118921-39-4; **13**, 118921-41-8; **14a**, 74221-86-6; **14b**, 118921-42-9; *cis*-**16a**, 118921-43-0; *trans*-**16a**, 118921-44-1; *cis*-**16b**, 118921-45-2; *trans*-**16b**, 118921-46-3; **16c**, 118921-47-4; **16d** (isomer 1), 118921-48-5; **16d** (isomer 2), 118921-49-6; **16f**, 118921-50-9; *cis*-**16g**, 118921-51-0; *trans*-**16g**, 118921-52-1; **16h**, 118921-53-2; **17a**, 26965-15-1; **17b**, 5312-86-7; **18**, 3569-36-6; *cis*-**20a**, 118921-54-3; *trans*-**20a**, 118921-55-4; **20b**, 118921-56-5; **20c** (isomer 1), 118921-57-6; **20c** (isomer 2), 118921-58-7; DIBAH, 1191-15-7; Al-*i*-Bu_3, 100-99-2; PHC≡CH, 536-74-3; 1-hexyne, 693-02-7; diethylaluminum chloride, 96-10-6; triethylaluminum, 97-93-8.

Soluble, Graphitic Ribbon Topologies. A Synthetic Strategy and First Model Studies

Karsten Blatter, Arnulf-Dieter Schlüter,* and Gerhard Wegner

Max-Planck-Institut für Polymerforschung, Postfach 3148, D-6500 Mainz, F.R.G.

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A strategy for the synthesis of graphitic, ribbon-shaped polymers is presented which is based on repetitive Diels–Alder (DA) methodology involving bifunctional, partially aromatic dienes and bifunctional dienophiles like benzoquinone. This paper describes related model studies, the results of which are interpreted as good evidence for the feasibility of the outlined strategy. The synthesis of novel, alkyl chain substituted polycyclic aromatic compounds **5**, **6**, **8**, **10b–d**, **11c,d**, and **13** is described. Compounds **10c,d** and **13** show surprisingly high solubilities in chloroform at room temperature. Finally, the structure of the "S"-shaped quinone derivative **11c** as derived from an X-ray analysis is presented.

Introduction

Ribbon-shaped (or ladder) polymers constitute an intriguing and aesthetically pleasing class of structures. For more than 20 years, chemists have focused attention on syntheses of such structures, because of their potential applications as either thermally stable, liquid crystalline, or electrically conducting materials; also, interesting mechanical properties may be anticipated for such materials. Ribbon structures which can be considered as part of the graphite lattice are of special interest, since their properties are expected to lie between those of known ladder polymers and that of graphite. In a survey of the literature, two main problems associated with ribbon syntheses are observed, namely, achieving a regular well-defined structure and proving the structure. Due to the multiple-stranded nature of ladder molecules, their synthesis involves formation of at least two bonds between each adjacent pair of monomer units, a situation prone to generate structural irregularities. Most ribbon-shaped structures, especially those with a high degree of unsaturation, e.g., graphitic ribbons, are rigid species and, hence, more or less insoluble. Consequently, a reliable elucidation of their structures turned out to be rather difficult, in many cases impossible.[1]

Up to now, progress in the synthesis of graphitic ribbons was achieved from two different directions. On the one hand, pyrolytic techniques were developed, converting suitable monomers to ribbons under harsh conditions.[2] Because no measures were taken to solubilize the ribbons obtained, these materials were intractable and the assignment of structure remained uncertain. The second approach was based on a stepwise construction of ribbon precursor topologies under mild conditions. Hart, Miller,

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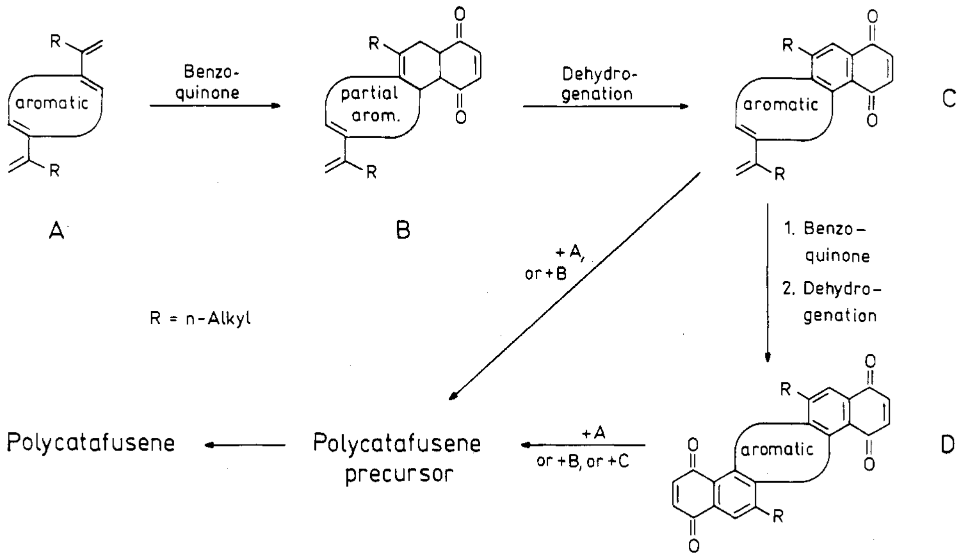
(1) Overberger, C. G.; Moore, J. A. *Adv. Polym. Sci.* **1970**, *7*, 113. Sastri, V. R.; Schulman, R.; Roberts, D. C. *Macromolecules* **1982**, *15*, 939. Lee, B. H.; Marvel, C. S. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 83. Kim, O.-K. *Mol. Cryst. Liq. Cryst.* **1984**, *105*, 161. Bi, X.-T.; Litt, M. H. *Polymer* **1987**, *28*, 2346. Ruan, J. Z.; Litt, M. H. *J. Polym. Sci., Part A: Polym. Chem.* **1987**, *25*, 285.

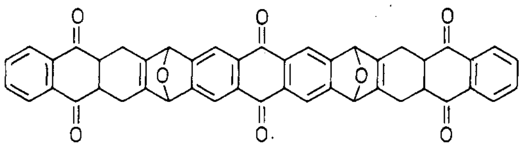
(2) Kaplan, M. L.; Schmidt, C.-H.; Chen; Walsh, W. M., Jr. *Appl. Phys. Lett.* **1980**, *36*, 867. Iqbal, Z.; Ivory, D. M.; Marti, J.; Bredas, J. L.; Baughman, R. H. *Mol. Cryst. Liq. Cryst.* **1985**, *118*, 103. Murakami, M.; Yoshimura, S. *J. Chem. Soc., Chem. Commun.* **1984**, 1649. Murakami, M.; Yoshimura, S. *Mol. Cryst. Liq. Cryst.* **1985**, *118*, 95. Murakami, M. *Synth. Met.* **1987**, *18*, 531.

0022-3263/89/1954-2396$01.50/0

Scheme I



and others utilized the repetitive Diels–Alder (DA) methodology successfully to prepare a variety of well-defined but short polyacene precursor ribbons.[3] They observed a rather dramatic decrease in the solubility of these compounds with increasing number of annelated rings. For example, 1, the longest polyacene derivative synthesized, was only sparingly soluble in chloroform. This finding underlines the importance of measures to increase solubility if synthesis of long ribbons is to be successful.



1

Some recent work concerned the question of how to increase the solubility of rigid species.[4] It is not possible as yet to predict the effect of a pendant group on the solubility of a given compound quantitatively, but from the data available, it can be concluded that attachment of flexible alkyl chains generally leads to a significantly increase in solubility.

Results and Discussion

Development of Strategy. A suitable target structure had to be chosen first. The synthesis of well-defined ribbons seemed more likely to be achieved if formation of only two bonds between each two adjacent monomer units was required. Hence, the search was concentrated on doubly stranded systems. Polyacenes, in principle very attractive graphitic ribbons, are known to be very reactive species.[5] Their angular annelated counterparts, the polycatafusenes,[6] ought to be more stable, according to Clar's rule.[7] Therefore, polycatafusenes were selected as the target class of ribbons for this study, and despite their anticipated greater stability compared with the isomeric polyacenes, it seemed reasonable to concentrate on polycatafusene precursors with regularly disrupted conjugation, so as to have materials that could certainly be handled under conventional laboratory conditions.

Our strategy for the synthesis of soluble polycatafusenes is based on Diels–Alder methodology as depicted in Scheme I. It involves bifunctional dienes (A) and the bifunctional dienophile benzoquinone undergoing sequences of Diels–Alder cyclizations followed by dehydrogenation reactions of the initial adducts. Thus, in the first step, adduct B is formed, which is then dehydrogenated to the AB-type monomer C. Monomer C has two options: either it undergoes a sequence of cyclization and dehydrogenation events or it adds another benzoquinone to give the new bifunctional dienophile D, having its own follow-up chemistry.

Some important features of this strategy should be mentioned briefly: (a) The potentially reactive centers in the bis dienes A are partially incorporated into an extended aromatic π-system. On the one hand, this leads to undesirable high activation barriers for the cycloaddition reactions. On the other hand, once the cycloaddition has occurred, the dehydrogenation of adduct B ought to be facilitated by the presence of the residual aromatic part of B, and this, most importantly, renders the DA reactions irreversible.

(b) Compounds A bear alkyl groups in the α-positions. This both serves the solubilization of the ribbons as discussed above and inhibits homopolymerization of these activated olefins.

(c) Benzoquinone is used as bifunctional dienophile. This compound is not only a powerful dienophile but also an efficient dehydrogenation agent. The same can be expected for all quinoid functions generated in the course of the reaction sequence. Consequently, to avoid problems of stoichiometry, either an even more powerful dehydrogenating agent has to be added or all reduced quinoid moieties have to be reoxidized permanently.

(d) Quinoid functions disrupt the π-conjugation regularly as required in our precursor concept.

(e) DA cyclizations of unsymmetrical components generally lead to the formation of isomers. Even though the resultant structural disorder is not aesthetically desirable in our case, it would help to increase the solubility of the ribbons.

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(3) Thomas, A. D.; Miller, L. L. *J. Org. Chem.* **1986**, *51*, 4160. Christopfel, W. C.; Miller, L. L. *Ibid.* **1986**, *51*, 4169. Chiba, T.; Kenny, P. W.; Miller, L. L. *Ibid.* **1987**, *52*, 4327. Jozefiak, T. H.; Miller, L. L. *J. Am. Chem. Soc.* **1987**, *109*, 6560. Kohnke, F. H.; Slawin, A. M. Z.; Stoddart, J. F.; Williams, D. J. *Angew. Chem.* **1987**, *99*, 941. Luo, J.; Hart, H. *J. Org. Chem.* **1987**, *52*, 4833. Luo, J.; Hart, H. *Ibid.* **1988**, *53*, 1343.

(4) See, for example: Ballauff, M. *Macromolecules* **1986**, *19*, 1366. Rehahn, M.; Schlüter, A.-D.; Wegner, G.; Feast, W. J. *Polymer*, in press. Opitz, K.; Schlüter, A.-D. *Angew. Chem.*, in press.

(5) Blome, H.; Clar, E.; Grundmann, C. In *Houben-Weyl, Methoden der Organischen Chemie*; Grundmann, C., Ed.; Thieme: Stuttgart, 1981; Vol. V/2b, p 361.

(6) Balaban, A. T.; Harary, F. *Tetrahedron* **1968**, *24*, 2505. Balaban, A. T. *Pure Appl. Chem.* **1982**, *54*, 1075.

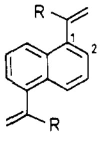
(7) Clar, E. *The Aromatic Sextet*; John Wiley: London, 1972.

Table I. Relative Reactivities of the Bis Dienes 2–4 toward TCNE (2 equiv) in C_6D_6, Determined by ^1H NMR Integration with Dioxane as Internal Standard

	monoadduct			diadduct		
compd	temp, °C	time	% yield	temp, °C	time	% yield
2	80	3 h	50 (**5**)	120	4 days	0
2	80	18 h	>95 (**5**)			
3	20	30 min	60 (**6**)	120	4 days	0
3	80	5 min	>95 (**6**)			
4	80	1 h	50 (**7**)	80	18 h	50 (**8**)

The project outlined in Scheme I is rather complex, and the outcome of the various reactions involved is difficult to predict. Therefore we decided to approach this challenging synthetic problem with model studies.

Reactivity of the Bis Dienes 2–4. In the initial experiments it was important to learn about the relative reactivities of some bifunctional dienes of type A. Therefore, the easily accessible bis dienes 2–4[8] were reacted with tetracyanoethylene (TCNE) as a test dienophile. The cycloaddition reactions were monitored by ^1H NMR spectroscopy under comparable reaction conditions (0.25 mM in hexadeuteriobenzene, 2 equiv of TCNE, sealed tubes under vacuum). All reactions proceeded cleanly; the results are summarized in Table I.



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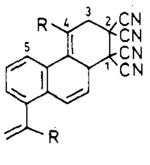

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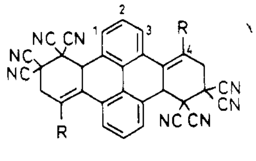

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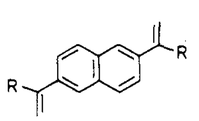

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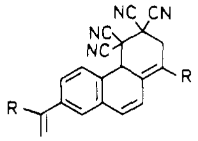
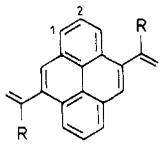


6

R = $(CH_2)_5CH_3$



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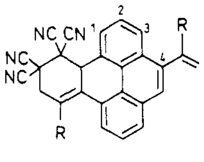
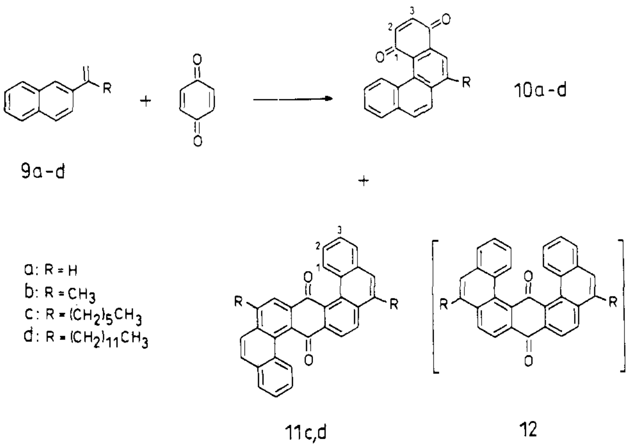


7

Already these qualitative kinetic data provide important insights into the feasibility of the outlined strategy. There is a dramatic loss in reactivity on going from the 2,6-disubstituted naphthalene derivative, **3**, to the 1,5-disubstituted, **2**.[9] Compound **3** is also significantly more reactive than the pyrene derivative **4**. The reactivities of the two functional groups in the bifunctional monomers **2** and **3** are not independent, thus, once the first DA adducts **5** and **6** are formed, a second cycloaddition reaction does not take place. In contrast, monoadduct **7**, derived from the pyrene derivative **4**, forms the diadduct **8** within a reasonable time. This reflects the different activation energies for the second DA step of the monoadducts **5**, **6**, and **7**, respectively. In compounds **5** and **6**, the benzenoid π-system is still intact and has to be disturbed, whereas a cycloaddition reaction of **7** involves the "isolated" double bond of a phenanthrene derivative only, leaving two benzene rings untouched. We concluded that since **3** is the most reactive diene in the first cycloaddition, it seems to be the most suited bifunctional diene for the polycycloaddition reactions, provided that the second DA step can be accomplished.

Scheme II



Cycloadducts **5**, **6**, and **8** were synthesized on a preparative scale, since they are interesting carbocyclic compounds in their own right.[10] Compound **7** was not isolated; its structure was unambiguously deduced from characteristic signals in the ^1H NMR spectra of raw mixtures.

Model Studies

In the next step, the bifunctional but less reactive dienophile benzoquinone was tested. The monofunctional diene **9c**, a model for **3**, was investigated first. Compound **9c** did not show any propensity to react with benzoquinone in benzene solution, even at 140 °C for 2 days. However, acetonitrile proved an effective solvent for this reaction. When **9c** was heated to 100 °C with 3 equiv of benzoquinone, adduct **10c** (Scheme II) was obtained as the major product in an isolated yield of 64%.

It is reasonable to assume that compound **10c** has been formed by dehydrogenation of the initial DA adduct of type B (Scheme I) by excess benzoquinone. This finding was not unexpected,[11] but was nevertheless important in view of the above discussion of the reactivity of the bifunctional diene **3** in the desired polycycloaddition reaction. It is also worth mentioning that the reaction conditions are rather mild. No isomerization[12] or homopolymerization of the starting olefin was observed.

Product **10c** was isolated by column chromatography. A mixture of starting material **9c** and one new compound,

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(8) Blatter, K.; Schlüter, A.-D. *Synthesis*, in press.

(9) We assume that steric hindrance caused by the hydrogen in the peri position is responsible for the low reactivity of the 1,5 derivative **2**.

(10) For analogous reactions with monofunctional aromatic dienes, see, e.g.: Klemm, L. H.; Solomon, W. C.; Kohlik, A. J. *J. Org. Chem.* **1962**, *27*, 2777.

(11) For benzoquinone as dehydrogenating agent, see, for instance, ref 5. See also ref 17.

(12) The question of the formation of isomers of **3** is addressed in ref 8.

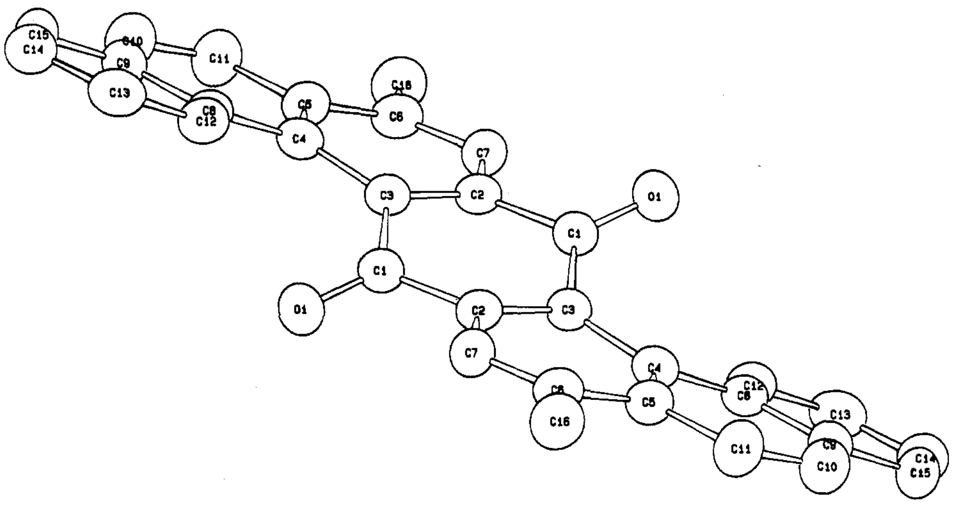


Figure 1. ORTEP plot of the structure of the "S"-shaped quinone derivative **11c**, omitting the hexyl chains except for the α-methylene groups (C(16)).

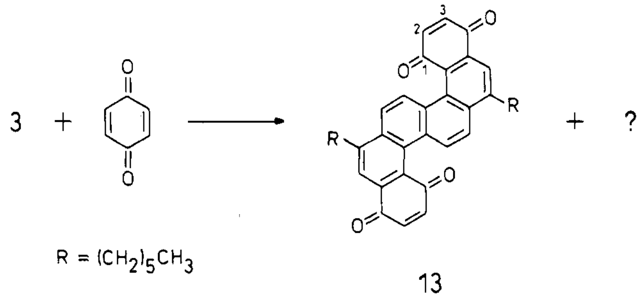
to which we ascribe structure **11c** (anti), was eluted as a small first fraction. **11c** was isolated in a yield of 4% and was fully characterized. Especially informative was the fact that **11c**, by symmetry, shows only one sharp ^{13}C NMR signal for the carbonyl carbons at $\delta = 185.8$ ppm.

Even though isomer **11c** has only been formed to a small extent, the formation itself provides valuable information in respect to the desired ribbon synthesis. Obviously, compound **10c** competes effectively with benzoquinone for diene **9c**, proving sufficient reactivity of the quinoid group in **10c** under the given conditions. This is encouraging evidence for the feasibility of the strategy.

Adducts **10c** and **11c** were isolated in a total yield of 68%, indicating a relatively high conversion in this model reaction. To get a more realistic figure for the actual conversion, the reaction between **9c** and benzoquinone was monitored ^{1}H NMR spectroscopically. The reaction proceeded cleanly, and conversions were determined by integration using dioxane as an internal standard. After 80 h at 100 °C in deuterioacetonitrile, adducts **10c** and **11c** had been formed in 78 (±5)% and 12 (±5)% yields, respectively, based on **9c**. This totals to a conversion of 90 (±5)%, which is quite promising with respect to the achievable molecular weight in the reaction of **3** with benzoquinone.

Formation of Isomers 11c/12. In the model reaction of **9c** with benzoquinone, only one of the two possible isomers **11c**/**12**, the anti adduct **11c**, was observed. Due to very minor uncertainties in the ^{1}H and ^{13}C NMR spectra of typical reaction mixtures, the formation of **12** can not be excluded rigorously. If it is formed, we estimate its yield to be less than 2%. This finding was somewhat unexpected but not unprecedented.[13] The reaction of the dodecyl-substituted olefin **9d** with benzoquinone gave essentially the same results as for **9c** (see Experimental Section).

Reaction of 3 with Benzoquinone. Having obtained these promising results in the monofunctional case, we felt encouraged to test the reactivity of the bis diene **3** toward benzoquinone. Thus, **3** was reacted with a large excess benzoquinone for 3 days at 100 °C in acetonitrile. No starting material **3** could then be detected by ^{13}C and ^{1}H NMR spectroscopy. After workup, the remaining material was separated by flash chromatography. A small, yellow fraction was obtained first, followed by a bright orange fraction, cleanly separated. The third and main fraction was black and was washed off the column by using tetrahydrofuran (THF) as eluent. The first fraction contained only traces of unidentified compounds and was not investigated further. The second fraction consisted of a pure compound, which was unambiguously identified as the dehydrogenated diadduct **13** (see Experimental Section). The yield of crystalline **13** was 15–20% based on **3**.



13

The diadduct **13** constitutes a very interesting key intermediate in the ribbon synthesis. It proves that **3** can act as a bifunctional species in the desired fashion. The formation of **13** also reflects the effectiveness of the dehydrogenation reaction following the first cycloaddition step of **3**. Otherwise the second addition of benzoquinone, finally yielding **13**, would not take place. It is interesting to note that the yield of diadduct **13** was quite low. This may suggest that the quinoid end groups of **13** effectively compete with benzoquinone, even when this is present in large excess.

It should be mentioned that compound **13** is of interest also in relation to other ribbon syntheses. Its bifunctionality, its kinked structure, and its solubilizing groups, together with its availability on the gram scale, make it a valuable AA-type building block for a variety of bifunctional dienes.[14]

The isolation of the diadduct **13** stimulated our interest in the nature of the main fraction. The structure and the molecular weight of this material are presently under investigation.

Structure of 11c. From the very beginning of this work, we considered detailed knowledge of the structures synthesized as very important. Hence, several attempts to grow single crystals were undertaken. In the case of compound **11c**, we were successful in growing single

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[13] For a related observation, see: Muschik, G. M.; Kelly, T. P.; Manning, W. B. *J. Org. Chem.* **1982**, *47*, 4709.

[14] Blatter, K.; Schlüter, A.-D. *Chem. Ber.*, in press.

Table II. Selected Bond Distances[a] of Compound 11c

atom 1	atom 2	distance	atom 1	atom 2	distance
O(1)	C(1)	1.217 (4)	C(6)	C(7)	1.376 (5)
C(1)	C(2)	1.503 (5)	C(8)	C(9)	1.423 (5)
C(1)	C(3)	1.483 (5)	C(8)	C(12)	1.414 (6)
C(2)	C(3)	1.376 (5)	C(9)	C(10)	1.426 (6)
C(2)	C(7)	1.408 (5)	C(9)	C(15)	1.403 (6)
C(3)	C(4)	1.444 (5)	C(10)	C(11)	1.329 (6)
C(4)	C(5)	1.426 (5)	C(12)	C(13)	1.365 (6)
C(4)	C(8)	1.450 (6)	C(13)	C(14)	1.402 (6)
C(5)	C(6)	1.418 (6)	C(14)	C(15)	1.361 (6)
C(5)	C(11)	1.429 (5)			

[a] In angstroms.

crystals of sufficiently good quality to obtain an X-ray crystal structure.[15] Figure 1 shows the molecular structure of compound **11c**. The most interesting feature of structure **11c** is its strong deviation from planarity. The seven annelated rings are twisted in a screwlike fashion. The reason for this distortion might be the steric constraint caused by the close proximity of the carbonyl oxygens and the hydrogens attached to C(12). This is illustrated by the dihedral angle O(1),C(1),C(2),C(7) = 30° and the bond angle C(3),C(1),O(1) = 125° indicating that oxygen and hydrogen move apart. Some of the bond lengths are summarized in Table II.

The most interesting bond distance is the one between C(10) and C(11), which is 1.329 (6) Å. Thus, this bond is almost an isolated CC double bond best compared with the corresponding bond in pyrene,[16] and this observation vindicates our approach to ribbons via polycatafusenes.

Solubility Study. Up to now, the solubilizing effect of the alkyl chains has not been discussed specifically although information could be inferred from the experimental techniques (column chromatography, NMR spectroscopy) applied, which all require good solubility. Since solubility is a matter of crucial importance to the feasibility of the strategy, the solubilities were determined quantitatively for some of these compounds; the results are summarized in Table III. Compound **10a** was prepared according to a literature procedure[17] and **10b** in analogy to **10c,d** (See Experimental Section).

Even though the list in Table III is not very extensive, there is one conclusion that can be drawn from it with certainty: Substitution with *n*-hexyl or *n*-dodecyl chains causes a dramatic increase in the solubilities. Whereas methyl substitution (**10b** versus **10a**) does not have a significant effect, substitution with longer chains as in **10c,d** increases the solubilities by a factor of 5–10. The very high solubility of compound **13**, comprising six annelated rings, nicely fits this picture.

Conclusion

The experiments described above illustrate our approach to a route to well-defined and soluble graphitic ribbons. A suitable bis diene (**3**) was selected and its ability to undergo a 2-fold DA reaction with benzoquinone was proved. It was also shown that the quinoid end group in **10c** , which is representative for other such groups appearing in the polyreaction, gives the expected DA adduct **11c** with very high conversion and surprisingly high isomeric purity. In light of these experiments and the excellent solubilities of the model compounds **10c,d** and **13**, the prognosis for the eventual success of the outlined strategy is good.

Experimental Section

Materials. All reagents were purchased from Aldrich Chemical Co. and used without further purification. Acetonitrile was distilled two times from P_2O_5 under nitrogen, and benzoquinone was freshly sublimed before use. Benzo[*c*]phenanthrene-1,4-quinone (**10a**) was prepared according to a literature procedure.[17] We are thankful to Prof. R. C. Schulz, Mainz, for providing us with 2-isopropenylnaphthalene (**9b**). Reactions that required temperatures above the boiling point of the corresponding solvent were carried out in thick-walled glass tubes equipped with Rotaflo taps; the reaction mixtures were degassed by applying several freeze/thaw cycles. Melting points were recorded on a Reichert Thermovar melting point microscope and are uncorrected. Mass spectra were obtained by using a Varian MAT 7A with EI ionization. IR spectra were recorded on a Perkin-Elmer 1430 spectrometer and NMR spectra on a Bruker AC 300 spectrometer (^{1}H NMR, 300 MHz; ^{13}C NMR, 75.5 MHz, δ (ppm), TMS as internal standard). UV spectra were measured on a Perkin-Elmer Lambda 3 UV–vis spectrometer.

General Procedure for the Preparation of Compounds 5, 6, and 8. The bis dienes **2**, **3**, and **4**, respectively (1.43 mmol), and tetracyanoethylene (185 mg, 1.43 mmol (**2**, **3**); 370 mg, 2.86 mmol (**4**)) were refluxed under nitrogen in $CHCl_3$ (5 mL) for 24 h (**2**), 2 h (**3**), and 60 h (**4**), respectively. The solvent was removed and the remaining brown liquid was chromatographed through silica (50 g) with petroleum ether/ether (10:1) as eluent.

1,1,2,2-Tetracyano-4-hexyl-1,2,3,10a-tetrahydro-8-(1-octen-2-yl)phenanthrene (5). Chromatography gave (i) a small fraction of unreacted **2** and (ii) compound **5** (510 mg, 75%) as a colorless liquid which rapidly turns yellow in the presence of air and/or light. MS (EI): m/z = 476 (5.8, M$^+$). IR (film): ν = 2250 (w). ^{1}H NMR ($CDCl_3$): δ = 0.85 (m, 6 H, 2CH_3), 1.20–1.62 (m, 16 H, CH_2 alkyl), 2.32 (t, 2 H, J = 7.7 Hz, CH_2 allyl), 2.40 (t, 2 H, J = 7.4 Hz, CH_2 allyl), 3.20 (dd, 1 H, J = 18.2 Hz, J = 2.4 Hz, H-3 syn), 3.35 (dd, 1 H, J = 18.2 Hz, J = 3.6 Hz, H-3 anti), 4.38 (m, 1 H, H-10a), 4.88, 5.38 (2 d, 1 H each, J = 1.6 Hz, =CH_2), 5.95 (dd, 1 H, J = 9.7 Hz, J = 1.9 Hz, H-10), 6.95 (dd, 1 H, J = 9.7 Hz, J = 3.0 Hz, H-9), 7.10–7.35 (m, 4 H, H aromat). ^{13}C NMR ($CDCl_3$): δ = 13.9, 14.0 (2 q), 22.4–31.7 (8 t), 33.0, 36.6 (2 t), 37.9 (s), 38.4 (t), 42.9 (s), 44.4 (d), 109.3, 110.4, 111.2, 111.3 (4 s), 115.6 (t), 121.4 (d), 127.0 (s), 127.3, 127.7 (2 d), 128.7 (s), 129.6, 130.1 (2 d), 130.2, 130.3 (2 s), 141.9 (s), 147.8 (s). Anal. Calcd for $C_{32}H_{36}N_4$: C, 80.63; H, 7.61; N, 11.75. Found: C, 80.60; H, 7.68; N, 11.61.

3,3,4,4-Tetracyano-1-hexyl-2,3,4,4a-tetrahydro-7-(1-octen-2-yl)phenanthrene (6). Compound **6** was obtained as a colorless liquid (610 mg, 90%) which decomposed quickly. MS (EI): m/z = 348 (1.25, M$^+$ − TCNE), 128 (28.3, TCNE). IR (film): ν = 2245 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 0.85 (m, 6 H, 2 CH_3), 1.10–1.60 (m, 16 H, CH_2 alkyl), 2.23 (m, 2 H, CH_2 allyl), 2.48 (t, 2 H, J = 7.0 Hz, CH_2 allyl), 3.08 (dd, 1 H, J = 18.6 Hz, J = 2.0 Hz, H-3 syn), 3.42 (dd, J = 18.6 Hz, J = 4.6 Hz, H-3 anti), 4.71 (m, 1 H, H-4a), 5.11, 5.30 (2 d, 1 H each, J = 1.2 Hz, =CH_2), 6.50, 6.60(2 d, 1 H each, J = 10.0 Hz, H-9/H-10), 7.22 (d, 1 H, J = 1.9 Hz, H-8), 7.38 (dd, 1 H, J = 8.1 Hz, J = 1.9 Hz, H-6), 7.70 (d, 1 H, J = 8.1 Hz, H-5). ^{13}C NMR ($CDCl_3$): δ = 13.9, 14.0 (2 q), 22.4–32.0 (9 t), 35.0, 35.8 (2 t), 40.2, 41.0 (2 s), 45.0 (d), 109.2, 110.5, 111.0, 112.2 (4 s), 113.2 (t), 122.8 (d), 124.4 (s), 124.7, 125.9, 126.1 (3 d), 126.9, 129.4 (2 s), 129.6 (d), 133.1 (s), 142.3 (s), 147.2 (s). Anal. Calcd for $C_{32}H_{36}N_4$: C, 80.63; H, 7.61; N, 11.75. Found: C, 80.32; H, 7.99; N, 11.40.

11,11,12,12-Tetracyano-9-*n*-hexyl-10,11,12,12a-tetrahydro-4-(1-octen-2-yl)benzo[*l*]pyrene (7). Some characteristic ^{1}H NMR data (C_6D_6): δ = 2.25, 2.92 (2 d, 1 H each, J = 18.5 Hz, H-10 (syn/anti)), 2.45 (t, 2 H, J = 7.1 Hz, CH_2 allyl), 4.37 (s, 1 H, H-12a), 5.15, 5.38 (2 d, 1 H each, J = 1.5 Hz, =CH_2).

6,6,7,7,13,13,14,14-Octacyano-4,11-di-*n*-hexyl-5,6,7,7a,12,13,14,14a-octahydrodibenzo[*e*,*l*]pyrene (8). As the main fraction, colorless crystals of compound **8** (260 mg, 73%) were obtained (mp 144 °C). MS (EI): m/z = 678 (0.4, M$^+$). IR

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(15) All calculations were performed on a Vax-11/730 Computer System (Digital Equipment) using the Structure Determination Package supplied from Enraf Nonius Delft. Tables of positional and thermal parameters and of bond lengths and bond angles are available as supplementary material (8 pages).

(16) Allmann, R.; *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.* **1970**, *132*, 129.

(17) Davies, W.; Porter, Q. N. *J. Chem. Soc.* **1957**, 4967.

Table III. Solubilities[a] of Various Quinoid Compounds in Chloroform at Room Temperature

compd	R	g/L	mol/L
10a	H	48	0.18
10b	CH_3	37	0.13
10c	*n*-hexyl	290	0.85
10d	*n*-dodecyl	480	1.15
13	*n*-hexyl	270	0.47

[a] In grams per liter and moles per liter of solution (±5%).

(KBr): ν = 2250 (w), 2240 (w) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 0.82 (t, 6 H, 2 CH_3), 1.10–1.65 (m, 16 H, CH_2 alkyl), 2.45 (m, 4 H, CH_2 allyl), 3.25 (dd, 2 H, *J* = 18.5 Hz, *J* = 1.6 Hz, H-5 (H-12) syn), 3.45 (dd, 2 H, *J* = 18.5 Hz, *J* = 3.4 Hz, H-5 (H-12) anti), 4.30 (m, 2 H, H-7a (H-14a)), 7.42 (d, 2 H, *J* = 7.8 Hz, H-3 (H-10)), 7.50 (dd, 2 H, *J* = 7.8 Hz, *J* = 7.0 Hz, H-2 (H-9)), 7.85 (d, 2 H, *J* = 7.0 Hz, H-1 (H-8)). ^{13}C NMR ($CDCl_3$): δ = 13.9 (q), 22.4–31.2, (4 t), 33.6 (t), 35.3 (t), 39.7 (s), 42.2 (s), 46.2 (d), 109.4, 110.2, 110.9, 112.1 (4 s), 125.7 (s), 126.6 (d), 128.7 (s), 128.8 (d), 130.0 (s), 130.1 (d), 130.6, 130.9 (2 s). Anal. Calcd for $C_{44}H_{38}N_8$: C, 77.85; H, 5.64; N 16.51. Found: C, 77.72; H, 5.60; N, 16.61.

6-Methylbenzo[*c*]phenanthrene-1,4-quinone (10b). 2-Isopropenylnaphthalene (**9b**) (1.0 g, 5.87 mmol) and benzoquinone (1.9 g, 17.6 mmol) were dissolved in acetonitrile (10 mL) and heated at 100 °C for 3 days. On cooling to room temperature, a red solid precipitated, which was washed with ethanol (50 mL) and dried in vacuum to yield **10b** as red crystals (550 mg, 34%, mp 223 °C). The mother layer still contained an undetermined amount of **10b**. MS (EI): *m*/*z* = 272 (100, M^+). IR (KBr): ν = 1663 (s), 1658 (s) cm^{-1}. UV (ethanol): λ_{max} (ϵ) = 230 (48 260), 370 (3120), 395 (5560). ^1H NMR ($CDCl_3$): δ = 2.79 (s, 3 H, CH_3), 6.90, 7.06 (2 d, 1 H each, *J* = 10.1 Hz, H-2, H-3), 7.44 (m, 1 H), 7.57 (m, 1 H), 7.74 (m, 3 H), 8.02 (s, 1 H, H-5), 8.27 (d, 1 H, *J* = 8.0 Hz, H-12). ^{13}C NMR ($CDCl_3$): δ = 20.4 (q), 121.3–127.9 (5 d), 129.4, 129.6 (2 s), 130.5, 130.7 (2 d), 130.8, 132.1, 133.3, 135.6 (4 s), 135.7, 140.1 (2 d), 141.1 (s), 185.4, 187.9 (2 s). Anal. Calcd for $C_{19}H_{12}O_2$: C, 83.81; H, 4.44. Found: C, 83.51; H, 4.43.

Diels–Alder Reaction of 9c,d and Benzoquinone. A thick-walled glass tube was charged with 2-(1-octen-2-yl)-naphthalene (**9c**) (1.0 g, 4.2 mmol), benzoquinone (1.37 g, 12.7 mmol), and acetonitrile (10 mL). This tube was degassed, sealed, and heated to 100 °C for 3 days. The resultant deep red solution was cooled, the solvent was removed, and the remaining dark brown residue was extracted four times with boiling water (30 mL each) to remove hydroquinone and excess benzoquinone. The crude product obtained was dissolved in $CHCl_3$ and dried over $MgSO_4$, and after the addition of silica (10 g), the solvent was removed completely. Flash chromatography with petroleum ether/ether (1:1) through silica (150 g) gave (i) starting material **9c** (50 mg); (ii) crude adduct **11c** (95 mg), which was recrystallized from hot ethanol (5 mL) to give pure **11c** (50 mg, 4% based on **9c**) as red crystals (mp 200 °C); and (iii) compound **10c** (920 mg, 64%) as yellow crystals, mp 128–130 °C. **6-Hexylbenzo[*c*]-phenanthrene-1,4-quinone (10c).** MS (EI): *m*/*z* = 342 (5, M^+). IR (KBr): ν = 1665 (s), 1655 (s) cm^{-1}. UV (*n*-hexane): λ_{max} (ϵ) = 250 (40 170), 333 (8685), 410 (3470). ^1H NMR ($CDCl_3$): δ = 0.90 (t, 3 H, CH_3), 1.25–1.85 (m, 8 H, CH_2 alkyl), 3.15 (t, 2 H, *J* = 7.7 Hz, CH_2 benzyl), 6.92, 7.08 (2 d, 1 H each, *J* = 10.2 Hz, H-2 (H-3)), 7.45, 7.60 (2 m, 1 H each, H aromat), 7.85 (m, 3 H, H aromat), 8.30 (s, 1 H, H-5), 8.03 (d, 1 H, *J* = 8.4 Hz, H-12). ^{13}C NMR ($CDCl_3$): δ = 14.0 (q), 22.5–33.6 (5 t), 121.1, 123.2, 124.9, 127.7, 127.9, (5 d), 129.5, 130.0, 130.4 (3 s), 130.5, 130.6 (2 d), 132.1, 133.2, 135.0 (3 s), 135.8 (d), 140.1 (d), 145.8 (s), 185.4 (s), 187.9 (s). Anal. Calcd for $C_{24}H_{22}O_2$: C, 84.18; H, 6.49. Found: C, 84.15; H, 6.41.

6,16-Dihexyldinaphtho[1,2-*a*:1′,2′-*h*]anthracene-9,18-quinone (11c). MS (EI): *m*/*z* = 576 (100, M^+). IR (KBr): ν = 1655 (s) cm^{-1}. UV (diethyl ether): λ_{max} (ϵ) = 225 (69 135), 337 (43 210), 410 (5555). ^1H NMR ($CDCl_3$): δ = 0.92 (t, 6 H, CH_3), 1.20–1.95 (m, 16 H, CH_2 alkyl), 3.25 (t, 4 H, *J* = 7.9 Hz, CH_2 benzyl), 7.50–8.05 (m, 10 H, H aromat), 8.30 (s, 2 H, H-8 (H-17)), 8.42 (d, 2 H, *J* = 8.2 Hz, H-1 (H-10)). ^{13}C NMR ($CDCl_3$): δ = 14.0 (q), 22.6–34.1 (5 t, CH_2 alkyl), 121.5, 123.7, 125.3, 127.8, 128.0 (5 d), 129.9 (s), 130.2, 130.4 (2 d), 132.2, 133.3, 134.5, 134.8 (4 s), 146.3 (s), 185.9 (s). Anal. Calcd for $C_{42}H_{40}O_2$: C, 87.46; H, 6.99. Found: C, 87.34; H, 7.03.

2-(1-Tetradecen-2-yl)naphthalene (9d) (1.20 g, 3.78 mmol) and benzoquinone (1.23 g, 11.35 mmol) were treated analogously. Flash chromatography through silica (150 g; eluent, petroleum ether/ether (10:1) gave (i) a red brown mass consisting of **11d** and some starting material **9d** (240 mg); repeated recrystallization from hot ethanol gave **11d** as yellow crystals (80 mg, 6%, mp 107 °C); (ii) compound **10d** as yellow crystals (810 mg, 50%), mp 65–67 °C. **6-Dodecylbenzo[*c*]phenanthrene-1,4-quinone (10d).** MS (EI): *m*/*z* = 426 (100, M^+). IR (KBr): ν = 1662 (s), 1605 (w) cm^{-1}. UV (CH_3CN): λ_{max} (ϵ) = 250 (40 220), 330 (8490), 410 (3330). ^1H NMR ($CDCl_3$): δ = 0.87 (t, 3 H, *J* = 6.2 Hz, CH_3), 1.20–1.90 (m, 20 H, CH_2 alkyl), 3.08 (t, 2 H, *J* = 7.4 Hz, CH_2 benzyl), 6.87, 7.04 (2 d, 1 H each, *J* = 10.3 Hz, H-2 (H-3)), 7.41–7.84 (m, 5 H, H aromat), 7.98 (s, 1 H, H-5), 8.24 (d, 1 H, *J* = 8.4 Hz, H-12). ^{13}C NMR ($CDCl_3$): identical with spectrum for **10c** except for the number of alkyl triplets. Anal. Calcd for $C_{30}H_{34}O_2$: C, 84.47; H, 8.03. Found: C, 84.24; H, 8.25.

6,16-Didodecyldinaphtho[1,2-*a*:1′,2′-*h*]anthracene-9,18-quinone (11d). MS (EI): *m*/*z* = 744 (100, M^+). IR (KBr): ν = 1660 (s) cm^{-1}. UV (ethanol): λ_{max} (ϵ) = 226 (65 560), 330 (35 920), 410 (5390). ^1H NMR ($CDCl_3$): δ = 0.92 (t, 6 H, 2 CH_3), 1.20–1.85 (m, 40 H, CH_2 alkyl), 3.25 (t, 4 H, *J* = 7.8 Hz, CH_2 benzyl), 7.50–8.05 (m, 10 H, H aromat), 8.28 (s, 2 H, H-8 (H-17)), 8.42 (d, 2 H, *J* = 8.2 Hz, H-1 (H-10)). ^{13}C NMR ($CDCl_3$): identical with spectrum for **11c** except for the number of alkyl triplets.

Diels–Alder Reaction of 3 and Benzoquinone. 2,6-Di-1-octen-2-ylnaphthalene (**3**) (4.0 g, 11.5 mmol) and benzoquinone (14.8 g, 138 mmol) in acetonitrile (40 mL) were reacted as described for compounds **9c,d**. Analogous workup followed by flash chromatography using petroleum ether/ether (1:1) as eluent gave (i) a yellow solid (400 mg), which was not further investigated; (ii) compound **13** as a fine, red powder, which was dried at 60 °C/10^{-2} hPa to remove traces of benzoquinone (yield 1.240 g, 20%; mp 123 °C); and (iii) a black powder (4.8 g), using THF as eluent. This powder still contained traces of hydroquinone. **6,14-Dihexyldibenzo[*c*,*l*]chrysene-1,4:9,12-diquinone (13).** MS (EI): *m*/*z* = 556 (100, M^+). IR (KBr): ν = 1660 (vs), 1610 (m) cm^{-1}. UV (ethanol): λ_{max} (ϵ) = 230 (40 935), 418 (2350), 488 (880). ^1H NMR ($CDCl_3$): δ = 0.90 (t, 6 H, 2 CH_3), 1.20–1.90 (m, 16 H, CH_2 alkyl), 3.12 (t, 4 H, *J* = 7.7 Hz, CH_2 benzyl), 6.93, 7.03 (2 d, 2 H each, *J* = 9.9 Hz, H-2 (H-10), H-3 (H-11)), 7.75 (d, 2 H, *J* = 9.1 Hz, H-7 (H-15)), 8.05 (s, 2 H, H-5 (H-13)), 8.12 (d, 2 H, *J* = 9.1 Hz, H-8 (H-16)). ^{13}C NMR ($CDCl_3$): δ = 13.9 (q), 22.5–31.7 (4 t), 33.6 (t), 118.5 (d), 123.4 (d), 129.1, 129.9, 131.7, 132.2 (4 s), 132.5 (d), 134.6 (s), 135.9 (d), 139.8 (d), 146.3 (s), 185.4 (s), 186.7 (s).

X-ray Diffraction Analysis Data of 11c.[15] Crystal data: monoclinic, $P\,2_1/m$, a = 7.115 (1) Å, b = 17.462 (1) Å, c = 12.529 (1) Å, β = 103.60 (1)°, z = 2, V = 1512.9 Å^3, D_{calcd} = 1.266 g/cm^3. Intensity data of 2537 reflections with $1° < \theta < 60°$ were collected on an Enraf Nonius CAD4 diffractometer with Cu K_α radiation. The structure was solved by direct methods (MULTAN) and refined by least-squares techniques to a final R value of R = 0.034 (R_w = 0.036) for 1080 reflections with $[F_o] > 6\sigma(F_o)$.

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Registry No. 2, 119796-11-1; 3, 119796-12-2; 4, 119796-13-3; 5, 119796-14-4; 6, 119796-15-5; 7, 119818-86-9; 8, 119796-16-6; **9b**, 3710-23-4; **9c**, 119796-17-7; **9d**, 119796-18-8; **10a**, 109699-80-1; **10b**, 119796-19-9; **10c**, 119796-20-2; **10d**, 119796-22-4; **11c**, 119796-21-3; **11d**, 119796-23-5; **13**, 119796-24-6; tetracyanoethylene, 670-54-2; benzoquinone, 106-51-4.

Supplementary Material Available: Tables of X-ray data (positional parameters, general displacement parameter expressions, bond distances and angles, and torsion angles) of compound **11c** (8 pages). Ordering information is given on any current masthead page.