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Easy Access to 3,8-Diaryldifurano[2,3-*a*:2′,3′-*f*]naphthalenes. A New Extended Aromatic System

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3,8-Diaryldifurano[2,3-*a*:2′,3′-*f*]naphthalenes were prepared in two simple steps. First, 1,5-dihydroxynaphthalene and 1-aryl-2-bromodecan-1-ones were condensed to the corresponding naphthalene 1,5-diethers. Second, these intermediates were cyclized using methanesulfonic acid in methylene chloride. Seven examples are given, three of which are doubly substituted with octyl chains to enhance the solubility. This increased solubility allowed further modification of the 3,8-aryl groups to attach electron-withdrawing groups (formyl, nitrile, dicyanovinyl, and benzoyl).

Introduction

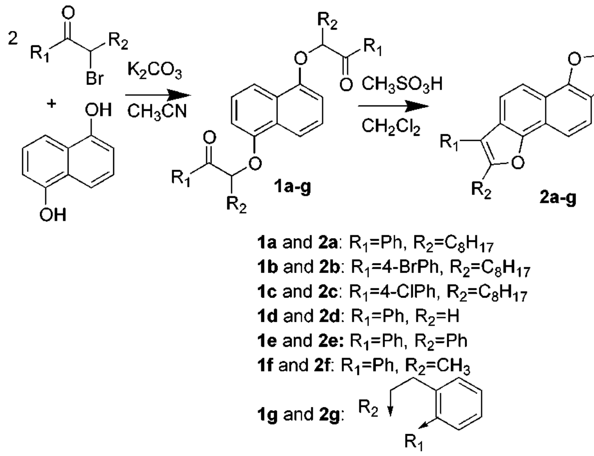
Extended aromatic systems have gained interest in diverse fields such as organic light-emitting diodes,[1] two-photon absorption materials,[2] second and higher order nonlinear optics and large (supramolecular) structures. New easily prepared building blocks with potential for further elaboration could add stimulus to these research areas.

In a search for new extended π-systems with possible applications in both two-photon absorption and electroactive polymers we have developed a synthesis of the hitherto unknown 3,8-diaryldifurano[2,3-*a*:2′,3′-*f*]naphthalene system (see Scheme 1). The parent compound difurano[2,3-*a*:2′,3′-*f*]naphthalene itself has been described only once in the literature.[3] Also the 3,8-dimethyl derivative of this compound has been prepared previously from 1,5-dipropynyloxynaphthalene by irradiation.[4] Further removed, but related, are the benzofuranes for which a somewhat similar synthetic strategy has been devised.[5]

Results and Discussion

A two-step synthetic procedure to the 3,8-diaryldifurano[2,3-*a*:2′,3′-*f*]naphthalenes **2a**−**g** was developed as outlined in Scheme 1. One equivalent of 1,5-dihydroxynaphthalene was reacted with 2 equiv of an α-bromoaryl ketone to produce the intermediary naphthalene 1,5-diethers **1a**−**g** in fair to good yields. Several methods for the dehydration step to form the difuranonaphthalenes **2a**−**g** were explored such as treatment with either concentrated sulfuric acid or polyphosphoric acid. The most general and satisfactorily method, however, was found to be anhydrous methanesulfonic acid in hot methylene chloride.

Scheme 1



When R_2 is hydrogen or methyl these compounds are only sparingly soluble in organic solvents. To improve the solubility a variant with octyl chains in the R_2 positions were obtained from 1-aryl-2-bromodecan-1-ones. The products **2a**−**c** substituted with two octyl chains in the 2 and 7 positions are very soluble at ambient temperature in common solvents facilitating further reactions shown in Scheme 2.

An Ullman-type reaction between **2b** and copper(I) cyanide in hot collidine gave the dinitrile **2h**. Exchange of the bromine atoms in compound **2b** with lithium atoms using *n*-butyllithium in THF and subsequent quenching of this intermediate with DMF produced the difuranonaphthalene dialdehyde **2i**. This compound was further modified by condensation with malodinitrile producing the bis(dicyanovinyl)difuranonaphthalene **2j**. A Friedel−Crafts reaction between the simple diphenyldifuranonaphthalene **2a** and benzoyl chloride with aluminum chloride in methylene chloride gave a mixture of mono- and dibenzoylated product. The latter was purified by column chromatography and proved to be the *meta*-substituted derivative **2k** by ^{1}H NMR. A singlet resulting

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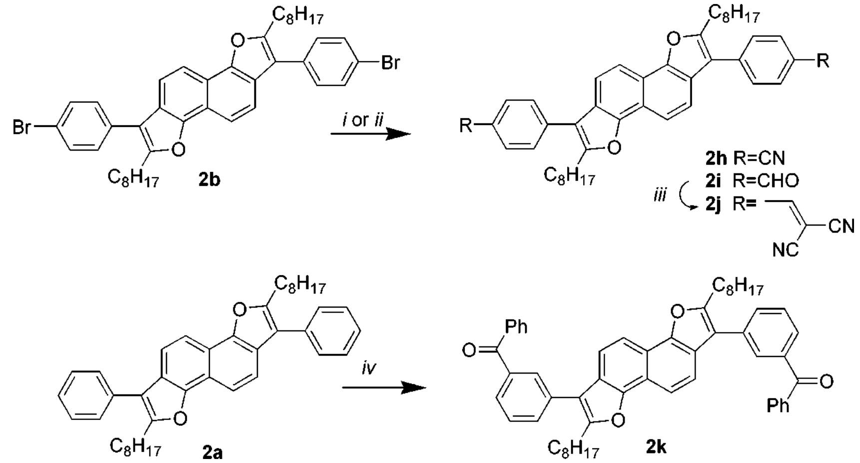
Scheme 2. Further Modifications of the 3,8-Diaryldifuranonaphthalene System[a]



[a] i: Cu(I)CN, ii: *n*-BuLi in THF at −78 °C, then DMF, iii: malodinitrile, iv: PhCOCl, $AlCl_3$.

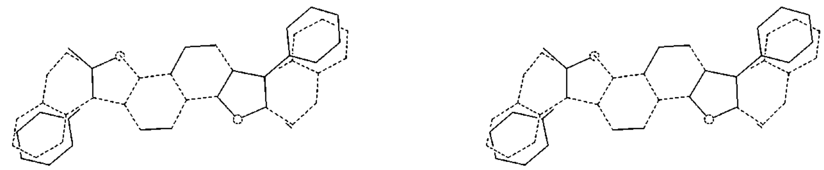


Figure 1. Stereoview of compound **2f** (solid) and **2g** (dotted) overlaid. It is noticeable that the substituent phenyl rings in compound **2g** are more in plane with the central part of the molecule than compound **2f**. This observation also hosts the explanation for the yellow color of compound **2g** as opposed to the colorless compound **2f**.

from the isolated protons on the phenyl rings is observed rather than a pattern due to, for example, a *para* substitution. This outcome of the reaction is somewhat surprising. The most reactive positions in the molecule for electrophilic substitution would be expected to be in the electron rich naphthalene nucleus rather than in the phenyl groups. And even if the phenyl groups are the preferred place of attack then *para*-substitution should be favored. When the aluminum chloride was added to the solution of **2a** in methylene chloride, a dark red color was observed indicating that a complex between the two had formed presumably via oxygen−aluminum contacts. This may explain the outcome of the reaction since it would lead to a deactivation of the central difuranonaphthalene moiety and at the same time favoring *meta*-substitution due to electron withdrawal from the phenyl groups.

X-ray Crystallography. The molecular conformation of compounds **2f** and **2g** was found to be very similar and in agreement with the proposed when considering the aromatic core. It was, however, puzzling that crystals of compound **2f** are colorless whereas crystals of compound **2g** had a pronounced yellow color. At first it was believed that this was due to a crystal packing effect. When considering the crystal structures this could, however, not be the case due to the more extensive overlap between neighboring molecules in compound **2f** as compared to compound **2g**. It was found that the ethylene bridge in compound **2g** forces the plane of the substituent phenyl ring to become more coplanar with the central aromatic part than observed in compound **2f**. The torsion angles defining the tilt of the substituent phenyl ring with respect to the plane of the central aromatic part was found to be, respectively, 44.633° for compound **2f** and 18.547° and 16.035° for compound **2g** (there is one molecule in the asymmetric of compound **2g** and thus two different torsion angles). This has been illustrated in Figure 1 where the molecular structures have been overlaid to emphasize the similarity in the central part of the molecule and the dissimilarity in the conformation of the substituent phenyl rings.

Experimental Section

General Section. Melting points are uncorrected. All commercially available chemicals were used without further purification. All solvent were reagent grade or better except for THF which was freshly distilled from sodium−benzophenone ketyl.

1,5-Bis(phenacyl-2-yloxy)naphthalenes (1a−g). General Procedure. 1,5-Dihydroxynaphthalene (3.20 g, 20.0 mmol), the appropriate 2-bromo-1-phenyl ketone (45 mmol), and dry K_2CO_3 (ca. 8 g) was mixed in HPLC grade acetone or acetonitrile (100 mL) and heated to reflux under argon 4 h. The cooled reaction mixture was then poured into water and filtered, washed with water, and then recrystallized from a suitable solvent.

3,8-Diaryldifurano[2,3-*a*:2′,3′-*f*]naphthalenes (2a−g). General Procedure. 1,5-Bis(phenacyloxy)-naphthalene (**1a**−**g**) in methylene chloride was added 10 equiv of CH_3SO_3H to give a deep red or violet solution/suspension. The reaction mixture was stirred 1 h at reflux and then poured onto ice and the solvent evaporated to precipitate the product. After filtering and washing with water, ethanol, and diethyl ether, the product was recrystallized.

3,8-Bis(4-cyanophenyl)difurano[2,3-*a*:2′,3′-*f*]naphthalene 2h. Compound **2b** (1.5 g, 2 mmol) and Cu(I)CN (3 g, 33 mmol) was mixed in collidine (25 mL) and heated to reflux overnight. The solvent was distilled in a vacuum and the residue extracted with methylene chloride. The organic phase was washed several times with dilute ammonia to remove copper salts. Evaporation in a vacuum gave a semisolid that could be crystallized from acetonitrile. Yield: 52%. mp 142−3 °C. 1H NMR (250.1 MHz, $CDCl_3$) δ: 0.90 (t, 6H, $J = 7$ Hz), 1.2−1.4 (m, 20H), 1.90 (p, 4H, $J = 7$ Hz), 2.99 (t, 4H, $J = 8$ Hz), 7.69 (d, 4H, $J = 8$ Hz), 7.73 (d, 2H, $J = 9$ Hz), 7.85 (d, 4H, J = 8 Hz), 8.20 (d, 2H, J = 9 Hz). 13C NMR (62.9 MHz, $CDCl_3$) δ: 14.5, 23.0, 27.4, 29.0, 29.6, 29.7, 29.8, 32.2, 111.1, 116.2, 117.3, 118.7, 119.0, 119.3, 123.2, 130.1, 133.1, 138.5, 150.4, 156.0 ppm. Anal. Calcd for $C_{44}H_{46}N_2O_2$: C, 83.24; H, 7.30; N, 4.41. Found: C, 82.94; H, 7.36; N, 4.38.

3,8-Bis(4-formylphenyl)difurano[2,3-*a*:2′,3′-*f*]naphthalene 2i. Dibromodifuranonaphthalene **2b** 5.0 g, 6.7 mmol was dissolved in dry THF (100 mL) in a three-necked flask with an argon bubbler and a septum and then cooled on a dry ice−acetone bath to −78 °C. *n*-Butyllithium in hexanes (15 mmol) was added and allowed to react at low temperature for 10 min. DMF (5 mL, excess) was added, and the cooling bath was removed. When the temperature had reached ambient after 30 min, dilute hydrochloric acid was added and the mixture evaporated to dryness in a vacuum. The solid was triturated with water and filtered to remove the salts. The dried product was recrystallized from acetonitrile. Yield 83% mp 124−5 °C. ^1H NMR (250.1 MHz, $CDCl_3$) δ: 0.88 (t, 6H, J = 7 Hz), 1.2−1.4 (m, 20H), 1.89 (p, 4H, J = 7 Hz), 7.74 (d, 4H, J = 8 Hz), 7.75 (d, 2H, J = 9 Hz), 8.04 (d, 4H, J = 8 Hz), 8.18 (d, 2H, J = 9 Hz). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ: 14.5, 23.0, 27.5, 29.1, 29.6, 29.7, 29.8, 32.2, 116.0, 117.8, 118.9, 119.0, 123.4, 130.0, 130.7, 135.4, 140.1, 150.4, 156.0, 192.2 ppm. Anal. Calcd for $C_{44}H_{48}O_4$: C, 82.46; H, 7.55. Found: C, 82.45; H, 7.51.

3,8-Bis(4-dicyanovinylphenyl)difurano[2,3-*a*:2′,3′-*f*]-naphthalene 2j. Diformyldifuranonaphthalene **2i** (1.0 g, 1.6 mmol) and malodinitrile (0.5 g, 7.6 mmol) was dissolved in methylene chloride (25 mL), and one drop of concentrated hydrochloric acid was added. The reaction mixture was heated to reflux for a few minutes and then evaporated to dryness and recrystallized from ethanol. Yield: 32%. mp 182−3 °C (color change from yellow to orange at ca. 140 °C). ^1H NMR (250.1 MHz, $CDCl_3$) δ: 0.87 (t, 6H, J = 7 Hz), 1.2−1.4 (m, 20H), 1.90 (p, 4H, J = 7 Hz), 3.01 (t, 4H, J = 8 Hz), 7.75 (d, 2H, J = 8 Hz), 7.77 (d, 4H, J = 8 Hz), 7.82 (s, 2H), 8.08 (d, 4H, J = 8 Hz), 8.19 (d, 2H, J = 8 Hz).). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ: 14.5, 23.0, 27.6, 29.1, 29.6, 29.7, 29.8, 32.2, 82.5, 113.2, 114.3, 116.3, 117.5, 118.9, 119.0, 123.1, 129.9, 130.3, 131.8, 140.6, 150.5, 156.7, 159.5 ppm. Anal. Calcd for $C_{50}H_{48}N_4O_2{*}CH_2Cl_2$: C, 74.90; H, 6.04; N, 6.72. Found: C, 75.29; H, 5.92; N, 6.77.

3,8-Bis(3-benzoylphenyl)difurano[2,3-*a*:2′,3′-*f*]naphthalene 2k. Compound **2a** (0.58 g, 1.00 mmol) and benzoyl chloride (0.35 g, 2.5 mmol) was dissolved in methylene chloride (25 mL). Aluminum chloride (0.45 g, 3.4 mmol) was added, and the dark red mixture was stirred at ambient temperature for 15 min and then quenched by addition of water. The solvents were removed in a vacuum, and the reddish residue was washed with ethanol and then crystallized from heptane. Further purification by chromatography on silica using hexane−ethyl acetate (3:1) as eluent gave the pure dibenzoylated product **2k**. Yield: 0.43 g 54%. mp 171−2 °C. ^1H NMR (250.1 MHz, $CDCl_3$) δ:0.89 (t, 6H, J = 7 Hz), 1.2−1.5 (m, 24H), 2.62 (t, 4H, J = 7 Hz), 7.2−7.4 (m, 16H, 7.78 (s, 2H), 7.91 (d, 4H, J = 8 Hz). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ: 14.5, 23.1, 27.0, 28.2, 29.5, 29.6, 29.8, 32.3, 115.7, 118.1, 119.8, 124.5, 127.7, 128.8, 129.2, 129.5, 130.4, 130.5, 132.4, 138.5, 149.3, 156.4, 198.6 ppm. Anal. Calcd for $C_{56}H_{56}O_4$: C, 84.81; H, 7.12. Found: C, 84.68; H, 7.02.

Crystallography Methods. Crystals of **2f** and **2g** were drawn directly from the mother liquor, coated with a thin layer of oil, mounted on glass needles using grease (Apiezon), and transferred quickly into the cold nitrogen stream on the diffractometer. Data were collected on a Siemens SMART Platform diffractometer with a CCD area sensitive detector. Absorption corrections were made using SADABS.[6] Direct methods for the structure solution and full-matrix least-squares refinements were used. Hydrogen atoms were included in calculated positions. Programs used were SMART, SAINT, and SHELXTL from Siemens.[7,8] The structures were checked for overlooked symmetry using MISSYM and for voids in PLATON.[9] The crystals scattered X-rays weakly and this posed particular problems for compound **2g** in terms of the data quality. What could be observed safely from the crystallographic data were molecular geometry and packing arrangements. Atomic coordinates and further crystallographic details have been deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England.

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Supporting Information Available: Product characterization data for the compounds **1a**−**g** and **2a**−**g**. Tables of fractional coordinates, equivalent isotropic and anisotropic thermal parameters, bond lengths and bond angles, powder diffractograms. This material is available free of charge via the Internet at http://pubs.acs.org..

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