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Phthalocyanines and Related Compounds: XXXIX.[1] Synthesis of Derivatives of Some Substituted 1-Phenylnaphthalene-2,3-dicarboxylic Acids

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Abstract—Derivatives (dinitriles, anhydrides, imides, *N*-phenylimides) of substituted 1-phenylnaphthalene-2,3-dicarboxylic and 1-phenylphenanthrene-2,3-dicarboxylic acids were prepared by the reactions of 2-bromomethylbenzophenones with various dienophiles. Starting from these derivatives, gallium complexes of substituted tetra-1-phenyl-2,3-naphthalocyanines and tetra(1-phenyl-2,3-phenanthro)porphyrazine were synthesized.

Annelated analogs of phthalocyanines, primarily isomeric 1,2- and 2,3-naphthalocyanines, are being extensively studied as compounds exhibiting strong absorption in the near IR range [2]. Metal complexes of tetra-1-phenyl-2,3-naphthalocyanines, showing increased solubility in organic solvents owing to the steric effect of the phenyl groups, are less studied. However, these compounds have already found applications, in particular, in photoconducting materials for information recording and in optical recording devices using semiconductor lasers [3].

These compounds were prepared from anhydrides of substituted 1-phenylnaphthalene-2,3-dicarboxylic acids, which, in turn, were synthesized by intermolecular condensation of phenylpropiolic acids in acetic anhydride, and also from the corresponding imides and dinitriles [2, 4, 5]. This route, however, allowed only preparation of compounds with the same substituents in the naphthalene core and phenyl group. Among other known routes to 1-phenylnaphthalene-2,3-dicarboxylic acid derivatives based on the Diels–Alder reaction of the intermediate 1-phenylisobenzofurans [6–12], the most attractive are the reactions of 2-(bromomethyl)benzophenones with esters and *N*-phenylimide of maleic acid, because of the availability of the starting chemicals and simple implementation [6]. It is suggested that 2-(bromomethyl)benzophenones **A**, being unstable, readily cyclize under the conditions of the Diels–Alder reaction to form the corresponding 1-phenylisobenzofurans **B**, which form with dienophiles adducts **C**. When heated, these adducts undergo dehydration catalyzed by the eliminated HBr and transform into 1-phenyl-2,3-disubstituted naphthalenes.

In this study we applied this method to preparing a series of 1-phenyl-substituted naphthalene-2,3-dicarboxylic acids and their annelated analogs, namely, dinitrile **I**, anhydride **II**, and imide **III** of 1-phenylnaphthalene-2,3-dicarboxylic acid; dinitrile **IV**, anhydride **V**, and imide **VI** of 7-*tert*-butyl-1-(*p*-*tert*-butylphenyl)naphthalene-2,3-dicarboxylic acid; dinitrile **VII**, anhydride **VIII**, imide **IX**, and *N*-phenylimide **X** of 1-(*p*-*tert*-butylphenyl)naphthalene-2,3-dicarboxylic acid; anhydride **XI** and imide **XII** of 7-*tert*-butyl-1-phenylnaphthalene-2,3-dicarboxylic acid; anhydride **XIII** and imide **XIV** of 1-(*p*-biphenylyl)naphthalene-2,3-dicarboxylic acid **XIV**; anhydride **XV** and imide **XVI** of 1-phenylphenanthrene-2,3-dicarboxylic acid. These compounds are of interest, in particular, as intermediates for preparing the corresponding substituted 2,3-naphthalocyanines.

The starting 2-methylbenzophenones, 2-methylbenzophenone **XVII**, 4,4'-di(*tert*-butyl)-2-methylbenzophenone **XVIII**, 4'-*tert*-butyl-2-methylbenzophenone **XIX**, 5-*tert*-butyl-2-methylbenzophenone **XX**, 4'-(*p*-biphenylyl)-2-methylbenzophenone **XXI**, and 1-benzoyl-2-methylnaphthalene **XXII**, were prepared by the Friedel–Crafts condensation in the presence of anhydrous aluminum chloride in benzene (for **XVII**) or in CS_2 (for **XVIII**–**XXII**) in 62–83% yields. Compounds **XVII**, **XXI**, and **XXII** were prepared by published procedures [13–15]. Methylbenzophenones **XVIII** and **XX** were prepared by the reactions of 4-*tert*-butyltoluene with 4-*tert*-butylbenzoyl chloride and benzoyl

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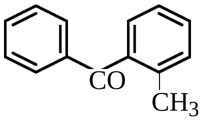
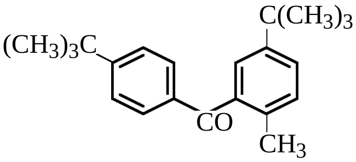
[1] For communication XXXVIII, see [1].

chloride, respectively, and methylbenzophenone **XIX**, by the reaction of *tert*-butylbenzene with 2-toluyl chloride; the products were purified by vacuum distillation.


XVII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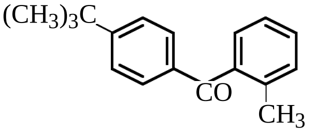
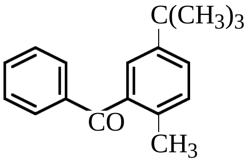
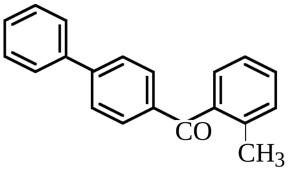
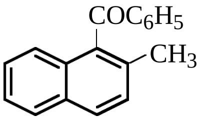
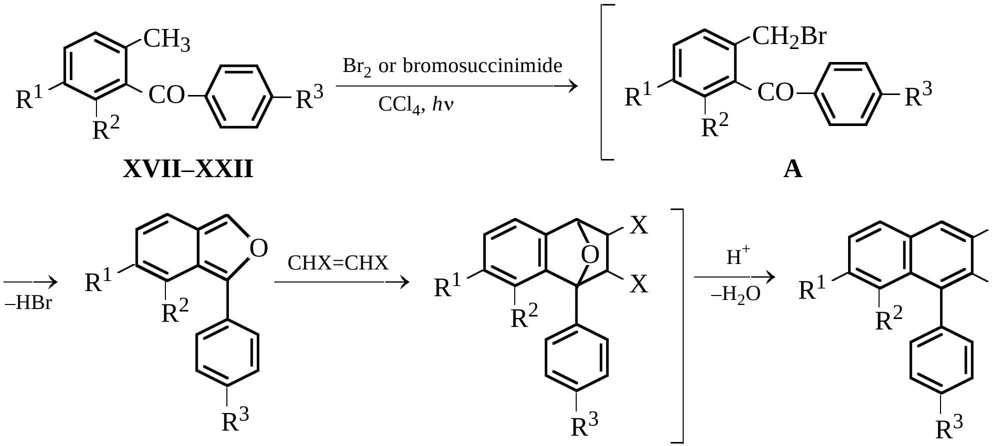

XIX


XX


XXI


XXII

Methylbenzophenones **XVII**–**XXII** were converted into the corresponding bromomethyl derivatives **A**, which were cyclized into isobenzofurans **B**, converted into Diels–Alder adducts **C**, and dehydrated to obtain the final products. The whole sequence of reactions was performed as one-pot synthesis without isolation of the intermediates. Methylbenzophenones **XVII**–**XX** were brominated with bromine and *N*-bromosuccinimide in CCl_4. To avoid bromination of the benzene ring, compound **XXI** was converted to benzyl bromide **A** with *N*-bromosuccinimide. Successful bromination of 1-benzoyl-2-methylnaphthalene **XXII** was possible only with bromine.



XVII–XXII **A** **B** **C** **I–XVI**

$R^1 = R^2 = R^3$ = H, X = CN (**I**), X, X = COOCO (**II**), CONHCO (**III**); $R^1 = R^3$ = *t*-Bu, R^2 = H, X = CN (**IV**), X, X = COOCO (**V**), CONHCO (**VI**); $R^1 = R^2$ = H, R^3 = *t*-Bu, X = CN (**VII**), X, X = COOCO (**VIII**), CONHCO (**IX**), CONPhCO (**X**); $R^2 = R^3$ = H, R^1 = *t*-Bu, X, X = COOCO (**XI**), CONHCO (**XII**); $R^1 = R^2$ = H, R^3 = Ph, X, X = COOCO (**XIII**), CONHCO (**XIV**); R^1, R^2 = CH=CHCH=CH, R^3 = H, X, X = COOCO (**XV**), CONHCO (**XVI**).

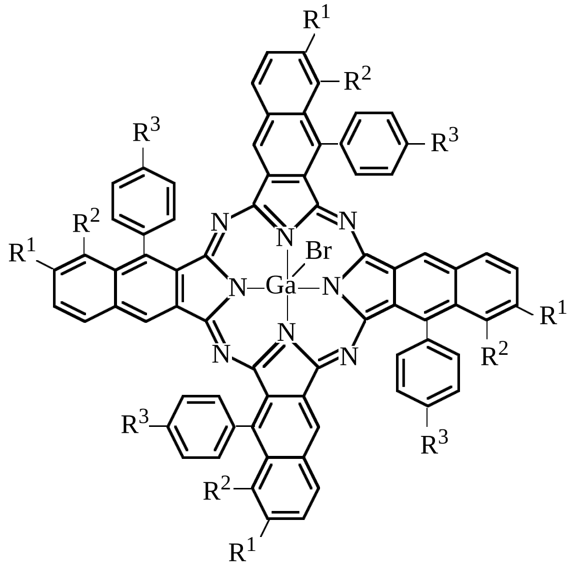
As dienophiles we used fumarodinitrile, maleic anhydride, maleimide, and *N*-phenylmaleimide. With fumarodinitrile, the reaction was complicated by partial hydrolysis of the dinitriles formed; along with these products, we isolated the corresponding imides in up to 8% yields. The final products **I**–**XVI** are

Yields, constants, elemental analyses, and mass spectra of **I**–**XVI**

Comp. no.	Yield, %	mp, °C (solvent for crystallization)	Found, %			Formula	Calculated, %			*M*		References
			C	H	N		C	H	N	*m/z* [M^+]	calculated	
I	53	213–214 (benzene–heptane)										[5]
II	61	246–247 (benzene)										[2, 4]
III	66	254–255 (chloroform)										[2, 3]
IV	49	215–216 (heptane)				$C_{26}H_{26}N_2$				366	366.51	[2]
V	60	190–191 (heptane)										[2]
VI	64	295–296 (benzene)										[2]
VII	46	232–233 (benzene–heptane)	85.03	5.89	8.87	$C_{22}H_{18}N_2$	85.13	5.84	9.02	310	310.39	
VIII	64	260–262 (benzene)	79.82	5.21		$C_{22}H_{18}O_3$	79.98	5.49				
IX	97	291–293 (benzene)	79.91	5.67	3.78	$C_{22}H_{19}NO_2$	80.22	5.81	4.25			
X	65	199–201 (chloroform)	82.67	5.47	3.19	$C_{28}H_{23}NO_2$	82.94	5.72	3.45			
XI	72	200–201 (benzene)	79.52	5.27		$C_{22}H_{18}O_3$	79.98	5.49				
XII	94	255–257 (benzene)	79.83	5.73	3.84	$C_{22}H_{19}NO_2$	80.22	5.81	4.25			
XIII	71	293–294 (heptane)	81.84	3.90		$C_{24}H_{14}O_3$	82.27	4.03				
XIV	78	304–305 (benzene)	82.13	4.10	3.70	$C_{24}H_{15}NO_2$	82.50	4.33	4.01	349	349.38	
XV	63	245–246 (benzene)	81.16	3.34		$C_{22}H_{12}O_3$	81.47	3.73				
XVI	96	304–306 (benzene)	81.60	3.71	3.98	$C_{22}H_{13}NO_2$	81.72	4.05	4.33	323	323.34	

crystalline substances. After recrystallization from appropriate solvent, we obtained their analytically pure samples in 46–78% yield. The physical properties, yields, mass spectra, and elemental analyses of **I**–**XVI** are listed in the table.

By the reactions of these anhydrides, imides, and dinitriles with $GaBr_3$ in a urea melt or in refluxing sulfolane, we prepared the gallium complexes of tetra-1-phenyl-2,3-naphthalocyanines (**XXIII**–**XXVII**) and tetra-1-phenyl-2,3-phenanthroporphyrazine (**XXVIII**); with the anhydrides and imides, the yields were higher. All the complexes are well soluble in organic solvents, which allowed their isolation in the analytically pure form by column chromatography on alumina, with benzene or chloroform as eluent. The complexes prepared from anhydrides and imides were mixtures of isomers differing in the relative position of phenyl groups. For complex **XXIII** prepared from dinitrile **I** by refluxing in sulfolane, the isomers were not detected chromatographically, which may be due to different orientation of the phthalogen molecules under the conditions of the template synthesis.



XXII–XXVIII

$R^1 = R^2 = R^3 = H$ (**XXIII**); $R^1 = R^3 =$ *t*-Bu, $R^2 = H$ (**XXIV**); $R^1 = R^2 = H$, $R^3 =$ *t*-Bu (**XXV**); $R^1 =$ *t*-Bu, $R^2 = R^3 = H$ (**XXVI**); $R^1 = R^2 = H$, $R^3 = Ph$ (**XXVII**); R^1, R^2 = CH=CHCH=CH, $R^3 = H$ (**XXVIII**).

Solutions of **XXIII**–**XXVII** in chloroform have an absorption spectrum typical of 2,3-naphthalocyanines. The spectra contain a strong long-wave band with a maximum at 820–826 nm (*Q* band), two well-resolved vibronic satellites at 700–780 nm, a weak broad band in the form of a shoulder at 406–435 nm, and a strong band in the UV range at 338–344 nm, related to the Soret band in porphyrazines. All the bands show a

10–15-nm bathochromic shifty relative to the corresponding bands in the spectrum of gallium tetra-5-*tert*-butyl-2,3-naphthalocyanine [16]. The low range in which the band positions vary in the series **XXIII**–**XXVII** indicates that the *tert*-butyl and phenyl groups in the positions remote from the macroring affect the chromophoric system insignificantly. On the other hand, these peripheral groups considerably increase the solubility of the complexes in organic solvents.

In the spectrum of **XXVIII**, the long-wave bands are somewhat shifted hypsochromically relative to the corresponding bands in the spectrum of gallium tetra-6-*tert*-butyl-2,3-naphthalocyanine, which is consistent with the previously published data for the related porphyrin systems [17, 18].

EXPERIMENTAL

The electronic absorption spectra of solutions of gallium complexes **XXIII**–**XXVIII** were recorded on a Hewlett–Packard HP-8453 spectrophotometer in plane-parallel cells, layer thickness 1 cm. The mass spectra of **XXIII** and **XXIV** were taken on a Finnigan-LCQ mass spectrometer, and those of the other compounds, on an LKB-2091 mass spectrometer.

2-Methylbenzophenones XVI–**XXII.** A 0.01-mol portion of appropriate hydrocarbon was added to a solution of 0.012 mol of anhydrous $AlCl_3$ in 20 ml of CS_2. The mixture was allowed to stand at room temperature for 20 min, after which a solution of 0.01 mol of appropriate acid chloride in 10 mol of CS_2 was added dropwise over a period of 10 min. The mixture was refluxed until the HCl evolution ceased, after which it was poured onto a mixture of ice and hydrochloric acid. The organic layer was extracted with diethyl ether; the ether extracts were washed with dilute NaOH and water. The solvent was distilled off, and the residue was distilled in a vacuum.

2-Methylbenzophenone XVII: yield 67%, bp 122–123°C (2 mm Hg) [13].

4,4'-Di(*tert*-butyl)-2-methylbenzophenone XVIII: yield 83%, bp 190–195°C (1 mm Hg). Mass spectrum, *m/z*: 308 $[M^+]$. Found, %: C 85.19; H 8.77. $C_{22}H_{28}O$. Calculated, %: C 85.66; H 9.15.

4'-*tert*-Butyl-2-methylbenzophenone XIX: yield 62%, bp 157–161°C (1 mm Hg). Mass spectrum, *m/z*: 252 $[M^+]$. Found, %: C 85.53; H 7.64. $C_{18}H_{20}O$. Calculated, %: C 85.67; H 7.99.

5-*tert*-Butyl-2-methylbenzophenone XX: yield 65%, bp 158–162°C (2 mm Hg). Mass spectrum, *m/z*: 252 $[M^+]$. Found, %: C 85.38; H 7.82. $C_{18}H_{20}O$. Calculated, %: C 85.67; H 7.99.

4'-(*p*-Biphenylyl)-1-methylbenzophenone XXI: yield 77%, mp 103–104°C (from hexane) [14].

1-Benzoyl-2-methylnaphthalene XXII: yield 82%, mp 74–75°C (from hexane) [15].

1-Phenyl-2,3-dicyanonaphthalene I. To a refluxing solution of 4.3 g of 2-methylbenzophenone **XVII** in 20 ml of CCl_4, illuminated with a 300-W lamp, we added dropwise a solution of 3.7 g of Br_2 in 20 ml of CCl_4. After the reaction completion, the lamp was switched off, and a solution of 1.7 g of fumarodinitrile in 10 ml of $CHCl_3$ was added. The mixture was refluxed for 20 h, after which imide **III** was filtered off; yield 0.5 g (8%), mp 238°C. The solvents were removed in a vacuum, and the residue was recrystallized from benzene–hexane. Yield of the dinitrile 2.6 g (53%), mp 213–214°C [5].

Dinitriles **IV** and **VII** were prepared similarly from benzophenones **XVIII** and **XIX**. Anhydrides **II**, **V**, **VIII**, **XI**, and **XV**, imides **III**, **VI**, and **XIV**, and *N*-phenylimide **X** were also prepared similarly starting from approprite maleic acid derivative (anhydride, imide, *N*-phenylimide).

1-(*p*-Biphenylyl)naphthalene-2,3-dicarboxylic anhydride XIII. A mixture of 2.7 g of methylbenzophenone **XXI** and 1.6 g of *N*-bromosuccinimide in 20 ml of CCl_4 was refluxed for 30 min under illumination with a 300-W lamp, after which a solution of 1 g of maleic anhydride in 30 ml of $CHCl_3$ was added. The mixture was refluxed for 20 h and cooled, the solvents were removed in a vacuum, and the residue was recrystallized from heptane; yield 2.48 g (71%), mp 293–294°C.

Imide **XIV** was prepared similarly starting from maleimide and was recrystallized from benzene.

1-(4-*tert*-Butylphenyl)naphthalene-2,3-dicarboxylic acid imide IX was prepared in 97% yield by fusion of anhydride **X** with urea.

7-*tert*-Butyl-1-phenylnaphthalene-2,3-dicarboxylic acid imide **XII** (yield 94%) and 1-phenylphenanthrene-2,3-dicarboxylic acid imide **XVI** (yield 96%) were prepared similarly, starting from anhydrides **XI** and **XV**, respectively.

(Tetra-1-phenyl-2,3-naphthalocyaninato)bromogallium XXIII. A mixture of 1.1 g of imide **III**, 0.31 g of $GaBr_3$, 3 g of urea, and a catalytic amount of ammonium molybdate was heated for 2 h at 270–290°C. After cooling, the fusion cake was treated with hot water, 5% HCl, again hot water, and diluted ethanol. The residue was treated with chloroform and chromatographed on alumina (eluent chloroform) to obtain the spectrally pure complex (0.58 g, 53%).

Electronic absorption spectrum in chloroform, λ, nm (log ε): 820 (5.30), 776 (4.52), 726 (4.57), 421 sh (4.44), 338 (4.87). Mass spectrum, *m/z*: 1167.5 [M^+]. Found, %: C 74.60; H 3.74; N 8.98. $C_{72}H_{40}BrGaN_8$. Calculated, %: C 74.17; H 3.46; N 9.61. Compound **XXIII** was also obtained in 17% yield by refluxing for 3 h a mixture of 0.1 g of dinitrile **I** and 0.03 g of $GaBr_3$ in 1 ml of sulfolane in the presence of a catalytic amount of ammonium molybdate.

[Tetra-7-*tert*-butyltetra-1-(4-*tert*-butylphenyl)-2,3-naphthalocyaninato]bromogallium XXIV was prepared from imide **VI**, $GaBr_3$, and a catalytic amount of ammonium molybdate by heating in a urea melt for 2 h at 270–290°C. The complex was purified by chromatography on alumina; eluent chloroform, yield 37%. Electronic absorption spectrum in chloroform, λ, nm (log ε): 826 (5.38), 782 (4.54), 732 (4.61), 434 sh (4.42), 340 (4.87). Mass spectrum, *m/z*: 1614 [M^+]. Found, %: C 77.81; H 6.83; N 6.41. $C_{104}H_{104}BrGaN_8$. Calculated, %: C 77.32; H 6.44; N 6.94.

[Tetra-1-(4-*tert*-butylphenyl)-2,3-naphthalocyaninato]bromogallium XXV was prepared similarly to **XXIII** from imide **IX** in 33% yield. Electronic absorption spectrum in chloroform, λ, nm (log ε): 825 (5.31), 779 (4.36), 731 (4.36), 433 sh (3.78), 342 (4.74). Found, %: C 75.44; H 5.17; N 7.62. $C_{88}H_{72}BrGaN_8$. Calculated, %: C 75.97; H 5.22; N 8.05.

(Tetra-7-*tert*-butyltetra-1-phenyl-2,3-naphthalocyaninato)bromogallium XXVI was prepared similarly to **XXIII** from imide **IX** in 40% yield. Electronic absorption spectrum in chloroform, λ, nm (log ε): 825 (5.31), 782 (4.40), 730 (4.46), 435 sh (3.95), 339 (4.04). Found, %: C 75.27; H 5.10; N 7.81. $C_{88}H_{72} \cdot BrGaN_8$. Calculated, %: C 75.97; H 5.22; N 8.05.

[Tetra(*p*-biphenylyl)-2,3-naphthalocyaninato]bromogallium XXVII. A mixture of 0.16 g of anhydride **XIII**, 1 g of urea, 0.5 g of ammonium sulfate, and a catalytic amount of ammonium molybdate was heated for 3 h at 280–300°C. After the standard work-up and chromatography of the residue on alumina, 0.065 g (40%) of **XXVII** was obtained. Electronic absorption spectrum in chloroform, λ, nm (log ε): 826 (5.30), 780 (4.58), 731 (4.56), 435 sh (4.28), 336 (4.89). Found, %: C 78.63; H 3.57; N 7.23. $C_{96}H_{56} \cdot BrGaN_8$. Calculated, %: C 78.38; H 3.84; N 7.62.

(Tetra-1-phenyl-2,3-phenanthroporphyrazinato)bromogallium XXVIII was prepared in 39% yield similarly to **XXIII**. Electronic absorption spectrum in chloroform, λ, nm (log ε): 795 (5.29), 756 (4.54), 707 (4.43), 406 sh (4.56), 344 (4.84). Found, %: C 77.89; H 3.90; N 7.72. $C_{88}H_{48}BrGaN_8$. Calculated, %: C 77.32; H 3.54; N 8.19.

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