The use of bisphthalonitriles in the synthesis of side-strapped 1,11,15,25-tetrasubstituted phthalocyanines

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Abstract: Nucleophilic aromatic substitution reactions of 3-nitrophthalonitrile yield 3-hydroxyphthalonitrile and 3-neopentoxyphtalocyanines, the latter of which condensed to 1,8,15,22-tetranopentoxyphtalocyanine as a mixture of isomers. Bisphthalonitriles such as 1,3-bis(2',3'-dicyanophenoyxy)-2,2-dipentylo propane, 1,3-bis(2',3'-dicyanophenoyxy)-2,2-diisopropyl propane, and 1,3-bis(2',3'-dicyanophenoyxy)-2-methyl-2-trimethylsilylmethyl propane all gave bis-crown-like 1,11,15,22-tetrasubstituted phthalocyanines as pure compounds when treated with lithium octoide in 1-octanol at 196°C. A host of other bisphthalonitriles including 1,5-bis(2',3'-dicyanophenoyxy)-3-oxapentane, 1,5-bis(2',3'-dicyanophenoyxy)methylcyclohexane, 1,2-bis(2',3'-dicyanophenoyxy)methyl benzene, and 2,5-bis(2',3'-dicyanophenoyxy)methyl furan did not dimerize to mononuclear phthalocyanines. The "gem dimethyl" effect was suggested as a reason for the successful macrocyclizations.

Key words: nucleophilic aromatic substitution, phthalonitriles, bisphthalonitriles, 1,11,15,22-tetrasubstituted phthalocyanines.

Résumé : Les réactions de substitutions aromatiques nucléophiles du 3-nitrophthalonitrile conduisent au 3-hydroxyphthalonitrile et au 3-neopentoxyphtalocyanine sous la forme d'un mélange d'isomères. Lorsqu'on soumet les bisphthalonitriles, tels que les 1,3-bis(2',3'-dicyanophenoxy)-2,2-dipentylo propane, 1,3-bis(2',3'-dicyanophenoxy)-2,2-diisopropyl propane, 1,3-bis(2',3'-dicyanophenoxy)-2,2-diisopropyl propane et 1,3-bis(2',3'-dicyanophenoxy)-methyl-2-trimethylsilylmethyl propane, à un traitement par de l'octoïlate de lithium en présence d'octanol à 196°C on obtient toujours des phthalocyanines 1,11,15,22-tétrasubstituées à l'état pur qui ressemblent à des couronnes doubles. Neuf autres bisphthalonitriles, y compris les 1,5-bis(2',3'-dicyanophenoxy)-3-oxapentane, 1,5-bis(2',3'-dicyanophenoxy)methylcyclohexane, 1,2-bis(2',3'-dicyanophenoxy)methyl benzène et 2,5-bis(2',3'-dicyanophenoxy)methyl furan, ne se démersisent pas en phthalocyanines mononucléaires. L'effet "gem-diméthyle" a été suggéré pour expliquer le succès des macrocyclisations qui ont réussi.

Mots clés : substitution aromatique nucléophile, phthalonitriles, bisphthalonitriles, phthalocyanines 1,11,15,22-tétrasubstituées.

Introduction

The synthesis of pure isomers of tetrasubstituted phthalocyanines (Pe) having one substituent in each of the benzene rings remains a difficult problem (1). Single isomers of 2,9,16,23(2), 2,9,17,24-(3), and 1,8,15,22-tetrasubstituted phthalocyanines (4), and a 1,2-naphthalocyanine (5) have been prepared capitalizing on reactive substrates (2) or electronic (3) or steric constraints (4, 5) but methods towards the synthesis of pure 1,11,15,25-tetrasubstituted phthalocyanines have been only briefly reported by us in a preliminary communication (6). Recently, some specific pure Pe isomers have been separated by chromatography (7). We decided upon a "constrained" approach towards the synthesis of phthalocyanines having substituents in the 1,11,15,25 positions. If we could dimerize bisphthalonitriles with appropriate bridging groups, then 1,11,15,25-tetrasubstituted phthalocyanines containing bridging substituents (side straps) in the 1,25 and 11,15 positions would be obtained. The difficulty in this approach is the fact that polymerization would compete with dimerization. After exploring many different conditions we found that that condensation of bisphthalonitriles under high dilution at high temperatures for short reaction times led in some cases to the desired phthalocyanines as shown below.

Results and discussion

Nucleophilic aromatic substitution reactions on 3-nitrophthalonitrile (1) (9) are not all that common (4, 8, 9) and hence we decided to examine some simple reactions of 1. Thus treatment of 1 with K2CO3 and NaNO2 in DMSO at reflux for 0.5 h, as for the preparation of 4-hydroxyphthalonitrile (10), led to 3-hydroxyphthalonitrile (2) in 43% yield. Similarly, treatment of 1 with neopenanol (2,2-dimethyl-1-propanol) and K2CO3 in DMSO at room temperature for 6 days gave 3-neopentoxyphtalocyanine in 63% yield. The long reaction times were necessary to drive the reaction to completion probably due to steric hindrance of the substitution at the 3-position (4, 8) and the bulky alcohol used. Conversion of 3 to its diiminioisoindoline 4 proceeded normally (11, 12). Condensation of 4 at 150°C in 2-N,N-dimethylaminoethanol (DMAE) (11, 12)
Scheme 1.

\[
\begin{align*}
\text{2} & \quad \text{CN} & \quad \text{K}_2\text{CO}_3, \text{NaNNO}_2 & \quad \text{DMSO} \\
\text{1} & \quad \text{CN} & \quad \text{H}_2\text{C}_2\text{C}_2\text{OH} & \quad \text{K}_2\text{CO}_3, \text{DMSO} \\
\text{3} & \quad \text{CN} & \quad \text{OCH}_2\text{CH}_2\text{OH} & \quad \text{K}_2\text{CO}_3, \text{DMSO} \\
\end{align*}
\]

NH\textsubscript{3}, MeOH

\[
\begin{align*}
\text{4} & \quad \text{NH} & \quad \text{MeOH} & \quad \text{MeO} & \quad \text{NH} \\
\text{5} \quad \text{R} = (\text{CH}_3)_3\text{CCH}_2\text{O} & \quad \text{OR} & \quad \text{OR} \\
\end{align*}
\]

gave 1,8,15,22-tetraneopentoxyphthalocyanine (5) in 16% yield as a mixture with its 1,8,15,25, 1,8,18,25, and 1,11,15,25 isomers (Scheme 1).

Having established that phthalocyanines containing bulky substituents at positions adjacent to the macrocyclic core are readily prepared, we directed our attention towards the preparation of bisphthalonitrides bridged at the 3-position, for eventual dimerization to 1,11,15,25-tetrasubstituted phthalocyanines. Earlier, we had suggested (12) that \( \beta \)-hydrogens on substituents could lead to \( \beta \)-elimination reactions under the basic conditions of Pc formation and hence we concentrated our attention on bridging groups containing no hydrogens at the \( \beta \)-position, particularly \( \beta, \beta \)-diaryl groups. Thus, treatment of 1 with a series of \( \beta, \beta \)-disubstituted-1,3-propanediols, such as the known 2-methyl-2-trityloxymethyl-1,3-propanediol (6), the commercially available 2,2-diethyl-1,3-propanediol (7), 2,2-dipenty1-1,3-propanediol (8), and 2,2-dioctyl-1,3-propanediol (9), and \( \text{K}_2\text{CO}_3 \) in dimethyl sulfoxide (DMSO) at 20°C while evacuated (4,6) gave the bisphthalonitrides 10–13 in 43–94% yields. Diols 8 and 9 were prepared by lithium aluminum hydride reduction of diethyl 2,2-dipentynylmalonate (13) and diethyl 2,2-diocetylmalonate (14), respectively. Dimerization of 10–13 under high-dilution conditions with lithium octoxide in 1-octanol at 196°C for 10 min gave the 1,2,5,11,15-bis(side-strapped) phthalocyanines 14–17 in 7–21% yields. Pcs 14, 16, and 17 were readily metallated to their phthalocyaninato zinc(II) compounds 18–20 in 90% yield by heating with zinc acetate in a 1:1 mixture of pyridine and \( N,N \)-dimethylformamide for 20 h at reflux conditions (Scheme 2). Attempts at cleavage of the side-strapped Pcs 14 and 19 as examples, using \( \text{BBr}_3 \) (15, 16) as previously described for 2,9,16,23-tetraneopentoxyphthalocyanine (17), simply gave recovered starting materials, while cleavage with \( \text{AlCl}_3 \) (18) gave decomposition of the phthalocyanine macrocycle.

Phthalocyanines 14 and 18 existed as an unequal mixture of cis and trans isomers as shown by NMR spectroscopy while Pc 15 was too insoluble for useful studies. Indeed, the insolubility of 15 and the attendant difficulties of purification meant that satisfactory analysis could not be obtained for this compound, although we feel that confirmation of structure is on firm ground with a good HRMS (see Experimental). The problems of working with 15 in fact led to the design of Pcs 16 and 17 having larger alkyl chains generating soluble, more readily characterized Pcs. Pcs 16, 17, 18, and 19 were all sufficiently soluble for easy separation and study. In an attempt to obtain symmetrical hydroxymethyl substituents at the \( \beta \)-position and also to tie back the \( \beta \)-substituents into a ring system so that subsequent cleavage might proceed more readily, 5,5-dihydroxyethyl-2-phenyl-1,3-dioxane (21) (19) and 1,1-dihydroxyethylcyclohexane (22) (20) were treated as above, but over a 12–16 day period, to give 5,5-bis(2′,3′-dicyanophenoxymethyl)-2-phenyl-1,3-dioxane (23) and 1,1-bis(2′,3′-dicyanophenoxymethyl)cyclohexane (24) in 73 and 65% yields, respectively (Scheme 3). Neither 23 nor 24 could be induced to undergo formation of mononuclear phthalocyanines and it appeared that only polymeric pigments were formed.

In attempts to make a larger variety of side-strapped phthalocyanines, including those of crown ethers and benzyl ethers that could be more readily cleaved (4), we treated a host 2

\[ \text{2} \quad \text{Side-products at higher temperatures and shorter reaction times included 2, ethers such as 3-(2′,3′-dicyanophenoxyl)2,2-diethylpropan-1-ol, and bis(2,3-dicyanophenyl)ether (BDPE), } \]

mp 223–226°C; Ft-Ir(CCl\textsubscript{4}) \textsuperscript{1} \textsuperscript{1}: 3087, 2023, 2238 (C\textsuperscript{1}C\textsuperscript{1}), 1565, 1461, 1270, 813; \textsuperscript{1}H NMR (acetone-d\textsubscript{6}) \textsuperscript{1} \textsuperscript{1} \textsuperscript{1}: 702 (m, 4H), 6.78 (d, 2H, \( J = 8 \text{ Hz} \)); \textsuperscript{13}C NMR (acetone-d\textsubscript{6}) \textsuperscript{1} \textsuperscript{1} \textsuperscript{1} \textsuperscript{1}: 158.29, 136.95, 131.18, 124.76, 118.24, 115.81, 113.02, 108.87; El-MS for \( \text{C}_{21}\text{H}_{16}\text{N}_{2}O_{3}, m/z \) (relative intensity): 270 (M\textsuperscript{+}, 100) 242 (13) 127 (10).

3

\[ \text{3} \quad \text{The trityl groups in 14 were removed by BB}_{3} \text{ to give a mixture in 31% yield of the appropriate cis and trans diols, as a light blue solid. EI-MS for } \text{C}_{6}\text{H}_{11}\text{N}_{2}O_{3}, m/z \text{ (relative intensity): 746 (M\textsuperscript{+}, 100), 716 (20), 355 (18), 281 (22), 207 (37), 119 (39), 73 (42).} \]
Scheme 2.

1, DMSO

\[ \text{K}_2\text{CO}_3, 20^\circ C \] evacuated

6 \( R = \text{CH}_3, R' = \text{CH}_2\text{OTr} \)
7 \( R = R' = \text{C}_2\text{H}_5 \)
8 \( R = R' = \text{C}_6\text{H}_{11} \)
9 \( R = R' = \text{C}_8\text{H}_{17} \)

(1) Li octoxide/1-octanol

(2) Zn(OAc)$_2$

10 \( R = \text{CH}_3, R' = \text{CH}_2\text{OTr} \)
11 \( R = R' = \text{C}_2\text{H}_5 \)
12 \( R = R' = \text{C}_6\text{H}_{11} \)
13 \( R = R' = \text{C}_8\text{H}_{17} \)

14 \( R = \text{CH}_3, R' = \text{CH}_2\text{OTr}, M = \text{H}_2 + \text{trans} \)
15 \( R = R' = \text{C}_2\text{H}_5, M = \text{H}_2 \)
16 \( R = R' = \text{C}_6\text{H}_{11}, M = \text{H}_2 \)
17 \( R = R' = \text{C}_8\text{H}_{17}, M = \text{H}_2 \)
18 \( R = \text{CH}_3, R' = \text{CH}_2\text{OTr}, M = \text{Zn}, + \text{trans} \)
19 \( R = R' = \text{C}_6\text{H}_{11}, M = \text{Zn} \)
20 \( R = R' = \text{C}_8\text{H}_{17}, M = \text{Zn} \)

Scheme 3.

1, DMSO

\[ \text{K}_2\text{CO}_3, 20^\circ C \]

21 \( R = R' = \text{H}, X = \text{O} \)
22 \( R = R' = \text{H}, X = \text{CH}_2 \)
23 \( R = R' = \text{H}, X = \text{O} \)
24 \( R = \text{Ph}, R' = \text{H}, X = \text{CH}_2 \)
of known symmetrical diols such as diethylene glycol (25), 1,2-dihydroxymethylbenzene (26), 2,2'-bis(hydroxymethyl)biphenyl (27) (21), 5-tert-butyl-1,3-dihydroxymethylbenzene (28) (22), 2,5-dihydroxymethylfuran (29), and cis-2,5-bis(hydroxymethyl)tetrahydrofuran (30) (23) as before to give the new bisphthalonitriles 31–37 in 19–56% yields. Unfortunately, none of 31–37 cyclized to bis side-strapped phthalocyanines under our standard conditions described above.

It is curious that among the 13 symmetrical bisphthalonitriles prepared for this study, only 10–13 underwent dimerization to mononuclear phthalocyanines. With hindsight it is possible to see that perhaps the "gem" dimethyl (Thorpe–Ingold) effect (24–26) is operating here as only 10–13 have noncyclic β,β-dialkyl substituents. The gem dimethyl effect was originally promulgated to explain favoured cyclization reactions in five- to seven-membered rings containing β,β-dimethyl substituents, but was later expanded to macrocyclic ring systems (27).

Spectroscopic and physical properties

It is well known that electron-donating substituents at the 1, 4, 8, 11, 15, 18, 22, and 25 positions of the phthalocyanine nucleus (cf. 5) result in an enhanced bathochromic shift of the Q-band in their UV–VIS spectra (1, 7, 28, 29), when compared to similar substitution at the 2, 3, 9, 10, 16, 17, 23, and 24 positions of the Pc nucleus. Thus, 5 shows a typical λ_max at 726 nm. Surprisingly, 14–17 exhibit λ_max values at 708–711 nm (Fig. 1) rather than the values at ~730 nm exhibited in related pure 1,8,15,22-alkoxy-substituted Pcs (4, 7) and another pure 1,11,15,25-alkoxy-substituted Pc (7). We believe that the nature of the alkoxy substituent constrained in a ring system may cause the lone pair of electrons to lie partially out of conjugation with the benzo groups. Cook et al. (29) noticed that in one of their octaalkoxyphthalocyanines containing additional chloro substituents at the 2, 3, 9, 10, 16, 17, 23, and 24 positions, the λ_max is shifted hypsochromically by about 20 nm relative to other octaalkoxyphthalocyanines, and this latter example could be regarded as a partially constrained phthalocyanine. As usual, the Pc zinc(II) derivatives 18–20 (Table 2, Fig. 2) exhibit λ_max values of the Q-band having a hypsochromic shift of 20–25 nm compared to their metal-free counterparts.

The UV–VIS spectrum of 19 (Fig. 2) showed a spectral profile consistent with a PcM of D_{4h} symmetry in which a single intense Q-band absorption is found. The single Q-band absorption in the UV–VIS spectrum (suggesting a PcM with D_{4h} symmetry) conflicts somewhat with the actual geometry of 19 in which the 1,25:11,15-bis(side-strapped) PcZn 18 is, on a macromolecular scale, of D_{2h} symmetry. This observation strongly suggests that the peripheral sidestrap substituents do not affect, or only very weakly affect, the Pc macrocyclic molecular orbitals involved in the Q-band HOMO–LUMO electron transition. These results are markedly different from other D_{2h} "opposite" Pcs in which Q-band splitting for metallophthalocyanines is observed (30, 31).

The 1H NMR of ZnPc 18 taken in THF-d_4 clearly showed the ABX splitting pattern generated by the aromatic hydrogens of the Pc macrocycle (doublet–triplet–doublet at 9.02, 7.99, and 7.68 ppm, respectively). As for metal-free 14, the presence of two possible side strap isomers generated two multiplets at 5.38 and 5.17 ppm for the methylene CH_2 hydro-
The NMR spectrum of 17 was examined in the most detail as it was the most soluble of the bis side-strapped Pcs. The 1H NMR spectrum of 17 in benzene-d6 clearly showed the doublet-triplet-doublet signals arising from the ABX-spin-type aromatic hydrogens, and a singlet signal corresponding to the CH2 hydrogens of the side straps. The internal N-H protons were evident as a broad proton signal shifted upfield to 6 ppm (6). Such a large upfield 1H NMR chemical shift of the N-H hydrogens is typical for Pcs at high concentration or for cofacial binuclear Pcs (12, 32). This upfield chemical shift is a reflection of the strong cone of aromaticity generated by the ring current of the Pc macrocycle (32). At high Pc concentrations, or for Pcs that have a tendency toward cofacial π-π interaction (i.e., Pc aggregates, cofacial binuclear Pcs), the shielding imparted by the Pc macrocycle has profound effects upon the chemical shifts of hydrogens of proximal Pc neighbours.

These shielding effects experienced by the aromatic, side-strap, and internal hydrogens were explored by the acquisition of 1H NMR spectra at varying concentrations of 17 in THF-d8 (Table 1, Fig. 3 and 4). These data indicate that as the Pc solution concentration increases, Pc aggregation (or π-π stacking) occurs, and results in shifts of Pc macrocycle (and side-strap) hydrogen signals to higher field. The shielding effects imparted by the Pc macrocycle affect the internal N-H hydrogens, the aromatic hydrogens, and the side-strap methylene (CH2) hydrogens to varying degrees. For instance, the internal N-H hydrogens show the largest changes in chemical shift (ΔΔ = 1.45 ppm), whereas the change in chemical shift of the side-strap hydrogens is smaller (ΔΔ = 0.41 ppm). It appears that, in general, the hydrogen atoms closest to the core of the phthalocyanine macrocycle are most strongly influenced by the cone of aromaticity and π-π stacking shielding effects. This information can be used in assigning the signals observed in the 1H NMR spectrum to the three types of Pc ring hydrogens. It would seem plausible that the aromatic hydrogen experiencing the greatest change in chemical shift as a result of changing the Pc concentration would be the aromatic hydrogen closest to the Pc core. In Pc isomers such as 17, these would be the hydrogens at the 4, 8, 18, and 22 positions of the macrocycle and would be represented by one of the two doublet signals observed in the aromatic region of the 1H NMR spectrum. The furthest downfield doublet signal (i.e., that closest to 8 ppm) exhibited the largest change of chemical shift (ΔΔ = 0.56 ppm) relative to the doublet found near 7 ppm (ΔΔ = 0.42 ppm). Even though there was only a one order of magnitude change in the concentration of Pc 17, the data obtained from this experiment suggest that the 4-, 8-, 18-, and 22-position hydrogens can be assigned to this most downfield doublet signal (H-a in Fig. 3). This allowed an assignment of the highest field aromatic doublet signal (ca. 7 ppm) to the hydrogens at the 2, 10, 16, and 24 positions (H-c, i.e., adjacent to the side strap) and, intuitively, the triplet signal (ca. 7.5 ppm) to the hydrogens at the 2, 9, 16, and 23 positions of the Pc macrocycle. These hydrogen assignments were confirmed upon acquisition of a NOESY-NMR spectrum of 17. Through-space NOE effects were observed between the side-strap CH2 and macrocycle H-c hydrogens (i.e., the hydrogens in the position ortho to the side-strap), further validating the Pc ring hydrogen assignments determined from the 1H NMR dilution shift experiment.

All new phthalocyanines and phthalonitriles exhibited parent ions in their FAB or EI mass spectra. IR data and good elemental analysis were consistent with the assigned structures. The directed syntheses of phthalocyanines having the unique substitution pattern at the 1,11,15,25 positions have been demonstrated by constraining the substitution pattern with bridges at the 1,25 and 1,11 positions.

**Experimental**

All organic solvents were dried by appropriate methods and distilled before use. All reagents were freshly distilled, or
were recrystallized and then dried under reduced pressure, before use. Anhydrous potassium carbonate (K₂CO₃) was finely ground, oven dried at 250°C for 36 h, and then stored in sealed vials. Unless otherwise noted, magnetic stirring methods under an inert atmosphere (Matheson High Purity argon) were utilized during distillation or reaction processes, and round-bottom glass vessels chosen such that the quantity of reagents and solvent did not exceed half of the available volume. Water-cooled condensers were used if reaction processes were held near, or at, reflux conditions. Melting points were determined using a Kofler hot-stage melting point apparatus and are reported uncorrected. Infrared spectroscopy was performed on either a Pye Unicam SP3-200 or a Perkin Elmer 1310 infrared spectrophotometer and FTIR spectroscopy was performed on a Unicam Mattson 3000 FTIR spectrometer using samples prepared as KBr discs unless otherwise noted. Mass spectral analyses were performed by Dr. B. Khouw (York University, North York, Ontario, Canada), Dr. R. Smith (McMaster University, Hamilton, Ontario, Canada), and Dr. R. N. Cerny (Midwest Center for Mass Spectrometry, University of Nebraska–Lincoln, Lincoln, Nebraska, U.S.A.). HRMS were performed by Dr. R. Smith (McMaster University, Hamilton, Ontario, Canada). Nuclear magnetic resonance (NMR) spectroscopy was performed at 295–300 K unless otherwise noted, using either a Bruker Aspect AM3000 or a Bruker ARX 400 high-field Fourier Transform instrument. Chemical shifts are reported in parts per million relative to a tetramethylsilane (TMS) internal standard. Splitting patterns of proton resonances are described as singlets (s), doublets (d), triplets (t), quadruplets (q), doublets of doublets (dd), multiplets (m), or as broad signals (bt). Coupling constants for signals other than singlets and multiplets are reported in hertz. ¹³C NMR resonances are reported as the proton-decoupled chemical shifts. In addition to one-dimensional (¹H) ¹H NMR and ¹³C NMR, compounds requiring absolute structure determination were elucidated using combinations of 2D ¹H NMR (COSY and NOESY) and 2D carbon–proton (XH) correlations.

3-Hydroxyphthalonitrile (2)

In a manner similar to that previously described in the preparation of 4-hydroxyphthalonitrile (10), 865 mg (5.00 mmol) of 3-nitrophthalonitrile (1) (8, 9) was dissolved in 5 mL of DMSO. K₂CO₃ (760 mg, 5.51 mmol) and NaN₃ (345 mg,
A solution of 467 mg (1.75 mmol) of diminoisouindole 4 in 3 mL of 2-N,N-dimethylaminoethanol (DMEA) was heated at 150°C (silicon oil bath) for 3 h. The mixture was cooled to RT and the dark green-black slurry poured into 15 mL of cold water. Cold methanol (30 mL) was added, the mixture homogenized, and the fine precipitate centrifuged and collected in six fractions. The supernatant liquid from each fraction was discarded, and the pellets were resuspended in 5 mL of methanol and centrifuged. This centrifugation procedure was repeated until the supernatant liquid was almost colourless (four cycles). The pellets were combined to give 148 mg of crude material that was purified by flash chromatography using toluene as the eluting solvent. The first product eluted was concentrated under reduced pressure to give 58.6 mg (16%) of Pch2 5 as a dark blue, shining solid (TLC: 2% 2-methoxyethanol-toluene, Rf = 0.70, mp > 325°C; UV–VIS (THF) λmax (nm): 318, 354, 630, 664, 696, 726; IR (cm−1): 3280 (N–H), 2950, 1580, 1490, 1330, 1250 (Ar–O–C), 1055, 1035, 1000, 740s; 1H NMR (THF-d8): 8: 9.30–7.54 (m, 12H), 4.74–4.23 (m, 8H), 1.64–1.19 (m, 36H), −0.18 (m, 2H); EI-MS m/e (%): 858 (M+100), 578 (17), 205 (30), 71 (18), 28 (29). Anal. calcd. for C59H54N204: C 72.73, H 6.76, N 13.05; found: C 72.56, H 6.60, N 12.87.

General methods of biphthalonitrile syntheses

Method 1 (refs. 4, 33)
The distilled or recrystallized diol was placed in a 50 mL round-bottom flask equipped with a magnetic stirrer and distilled DMSO or DMF was added (5 mL/mmol diol) and heated to 50°C. Anhydrous K2CO3 (3–4 mol equiv.) and 2,2’-2,5 equivalents of 3-nitrophthalonitrile (1) (8, 9) were added, the joint was well greased, fitted with a MgSO4 drying tube, and the slurry stirred at rt, producing a pink-red coloured heterogeneous mixture. Two additional 0.25 equivalents of K2CO3 were then added at 24 h intervals and the mixture stirred for an additional 3 days or until all of 1 had been consumed. At each 24 h interval, the reaction slurry was briefly homogenized by sonication and the component profile monitored by TLC (10% CH3CN–Bz).

At the end of the reaction period the mixture was poured into ice-water, the flask rinsed with water, and the rinsings were added to the ice-water. The orange-brown precipitate was collected by centrifugation, washed with 40 mL of 10% NaHCO3 (aq.) (removing red-coloured products and yellow-coloured 3-hydroxyphthalonitrile (2)), and then with water. The residue was then washed with methanol, removing yellow coloured materials (mono-reacted diol and any excess 1). The crude off-white coloured product was analyzed by TLC and recrystallized from either hot ethyl acetate, methanol, acetone, benzene, or acetonitrile. If TLC analysis indicated the presence of impurities (in particular, BDPE) in excess of approx-
imately 15%, the crude product was first purified by column chromatography using silica gel adsorbant and 10% CH₂CN–Bz as the eluting solvent and then recrystallized. The white bisphthalonitrile was dried overnight at 70°C at 10⁻³ Torr (1 Torr = 133.3 Pa).

**Method II**

The distilled or recrystallized diol was placed in a 50 mL round-bottom flask equipped with a magnetic stirrer and distilled DMSO was added (5 mL/mmol diol). Anhydrous K₂CO₃ (0.54 equiv.) and 0.50 equivalent of 1 were added; the joint was well greased and then fitted with a Quick-Fit stopcock valve. The flask was evacuated to an internal pressure of approximately 20 Torr, the valve closed, and the mixture stirred rapidly at rt, immediately producing a pale pink heterogeneous mixture.

At 24 h intervals, the reaction slurry was briefly homogenized by brief sonication (with swirling) and the component profile monitored by TLC (10% CH₃CN–Bz). The flask was reevacuated and the slurry stirred. If all of 1 had been consumed, additional aliquots of carbonate (0.54 equiv.) and of 1 (0.50 equiv.) were added prior to evacuation and stirring. After the addition of 2.20–2.50 equivalents of 1, the mixture was stirred for an additional 24 h and then monitored by TLC. Additional K₂CO₃ (0.5–1.5 equiv.) was added if unreacted 1 was present and the mixture stirred for a further 24–96 h. The reaction mixture was then worked up as for Method I. 2,2-Dipentylopropan-1,3-diol (8)

In a manner similar to that previously described (19), a solution of 3.00 g (10.0 mmol) of diethyl 2,2-dipentylomalonate (13) in 4 mL of Et₂O was added dropwise to a stirred 5–10°C suspension of 1.15 g (30.3 mmol) of lithium aluminum hydride (LiAlH₄) in 25 mL of Et₂O. After addition of the diester, the mixture was heated at reflux for 2 h and then stirred at RT overnight. Active LiAlH₄ was quenched by addition of 2 mL of EtOAc and then 2 mL of 95% EtOH. The inorganic salts were removed by filtration through Celite, washed with Et₂O, and the filtrate was concentrated to dryness under reduced pressure. The oily residue was dissolved in 30 mL of EtOAc and extracted successively with 20 mL portions of 6 M NaOH, 4 M HCl, twice with 40 mL of H₂O, and finally with one 10 mL portion of brine. The organic phase was dried over MgSO₄ and evaporated under reduced pressure to give a yellowish oil. Distillation of the residue under reduced pressure gave 4.13 g (69%) of diol 9 as a colourless viscous oil that slowly solidified to a white wax at RT (23°C), bp 159–162°C/5 × 10⁻³ Torr; IR (cm⁻¹): 3500–3200 br (OH), 2950, 2980, 1470, 1380, 1030, 720; 1H NMR (CDCl₃) δ: 3.56 (s, 4H), 1.27–1.22 (br m, 30H), 0.88 (t, 6H, J = 7 Hz); 13C NMR (CDCl₃) δ: 69.47 (CH₂OH), 41.00 (4°C), 31.88, 30.79, 30.58, 29.55, 29.32, 22.85, 22.66, 14.08 (CH₃CH₂); EI-MS m/z (%): 282 (2), 269 (22), 252 (19), 154 (22), 139 (27), 111 (33), 97 (60), 83 (79), 69 (100). Anal. calcd. for C₁₀H₁₆O₂: C 76.00, H 13.42; found: C 76.43, H 13.96.

### 1.3-Bis(2',3'-dicyanophenoxy)-2-methyl-2-trityloxyethylpropane (10)

Bisphthalonitrile 10 was prepared by Method II from 0.900 g (2.49 mmol) of diol 6 (12), 1.159 g (6.70 mmol) of 3-arylphthalonitrile (1), and 1.460 g (10.6 mmol) of K₂CO₃ in 20 mL of DMSO at RT over a 6 day period. Aqueous work-up and EtOH washing of the crude product gave a pink coloured crude product. Recrystallization of this crude product from EtOAc–hexanes gave 1.44 g (94%) of white crystalline 10 (TLC: 10% CH₃CN–Bz, Rf = 0.85), mp 233–235°C; IR (cm⁻¹): 3090, 2920, 2220 (C≡N), 1580, 1450, 1290, 1060, 790, 700; 1H NMR (CD₃CN): δ: 7.72 (t, 2H, J = 8 Hz), 7.5–7.2 (m, 19H), 4.22 (2, 4H), 3.30 (2, 2H), 1.27 (3, 3H); 13C NMR (acetone-d₆) δ: 162.02, 144.71, 136.30, 129.42, 128.63, 127.84, 126.46, 118.73, 117.00, 116.25, 113.76, 105.07, 87.43, 72.02, 64.50, 41.83, 17.58; EI-MS m/z (%): 614 (M⁺), 537 (9), 243 (100), 165 (35), 105 (29). Anal. calcd. for C₉₀H₆₂O₈N₄: C 78.19, H 4.88, N 9.12; found: C 77.66, H 4.75, N 9.30.

### 1.3-Bis(2',3'-dicyanophenoxy)-2,2-diethylpropane (11)

Bisphthalonitrile 11 was prepared by Method II from 692 mg (5.23 mmol) of commercially available 2,2-diethylpropan-1,3-diol (7), 2.00 g (11.56 mmol) of I, and 3.05 g (22.11 mmol) of K₂CO₃ in 10 mL of DMSO over a 7 day period. The yield of off-white solid 11, after purification by column chromatography using 10% acetonitrile–benzene as eluting solvent and recrystallization from acetonitrile, was 870 mg (43%) (TLC: 10% CH₃CN–Bz, Rf = 0.79), mp 216–218°C; IR (cm⁻¹): 3080, 2960, 2220 (C≡N), 1580s, 1470, 1450, 1290, 1050 (C-O), 795s; 1H NMR (CD₃CN): δ: 7.67 (t, 2H, J = 8 Hz), 7.35 (d, 2H, J = 8 Hz); 13C NMR (acetone-d₆) δ: 162.25, 136.34, 126.46, 119.03, 116.96, 112.33, 113.94, 104.99, 71.98, 42.14, 23.69, 7.42; EI-MS m/z (%): 384 (M⁺), 259 (4), 241 (50), 145 (38), 97 (80), 55 (100). Anal. calcd. for C₉₂H₆₂O₈N₄: C 71.88, H 5.21, N 14.58; found: C 72.24, H 4.78, N 14.99.

### 1.3-Bis(2',3'-dicyanophenoxy)-2,2-dipentylopropane (12)

Bisphthalonitrile 12 was prepared by Method II from 0.72 g
(3.3 mmol) of 2,2-dipentylpropan-1,3-diol (8), 1.40 g (8.1 mmol) of 1, and 2.1 g (15.2 mmol) of K₂CO₃ in 7 mL of DMSO at RT over a 9 day period. Aqueous work-up and methanol washing of the solid reaction products gave a yellowish crude solid. Recrystallization of the crude product from acetone gave 0.81 g (52%) of white crystalline 12 (TLC: 10% CH₃CN-Bz, Rf = 0.78), mp 173–174°C; IR (cm⁻¹): 3080, 2960, 2210 (C=O=N), 1585, 1285, 1055, 795. ^1H NMR (CD₂CN) δ: 7.71 (t, 2H, J = 8 Hz), 7.45 (m, 4H), 4.13 (s, 4H), 1.54 (m, 4H), 1.3 (m, 12H), 0.86 (s, 6H, J = 7 Hz). ^13C NMR (acetone-d₆) δ: 162.27, 136.34, 126.48, 119.08, 116.23, 113.95, 104.97, 72.56, 42.05, 33.25, 31.80, 23.05, 22.92, 14.22; El-MS m/z (%): 469 (M⁺ + 1, 50), 453 (10), 439 (18), 397 (21), 368 (30), 325 (72), 144 (100). Anal. calc. for C₂₆H₂₅N₂O₂: C 74.36, H 6.84, N 11.97; found: C 74.20, H 6.93, N 12.00.

1,3-Bis(2',3'-dicyanophenoxy)-2,2-dioclytpropane (13) Biphthalonitrile 13 was prepared by Method II from 3.05 g (10.2 mmol) of 2,2-dioclytpropan-1,3-diol (9), 3.9 g (22.5 mmol) of 1, and 7.4 g (54 mmol) of K₂CO₃ in 25 mL of DMSO at RT over an 8 day period. Aqueous work-up and methanol washing of the solid reaction products gave a yellowish solid that was recrystallized from acetone. A second recrystallization from ethyl acetate gave 3.17 g (57%) of white crystalline 13 (TLC: 10% CH₃CN-Bz, Rf = 0.80), mp 163–165°C; FT-IR (cm⁻¹): 3083, 2927, 2862, 2225 (C=N), 1518, 1463, 1294, 1045, 798. ^1H NMR (acetone-d₆) δ: 7.86 (t, 2H, J = 8 Hz), 7.71 (d, 2H, J = 8 Hz), 7.55 (d, 2H, J = 8 Hz), 4.31 (s, 4H), 1.64 (m, 4H), 1.32 (m, 24H), 0.84 (s, 6H, J = 7 Hz); ^13C NMR (acetone-d₆) δ: 162.26, 136.35, 126.46, 109.16, 116.95, 116.22, 113.94, 104.99, 72.48, 42.06, 32.54, 31.66, 30.94, 29.88, 23.26, 23.11, 14.30; El-MS m/z (%): 552 (M⁺, 4), 523 (4.6), 509 (2.8), 495 (2.4), 469 (3.4), 409 (55), 145 (22), 43 (100). Anal. calc. for C₂₆H₂₅N₂O₂: C 76.09, H 7.97, N 10.14; found: C 75.92, H 8.52, N 10.27.

General method of bis side-strapped phthalocyanine synthesis A solution of the biphthalonitrile was made using 1-octanol, tetrahydrofuran (THF), or mixtures of 1-octanol and THF. A syringe pump was used to add the biphthalonitrile dropwise (ca. 0.02 mmol/min) to lithium octoxide in 1-octanol heated at reflux (ca. 196°C) in a modified air-cooled distillation apparatus that allowed rapid removal of cosolvent. In general, 10 mL of 1-octanol containing excess lithium metal was used for every 100 mg of biphthalonitrile added. Pd catalyst was usually evident after 20 s of biphthalonitrile addition. Upon addition of the biphthalonitrile, the mixture was heated at reflux for an additional 2–10 min and then allowed to cool to RT. Water was then added and the mixture neutralized by addition of HCl (aq.) (ca. pH 7), giving a suspension that was homogenized by ultrasound. The mixture was then concentrated to near dryness under reduced pressure and the crude Pd product purified by centrifugation and chromatographic and recrystallization techniques. 1,25:11,15-Bis(2'-methyl-2'-trityl oxyethylpropan-1'-3'-dioxy)phthalocyanine (14) Pd₄Cl₄ 14 was prepared, using the general method, by an 18 min dropwise addition of a solution of 300 mg (0.49 mmol) bisphthalonitrile 6 in 7 mL of THF to 30 mL of 1-octanol containing 50 mg (2.2 mmol) of cleaned lithium metal at 200°C. After addition of 6, the mixture was heated at reflux for an additional 5 min and then cooled to RT. A general method work-up (similar to that of 17) gave 200 mg of blue-green crude solid. The solid was dissolved in THF, adsorbed on normal grade silica gel, then purified by flash chromatography (benzene as eluant) to yield a first fraction of almost pure 14 (detected by TLC). Pd₄Cl₄ 14 was rechromatographed under the same conditions to yield 48 mg (16%) of 14 as a dark blue solid, mp >350°C; IR (cm⁻¹): 3280 (N-H), 3050, 2910, 2860, 1580, 1480, 1250 (Ar-O-C), 1030, 745, 700; UV–VIS (THF) λmax nm log ε: 330 (4.75), 618 (4.45), 656 (4.64), 680 (5.11), 712 (5.13); ^1H NMR (380 K)pyridine-d₅ δ: 9.07 (m, 4H), 8.06 (m, 16H), 7.84 (d, 4H, J = 6 Hz), 7.57 (m, 14H), 7.40 (t, 4H, J = 7 Hz), 5.41 (m, 4H), 5.21 (m, 4H), 4.00 and 3.99 (2s, 4H), 1.93 and 1.92 (2s, 6H). −1.70 (br s, 2H); +FAB–MS m/z 1231 (M⁺ + 1). Anal. calc. for C₆H₄₂N₄O₄: C 78.05, H 5.04, N 9.11; found: C 77.93, H 5.21, N 8.88.
from dimeric and oligomeric Pc products by flash column chromatography (3% Bz-toluene as eluting solvent) as a fast moving blue pigment F1. A slower moving blue-green component was eluted after changing the eluting solvent to 1% THF-toluene. The desired fast moving mononuclear Pc pigment 16 was then treated twice by flash column chromatography (3% Bz-toluene as eluting solvent). This pigment was recrystallized from pyridine to yield 11.1 mg (21%) of PcH₂, 16 as a bright blue solid, mp >330°C; IR (cm⁻¹): 3300 (N-H), 2940, 2935, 1585w, 1460, 1230 (Ar-O-C), 1035, 800w, 745s; UV-VIS (THF) λₘₐₓ nm (log e): 329.5 (4.76), 314.7 (4.53), 645 (4.70), 674 (5.19), 709 (5.14); ¹H NMR (benzene-d₆): 8.87 (d, 4H, J = 8 Hz), 8.28 (m, 4H, J = 8 Hz), 4.83 (s, 8H), 1.90 (m, 8H), 5.14 (m, 8H). 0.80 (m, 12H), -4.5 (s, 2H); +FAB-MS m/z (%): 490 (M⁺, 2), 869 (1.2), 772 (1), 759 (1), 687 (0.5), 614 (1.5), 460 (5), 307 (34), 154 (100). Anal. calcd. for C₃₃H₂₆N₈O₄: C 76.05, H 8.02, N 10.14; found: C 75.92, H 8.52, N 10.27.

1.25:11,15-Bis(2',2'-dicyclopropyl-1',3'-dioxy)phthalocyaninato zinc(II) (20)

PcH₂, 17 was prepared as for 15 from a 20 mL THF/1-octanol (2:1) solution of 1.11 g (2.02 mmol) of bisphthalonitrile 13 added after a 7 min period to 75 mL of 1-octanol containing 85 mg (12.1 mmol) of lithium metal at 195–200°C. The mixture was heated for an additional 5 min, cooled to RT and worked up as previously described. The desired PcH₂, 17 was separated from oligomeric Pc pigments by flash chromatography (benzene as eluting solvent). Flash chromatography of this nearly pure pigment (benzene as eluting solvent) gave 207 mg (19%) of 17 as a dark blue, shining solid, mp >330°C; IR (cm⁻¹): 3290 (N-H), 2930, 2850, 1590w, 1460w, 1255 (Ar-O-C), 1030, 805w, 740s; UV-VIS (THF) λₘₐₓ nm (log e): 325.2 (4.79), 613 (4.58), 646 (4.73), 675 (5.12), 709 (5.17); ¹H NMR (benzene-d₆): 7.92 (d, 4H, J = 7 Hz), 7.25 (t, 4H, J = 7 Hz), 6.88 (d, 4H, J = 7 Hz), 4.44 (s, 8H), 1.58–1.88 (m, 8H), 1.15 (t, 12H, J = 6.8 Hz), −5.99 (s, 2H) (see Table 3); El-MS m/z (%): 1107 (M⁺ + 1, 32), 1077 (5), 806 (8), 660 (18), 556 (100). Anal. calcd. for C₃₃H₂₆N₈O₄: C 75.91, H 8.19, N 10.12; found: C 75.58, H 8.52, N 9.88.

5.5-Bis(2',3'-dicyanophenoxymethyl)-2-phenyl-1,3-dioxane (23)

Bisphthalonitrile 23 was prepared by Method II from 1.11 g (5 mmol) of 5,5-dihydroxymethyl-2-phenyl-1,3-dioxane (21) (19), 1.75 g (10.1 mmol) of 1, and 3.1 g (22.5 mmol) of K₂CO₃ in 25 mL of DMSO at RT over a 16 day period. Aqueous work-up and methanol washing of the reaction products gave a pink-coloured solid. Double recrystallization of the pink solid from EtOAc gave 1.83 g (77%) of white crystalline 23 (TLC: 5% CH₃CN–Bz, Rₜ = 0.43), mp 180–182.5°C; IR (cm⁻¹): 3180, 3100w, 2990, 2880, 2245 (C≡N), 1585s, 1470v, 1395, 1300br, 1115, 1060br, 800s, 740, 700s; ¹H NMR (CDCl₃): 8.74 (t, 2H, J = 8 Hz), 7.60 (d, 2H, J = 8 Hz), 7.50–7.37 (m, 7H), 5.59 (s, 1H), 4.70 (s, 2H), 4.55 (d, 2H, J = 12 Hz), 4.19 (s, 2H), 4.12 (d, 2H, J = 12 Hz); ¹³C NMR (DMSO-d₆): 160.74 and 160.53, 137.95, 136.09 and 136.02, 129.07, 128.19, 126.31, 126.20, 119.84 and 118.69, 115.73 and 115.70, 115.29 and 115.27, 113.48 and 113.39, 103.45 and 113.38, 101.40, 68.85, 68.42, 67.82, 38.36; El-MS m/z (%): 476 (M⁺, 63), 475 (23), 399 (5), 197 (60), 157 (25), 105 (77); ²²Na). Anal. calcd. for C₅₃H₄O₄: C 70.58, H 4.23, N 11.76; found: C 70.25, H 4.66, N 12.00.

1.1-Bis(2',3'-dicyanophenoxymethyl) cyclohexane (24)

Bisphthalonitrile 24 was prepared by Method II from 0.72 g (5 mmol) of 1,1-dihydroxymethylcyclohexane (22) (20), 2.25 g (13 mmol) of 1, and 2.65 g (19 mmol) of K₂CO₃ in 20 mL of
DMSO over a 12 day period at RT. Aqueous work-up and methanol washing gave a pink coloured crude product. Double recrystallization of the crude product from acetone gave 1.28 g (63%) of bisphthalonitrile 24 as colourless crystals (TLC: 10% CH2CN-Bz, Rf = 0.63), mp 246-247°C; IR (cm–1): 3080s, 2910, 2850, 2220 (C==N), 1775s, 1450b, 1290b, 1050, 930, 790s, 730; 1H NMR (CD2CN) δ: 7.72 (t, 2H, J = 8 Hz), 7.48 (d, 2H, J = 8 Hz), 7.42 (d, 2H, J = 8 Hz), 4.42 (s, 4H), 1.69–1.53 (m, 10H); 13C NMR (DMSO-d6) (330 K) δ: 160.84, 135.40, 125.21, 118.60, 115.17, 114.94, 103.06, 72.24, 38.02, 28.87, 25.16, 20.32; El-MS m/z (%): 396 (M+), 32, 252 (100), 157 (77), 144 (87), 127 (93). Anal. calcd. for C24H19N4O2: C 72.73, H 5.05, N 14.14; found: C 73.03, H 4.77, N 13.78.

1,3-Bis(2′,3′-dicyanophenoxymethyl)-3-oxapentane (31) Bisphthalonitrile 31 was prepared by Method II from 0.795 g (7.50 mmol) of diethylene glycol (25), 2.17 g (18.3 mmol) of I, and 3.04 g (22.1 mmol) of K2CO3 in 10 mL of DMSO at 50°C over a 6 day period. After work-up by Method I, bisphthalonitrile 31 was obtained from the crude product by column chromatography (15% CH2CN-Bz as the eluting solvent) as the first fraction collected. After recrystallization from acetone, 509 mg (19%) of 31 was obtained as white needles (TLC: 15% CH2CN-Bz, Rf = 0.50), mp 223–224°C; IR (cm–1): 3090, 2920, 2220 (C==N), 1580, 1470, 1300, 1140, 1065, 795; 1H NMR (CD2CN) δ: 7.70 (t, 2H, J = 8 Hz), 7.45 (d, 2H, J = 8 Hz), 7.44 (d, 2H, J = 8 Hz), 4.34 (s, 4H, J = 4 Hz); 3.94 (t, 4H, J = 4 Hz); 13C NMR (DMSO-d6) (330 K) δ: 160.73, 135.21, 125.49, 118.64, 115.25, 114.03, 69.35, 68.57; El-MS m/z (%): 358 (M+), 215 (17), 171 (100), 145 (25), 116 (14). Anal. calcd. for C23H18N4O2: C 76.04, H 3.91, N 15.64; found: C 76.73, H 3.87, N 15.42.

A second fraction eluted from the column consisted of a mixture (by TLC) of BDPE2 and a monosubstitution product (ethanol).

1,2-Bis(2′,3′-dicyanophenoxymethyl)benzene (32) Bisphthalonitrile 32 was prepared by Method II from 1.068 g (7.55 mmol) of 1,2-dihydroxybenzene (26) (Aldrich), 3.0 g (17.3 mmol) of I, and 3.0 g (21.7 mmol) of K2CO3 in 10 mL of DMSO at RT over a 6 day period. After aqueous work-up and washing with MeOH an off-white crude product was recovered. Recrystallization of the crude product from acetone gave 760 mg (26%) of white 32 as an amorphous solid (TLC: 5% CH2CN–Bz, Rf = 0.24), mp 254–256°C; FT-IR (cm–1): 3167, 3085, 2924, 2225 (C==N), 1583a, 1469, 1453, 1372, 1037, 802, 767, 734; 1H NMR (CDCl3) δ: 7.83 (t, 2H, J = 8 Hz), 7.73 (d, 2H, J = 8 Hz), 7.61 (m, 4H), 7.46 (m, 2H), 5.54 (s, 4H); 13C NMR (CDCl3) δ: 169.24, 135.28, 133.34, 128.66, 128.52, 125.69, 118.64, 115.24, 115.20, 113.09, 103.24, 68.88; El-MS m/z (%): ion signals not observed. Anal. calcd. for C23H18N4O2: C 73.85, H 3.59, N 14.36; found: C 73.64, H 3.57, N 14.45.

Cis-2,5-Bis(2′,3′-dicyanophenoxymethyl)tetrahydrofuran (36) Bisphthalonitrile 36 was prepared by Method II from 0.66 g (5 mmol) of cis-2,5-bis(hydroxymethyl)tetrahydrofuran (30) (23), 2.10 g (12.1 mmol) of I, and 2.40 g (17.4 mmol) of K2CO3 in 10 mL of DMSO at RT over a 10 day period. Work-up and recrystallization from methanol gave 820 mg (43%) of greyish-yellow crystalline 36 (TLC: 15% CH2CN–Bz, Rf = 0.55), mp 186-188°C; FT-IR (cm–1): 3085, 2977, 2897, 2226 (C==N), 1563s, 1465s, 1260, 1100, 789; 1H NMR (acetone-d6)
\[ \delta: 7.81 \text{ t}, 2 \text{ H}, J = 8 \text{ Hz}; \ 7.62 \text{ d}, 2 \text{ H}, J = 8 \text{ Hz}; \ 7.53 \text{ d}, 2 \text{ H}, J = 8 \text{ Hz}; \ 4.39 \text{ m}, 2 \text{ H}; \ 4.34 \text{ m}, 2 \text{ H}, J = 4.2 \text{ Hz}; \ 4.29 \text{ m}, 2 \text{ H}, J = 4.2 \text{ Hz}; \ 2.15 \text{ t}, 4 \text{ H}; \ ^{13} \text{C NMR (acetone-\text{d}_6)} \delta: 162.44, 135.12, 126.36, 119.09, 117.11, 116.31, 114.20, 104.90, 78.69, 72.72, 28.30; \ +\text{FAB-MS m/z} (\%): 385 (M^+ + 1, 100).

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