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Phthalocyanines and Related Compounds: XLI.[1] Synthesis of 9,10-Diphenylanthracene-2,3-dicarboxylic Acid Derivatives

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Abstract — Derivatives of 9,10-diphenylanthracene-2,3-dicarboxylic acid were synthesized by the Diels–Alder reaction of 1,3-diphenylisobenzofuran with adducts of furan (or silvan) and the corresponding maleic (fumaric) acid derivative or with *trans*-cyclohex-4-ene-1,2-dicarbonitrile, followed by aromatization.
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In the preceding communication we described the synthesis of 1-phenylnaphthalene-2,3-dicarboxylic acid derivatives by the reaction of 2-bromomethylbenzophenones with derivatives of maleic acid, which was accompanied by intermediate formation of the corresponding Diels–Alder adducts [1]. In the present work we used the Diels–Alder reaction to obtain derivatives of 9,10-diphenylanthracene-2,3-dicarboxylic acid which attract interest as, e.g., fluorescent labels for the determination of singlet oxygen in aqueous medium [2]. Some of these compounds are starting materials in the synthesis of tetra-2,3-(9,10-diphenylanthraceno)porphyrazines (linearly fused anthracene analogs of phthalocyanines) whose long-wave absorption maximum in the electronic spectrum is located in the near IR region; such substances may be used in optical data storage devices [3–6].

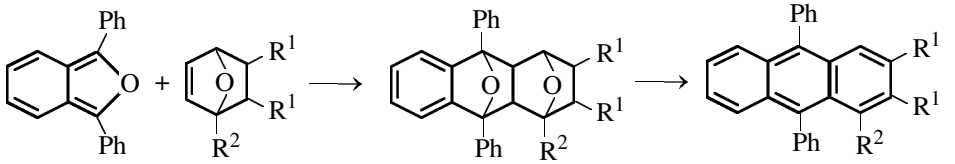
Rigaudy et al. [7, 8] reported on the synthesis of 9,10-diphenylanthracene-2,3-dicarboxylic acid ester and 9,10-diphenylanthracene-2,3-dicarbonitrile in 5–35% yield via cycloaddition of dimethyl acetylenedicarboxylate and but-2-yne-1,4-dinitrile, respectively, at the 1,4 positions of 9,10-diphenylanthracene. However, the described procedures can hardly be regarded as preparative because of difficult isolation of the esters and low accessibility of dicyanoacetylene; the synthesis of the latter is poorly reproducible but highly explosive.

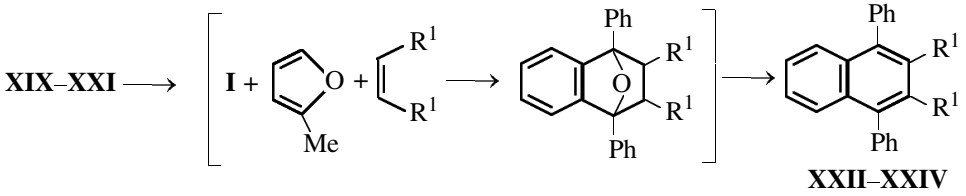
Dimethyl 9,10-diphenylanthracene-2,3-dicarboxylate was also synthesized by the Diels–Alder reaction of 1,3-diphenyl-2-benzofuran (**I**) with the furan–dimethyl maleate adduct in boiling chloroform. It was found that the initially formed diepoxy compound lost two water molecules on treatment with dehydrating agents to afford the corresponding anthracene [2, 9]. We believed that the above scheme may be convenient for the synthesis of various 9,10-diphenylanthracene-2,3-dicarboxylic acid derivatives, namely its anhydride **II**, imide **III**, *N*-phenylimide **IV**, and dinitrile **V**, as well as of 1-methyl-9,10-diphenylanthracene-2,3-dicarboximide (**VI**) and 1-methyl-9,10,*N*-triphenylanthracene-2,3-dicarboximide (**VII**). As dienophiles in the Diels–Alder reaction with 1,3-diphenyl-2-benzofuran we used cyclic adducts derived from furan and maleic anhydride, maleimide, and Nphenylmaleimide: 3,6-epoxy-1,2,3,4-tetrahydrophthalic anhydride (**VIII**), 3,6-epoxy-1,2,3,4-tetrahydrophthalimide (**IX**), and 3,6-epoxy-*N*-phenyl-1,2,3,4-tetrahydrophthalimide (**X**), respectively. Also, the adduct of furan with fumaronitrile, 3,6-epoxy-1,2,3,4-tetrahydrophthalonitrile (**XI**) and analogous 2-methylfuran (silvan) adducts, 3,6-epoxy-1-methyl-1,2,3,4-tetrahydrophthalimide (**XII**), 3,6-epoxy-1-methyl-*N*-pheny-1,2,3,4-tetrahydrophthalimide (**XIII**), and 3,6-epoxy-1-methyl-1,2,3,4-tetrahydrophthalic anhydride (**XIV**), were used. Taking into account that adducts **VIII**–**XIV** are unstable (they are capable of undergoing thermal retro-Diels–Alder decomposition), the reactions with 1,3-diphenyl-2-benzofuran were carried out by keeping mixtures of the reactants in chloroform for several days at room temperature. The reaction was assumed to be complete when a yellow–green luminescence intrinsic to the initial diene disappeared and an abundant white crystalline solid (adduct **XV**–**XXI**) separated. The products were then subjected to aromatization by treatment with acid reagents. Adducts **XV**–**XVII** re-

[1] For communication XL, see [1].

adily lost water on heating with $BF_3 \cdot Et_2O$ in boiling acetonitrile to give anthracenes **II**–**V** in 47–79% yield. Compounds **II**–**V** were isolated as bright yellow substances showing luminescence in solution. The aromatization of compound **XVIII** was accompanied by partial hydrolysis of dinitrile **V** to imide **III**. The latter was the only isolated compound when a solution of **XVIII** in methanol was heated under reflux while bubbling dry hydrogen chloride therethrough.

Analogous treatment of silvan adducts **XIX** and **XX** resulted in formation of the corresponding anthracenes **VI** and **VII** with a much lower yield (19–23%). Apart from compounds **VI** and **VII**, we isolated crystalline products which were initially assigned the structure of the corresponding monoepoxy derivatives, 1,4-epoxy-9,10-diphenyl-1,2,3,4-tetrahydroanthracenes, which could be formed via elimination of one water molecule from **XIX** and **XX** [2]. However, the data of elemental analysis and the mass spectra indicated that these compounds are substituted naphthalenes, 1,4-diphenylnaphthalene-2,3-dicarboximide (**XXII**) and 1,4,*N*-triphenylnaphthalene-2,3-dicarboximide (**XXIII**). 1,4-Diphenylnaphthalene-2,3-dicarboxylic anhydride (**XXIV**)was the only aromatization product obtained from compound **XXI**. The electron-impact mass spectrum of diepoxy derivative **XXI** lacked molecular ion peak, and the base peak with *m/z* 270 belonged to 1,3-diphenyl-2-benzofuran. The mass spectrum of the aromatization product contained a strong peak with *m/z* 350 due to naphthalene derivative **XXIV**. Most probably, diepoxy compounds **XIX**–**XXI** under the aromatization conditions undergo partial (compounds **XIX** and **XX**) or complete (**XXI**) retro-Diels–Alder decomposition into the initial components, and diene **I** thus formed reacted with maleic acid derivative. As a result, the yield of anthracene derivative was considerably reduced or it was not formed at all. Compounds **XXIII** and **XXIV** were identical to those obtained by the direct reactions of diene **I** with *N*-phenylmaleimide and maleic anhydride [10, 11].

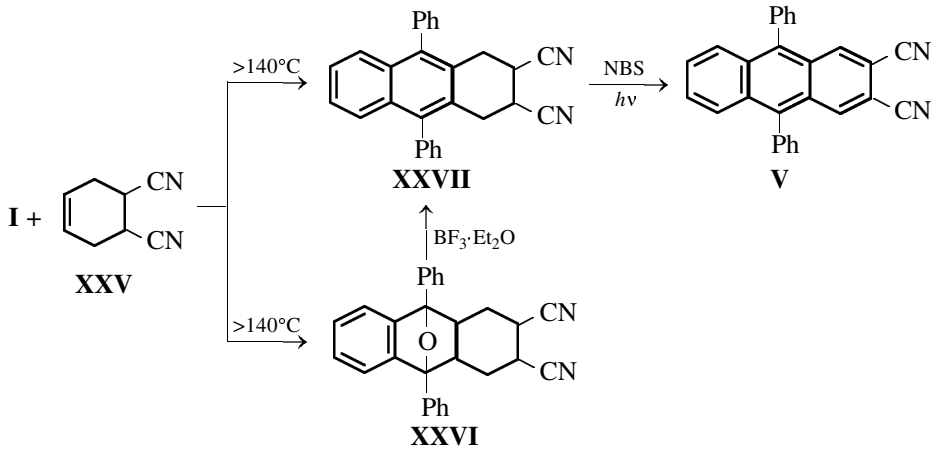




II, VIII, XV, R^2 = H, R^1R^1 = OCOCO; **III, IX, XVI**, R^2 = H, R^1R^1 = OCNHCO; **IV, X, XVII**, R^2 = H, R^1R^1 = OCNPhCO; **V, XI, XVIII**, R^1 = CN; **VI, XII, XIX, XXII**, R^2 = Me, R^1R^1 = OCNHCO; **VII, XIII, XX, XXIII**, R^2 = Me, R^1R^1 = OCNPhCO; **XIV, XXI, XXIV**, R^2 = Me, R^1R^1 = OCOCO.

These results indicate lower a stability of silvan adducts **XIX**–**XXI**, as compared to the corresponding furan derivatives; a probable reason is *peri* arrangement of the phenyl and methyl groups.

We have developed an alternative procedure for the synthesis of dinitrile **V** via Diels–Alder reaction of 1,3-diphenyl-2-benzofuran with excess trans-cyclohex-4-ene-1,2-dicarbonitrile (**XXV**). Thermal dehydration of primary adduct **XXVI** gave 9,10-diphenyl-1,2,3,4-tetrahydroanthracene-2,3-dicarbonitrile (**XXVII**). When the reaction was carried out below 140°C, we isolated 9,10-epoxy-9,10-diphenyl-1,2,3,4,4a,9,9a,10-octahydroanthracene-2,3-dicarbonitrile (**XXVI**) which was treated with $BF_3 \cdot Et_2O$ to obtain tetrahydro derivative **XXVII** as a result of elimination of water molecule. Aromatization of **XXVII** by treatment with *N*-bromosuccinimide (NBS) under conditions of radical initiation gave 9,10-diphenylanthracene-2,3-dicarbonitrile (**V**). The mass spectrum of **XXVI**, as well as of diepoxy compound **XXI**, contained a strong peak with *m/z* 270, which belongs to the molecular ion derived from diene **I**. Samples of dinitrile **V** synthesized by the two methods were



identical, and their characteristics coincided with those reported in [8].

The structure and purity of compounds **II**–**XXVII** were confirmed by elemental analysis, electronic spectroscopy, mass spectrometry, and thin-layer chromatography.

EXPERIMENTAL

The mass spectra were recorded on an LKB-2091 mass spectrometer (Sweden). Column chromatography was performed using silica gel L 40/100 μm. The purity of the products was checked by thin-layer chromatography on Silufol UV-254 plates. Commercial furan and 1,3-diphenyl-2-benzofuran (from Aldrich) were used. 2-Methylfuran (bp 63–64°C) was synthesized by the procedure described in [12].

***trans*-Cyclohex-4-en-1,2-dicarbonitrile (XXV)** was synthesized by reaction of fumaronitrile with 2,5-dihydrothiophene-1,1-dioxide (butadiene adduct with sulfur anhydride). Yield of 80%, mp 128–130°C; published data [13]: mp 125°C.

3,6-Epoxy-1,2,3,6-tetrahydrophthalic anhydride (VIII) was synthesized by mixing 2 g of maleic anhydride with 1.5 ml of furan in 5 ml of diethyl ether. Yield quantitative, mp 125°C (decomp.) [14].

3,6-Epoxy-1,2,3,6-tetrahydrophthalimide (IX) was synthesized by reaction of 2 g of maleimide with 5 ml of furan in 25 ml of diethyl ether. Yield quantitative, mp 131°C (decomp.); published data [15]: mp 130–132°C (decomp.).

3,6-Epoxy-*N*-phenyl-1,2,3,6-tetrahydrophthalimide (X) was synthesized by reaction of 5 ml of furan with 8.7 g of *N*-phenylmaleimide in 50 ml of chloroform. Yield 90%, mp 163–165°C; published data [16]: mp 165.5°C.

3,6-Epoxy-1,2,3,6-tetrahydrophthalonitrile (XI) was synthesized from 3 g of fumaronitrile and 4 ml of furan in 15 ml of dioxane. Yield 33%, mp 111°C; published data [17]: mp 111°C.

3,6-Epoxy-3-methyl-1,2,3,6-tetrahydrophthalimide (XII) was synthesized as described above for compound **IX** from silvan and maleimide. Yield 90%, mp 163–165°C; published data [18]: mp 163–165°C.

3,6-Epoxy-3-methyl-1,2,3,6-tetrahydrophthalic anhydride (XIV) was synthesized by the procedure described in [12]. Yield 93%, mp 74–75°C (decomp.).

9,10-Diphenylanthracene-2,3-dicarboxylic anhydride (II). A solution of 0.27 g of 1,3-diphenyl-2-benzofuran and 0.17 g of adduct **VIII** in 5 ml of chloroform was kept at room temperature until the reaction was complete. The white solid was filtered off, washed with chloroform, dried, and mixed with a solution of 1 ml of $BF_3 \cdot Et_2O$ in 4 ml of acetonitrile, and the mixture was heated for 4 h under reflux, cooled, and poured into water. The precipitate was filtered off, washed with water, dried, and recrystallized from benzene. Yield 0.28 g (70%), mp >360°C; published data [9]: mp 382–383°C; R_f 0.62 (chloroform). Mass spectrum, *m/z*: 400 $[M]^+$. Calculated: *M* 400.43.

9,10-Diphenylanthracene-2,3-dicarboximide (III). *a*. A solution of 0.54 g of 1,3-diphenyl-2-benzofuran and 0.32 g of adduct **IX** in 15 ml of chloroform was kept at room temperature until the reaction was complete. The precipitate was filtered off, washed with chloroform, dried, and mixed with 15 ml of methanol, and the mixture was heated for 4 h under reflux while bubbling dry hydrogen chloride. The mixture was cooled, poured into water, and neutralized with sodium carbonate, and the yellow precipitate was filtered off, washed with methanol, and recrystallized from benzene–hexane. Yield 0.63 g (79%), mp >360°C, R_f 0.77 (benzene–ethyl acetate, 4 : 1).

Mass spectrum, *m/z*: 399 $[M]^+$. Calculated: *M* 399.45. Found, %: C 84.41; H 4.30; N 3.39. $C_{28}H_{17}NO_2$. Calculated, %: C 84.19; H 4.29; N 3.51.

b. Compound **III** was synthesized from 0.146 g of 1,3-diphenyl-2-benzofuran and 0.088 g of adduct **IX** in 4 ml of dioxane; a solid separated and was dissolved in 4 ml of methanol, and the solution was heated under reflux while bubbling dry hydrogen chloride through the solution over a period of 2 h. Yield 0.11 g (51%), mp >360°C (from benzene–hexane).

9,10,*N*-Triphenylanthracene-2,3-dicarboximide (IV) was synthesized as described above for compound **II** from 0.27 g of 1,3-diphenyl-2-benzofuran and 0.24 g of adduct **X**. Yield 73%, mp 344–345°C (decomp.), R_f 0.54 (chloroform). Found, %: C 85.49; H 4.49; N 2.97. $C_{34}H_{21}NO_2$. Calculated, %: C 85.87; H 4.45; N 2.95.

9,10-Diphenylanthracene-2,3-dicarbonitrile (V). *a*. Compound **V** was synthesized from 0.83 g of 1,3-diphenyl-2-benzofuran and 0.45 g of adduct **XI** in 25 ml of dioxan. After treatment with $BF_3 \cdot Et_2O$, the mixture was subjected to column chromatography on silica gel. We isolated 0.55 g (47%) of compound **V**, mp 351–353°C (from MeCN); published data [8]: mp 351–352°C; R_f 0.36 (chloroform), and 0.25 g (21%) of imide **III**, mp >360°C (from benzene–hexane), R_f 0.77 (benzene–ethyl acetate, 4 : 1).

b. A mixture of 0.3 g of compound **XXVII** and 0.4 g of *N*-bromosuccinimide in 10 ml of carbon tetrachloride was heated for 4 h under reflux on exposure light produced by a 60-W lamp. The mixture was evaporated to dryness, and the solid residue was washed with hot water and recrystallized from acetonitrile. Yield 0.24 g (80%), mp 353–354°C; published data [8]: mp 351–352°C; R_f 0.36 (chloroform).

9,10-Epoxy-9,10-diphenyl-1,2,3,4,4a,9,9a,10-octahydroanthracene-2,3-dicarbonitrile (XXVI). A mixture of 0.54 g of diene **I** and 1.42 g of compound **XXV** in 2 ml of xylene was heated for 5 h at 130–140°C. The solvent was evaporated to dryness, and the residue was subjected to vacuum sublimation to remove excess initial compound **XXV**. The residue was recrystallized from hexane to isolate 0.72 g (90%) of compound **XXVI** with mp 225–227°C (decomp.). Found, %: C 83.89; H 5.17; N 7.23. $C_{28}H_{22}N_2O$. Calculated, %: C 83.56; H 5.51; N 6.96.

9,10-Diphenyl-1,2,3,4-tetrahydroanthracene-2,3-dicarbonitrile (XXVII). *a*. A mixture of 0.7 g of compound **XXVI** and 11 ml of $BF_3 \cdot Et_2O$ in 35 ml of acetonitrile was heated for 3 h under reflux. The mixture was cooled, and the precipitate was filtered off and recrystallized from acetonitrile. Yield 0.57 g (83%), mp 277–279°C (decomp.). Mass spectrum, *m/z*: 384 $[M]^+$. Calculated: *M* 384.48.

b. A mixture of 0.05 g of 1,3-diphenyl-2-benzofuran and 0.14 g of compound **XXV** in 0.5 ml of xylene was heated for 5 h at 140–150°C. It was then cooled, and the precipitate was filtered off. Yield 0.05 g (68%), mp 277–279°C (decomp.).

1-Methyl-9,10-diphenylanthracen-2,3-dicarboximide (VI) was synthesized in 23% yield from 1,3-diphenyl-2-benzofuran and adduct **XII** following the procedure described above for compound **III**. mp 310–312°C (from benzene–hexane), R_f 0.81 (benzene–ethyl acetate, 4 : 1). Mass spectrum, *m/z*: 413 $[M]^+$. Calculated: *M* 413.48. Found, %: C 83.57; H 4.70; N 4.17. $C_{29}H_{19}NO_2$. Calculated, %: C 84.24; H 4.63; N 3.39.

From the filtrate we isolated imide **XXII**. Yield 42%, mp 318–319°C, R_f 0.75 (benzene–ethyl acetate, 4 : 1). Found, %: C 82.28; H 4.41; N 4.00. $C_{24}H_{15}NO_2$. Calculated, %: C 82.50; H 4.33; N 4.01.

1-Methyl-9,10,*N*-triphenylanthracene-2,3-dicarboximide (VII) was synthesized as described above for compound **IV** from 1,3-diphenyl-2-benzofuran and adduct **XIII**. Yield 19%, mp 348–349°C (decomp., from benzene–hexane), R_f 0.42 (benzene). Found, %: C 85.09; H 4.70; N 2.83. $C_{35}H_{23}NO_2$. Calculated, %: C 85.87; H 4.73; N 2.86. The mother liquir was evaporated, and the residue was recrystallized from benzene–hexane to isolate imide **XXIII**. Yield 40%, mp 295–296°C; published data [10]: mp 297–298°C, R_f 0.39 (benzene). Mass spectrum, *m/z*: 425 $[M]^+$. Calculated *M*: 425.49.

1,4-Diphenylnaphthalene-2,3-dicarboxylic anhydride (XXIV) was synthesized as described above for compound **II** from 0.11 g of diene **I** and 0.08 g of adduct **XIV**. Yield 53%, mp 273–275°C [11], R_f 0.62 (chloroform). Mass spectrum, *m/z*: 350 $[M]^+$. Calculated: *M* 350.37.

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