

Facile Synthesis and X-ray Structure of Alkoxy-Functionalized Dibenzo[*fg,op*]naphthacenes

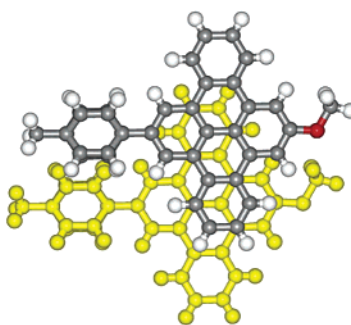
Xiao Hong Cheng,[†] Sigurd Höger,^{*,†} and Dieter Fenske[‡]

Polymer-Institut, Universität Karlsruhe, Hertzstrasse 16, 76187 Karlsruhe, Germany,
and Institut für Anorganische Chemie, Universität Karlsruhe, Engesserstrasse 15,
76128 Karlsruhe, Germany

hoeger@chemie.uni-karlsruhe.de

Received April 11, 2003

ABSTRACT



1,3-Bis(2-bromophenyl)-2,5-diphenylbenzenes are readily available by the condensation of phenylacetates with the corresponding pyrylium salts and undergo a palladium-catalyzed dehydrohalogenation to give functionalized dibenzo[*fg,op*]naphthacenes.

Polycyclic aromatic hydrocarbons (PAHs) played a major role in the development of industrial organic chemistry.¹ During the last years, the interest in these compounds was renewed because of their electronic and optoelectronic properties.² In general, columnar packing motives with a strong π - π overlap are found only in materials with a minimum size of the polycyclic aromatic backbone. To keep these structures tractable solubilizing side chains have to be attached to the aromatics. Therefore, methods which are mild

enough to prepare the polycyclic backbone in the presence of the side chains as well as strategies for the simple synthesis of the noncondensed precursors are of high interest both for the extension of the existing synthetic toolkit and for the preparation of functional materials.³ Recently, we have explored the synthetic potential of the transformation of 2,4,6-triarylpyrylium salts to the corresponding 1,2,3,5-tetraarylbenzenes by the condensation with sodium phenylacetate.⁴ We could show that this reaction is compatible with the presence of halogens in the compounds and could use the resulting functionalized 4,4''-diiodo-*m*-terphenyls for the synthesis of shape-persistent macrocycles.⁵

This led us to the idea that functionalized 1,2,3-triarylbenzenes containing properly located bromo or iodo groups might undergo a transition metal-catalyzed dehydrohaloge-

[†] Polymer-Institut.

[‡] Institut für Anorganische Chemie.

(1) (a) Clar, E. *Polycyclic Hydrocarbons*; Academic Press: New York, 1964. (b) Zander, M. *Polycyclische Aromaten*; Teubner: Stuttgart, Germany, 1995. (c) Harvey, R. G. *Polycyclic Aromatic Hydrocarbons*; Wiley-VCH: New York, 1997.

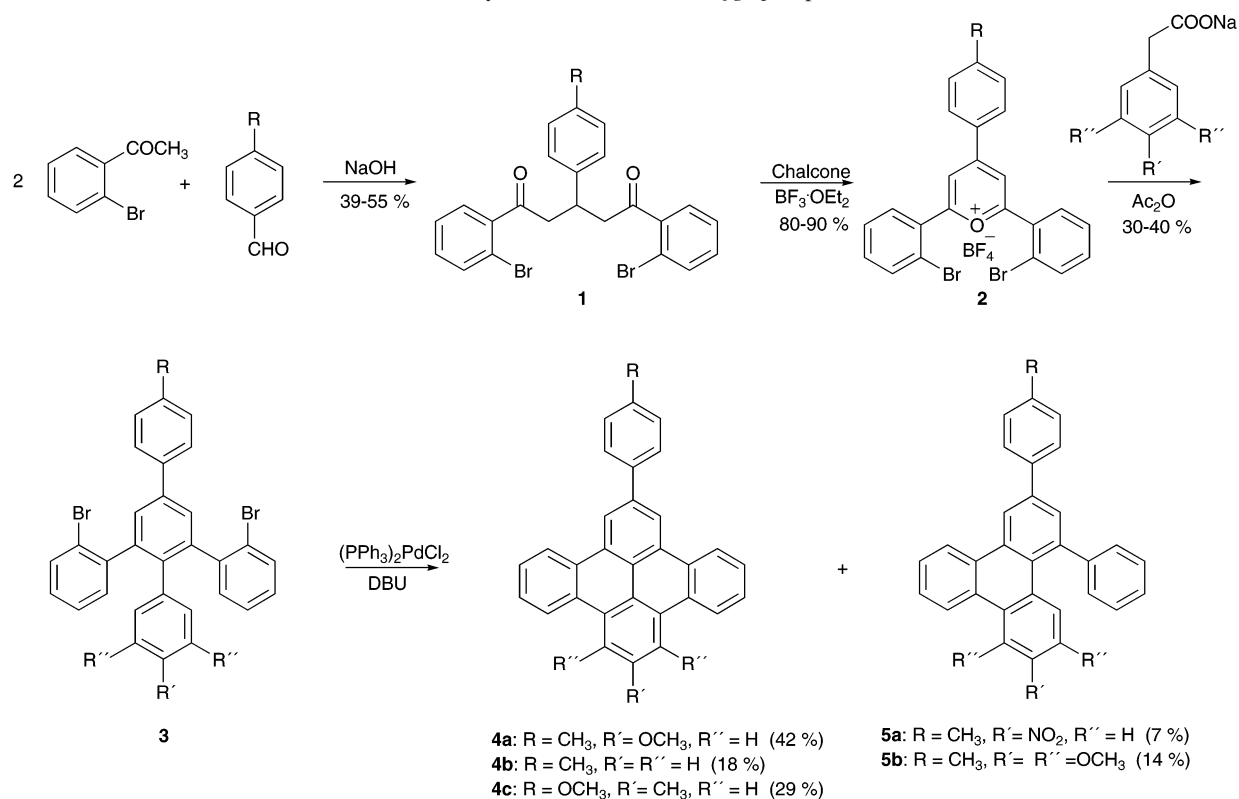
(2) (a) Adam, D.; Schuhmacher, P.; Simmerer, J.; Häussling, L.; Siemensmeyer, K.; Eitzbach, K. H.; Ringsdorf, H.; Haarer, D. *Nature* **1994**, *371*, 141. (b) Schmidt-Mende, L.; Fechtenkötter, A.; Müllen, K.; Moons, E.; Friend, R. H.; MacKenzie, J. D. *Science* **2001**, *293*, 1119. (c) Percec, V.; Glodde, M.; Bera, T. K.; Miura, Y.; Shiyonovskaya, I.; Singer, K. D.; Balagurusamy, V. S. K.; Heiney, P. A.; Schnell, I.; Rapp, A.; Spiess, H.-W.; Hudson, S. D.; Duan, H. *Nature* **2002**, *417*, 384.

(3) Hagen, S.; Hopf, H. *Top. Curr. Chem.* **1998**, *196*, 45.

(4) Zimmermann, T.; Fischer, G. W. *J. Prakt. Chem.* **1987**, *329*, 975.

(5) Höger, S.; Rosselli, S.; Ramminger, A.-D.; Enkelmann, V. *Org. Lett.* **2002**, *4*, 4269.

Scheme 1. Synthesis of the Dibenzo[*fg,op*]naphthacenes



nation to form functionalized dibenzo[*fg,op*]naphthacenes. So far only two procedures for the synthesis of alkoxy-functionalized dibenzo[*fg,op*]naphthacenes have been described, both of them leading to highly substituted materials by using an oxidative dehydrogenation reaction.⁶ Here we show that these aromatics with only one alkoxy group at a defined position are available by a simple Pd(0)-catalyzed dehydrohalogenation procedure. Key compounds in our synthesis are the pyrylium salts **2** containing bromine at the 2 and 2'' position. Pyrylium salts with substituents in this position are only rarely described and initial attempts to synthesize them directly from 2-bromo acetophenone and the corresponding benzaldehyde failed. In contrast, acceptable to good yields were obtained by applying a two-step route preparing first the 1,5-diketone **1** and then performing the cycloaromatization with chalcone as oxidant (Scheme 1). Although first attempts to prepare **1** under conventional conditions (EtOH, aq NaOH, reflux) gave the product in only 8% yield, solvent-free conditions improved the yield dramatically up to 55%.⁷ Condensation of **2** with the corresponding sodium phenyl acetates formed the aromatic dibromides in good yields. The dehydrohalogenation was performed by heating **3** in dimethylacetamide (DMA) in the presence of DBU and (PPh₃)₂PdCl₂ at 160 °C for 12 h. The end of the reaction becomes easily visible by the precipitation of palladium black in the former slightly tan solution.

Dibenzo[*fg,op*]naphthacenes were obtained in variable yields depending on the substitution pattern of the phenyl acetate (isolated yields of the main reaction products are given in Scheme 1). Good yields were obtained for **4a** and moderate yields for **4b** and **4c**, while in the case of **5a** and **5b** only the formation of minor amounts of the corresponding triphenylenes was observed. The product distribution and yield can be explained by the assumption that after the oxidative addition of the Pd(0) to the arylbromide the newly formed Pd(II) species electrophilically attacks the phenyl ring containing the R' and R'' substituents.⁸ Alternatively, dehalogenation leads to the dehalogenated products. The actual outcome of the reaction depends strongly on the steric and electronic properties of the electrophilically attacked aryl ring. If its electron density is reduced (as going from **4a** to **5a**) or if steric crowding (**5b**) hinders a fast attack, the competitive dehalogenation becomes the predominant reaction. Exchange of the catalyst did not improve the yields. When the cyclizations were performed with (P(*o*-tol)₃)₂PdCl₂ under otherwise identical conditions, the yield of the main product decreased from 42% to 24% (**4a**) and from 7% to 5% (**5a**), respectively.

4a was crystallized from benzene/CHCl₃ to afford slightly yellow crystals suitable for X-ray investigation (Figure 1).⁹ The nearly perfectly planar polycyclic aromatics form infinite stacks which are arranged in a herringbone-like motif. The

(6) (a) Musgrave, O. C.; Webster, C. J. *Chem. Commun.* **1969**, 712. (b) Kumar, S.; Naidu, J. J.; Rao, D. S. S. *J. Mater. Chem.* **2002**, *12*, 1335.

(7) Cave, G. W. V.; Raston, C. L.; Scott, J. L. *Chem. Commun.* **2001**, 2159.

(8) (a) Martín-Matute, B.; Mateo, C.; Cárdenas, D. J.; Echavarren, A. M. *Chem. Eur. J.* **2001**, *7*, 2341. (b) Hennings, D. D.; Iwasa, S.; Rawal, V. H. *J. Org. Chem.* **1997**, *62*, 2. (c) Echavarren, A. M.; Gómez-Lor, B.; González, J. J.; de Frustos, O. *Synlett* **2003**, 585.

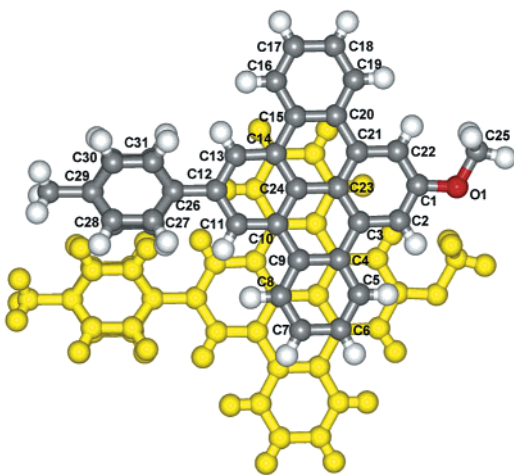


Figure 1. Crystal structure of **4a** (view of two adjacent molecules projected onto the PAH planes showing the displacement of the molecules in the stack).

attached phenyl substituent is disordered, adopting torsion angles of 21.8° and -27.4° , respectively, relative to the polycyclic part of the molecule. The bond lengths of the dibenzo[*fg,op*]naphthacene agree with the local molecular symmetry and are in accordance with Clar's sextet rule.¹⁰ Figure 1 displays the normal projection of two molecules of

(9) Crystal data for **4a**: $C_{32}H_{22}O$, monoclinic, space group $P2_1/c$ (no. 14), $Z = 4$, $a = 23.903(5)$ Å, $b = 5.0540(10)$ Å, $c = 17.002(3)$ Å, $\beta = 92.29(3)^\circ$, $V = 2052.3(7)$ Å³, $D_c = 1.367$ g cm⁻³, $\mu(\text{Mo K}\alpha) = 0.082$ mm⁻¹; $T = 200$ K. Data collection: Stoe-IPDSII; $2\theta_{max} = 63.3^\circ$; 14344 reflections and 4893 with $I > 2\sigma(I)$; 438 parameters (C, O anisotope, H isotrope); maximum residual electron density 0.24 e Å⁻³; $R_1 = 0.062$, $wR_2 = 0.19$. The structure was solved and refined on F by using the SHELXS-97 program. CCDC reference number CCDC 201035.

4a reminiscent of that of graphite with a center-to-center offset of about 3.8 Å.¹¹ Remarkable is the small intermolecular distance between C19 and C23 (3.29 Å), C8 and C24 (3.32 Å), and C4 and C21 (3.34 Å), all below the layer distance in graphite (3.35 Å).¹²

All in all we present here a simple approach toward alkoxy-functionalized dibenzo[*fg,op*]naphthacenes. Current activities study the scope and limit of this synthetic methodology as well as the incorporation of these PAHs into complex molecular architectures. This includes also the reaction sequence $\text{OMe} \rightarrow \text{OH} \rightarrow \text{OTf}$ that allows further transition metal-catalyzed C–C coupling reactions.¹³

Acknowledgment. The authors thank the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the BMBF for support.

Supporting Information Available: Experimental procedures and characterization as well as X-ray data for **4a**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OL034626G

(10) Selected bond distances (Å): C(1)–C(2) 1.387(3), C(1)–C(22) 1.382(2), C(2)–C(3) 1.385(2), C(3)–C(4) 1.462(2), C(3)–C(23) 1.419(2), C(4)–C(5) 1.405(2), C(4)–C(9) 1.404(2), C(5)–C(6) 1.371(3), C(6)–C(7) 1.386(3), C(7)–C(8) 1.374(3), C(8)–C(9) 1.401(2), C(9)–C(10) 1.464(2), C(10)–C(11) 1.392(2), C(10)–C(24) 1.411(2), C(11)–C(12) 1.390(3), C(12)–C(13) 1.388(3), C(12)–C(26) 1.484(2), C(13)–C(14) 1.383(3), C(14)–C(15) 1.461(2), C(14)–C(24) 1.420(2), C(15)–C(16) 1.410(2), C(15)–C(20) 1.397(2), C(16)–C(17) 1.366(3), C(17)–C(18) 1.389(3), C(18)–C(19) 1.367(3), C(19)–C(20) 1.406(2), C(20)–C(21) 1.461(2), C(21)–C(22) 1.390(2), C(21)–C(23) 1.415(2), C(23)–C(24) 1.431(2).

(11) Goddard, R.; Haenel, M. W.; Herndon, W. C.; Krüger, C.; Zander, M. *J. Am. Chem. Soc.* **1995**, *117*, 30.

(12) The intermolecular distance between C(25) and O(1) (4.15 Å) is too long for a hydrogen bond that it might be responsible for a stabilization of the packing motive. However, it exists as a short intercolumnar contact between H(5) and O(1) (2.51 Å).

(13) Cheng, X. H.; Höger, S. In preparation.