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Syntheses of various symmetrical naphthalenophanes and anthracenophanes *via* a Diels–Alder reaction between *syn*-[2.2](5,8)phthalazinophane derivatives and some selected dienophiles as well as the synthesis of other symmetrical heterophanes

Ashraf A. Aly
Department of Chemistry, Faculty of Science, El-Minia University, El-Minia, Egypt.
E-mail: ashraf160@yahoo.com

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The syntheses of various classes of unreported naphthalenophanes, anthracenophanes and heterophanes are herein reported. The key to their successful preparation depends on the synthesis of *syn*-4,7,14,17-tetra(phenyl and chloro)-[2.2](5,8)phthalazinophanes as well as *syn*-4,5,6,7,14,15,16,17-octahydro[2.2](5,8)phthalazinophane-4,7,14,17-tetraone and 4,5,12,13-tetrakis(methoxycarbonyl)-[2.2]paracyclophane.

Introduction

[2.2]Paracyclophane is the smallest stable member of the [*m*,*n*]cyclophane series. The close proximity of the two benzene rings in [2.2]paracyclophane leads to a strong interaction of the π-systems.[1–4] The chemical behavior of [2$_n$]cyclophanes is determined, on the one hand, by interannular π-interactions between the benzene ″decks″ and by the strain of the polycyclic systems, on the other, making them far more reactive as compared with classical aromatic systems.[5] More importantly, [2.2]paracyclophanes containing polycyclic aromatic subunits constitute a class of compounds, which contain conjugated π-systems and show interesting electronic[6–8] and stereochemical[9,10] properties. The incorporation of heteroatoms into conjugated polycyclic cyclophanes will effectively increase their electronic properties and may also be of interest from a biological prospective. The syntheses of cyclophanes having one or more condensed polycyclic aromatic subunits generally involve multiple steps, often resulting in low overall yields of the desired products.[11–14] Although, many tetrasubstituted-[2.2]paracyclophanes have been synthesized by cycloaddition reactions between symmetrical acetylenes and hexa-1,2,4,5-tetraene,[15] their chemistry has been hitherto little investigated.[15,16] Recently, we have worked to find efficient, facile and elegant methods for the preparation of novel symmetrical polycyclic heterophanes such as [2.2](3,8)pyridazinophane and quinolinophane-2(1*H*)-one as well as the synthesis of [2](5,8)quinolinophanes and fused spiro-pyranoindanoparacyclophanes.[17] Herein, we report an investigation into the synthesis of various symmetrical naphthalenophanes and anthracenophanes from the newly prepared *syn*-4,7,14,17-tetra(phenyl and chloro)[2.2](5,8)phthalazinophanes (**2** and **13**) in addition to *syn*-4,5,6,7,14,15,16,17-octahydro[2.2](5,8)phthalazinophane-4,7,14,17-tetraone (**10**). These syntheses depend upon the use of the Diels–Alder cycloaddition reaction in the reactions of compounds **2**, **10** and **13** with some selected dienophiles such as dimethyl acetylenedicarboxylate (DMAD) and dimethyl maleate (DMM). Moreover, the resulting polycyclic cycloadducts can be used as precursors to prepare many symmetrical heterophanes. On the other hand, some heterophanes can be successfully prepared by the reaction of 4,5,12,13-tetrakis(methoxycarbonyl)-[2.2]paracyclophane (**9**) with a range of binucleophilic compounds.

Results and discussion

Synthesis

By gently heating a mixture of 4,5,12,13-tetrabenzoyl[2.2]paracyclophane (**1**)[15] with an excess amount of hydrazine hydrate in DMF, *syn*-4,7,14,17-tetraphenyl[2.2](5,8)phthalazinophane (**2**) was obtained in 80% yield (Scheme 1). Primarily, we believe that compound **2** is a good diene system for [4π + 2π]cycloaddition reactions. Moreover, owing to the symmetrical structure, compound **2** also has the ability to behave in a similar way to *s*-tetrazines in cycloaddition reactions. Consequently, reaction of **2** with DMAD in refluxing toluene gave, after 5 days, *syn*-[2.2](1,4)naphthalenophane derivative **3** in 92% yield (Scheme 1). The synthesis of nitrogen-containing heterophanes led to the idea that the heterophane **4** could be obtained from the naphthalenophane **3**. The presence of the two *ortho*-groups in **3** is taken advantage of in the reaction with aromatic amines, such as aniline, resulted in [2.2](5,8)benzo[*f*]isoindolophanetetraone derivative **4** in 92% yield (Scheme 1). On applying the same procedure used to prepare **2**, reaction of **3** with hydrazine hydrate afforded the aza-derivative of *syn*-[2.2](1,4)anthracenophane **5** in 80% yield (Scheme 1).

Surprisingly, treatment of **5** with DMAD in an acetic acid and acetic anhydride mixture gave the polynuclear hydrocarbon *syn*-[2.2](1,4)anthracenophane derivative **6** in 95% yield (Scheme 1).

Elemental analyses and mass spectra confirmed the molecular formula of both **4** and **6** as $C_{64}H_{42}N_2O_4$ and $C_{72}H_{56}O_{16}$, respectively. The mass spectra indicated that the number of carbon atoms of **4** and **6** exceeded those in C_{60} chemistry. Therefore, compounds **4** and **6** obviously constitute a new class in the field of polycyclic cyclophane and heterocyclic chemistry.

The proposed mechanism describing the formation of **6** is undoubtedly based on an initial acetylated product **7**, followed by a [4π + 2π]cycloaddition reaction between **7** and DMAD to form the intermediate **8**. Aromatization and elimination of two moles of nitrogen molecules from **8** give **6** (Fig. 1).

The chemistry of another example of a tetrasubstituted-[2.2]paracyclophanes, namely 4,5,12,13-tetrakis(methoxycarbonyl)[2.2]paracyclophane (**9**) (Scheme 2). Reaction of **9** with hydrazine hydrate in DMF afforded *syn*-4,5,6,7,14,15,16,17-octahydro[2.2](5,8)phthalazinophane-4,7,14,17-tetraone (**10**)

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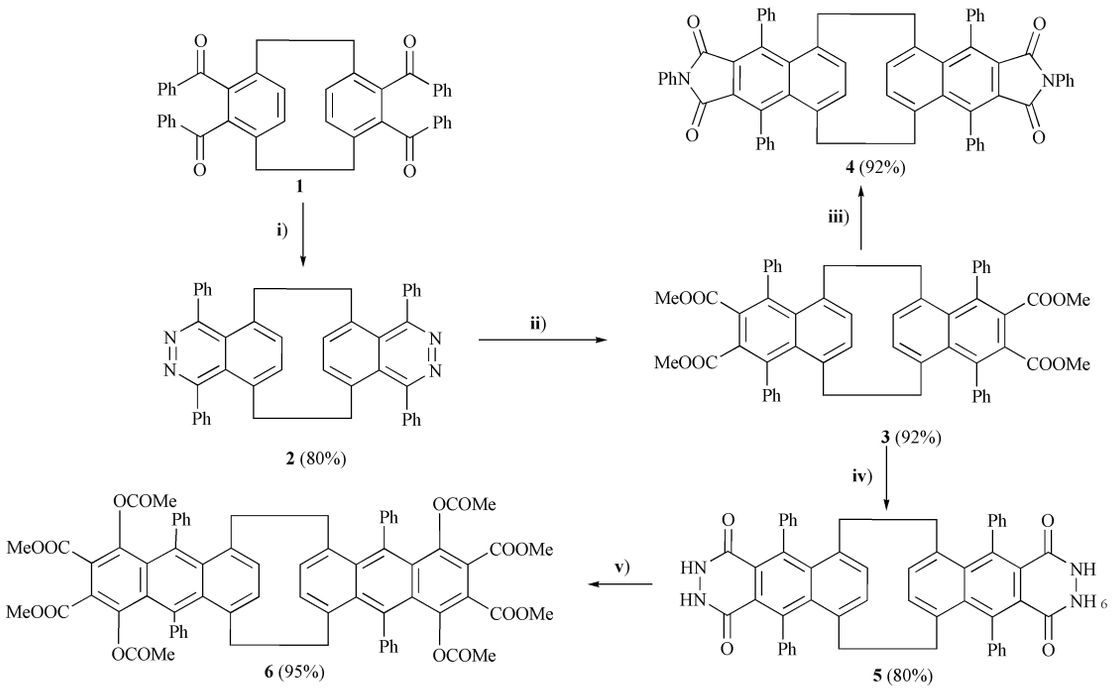


Scheme 1 *Reagents and conditions*: i) NH_2–NH_2, DMF, 80 °C, 10 h; ii) DMAD, toluene, reflux, 5 d; iii) aniline, EtOH, reflux, 2 d; iv) NH_2–NH_2, DMF, 80 °C, 12 h; v) DMAD, AcOH, Ac_2O, reflux, 5 d.

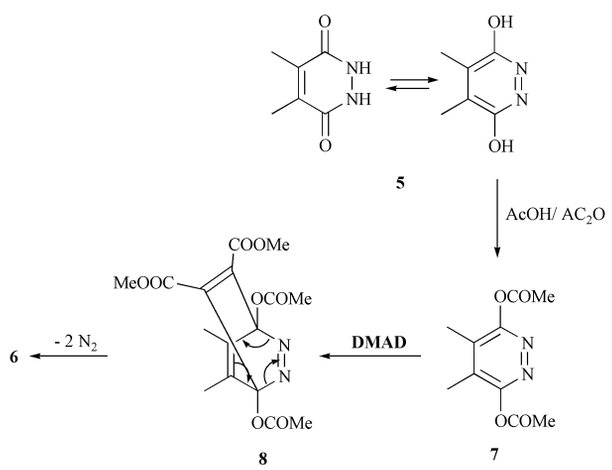


Fig. 1

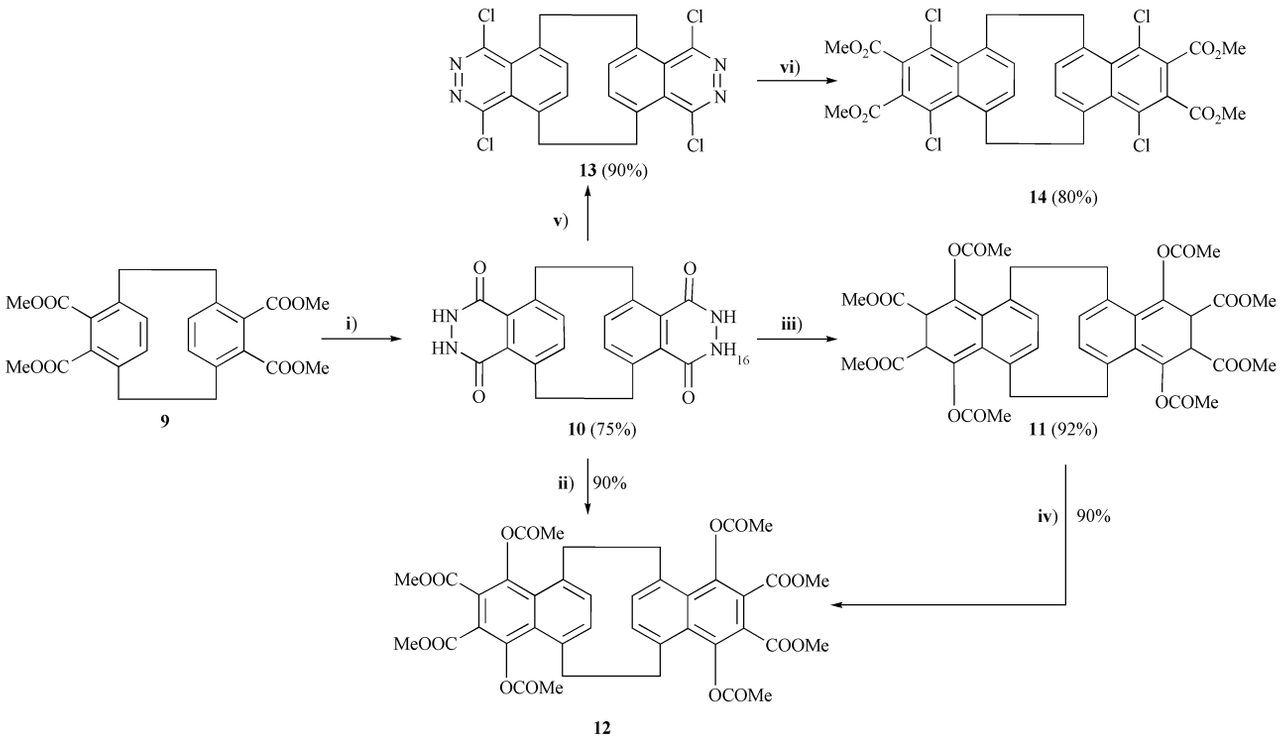
in 75% yield (Scheme 2). The chemistry of **10** with DMAD, DMM and phosphorus pentachloride was then examined.

Inspired by the success obtained in the synthesis of **6**, we decided to investigate the reaction of **10** with two equivalents of DMAD under the same reaction conditions. The former reaction afforded the desired hexacetylated cycloadduct **12** (**Method A**) in 90% yield (Scheme 2). Compound **12** was proved and identified as *syn*-5,6,15,16-tetrakis(methoxycarbonyl)-4,7,14,17-tetraacetoxy[2.2](1,4)naphthalenophane, which is considered to be a derivative of compound **3**. Having established that the optimum conditions for the synthesis of either anthracenophane **6** or naphthalenophane **12** involved the use of an acetic acid and acetic anhydride mixture in a Diels–Alder reaction of either **5** or **10** with DMAD, our attention finally turned to the use of this mixture in the reaction between **10** and another dienophile such as DMM. This reaction of **10** with DMM afforded, within 3 days, product **11** in 92% yield (Scheme 2). With the aim of preparing **12**, oxidation of **11** using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) was succeeded to form **12** in 90% yield (**Method B**, Scheme 2). Structural assignments of compounds **10**–**12** showed symmetrical features in their ^{1}H, ^{13}C NMR and mass spectra (see Experimental section). Similarly, the proposed mechanism describing the formation of either **11** or **12** is based upon the same steps for the formation of **6**.

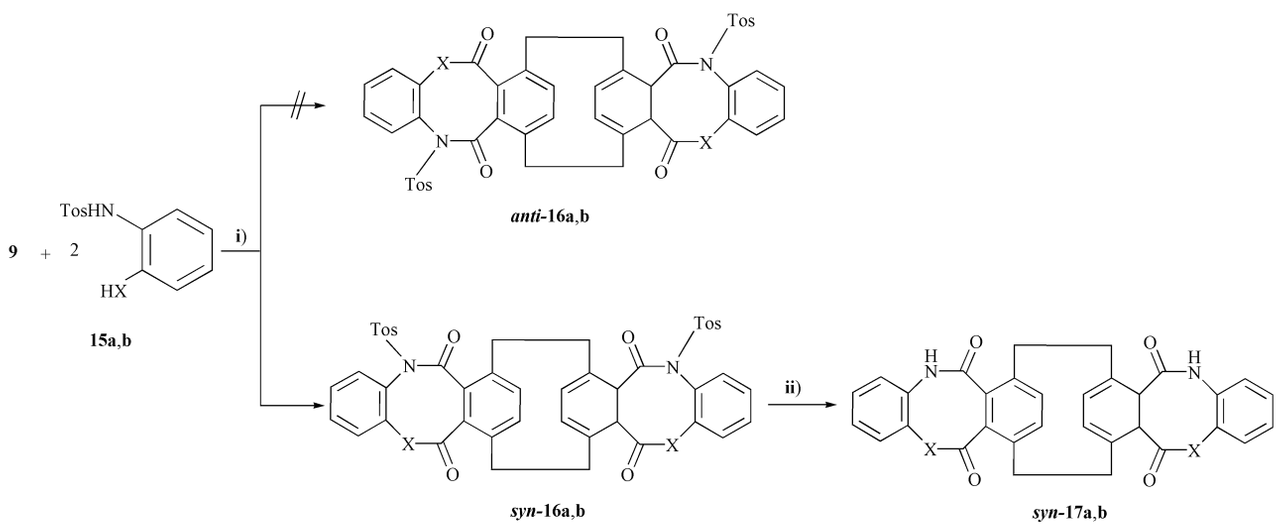
One reason for the use of phosphorus pentachloride is its reaction with phthalazine-1,4(2*H*,3*H*)-dione derivatives to prepare 1,4-dichlorophthalazine derivatives, which are considered as intermediates in the synthesis of heterocyclic compounds.[18,19] In the reaction of phosphorus pentachloride with compound **10**, *syn*-4,7,14,17-tetrachloro[2.2](5,8)phthalazinophane (**13**) was obtained in 90% yield (Scheme 2). The similarities of the chemistry in Schemes 1 and 2, prompts us to synthesize the *syn*-tetrachloronaphthalenophane derivative **14**. Transformation of **13** into **14** was accomplished, in 80% yield, by refluxing of **13** with DMAD in an acetic acid and acetic anhydride mixture (Scheme 2). In comparison with compounds **3** and **12** discussed above, the molecular symmetry of **14** also causes slight differences in the resonances of the bridge and paracyclophanyl protons in its ^{1}H NMR spectrum (see Experimental section). The distinctive differences in δ_C values in the ^{13}C NMR spectra of the former compounds are also attributed to the effect of the various substitutents on the ring-current of the carbons in the naphthalenoid rings (see Experimental section).

It was reported that the reaction of **9** with aniline afforded the corresponding *syn*-isoindolenophane.[16] Interestingly, we have also investigated the synthesis of the heterophanes **17a**,**b** as a general method for preparing this class of compound, so as to facilitate their future synthesis. Attempts to prepare the heterophanes **17a**,**b** from the reaction of **9** with binucleophilic compounds such as 2-aminophenol and 2-aminothiophenol proceeded, but in very low yields of the desired products. Thus, it is believed that the reaction between **9** and these nucleophiles have to proceed *via* protection of their amino groups. Therefore, we prepared *N*-tosyl-2-aminophenol (**15a**) and *N*-tosyl-2-aminothiophenol (**15b**) by applying the procedures mentioned in references 20 and 21 (Scheme 3). Treatment of compound **9** with **15a**,**b** under basic condition led to the formation of the *syn*-heterophanes **16a**,**b** (Scheme 3). Hydrolysis of the tosyl groups in **16a**,**b** using sulfuric acid gave the desired products **17a**,**b** (Scheme 3).

Compounds **16a**,**b** and **17a**,**b** are described as having a *syn*-structure (pseudo-*meta*) rather than an *anti*-one (pseudo-*para*). This is based on the knowledge of the ^{1}H NMR spectra of compounds which have relatively similar structures to **16a**,**b**



Scheme 2 *Reagents and conditions*: i) NH_2–NH_2, DMF, 80 °C, 6 h; ii) DMAD, AcOH, Ac_2O, reflux, 2 d **(Method A)**; iii) DMM, AcOH, Ac_2O, reflux, 3 d; iv) DDQ PhCl, reflux, 24 h **(Method B)**; v) PCl_5, DMF, 100 °C, 3 h; vi) DMAD, AcOH, Ac_2O, reflux, 24 h.



15-17		yield (%) of **16**	yield (%) of **17**
a	X = O	75	85
b	X = S	77	80

Scheme 3 *Reagents and conditions*: i) EtOH, Et_3N, reflux, 24 h; ii) H_2SO_4, H_2O.

and **17a**,**b**.[10] The multiplet pattern in the ^{1}H NMR spectra of the methylene bridges reflects the molecular symmetry of the aforementioned structures.[10,22] The ethano-bridges in the *syn*-structure are in different environments but each bridge is symmetrical and has two sets of two chemically equivalent but magnetically non-equivalent protons. Therefore, the ^{1}H NMR spectra of **16a**,**b** and **17a**,**b** revealed two different AA′XX′ spectra of the bridge hydrogen atoms (see Experimental section). On the other hand, the *anti*-isomer (pseudo-*para*) has two equivalent bridges, each containing four chemically non-equivalent protons; hence they give one AKRX spectrum.

In conclusion, we have demonstrated very convenient procedures by which various *syn*-naphthalenophanes, anthracenophanes and heterophanes can be synthesized. The advantages of these methodologies is the very high yields of the desired products and the ease with which polycyclic cyclophanes can be converted into the corresponding heterophanes. The former results also indicate, beyond doubt, the extraordinary reactivity of **2** and **9** in their reactions with various reagents; such behaviour has not been observed in classic aromatic systems. Consequently, much effort is required to discover more about cyclophane chemistry.

Experimental

Melting points are uncorrected values. The IR spectra were recorded on a Nicolet 320 FT-IR using KBr pellets. The UV spectra were measured on a Beckman UV 5230 spectrophoto-

meter.^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker AM 400 (400.134 MHz and 100.60 MHz) instrument in $CDCl_3$ and DMSO-d_6. The chemical shifts (δ's) were measured relative to the internal standard TMS. Coupling constants were expressed in Hz. Mass spectra were performed using Finnigan MAT 8430 spectrometer at 70 eV. Elemental analyses were performed by the Microanalysis Center of the Institut für Anorganische Chemie, Technische Universität Braunschweig. Column chromatography was performed on silica gel 7714 (Merck). Zones of eluted material were detected by quenching of indicator fluorescence upon exposure to 254 nm UV light. The dienophiles and the other reagents were commercial products bought from either Aldrich or Fluka.

syn-4,7,14,17-Tetraphenyl[2.2](5,8)phthalazinophane (2)

A mixture of **1** (0.62 g, 1 mmol) and hydrazine hydrate (3.20 g, 10 mmol) in DMF (25 cm^3) was heated in an oil bath at 80 °C for 10 h. The reaction mixture was then cooled (0 °C) and ethanol (150 cm^3) was added. The yellow precipitate formed was isolated by filtration. The precipitate was washed several times with water and ethanol. Compound **2** was recrystallized from ethyl acetate as yellow needles. Yield 0.49 g (80%), mp > 300 °C (Found: C, 85.80; H, 5.22; N, 9.15. $C_{44}H_{32}N_4$ requires C, 85.69; H, 5.23; N, 9.08%); ν_{max} (KBr)/cm^{-1} 3058–3010 (Ar–CH), 2980–2968 (Ali.–CH), 1117 (N=N); λ_{max} (CH_2Cl_2)/nm (log ε/dm^3 mol^{-1} cm^{-1}) 390 (3.92); δ_H(400.134 MHz, DMSO-d_6) 2.48–2.60 (4H, m, CH_2–CH_2), 3.60–3.82 (4H, m, CH_2–CH_2), 6.60 (4H, s, PC–H) (PC = [2.2]paracyclophane), 7.35–7.62 (20H, m, Ph–H); δ_C (100.60 MHz, DMSO-d_6) 28.90 (CH_2–CH_2), 126.40, 128.40, 130.80, 135.60 (PC–CH, Ph–CH), 132.80, 138.00, 142.00 (PC–C, Ph–C), 158.90 (C-3); *m*/*z* (EI) 617 (M + 1, 18%), 616 (M$^+$, 38), 588 (14), 510 (12), 410 (14), 308 (100), 280 (20), 204 (16), 126 (20), 102 (34), 77 (30).

syn-5,6,15,16-Tetrakis(methoxycarbonyl)-4,7,14,17-tetraphenyl-[2.2](1,4)-naphthalenophane (3)

A stirred mixture of **2** (0.62 g, 1 mmol) and DMAD (0.28 g, 2 mmol) in toluene (70 cm^3) was refluxed for 5 d (the reaction progress was followed by TLC analysis). The solvent was then removed *in vacuo* and the residue was applied to a column chromatograph using CH_2Cl_2 as eluent. To the oily substance formed, ethanol was added dropwise with stirring at room temperature over 30 min. The yellow precipitate obtained by filtration was recrystallized from acetone as yellow crystals of **3**. Yield 0.78 g (92%), mp 230 °C (Found: C, 79.40; H, 5.20. $C_{56}H_{44}O_8$ requires C, 79.60; H, 5.25%); ν_{max} (KBr)/cm^{-1} 3110–3040 (Ar–CH), 2980–2880 (Ali.–CH), 1734–1700 (CO); λ_{max} (CH_3CN)/nm (log ε/dm^3 mol^{-1} cm^{-1}) 398 (3.94); δ_H(400.134 MHz, $CDCl_3$) 2.75–3.04 (m, 4H, CH_2–CH_2), 3.64–3.80 (m, 4H, CH_2–CH_2), 3.90 (s, 12H, CH_3-ester), 6.40 (s, 4H, PC–H), 7.40–7.66 (m, 20H, Ph–H); δ_C(100.60 MHz, $CDCl_3$) 32.30 (CH_2–CH_2), 50.90 (*C*H$_3$-ester), 124.80 (=*C*–COOCH$_3$), 128.12, 130.14, 132.60, 134.66 (PC–CH, Ph–CH), 135.42, 136.20, 137.02, 148.90 (PC–C, Ph–C), 172.00 (*C*OO-ester); *m*/*z* (EI) 844 (M$^+$, 40%), 828 (30), 784 (34), 770 (22), 724 (18), 422 (100), 406 (18), 362 (28), 226 (34), 150 (18), 143 (12), 104 (22).

4,6,8,15,17,19-Hexaphenyl[2.2](5,8)benzo[*f*]isoindolophane-5,7,16,18(6*H*,17*H*)-tetraone (4)

A stirred mixture of **3** (0.42 g, 0.5 mmol) and aniline (0.09 g, 1 mmol) in absolute ethanol (200 cm^3) was refluxed for 2 d (the reaction was followed by TLC analysis). The yellow precipitate formed was collected by filtration. The precipitate was dissolved in CH_2Cl_2 (100 cm^3) and the solution was concentrated *in vacuo*. The residue was applied to a column chromatograph coated with silica gel using CH_2Cl_2 as eluent. The solvent was evaporated *in vacuo* and the product obtained was recrystallized from ethanol as yellow crystals of **4**. Yield 0.42 g (92%), mp 260 °C (Found: C, 85.30; H, 4.60; N, 3.00. $C_{64}H_{42}N_2O_4$ requires C, 85.12; H, 4.69; N, 3.10%); ν_{max} (KBr)/cm^{-1} 3118–3060 (Ar–CH), 2985–2870 (Ali.–CH), 1720 (CO); λ_{max} (CH_2Cl_2)/nm (log ε/dm^3 mol^{-1} cm^{-1}) 400 (3.98); δ_H(400.134 MHz, DMSO-d_6) 2.60–2.78 (4H, m, CH_2–CH_2), 3.60–3.76 (4H, m, CH_2–CH_2), 6.56 (4H, s, PC–H), 7.18–7.48 (20H, m, Ph–H), 7.64–7.72 (6H, m, Ph–H), 7.90–8.04 (4H, m, Ph–H); δ_C(100.60 MHz, DMSO-d_6) 32.60 (CH_2–CH_2), 125.12, 128.60, 130.18, 132.40, 134.22, 134.80, 138.60 (PC–CH, Ph–CH), 128.00, 132.60, 134.90, 136.40, 138.02, 148.60 (PC–C, Ph–C), 172.00 (CO); *m*/*z* (EI) 904 (M + 1, 24%), 903 (M$^+$, 100), 826 (22), 756 (16), 452 (68), 306 (16), 146 (26), 158 (18), 104 (16), 77 (38).

syn-5,8,17,20-tetraoxo-4,9,16,21-tetraphenyl-5,6,7,8,17,18,19,20-octahydro[2.2](6,9)benzo[*g*]phthalazinophane (5)

Compound **5** was prepared using the same procedure as that used for **2**. A stirred mixture of **3** (0.43 g, 0.5 mmol) and hydrazine hydrate (1.60 g, 5 mmol) in DMF (20 cm^3) was heated in an oil bath at 80 °C for 12 h. Compound **5** was recrystallized from DMF–ethanol as orange needles. Yield 0.32 g (80%), mp 280–282 °C (decomp.) (Found: C, 79.80; H, 4.62; N, 7.15. $C_{52}H_{36}N_4O_4$ requires C, 79.98; H, 4.65; N, 7.17%); ν_{max} (KBr)/cm^{-1} 3136–3065 (Ar–CH), 2990–2890 (Ali.–CH), 1690 (CO); λ_{max} (CH_2Cl_2)/nm (log ε/dm^3 mol^{-1} cm^{-1}) 398 (3.94); δ_H(400.134 MHz, DMSO-d_6) 2.55–2.72 (4H, m, CH_2–CH_2), 3.62–3.80 (4H, m, CH_2–CH_2), 5.00 (4H, br s, 4NH), 6.70 (4H, s, PC–H), 7.40–7.60 (20H, m, Ph–H); δ_C(100.60 MHz, DMSO-d_6) 30.80 (CH_2–CH_2), 126.40, 129.60, 130.42, 134.60 (PC–CH, Ph–CH), 132.40, 133.00, 135.30, 137.40, 146.40, (PC–C, Ph–C), 167.90 (CO-amide); *m*/*z* (EI) 781 (M + 1, 20%), 780 (M$^+$, 100), 750 (16), 694 (24), 616 (20), 538 (18), 390 (60), 304 (22), 226 (14), 110 (14), 77 (34), 60 (18).

syn-6,7,18,19-Tetrakis(methoxycarbonyl)-5,8,17,20-tetra-acetoxy-4,9,16,21-tetraphenyl[2.2](1,4)anthracenophane (6)

A stirred mixture of **5** (0.39 g, 0.5 mmol) and DMAD (0.14 g, 1 mmol) in acetic acid (30 cm^3) and acetic anhydride (5 cm^3) was refluxed for 5 d (the reaction progress was followed by TLC analysis). The yellow precipitate formed was collected by filtration. The precipitate was washed several times with water until the odor of the acid mixture was nearly removed. The precipitate was then dried *in vacuo* and recrystallized from DMF–ethanol as yellow crystals of **6**. Yield 0.56 g (95%), mp > 300 °C (Found: C, 73.30; H, 4.74. $C_{72}H_{56}O_{16}$ requires C, 73.46; H, 4.79%); ν_{max} (KBr)/cm^{-1} 3160–3008 (Ar–CH), 2985–2895 (Ali.–CH), 1738–1710 (CO), 1112 (OCH_3); λ_{max} ($CHCl_3$)/nm (log ε/dm^3 mol^{-1} cm^{-1}) 414 (4.12); δ_H(400.134 MHz, DMSO-d_6) 2.15 (12H, s, $OCOCH_3$), 2.75–3.10 (4H, m, CH_2–CH_2), 3.78–3.98 (16H, m, CH_2–CH_2, CH_3-ester), 6.68 (4H, s, PC–H), 7.60–7.78 (20H, m, Ph–H); δ_C(100.60 MHz, DMSO-d_6) 15.40 (OCO*C*H$_3$) 32.10 (CH_2–CH_2), 50.90 (*C*H$_3$-ester), 125.00 (=*C*-methyl-ester), 128.18, 128.40, 130.60, 132.40 (PC–CH, Ph–CH), 134.00, 134.80, 135.40, 136.10, 136.42, 144.68 (PC–C, =*C*–OCOCH$_3$), 166.90 (O*C*O-ester), 170.00 (*C*OO-ester); *m*/*z* (FAB) 1177 (M$^+$, 100%).

syn-4,5,6,7,14,15,16,17-Octahydro[2.2](5,8)phthalazinophane-4,7,14,17-tetraone (10)

By applying the same procedure mentioned in case of the synthesis of compound **2**, a mixture of **9** (0.44 g, 1 mmol) and hydrazine hydrate (3.20 g, 10 mmol) was heated for 6 h. Compound **10** was recrystallized from acetone as orange needles. Yield 0.28 g (75%), mp > 300 °C (Found: C, 63.30; H, 4.20; N, 14.85. $C_{20}H_{16}N_4O_4$ requires C, 63.38; H, 4.28; N, 14.89%); ν_{max} (KBr)/cm^{-1} 3236 (NH), 3040–3000 (Ar–CH), 2996–2985 (Ali.–CH), 1694 (CO); λ_{max} (CH_3CN)/nm (log ε/dm^3 mol^{-1} cm^{-1}) 386 (3.90); δ_H(400.134 MHz, $CDCl_3$) 2.70–3.00 (4H, m, CH_2–CH_2), 3.75–4.00 (4H, m, CH_2–CH_2), 5.00 (4H, br s, 4NH),

6.75 (4H, s, PC–H); δ_C(100.60 MHz, $CDCl_3$) 29.90 (CH_2–CH_2), 131.80 (PC–CH), 135.00, 139.40 (PC–C), 167.60 (CO-amide); *m*/*z* (EI) 376 (M^+, 40%), 360 (40), 346 (94), 332 (10), 303 (14), 203 (40), 188 (100), 159 (20), 143 (12), 133 (44), 103 (22), 77 (18).

syn-5,6,15,16-Tetrakis(methoxycarbonyl)-4,7,14,17-tetraacetoxy-[2.2](1,4)naphthalenophane (12) (Method A)

A stirred mixture of **10** (0.76 g, 2 mmol) and DMAD (0.57 g, 4 mmol) in acetic acid (50 cm^3) and acetic anhydride (5 cm^3) was refluxed for 2 d (the reaction progress was followed by TLC analysis). The yellow precipitate formed was collected by filtration. The precipitate was washed several times with water until the odor of the acid mixture was removed. The precipitate was dried *in vacuo* and recrystallized from $CHCl_3$–methanol as yellow crystals of **12**. Yield 1.39 g (90%), mp 260 °C (Found: C, 62.00; H, 4.70. $C_{40}H_{36}O_{16}$ requires C, 62.18; H, 4.70%); ν_{max} (KBr)/cm^{-1} 3030–3000 (Ar–CH), 2990–2895 (Ali.–CH), 1734–1708 (CO), 1115 (OCH_3); λ_{max} ($CHCl_3$) (log ε/dm^3 mol^{-1} cm^{-1})/nm 390 (3.92); δ_H(400.134 MHz, $CDCl_3$) 2.18 (s, 12H, $OCOCH_3$), 2.80–3.15 (m, 4H, CH_2–CH_2), 3.70–3.88 (m, 4H, CH_2–CH_2), 3.91 (s, 12H, CH_3-ester), 6.64 (s, 4H, PC–H); δ_C(100.60 MHz, $CDCl_3$) 15.40 (OCOCH_3), 32.80 (CH_2–CH_2), 50.80 (CH_3-ester), 124.20 (=*C*–$COOCH_3$), 126.60 (PC–CH), 129.0, 134.60, 148.68 (PC–C, =*C*–$OCOCH_3$), 168.80 (O*C*O-ester), 172.00 (*C*OO-ester); *m*/*z* (EI) 772 (M^+, 60%), 756 (46), 742 (24), 712 (20), 654 (18), 416 (12), 386 (100), 312 (30), 300 (14), 296 (18), 242 (22), 144 (16), 132 (34), 102 (12), 59 (14).

syn-5,6,15,16-Tetrakis(methoxycarbonyl)-4,7,14,17-tetraacetoxy-5,6,15,16-tetrahydro[2.2](1,4)naphthalenophane (11)

By applying the same procedure mentioned in preparing **12**, a stirred mixture of **10** (0.76 g, 2 mmol) and DMM (0.58 g, 4 mmol) in acetic acid (50 cm^3) and acetic anhydride (5 cm^3) was refluxed for 3 d (the reaction progress was followed by TLC analysis). Compound **11** was recrystallized from ethanol as pale yellow needles. Yield 1.42 g (92%), mp 290–292 °C (Found: C, 61.94; H, 5.14. $C_{40}H_{40}O_{16}$ requires C, 61.85; H, 5.19%); ν_{max} (KBr)/cm^{-1} 3050–3008 (Ar–CH), 2998–2892 (Ali.–CH), 1736–1704 (CO), 1112 (OCH_3); λ_{max} ($CHCl_3$) (log ε/dm^3 mol^{-1} cm^{-1})/nm 382 (3.80); δ_H(400.134 MHz, DMSO-d_6) 2.10 (12H, s, $OCOCH_3$), 2.78–3.10 (4H, m, CH_2–CH_2), 3.60–4.00 (20H, m, CH_2–CH_2, H-6, H-6′, H-7, H-7′, CH_3-ester), 6.50 (4H, s, PC–H); δ_C(100.60 MHz, DMSO-d_6) 15.30 (OCOCH_3), 32.40 (CH_2–CH_2), 38.40 (*C*H–ester), 50.98 (CH_3-ester), 125.20 (PC–CH), 128.40, 133.90, 140.68 (PC–C), 168.90 (O*C*O-ester), 172.00 (*C*OO-ester); *m*/*z* (EI) 776 (M^+, 70%), 760 (40), 746 (16), 716 (12), 658 (22), 388 (100), 308 (16), 262 (20), 188 (20), 144 (16), 60 (18).

Oxidation of 11; another method for the synthesis of 12 (Method B)

A mixture of **11** (0.78 g, 1 mmol) and **DDQ** (0.46 g, 2 mmol) in chlorobenzene (40 cm^3) was refluxed for 1 d. The reaction mixture was cooled and the precipitate of **DDQ**–H_2 formed was separated by filtration. The precipitate was washed with $CHCl_3$ (200 cm^3) and the filtrate was then concentrated *in vacuo*. The residue was applied to a column chromatograph using $CHCl_3$ as eluent to give compound **12**, which on recrystallization gave 0.70 g (90%) yield, mp 260 °C. The physical and analytical data of **12** are the same as given before.

syn-4,7,14,17-Tetrachloro[2.2](5,8)phthalazinophane (13)

A 100 cm^3 three-necked round bottom flask was equipped with a condenser and a magnetic stirrer. The system was flame-dried under a strong flow of N_2 gas and then cooled to room temperature. To a stirred ice-cold solution (−15 °C) of **10** (0.38 g, 1 mmol) in DMF (40 cm^3) under N_2 gas, a solution of phosphorus pentachloride (0.94 g, 4.5 mmol) in DMF (5 cm^3) was added dropwise over 30 min. The color of the reaction mixture turned from orange to black after stirring for 1 h at ambient temperature. The reaction mixture was further heated in an oil bath (100 °C) for 3 h. The cooled organic layer was extracted with CH_2Cl_2 and washed several times with water. The organic layer was dried over magnesium sulfate. The solvent was concentrated *in vacuo* and the residue was applied to a column chromatograph using $CHCl_3$–hexane (5 : 1) as eluent. The elution afforded compound **13**, which recrystallized from ethyl acetate as pale yellow crystals. Yield 0.41 g (90%), mp 212 °C (Found: C, 53.30; H, 2.66; Cl, 31.45; N, 12.54. $C_{20}H_{12}Cl_4N_4$ requires C, 53.36; H, 2.69; Cl, 31.50; N, 12.45%); ν_{max} (KBr)/cm^{-1} 3055–3010 (Ar–CH), 2988–2855 (Ali.–CH), 1115 (N=N); λ_{max} ($CHCl_3$)/nm (log ε/dm^3 mol^{-1} cm^{-1}) 375 (3.82); δ_H(400.134 MHz, $CDCl_3$) 2.95–3.15 (4H, m, CH_2–CH_2), 3.82–3.98 (4H, m, CH_2–CH_2), 6.64 (4H, s, PC–H); δ_C(100.60 MHz, $CDCl_3$) 30.10 (CH_2–CH_2), 129.80 (PC–CH), 134.80, 136.80, 154.20 (PC–C); *m*/*z* (EI) 454 (M + 4, 10%), 452 (M + 2, 52), 450 (M^+, 100), 448 (22), 422 (35), 416 (20), 414 (40), 380 (18), 378 (32), 306 (20), 228 (18), 226 (56), 190 (18), 188 (36), 174 (10), 172 (24), 146 (18), 104 (14).

syn-4,7,14,17-Tetrachloro-5,6,15,16-tetrakis(methoxycarbonyl)-[2.2](1,4)naphthalenophane (14)

On applying the same procedure mentioned in preparing **12**, a stirred mixture of **13** (0.45 g, 1 mmol) and DMAD (0.28 g, 2 mmol) in acetic acid (50 cm^3) and acetic anhydride (5 cm^3) was refluxed for 24 h. Compound **14** was recrystallized from ethanol as pale yellow needles. Yield 0.54 g (80%), mp 248–250 °C (Found: C, 56.50; H, 3.60; Cl, 20.86. $C_{32}H_{24}Cl_4O_8$ requires C, 56.66; H, 3.57; Cl, 20.91%); ν_{max} (KBr)/cm^{-1} 3036–3008 (Ar–CH), 2994–2985 (Ali.–CH), 1732–1704 (CO), 1112 (OCH_3); λ_{max} ($CHCl_3$)/nm (log ε/dm^3 mol^{-1} cm^{-1}) 392 (3.90); δ_H(400.134 MHz, $CDCl_3$) 2.75–3.06 (m, 4H, CH_2–CH_2), 3.65–3.84 (m, 4H, CH_2–CH_2), 3.95 (s, 12H, CH_3-ester), 6.54 (s, 4H, PC–H); δ_C(100.60 MHz, $CDCl_3$) 32.40 (CH_2–CH_2), 50.92 (CH_3-ester), 125.00 (=*C*–$COOCH_3$), 124.70 (PC–CH), 128.70, 135.00, 146.90 (PC–C, =*C*–Cl), 172.60 (*C*OO-ester); *m*/*z* (EI) 682 (M + 4, 10%), 680 (M + 2, 50), 678 (M^+, 100), 676 (80), 642 (18), 640 (30), 584 (22), 550 (16), 548 (40), 340 (30), 388 (80), 302 (20), 194 (16), 192 (34), 152 (18), 150 (28).

Reaction of 9 with *N*-tosylamine derivatives (15a,b): general procedure

To a stirred solution of **9** (0.44 g, 1 mmol) in absolute ethanol (500 cm^3) containing a few drops of triethylamine, a solution of either **15a** or **15b** (2 mmol) in absolute ethanol (100 cm^3) was added dropwise with stirring over 30 min. The color of the reaction mixture changed from yellow to red then became brown after stirring for 1 h at room temperature. The reaction mixture was refluxed for 24 h (the reaction progress was monitored using TLC analysis). The mixture was then cooled (0 °C) and the precipitate of either **16a** or **16b** that formed was filtered, washed with cooled ethanol and recrystallized from the stated solvents.

Compound 16a. Yellow crystals (acetone). Yield 0.63 g (75%), mp > 300 °C (Found: C, 65.70; H, 4.00; N, 3.25; S, 7.68. $C_{46}H_{34}N_2O_{10}S_2$ requires C, 65.86; H, 4.09; N, 3.34; S, 7.64%); ν_{max} (KBr)/cm^{-1} 3040–3008 (Ar–CH), 2986–2860 (Ali.–CH), 1735–1700 (CO), 1690, 1630, 1600; λ_{max} ($CHCl_3$)/nm (log ε/dm^3 mol^{-1} cm^{-1}) 430 (4.10); δ_H(400.134 MHz, $CDCl_3$) 2.30–2.45 (8H, m, CH_2–CH_2, CH_3, AA′XX′, J_{gem} 14.0, J_{trans} 7.5, J_{cis} 7.0 Hz), 2.68–2.75 (2H, m, CH_2–CH_2, AA′XX′, J_{gem} 13.5, J_{trans} 8.5, J_{cis} 8.8 Hz), 3.45–3.52 (2H, m, CH_2–CH_2, AA′XX′, J_{gem} 13.5, J_{trans} 8.2, J_{cis} 8.8 Hz), 4.00–4.08 (2H, m, CH_2–CH_2, AA′XX′, J_{gem} 14.2, J_{trans} 7.2, J_{cis} 6.8 Hz), 6.20 (2H, d, *J* 7.8 Hz, PC–H), 6.65 (2H, d, *J* 7.8 Hz, PC–H), 7.10 (2H, d, *J* 8.0 Hz),

7.35 (2H, d, *J* 8.2 Hz), 7.56–7.62 (4H, m), 7.70 (2H, dt, *J* 7.8, 1.8 Hz), 7.84 (2H, dt, *J* 7.8, 1.8 Hz), 8.12 (2H, dd, *J* 7.8, 1.8 Hz), 8.18 (2H, dd, *J* 7.8, 1.8 Hz); δ_C(100.60 MHz, $CDCl_3$) 22.10 (CH_3), 31.80, 34.00 (CH_2–CH_2), 124.18, 125.18, 126.40, 126.80, 127.64, 128.82, 128.98, 129.18, 130.14, 131.18, 131.40, 132.60, 132.80, 134.00, 135.10, 144.18, 144.80, 150.20 (PC–CH, PC–C, Ar–CH, Ar–C), 168.80, 174.00 (CO); *m*/*z* (EI) 839 (M + 1, 10%), 838 (M^+, 100), 806 (10), 682 (20), 578 (14), 520 (14), 420 (60), 264 (22), 160 (16), 104 (14), 77 (20).

Compound 16b. Yellow crystals (acetone). Yield 0.67 g (77%), mp > 300 °C (Found: C, 63.30; H, 3.90; N, 3.18; S, 14.64. $C_{46}H_{34}N_2O_8S_4$ requires C, 63.43; H, 3.93; N, 3.22; S, 14.73%); ν_{max} (KBr)/cm^{-1} 3048–3010 (Ar–CH), 2990–2875 (Ali.–CH), 1736–1704 (CO), 1692, 1628, 1600; λ_{max} ($CHCl_3$)/nm (log ε/dm^3 mol^{-1} cm^{-1}) 442 (4.24); δ_H(400.134 MHz, $CDCl_3$) 2.32–2.48 (8H, m, CH_2–CH_2, AA′XX′, CH_3, AA′XX′, J_{gem} 13.8, J_{trans} 7.5, J_{cis} 7.2 Hz), 2.70–2.78 (2H, m, CH_2–CH_2, AA′XX′, J_{gem} 13.6 J_{trans} 8.7, J_{cis} 9.0 Hz), 3.42–3.50 (2H, m, CH_2–CH_2, AA′XX′, J_{gem} 13.5, J_{trans} 8.5, J_{cis} 8.8 Hz), 3.98–4.04 (2H, m, CH_2–CH_2, AA′XX′, J_{gem} 13.5, J_{trans} 8.5, J_{cis} 8.6 Hz), 6.22 (2H, d, *J* 7.8 Hz, PC–H), 6.68 (2H, d, *J* 7.8 Hz, PC–H), 7.08 (2H, d, *J* 8.0 Hz), 7.32 (2H, d, *J* 8.2 Hz), 7.54–7.60 (4H, m), 7.78 (2H, dt, *J* 7.8, 1.8 Hz), 7.82 (2H, dt, *J* 7.8, 1.8 Hz), 8.10 (2H, dd, *J* 7.8, 1.8 Hz), 8.20 (2H, dd, *J* 7.8, 1.8 Hz); δ_C(100.60 MHz, $CDCl_3$) 21.80 (CH_3), 32.00, 33.88 (CH_2–CH_2), 125.20, 126.00, 126.64, 126.86, 127.80, 128.90, 129.10, 129.32, 130.64, 131.48, 131.66, 132.60, 133.00, 134.40, 135.30, 144.44, 144.98, 150.60 (PC–CH, PC–C, Ar–CH, Ar–C), 168.64, 173.88 (CO); *m*/*z* (EI) 872 (M + 1, 8%), 871 (M^+, 100), 839 (20), 824 (14), 716 (14), 594 (18), 536 (24), 436 (62), 435 (58), 282 (12), 280 (20), 176 (18), 120 (24), 76 (14).

Hydrolysis of 16a,b: general procedure

Concentrated sulfuric acid (5 cm^3) was added with stirring to the *N*-tosylamine derivatives **16a**,**b** (0.5 mmol) in a sealed flask. After 30 min of stirring at room temperature, the reaction mixture was cooled to 0 °C and water (200 cm^3) was added dropwise with vigorous stirring. The formed precipitate of **17a** or **17b** was filtered and recrystallized from the stated solvents.

Compound 17a. Pale yellow crystals ($CHCl_3$–ethanol). Yield 0.23 g (85%), mp 280–282 °C (Found: C, 72.30; H, 4.14; N, 5.20. $C_{32}H_{22}N_2O_6$ requires C, 72.45; H, 4.18; N, 5.28%); ν_{max} (KBr)/cm^{-1} 3200 (NH), 3030–3012 (Ar–CH), 2990–2890 (Ali.–CH), 1730–1690 (CO), 1510, 1450, 1380; λ_{max} ($CHCl_3$)/nm (log ε/dm^3 mol^{-1} cm^{-1}) 388 (3.90); δ_H(400.134 MHz, DMSO-d_6) 2.36–2.44 (2H, m, CH_2–CH_2, AA′XX′, J_{gem} 14.0, J_{trans} 7.8, J_{cis} 7.6 Hz), 2.54–2.62 (2H, m, CH_2–CH_2, AA′XX′, J_{gem} 13.2, J_{trans} 6.8, J_{cis} 7.0 Hz), 3.45–3.52 (2H, m, CH_2–CH_2, AA′XX′, J_{gem} 13.5, J_{trans} 7.5, J_{cis} 6.8 Hz), 3.80–3.86 (2H, m, CH_2–CH_2, AA′XX′, J_{gem} 13.8, J_{trans} 7.6, J_{cis} 7.5 Hz), 6.12 (2H, d, *J* 7.8 Hz, PC–H), 6.46 (2H, d, *J* 7.8 Hz, PC–H), 6.70–6.80 (4H, m), 7.76 (2H, dt, *J* 7.8, 1.8 Hz), 7.78 (2H, dt, *J* 7.8, 1.8 Hz), 8.90 (2H, s, NH); δ_C(100.60 MHz, DMSO-d_6) 29.60, 32.88 (CH_2–CH_2), 124.60, 126.78, 128.98, 130.60, 131.64, 132.28, 133.00, 133.80, 134.70, 138.40, 140.48, 146.60 (PC–CH, PC–C, Ar–CH, Ar–C), 168.00, 173.80 (CO); *m*/*z* (EI) 530 (M^+, 100%), 422 (24), 366 (18), 266 (28), 265 (60), 220 (14), 178 (14), 104 (16).

Compound 17b. Pale yellow crystals ($CHCl_3$–ethanol). Yield 0.23 g (80%), mp 275–277 °C (Found: C, 68.20; H, 3.90; N, 4.90; S, 11.34. $C_{32}H_{22}N_2O_4S_2$ requires C, 68.31; H, 3.94; N, 4.98; S, 11.40%); ν_{max} (KBr)/cm^{-1} 3218 (NH), 3034–3018 (Ar–CH), 2996–2896 (Ali.–CH), 1732–1692 (CO), 1510, 1450, 1380; λ_{max} ($CHCl_3$)/nm (log ε/dm^3 mol^{-1} cm^{-1}) 396 (3.98); δ_H(400.134 MHz, DMSO-d_6) 2.32–2.40 (2H, m, CH_2–CH_2, J_{gem} 13.8, J_{trans} 7.5, J_{cis} 7.0 Hz), 2.52–2.60 (2H, m, CH_2–CH_2, J_{gem} 13.6, J_{trans} 7.3, J_{cis} 6.6 Hz), 3.42–3.50 (2H, m, CH_2–CH_2, AA′XX′, J_{gem} 13.5, J_{trans} 7.2, J_{cis} 6.8 Hz), 3.78–3.84 (2H, m, CH_2–CH_2, AA′XX′, J_{gem} 13.8, J_{trans} 7.5, J_{cis} 7.0 Hz), 6.14 (2H, d, *J* 7.8 Hz, PC–H), 6.50 (2H, d, *J* 7.8 Hz, PC–H), 6.68–6.78 (4H, m), 7.74 (2H, dt, *J* 7.8, 1.8 Hz), 7.76 (2H, dt, *J* 7.8, 1.8 Hz), 8.94 (2H, s, NH); δ_C(100.60 MHz, DMSO-d_6) 30.40, 32.94 (CH_2–CH_2), 125.78, 126.82, 128.90, 130.64, 131.66, 132.32, 133.10, 133.78, 134.66, 138.42, 140.50, 146.80 (PC–CH, PC–C, Ar–CH, Ar–C), 168.40, 173.60 (*C*O); *m*/*z* (EI) 562 (M^+, 100%), 438 (20), 382 (18), 282 (64), 234 (20), 160 (18), 104 (20).

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