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The 'inverse electron-demand' Diels–Alder reaction in polymer synthesis. Part 5: Preparation and model reactions of some electron-rich bis-dienamines☆

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Dedicated to Professor Károly Lempert on the occasion of his 80th birthday

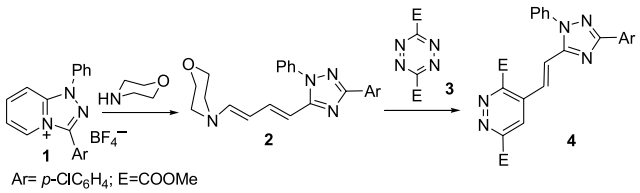
Abstract—The *m*- and *p*-phenylene-bridged bis-azolopyridinium salts have been synthesized and converted into the corresponding bis-dienamines by reaction with pyrrolidine. These dienamines react readily with dimethyl 1,2,4,5-tetrazine-dicarboxylate to yield the bis-azolylvinyl-pyridazines.

1. Introduction

As part of our investigation into the synthesis of 'high-performance' aromatic and heteroaromatic polymers, we have developed an interest in the 'inverse electron-demand' Diels–Alder reactions of bifunctional substrates. To this end synthetic routes to bis-alkynes,[2] bis-(1,2,4-triazines)[3] and bis-(1,2,4,5-tetrazines)[1] have been established; however the bis-alkynes have proved insufficiently reactive towards the above bis-azadienes, and the search for more electron-rich bis-dienophiles has therefore been further extended.

It has been reported[4,5] that dienamines, formed by the ring opening of condensed azolopyridinium salts, react smoothly with tetrazines to give azolylvinylpyridazines in good yield. Thus the triazolyl-dienamine **2**, formed by the reaction of morpholine with the triazolopyridinium salt **1**, reacts readily with dimethyl 1,2,4,5-tetrazine-3,6-dicarboxylate **3** to form the triazolylvinylpyridazine **4** (Scheme 1). The reaction takes place selectively on the sterically less hindered 3,4-double bond of the diene, and the geometry of the 1,2-double bond in **2** is retained in most cases during the process.[6]

We have aimed to exploit this exceptional reactivity of



Scheme 1.

dienamines towards electron-deficient dienes by extending the synthetic route to bis-dienamines. A potential benefit of polymers arising from bis-dienamines and bis-azadienes is that they also incorporate double bonds which can then easily be functionalised, allowing for the subsequent modification of the polymer chain, or else can provide sites where cross linking can occur.

2. Results and discussion

To overcome the difficulties which regularly arise in the synthesis of bis-functionalised molecules (mono-functionalisation, separation of products, etc.) we had to choose as targets such bis-salts where the synthesis appeared to be straightforward and the interference of a second functionality in the molecule could be minimized during the preparation. Both the [1,2,4]triazolo[4,3-*a*]pyridinium and the [1,2,3]triazolo[1,5-*a*]pyridinium systems were promising candidates, as the preparation of these heterocycles utilizes selective ring closure procedures.[6,7] Another advantage of these ring syntheses is that the central phenylene linking units are not only stable but are ultimately

☆ See Ref. 1.

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derivable from commonly available starting materials, namely isophthaloyl and terephthaloyl chloride.

To prepare the bis-[1,2,4]triazolopyridinium salts, 1-phenyl-1-(2-pyridyl)hydrazine **6**[8] was acylated with isophthaloyl and terephthaloyl chloride **5a–b**. These reactions yielded the bis-hydrazides **7a–b** as the sole products. Compounds **7a** and **7b** were converted into the bis-[1,2,4]triazolo[4,3-*a*]pyridinium salts **8a–b** by heating with phosphoryl chloride and workup with tetrafluoroboric acid (Scheme 2). Under these conditions no partially cyclised products were observed.

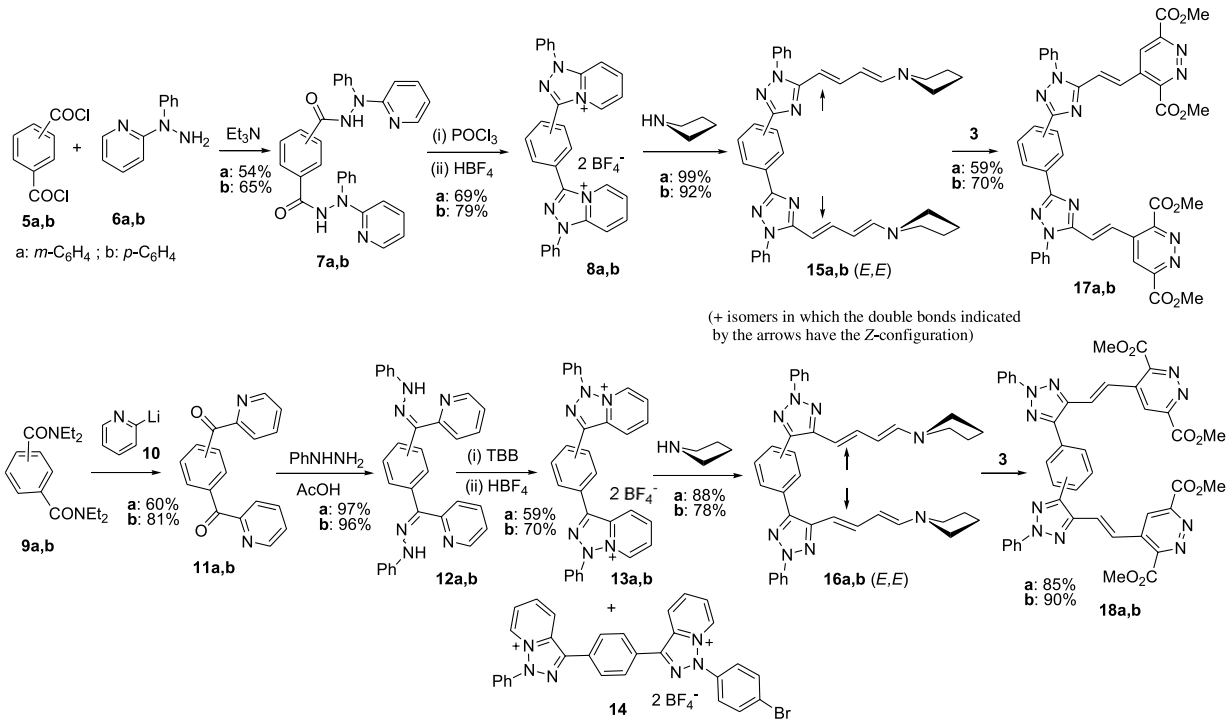
The synthesis of the [1,2,3]triazolo analogues of **8** started from iso- and terephthaloyl bis-diethylamides **9a–b**. The bis-amides were reacted with 2-lithiopyridine **10**—prepared in situ from 2-bromopyridine and *n*-butyllithium[10]—to give the 2-pyridoylbenzenes **11a–b** in moderate to high yield. The bis-ketones **11a–b** were converted into their phenylhydrazones **12a–b** using phenylhydrazine in acetic acid. The ^{1}H NMR spectra of **12a** and **12b** show the presence of all three possible *syn–anti* isomers. After the separation of the three isomers by preparative TLC, the ^{1}H NMR spectrum of each fraction shows the same complex pattern again, which suggests the fast equilibration of the three forms in solution. The crude hydrazones **12a–b** were oxidized to the bis-[1,2,3]triazolo[1,5-*a*]pyridinium salts **13a–b** by 2,4,4,6-tetrabromocyclohexa-2,5-dienone ('tribromophenol-bromine', TBB)[11] in good yield (Scheme 2). In the case of **12b**, a by-product of this oxidation is the mono-(*p*-bromophenyl) analogue **14**: this was detected by ^{1}H, ^{13}C and ^{15}N NMR as a minor component of the unpurified reaction product.

To test the applicability of the bis-triazolopyridinium salts as precursors for bis-dienamines, compounds **8a–b** and **13a–b** were reacted with pyrrolidine. The reactions proceeded readily in each case and the bis-dienamines **15a–b** and **16a–b** were formed in good yield. In accordance with earlier findings[4] for mono-dienamines, all of these bis-dienamines consisted of a mixture of the *E*,*E* and *Z*,*E* side-chain isomers. The preliminary product of the ring opening reaction has a *Z*,*E* geometry, but the dienamines are capable of isomerisation to the preferred *E*,*E* isomer in solution under the applied conditions.[12]

For the above reasons the separation of dienamine isomers is very tedious—if indeed it is possible at all—and the use of mixtures of *Z*,*E* and *E*,*E* isomers could lead in principle to isomeric products. To overcome this undesired result we carried out the inverse electron-demand Diels–Alder reaction of the bis-dienamines with tetrazinedicarboxylic ester **3** in a solvent, where the isomerisation of the intermediates formed in the cycloaddition might occur.[5] The bis-triazolyldienamines **15a–b** and **16a–b** were reacted with the tetrazine **3** at room temperature in dichloromethane, and only the *E*-bis-triazolylvinyl-pyridazines **17a–b** and **18a–b** were isolated from the reaction mixtures, in nearly quantitative yield.

3. Conclusion

In summary we demonstrated that bis-azolopyridinium salts might be prepared in good yield utilizing easily available starting materials and a straightforward synthetic strategy. Analogously to the simple azolopyridinium salts the bis-salts undergo facile ring opening with secondary amines to give bis-dienamines. The formed bis-dienamines are promising building blocks for heterocyclic polymers as they react readily with electron deficient azadienes. The simple and high yielding reactions make this approach



Scheme 2.

attractive for the synthesis of new polymers utilizing the inverse electron-demand Diels–Alder approach. This is currently under investigation.

4. Experimental

4.1. General

Melting points were determined on a hot-stage microscope and are uncorrected. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX-500 spectrometer in $CDCl_3$ and CD_3SOCD_3 and chemical shifts are given in ppm. For NMR spectra the residual peak of $CHCl_3$ (7.26 ppm) and the central peaks of DMSO (δ_H 2.50 ppm), $CDCl_3$ (δ_C 77.0) and DMSO-d_6 (δ_H 39.43) were used as the internal reference. In this paper DMSO-d_6 was used as the solvent unless otherwise indicated. Direct C–H correlations were obtained in each case by 2D-HMQC spectra. Since direct measurement of the nitrogen resonances was impossible in CD_3CN, ^{15}N NMR signals were indirectly obtained with the same instrument by detection of protons (2D-HMBC); the chemical shifts are given upfield from nitromethane (δ_N=0) as external reference. The 2D-HMQC and 2D-HMBC spectra were obtained by using the standard Bruker pulse programs INV4GS and INV4GSLPLRND respectively.

4.1.1. Iso- and terephthaloyl bis-[2-phenyl-2-(2-pyridyl)]hydrazide (7a–b). A mixture of *N*-phenyl-*N*-(2-pyridyl)-hydrazine[8] **6** (3.70 g, 20 mmol) and isophthaloyl or terephthaloyl chloride (2.03 g, 10 mmol) was heated under reflux in pyridine (20 ml) for 3 h, then stirred at ambient temperature overnight and poured into water. The bis-hydrazide was filtered off and recrystallised from dimethylformamide–water.

7a: Yield: 2.72 g (54%), white solid, mp: 279–280 °C; IR 3238, 1671, 1588, 1432, 1324, 1279, 697 cm^{-1}; ^{1}H NMR: 11.46 (s, 2H), 8.56 (s, 1H), 8.19 (d, 2H, *J*=7.4 Hz), 8.16 (br s, 2H), 7.72 (t, 1H, *J*=7.4 Hz), 7.64 (t, 2H, *J*=7.1 Hz), 7.48 (d, 4H, *J*=7.2 Hz), 7.37 (br t, 4H), 7.14 (t, 2H, *J*=6.8 Hz), 6.92 (d, 2H, *J*=8.3 Hz), 6.86 (t, 2H, *J*=5.3 Hz); ^{13}C NMR: 166.26, 157.76, 148.25, 144.77, 138.90, 133.75, 131.82, 129.95, 129.57, 127.90, 125.27, 124.00, 116.88, 109.71; Anal. Calcd For $C_{30}H_{24}N_6O_2$: C, 71.99; H, 4.83; N, 16.79; found C, 72.13; H, 4.79; N, 17.11%.

7b: Yield: 3.25 g (65%), white solid, mp: >290 °C; IR 3239, 1660, 1589, 1432, 1324, 1283, 697 cm^{-1}; ^{1}H NMR: 11.44 (s, 2H), 8.16 (d, 2H, *J*=7.3 Hz), 8.11 (s, 4H), 7.64 (t, 2H, *J*=7.1 Hz), 7.48 (d, 4H, *J*=7.8 Hz), 7.37 (t, 4H, *J*=7.5 Hz), 7.14 (t, 2H, *J*=7.3 Hz), 6.91 (d, 2H, *J*=8.5 Hz), 6.88 (t, 2H, *J*=6.3 Hz); ^{13}C NMR: 166.13, 157.71, 148.28, 144.72, 138.93, 136.30, 129.59, 128.73, 125.28, 123.95, 116.92, 109.71; Anal. Calcd For $C_{30}H_{24}N_6O_2$: C, 71.99; H, 4.83; N, 16.79; found C, 72.24; H, 5.01; N, 17.06%.

4.1.2. 3,3′-*m*-, and 3,3′-*p*-Phenylenebis(1-phenyl-[1,2,4]triazolo[4,3-*a*]pyridinium) bis-tetrafluoroborates 8a and 8b. A mixture of the appropriate hydrazide **7a** or **7b** (2.00 g, 4 mmol) and phosphoryl chloride (15 ml) was heated under reflux for 2 h. The resulting mixture was cooled to room temperature and the solvent evaporated under reduced pressure. The residue was dissolved in boiling water (30 ml), the mixture filtered, and the filtrate treated with 40% tetrafluoroboric acid (3 ml) and cooled to 0 °C. The resulting precipitate was filtered off, washed with water, dried and recrystallised from butan-1-ol.

8a: Yield: 1.77 g (69%), white solid, mp: >290 °C; IR 1646, 1513, 1341, 1059, 756 cm^{-1}; ^{1}H NMR: 9.16 (d, 2H, *J*=7.0 Hz), 8.61 (s, 1H), 8.46–8.44 (m, 4H), 8.40 (t, 2H, *J*=7.8 Hz), 8.20 (t, 1H, *J*=7.8 Hz), 7.94 (d, 4H, *J*=7.5 Hz), 7.83–7.79 (m, 6H), 7.75 (t, 2H, *J*=7.4 Hz); ^{13}C NMR: 146.40, 143.82, 140.73, 135.60, 134.31, 132.22, 131.93, 131.68, 131.39, 128.27, 125.21, 124.66, 120.63, 112.21; Anal. Calcd For $C_{30}H_{22}N_6B_2F_8$: C, 56.29; H, 3.46; N, 13.13; found C, 56.44; H, 3.49; N, 12.82%.

8b: Yield: 2.03 g (79%), white solid, mp: >290 °C; IR 1644, 1522, 1341, 1083, 764 cm^{-1}; ^{1}H NMR: 9.21 (d, 2H, *J*=6.8 Hz), 8.46 (d, 2H, *J*=9.1 Hz), 8.42–8.39 (m, 6H), 7.96 (d, 4H, *J*=7.9 Hz), 7.85–7.81 (m, 6H), 7.76 (t, 2H, *J*=7.4 Hz); ^{13}C NMR: 146.50, 144.05, 140.77, 135.70, 131.85, 131.75, 131.45, 128.34, 126.83, 125.31, 120.75, 112.34; Anal. Calcd For $C_{30}H_{22}N_6B_2F_8$: C, 56.29; H, 3.46; N, 13.13; found C, 56.47; H, 3.39; N, 12.82%.

4.1.3. 1,3- and 1,4-Bis(2-pyridoyl)benzene (11a and 11b). A solution of 2-lithiopyridine **10**, prepared from 2-bromopyridine (2.24 g, 14.2 mmol) and *n*-butyllithium (9.0 ml, 1.6 M in hexanes) in dry ether (10 ml) at −78 °C, was added dropwise at the same temperature to the slurry of isophthaloyl or terephthaloyl bis(diethylamide)[9] **9a** or **9b** (1.93 g, 7 mmol) in dry ether (20 ml). The mixture was left to warm to room temperature, stirred overnight, then treated with saturated aqueous ammonium chloride solution and extracted with dichloromethane. The combined organic phases were dried and the solvent evaporated, and the crude product was recrystallised from ethanol.

11a: 1.47 g (60%), white solid, mp: 128–130 °C; IR 1668, 1594, 1303, 1121, 1013, 696 cm^{-1}; ^{1}H NMR: 8.75 (d, 2H, *J*=4.5 Hz), 8.61 (s, 1H), 8.28 (d, 2H, *J*=7.8 Hz), 8.12–8.07 (m, 4H), 7.75–7.69 (m, 3H); ^{13}C NMR: 193.23, 155.10, 149.00, 137.48, 136.66, 135.37, 134.31, 128.47, 126.77, 125.08; Anal. Calcd For $C_{18}H_{12}N_2O_2$: C, 74.99; H, 4.20; N, 9.72; found C, 75.11; H, 4.25; N, 9.61%.

11b: 1.63 g (81%), white solid, mp: 184–6 °C; IR 1667, 1580, 1310, 936 cm^{-1}; ^{1}H NMR: 8.74 (d, 2H, *J*=4.5 Hz), 8.10–8.07 (m, 4H), 8.06 (s, 4H), 7.70 (dd, 2H, *J*=7.6, 4.5, 1.7 Hz); ^{13}C NMR: 193.67, 154.31, 149.19, 139.77, 138.24, 130.51, 127.61, 124.70; Anal. Calcd For $C_{18}H_{12}N_2O_2$: C, 74.99; H, 4.20; N, 9.72; found C, 74.67; H, 4.26; N, 9.52%.

4.1.4. 1,3- and 1,4-Bis(2-pyridoyl)benzene bis-phenylhydrazones (12a and 12b). A mixture of the appropriate bis-(2-pyridoyl)benzene **11a** or **11b** (0.59 g, 2 mmol), phenylhydrazine (0.45 g, 4.2 mmol), acetic acid (3 ml) and 48% hydrobromic acid (1 drop) was stirred at ambient temperature overnight to give a red solution which was

poured into cold water. The resulting precipitate was filtered off, washed with cold water and dried. The crude products, which consist in each case of a mixture of three isomers (*syn*,*syn*; *syn*,*anti*; *anti*,*anti*) were used in the subsequent step without further purification.

12a: Yield: 0.91 g (97%), yellow solid; **12b**: Yield: 0.90 g (96%), yellow solid.

4.1.5. 1,1′-*m*-, and 1,1′-*p*-Phenylenebis(3-phenyl-[1,2,3]triazolo[1,5-*a*]pyridinium) bis-fluoroborate 13a and 13b. Solutions of 2,4,4,6-tetrabromocyclohexa-2,5-dienone[13] (1.05 g, 2.5 mmol) in dichloromethane (3 ml) and of the appropriate hydrazone **12a** or **12b** (0.20 g, 0.4 mmol) in dichloromethane (2 ml) were mixed and stirred at ambient temperature for 30 min. Ether was added to the resulting mixture and the precipitate was filtered off, dissolved in nitromethane and the solution treated with cyclohexene (1 ml). Ether was then added to the solution, and the resulting precipitate was filtered off; the crude bromide salt was converted into the tetrafluoroborate by addition of acetonitrile (3 ml) followed by 40% tetrafluoroboric acid (4 drops). The resulting solution was diluted with water and extracted with nitromethane. The combined organic extracts were dried, the solvent evaporated and the crude product recrystallised from dimethylformamide–water.

13a: Yield: 0.15 g (59%), white solid, mp: 268–269 °C (dec); IR 1624, 1492, 1124, 1084, 1039, 694 cm^{-1}; ^1H NMR: 9.40 (d, 2H, *J*=7.0 Hz), 9.04 (d, 2H, *J*=8.8 Hz), 8.70 (br s, 1H), 8.47 (d, 2H, *J*=7.7 Hz), 8.41 (br t, 2H, *J*=7.6 Hz), 8.09–8.01 (m, 7H), 7.89–7.86 (m, 6H), 7.75; ^{13}C NMR: 141.47, 136.21, 134.58, 134.13, 133.72, 131.70, 131.08, 130.31, 129.18, 128.11, 127.63, 126.20, 124.79, 121.55; Anal. Calcd For $C_{30}H_{22}N_6B_2F_8$: C, 56.29; H, 3.46; N, 13.13; found C, 55.90; H, 3.55; N, 13.40%.

13b: 0.18 g (70%), white solid, mp: >290 °C; IR 1627, 1494, 1427, 1126, 1060, 850, 742 cm^{-1}; ^1H NMR: 9.38 (d, 2H, *J*=7.0 Hz), 9.05 (d, 2H, *J*=8.7 Hz), 8.46 (s, 4H), 8.40 (dd, 2H, *J*=8.9, 7.0 Hz), 8.13–7.98 (m, 8H), 7.91–7.87 (m, 4H); ^{13}C NMR: 141.27, 136.20, 134.80, 134.56, 134.14, 133.75, 131.70, 130.29, 128.10, 126.24, 124.79, 121.55; Anal. Calcd For $C_{30}H_{22}N_6B_2F_8$: C, 56.29; H, 3.46; N, 13.13; found C, 56.44; H, 3.32; N, 12.91%.

4.1.6. General procedure for the ring opening of the bis-triazolopyridinium salts (8a–b, 13a–b) with pyrrolidine. The synthesis of bis-dienamines. Pyrrolidine (0.7 ml) was added to a slurry of the appropriate bis-salt (0.32 g, 0.5 mmol) in acetonitrile (5 ml) and the resulting mixture was stirred at room temperature for 3 days. The precipitate which formed was filtered off, washed, and dried to give the crude dienamine, which was used without further purification in the subsequent step.

15a: Yield: 0.30 g (99%), yellow solid, a 70:30 mixture of *E*,*E*–*E*,*E* and *Z*,*E*–*E*,*E* isomers; ^1H NMR ($CDCl_3$): (*E*,*E*–*E*,*E*) 9.01 (s, 1H), 8.22 (d, 2H, *J*=7.7 Hz), 7.59–7.40 (m, 13H), 6.86 (d, 2H, *J*=12.1 Hz), 5.93 (d, 2H, *J*=14.7 Hz), 5.07 (t, 2H, *J*=11.9 Hz), 3.25–3.20 (m, 8H), 1.92–1.87 (m, 8H); (*Z*,*E*–*E*,*E*) 9.09 (s, 1H), 8.26 (d, 2H, *J*=7.7 Hz), 7.59–7.40 (m, 12 H), 6.90 (t, 1H, *J*=11.7 Hz), 6.86 (d, 1H, *J*=12.1 Hz), 6.84 (t, 1H, *J*=12.0 Hz), 6.45 (t, 1H, *J*=9.0 Hz), 5.93 (d, 1H, *J*=14.7 Hz), 5.56 (d, 1H, *J*=9.0 Hz), 5.07 (t, 1H, *J*=11.9 Hz), 3.24–3.20 (m, 4H), 3.38–3.34 (m, 4H), 1.91–1.87 (m, 4H), 1.84–1.80 (m, 4H).

15b: Yield: 0.28 g (92%), yellow solid, a 40:60 mixture of *E*,*E*–*E*,*E* and *Z*,*E*–*E*,*E* isomers; ^1H NMR ($CDCl_3$): (*E*,*E*–*E*,*E*) 8.28 (s, 4H), 7.57–7.38 (m, 12H), 6.87 (d, 2H, overlapping signals), 5.91 (d, 2H, *J*=14.8 Hz), 5.06 (t, 2H, *J*=12.1 Hz), 3.25–3.21 (m, 8H), 1.90–1.84 (m, 8H); (*Z*,*E*–*E*,*E*) 8.32 (d, 2H, *J*=4.8 Hz), 8.27 (d, 2H, *J*=5.1 Hz), 7.59–7.40 (m, 11 H), 6.87–6.84 (m, 3H), 6.46 (dd, 1H, *J*=11.0, 10.2 Hz), 5.91 (d, 1H, *J*=14.8 Hz), 5.53 (d, 1H, *J*=11.0 Hz), 5.06 (dd, 1H, *J*=14.8, 10.2 Hz), 3.39–3.35 (m, 4H), 3.23–3.20 (m, 4H), 1.98–1.93 (m, 4H), 1.89–1.84 (m, 4H).

16a: Yield: 0.265 g (88%), yellow solid, a 90:10 mixture of *E*,*E*–*E*,*E* and *Z*,*E*–*E*,*E* isomers; ^1H NMR ($CDCl_3$): (*E*,*E*–*E*,*E*) 8.10 (1H, t, *J*=1.5 Hz), 8.07 (4H, d, *J*=7.7 Hz), 7.71 (2H, dd, 7.7, *J*=1.5 Hz), 7.49 (1H, t, *J*=7.7 Hz), 7.39 (4H, t, *J*=7.7 Hz), 7.22 (2H, t, *J*=7.7 Hz), 7.16 (2H, dd, *J*=15.2, 10.9 Hz), 6.65 (2H, d, *J*=13.2 Hz), 6.18 (2H, d, *J*=15.2 Hz), 5.09 (2H, dd, *J*=13.2, 10.9 Hz), 3.12 (8H, t, *J*=6.8 Hz), 1.81 (8H, t, *J*=6.8 Hz); ^{13}C NMR ($CDCl_3$): 146.60, 145.30, 142.10, 140.40, 135.90, 132.30, 129.50, 129.30, 128.40, 128.35, 127.00, 118.90, 106.00, 99.30, 49.30, 25.70.

16b: Yield: 0.235 g (78%), yellow solid, a 85:15 mixture of *E*,*E*–*E*,*E* and *Z*,*E*–*E*,*E* isomers; ^1H NMR ($CDCl_3$): (*E*,*E*–*E*,*E*) 8.17 (4H, d, *J*=7.7 Hz), 7.91 (4H, s), 7.50 (4H, t, *J*=7.7 Hz), 7.33 (2H, t, *J*=7.7 Hz), 7.26 (2H, dd, *J*=15.3, 12.7 Hz), 6.78 (2H, d, *J*=12.9 Hz), 6.27 (2H, d, *J*=15.3 Hz), 5.19 (2H, t, *J*=12.7 Hz), 3.25 (8H, t, *J*=6.2 Hz), 1.94 (8H, t, *J*=6.2 Hz); ^{13}C NMR ($CDCl_3$): 146.6, 145.2, 142.1, 140.4, 135.9, 131.6, 129.5, 128.8, 127.0, 118.9, 106.0, 99.1, 49.3, 25.7.

4.1.7. General procedure for the inverse electron-demand Diels–Alder reaction of bis-dienamines (14a–b, 15a–b) with dimethyl 1,2,4,5-tetrazine-3,6-dicarboxylate (3). The tetrazine diester **3**[14] (0.070 g, 0.35 mmol) was added in one portion to the slurry of the appropriate bis-dienamine **15a–b** or **16a–b** (0.097 g, 0.16 mmol) in dichloromethane (5 ml) and the mixture was stirred for 6 h. After evaporation of the solvent the residue was washed with ether and the crude product recrystallised from aqueous dimethylformamide.

17a: Yield: 0.15 g (59%), white solid, mp: 215–216 °C (dec.); IR 1730, 1499, 1264, 1137, 772, 693 cm^{-1}; ^1H NMR: 8.86 (s, 1H), 8.48 (s, 2H), 8.22 (d, 2H, *J*=8.3 Hz), 8.06 (d, 2H, *J*=16.1 Hz), 7.73–7.61 (m, 11H), 7.37 (d, 2H, *J*=16.1 Hz), 4.00 (s, 6H), 3.98 (s, 6H); ^{13}C NMR: 165.46, 164.92, 164.50, 161.64, 153.10, 153.00, 152.15, 135.79, 130.67, 130.46, 130.21, 128.25, 126.39, 126.29, 124.50, 124.07, 122.91, 54.23, 54.09; Anal. Calcd For $C_{42}H_{32}N_{10}O_8$: C, 62.68; H, 4.01; N, 17.40; found C, 62.34; H, 4.16; N, 17.32%.

17b: Yield: 0.18 g (70%), white solid, mp: >290 °C (dec.

starting around 240 °C); IR 1726, 1500, 1265, 1138, 775, 692 cm^{-1}; ^1H NMR: 8.53 (s, 2H), 8.28 (s, 4H), 8.08 (d, 2H, J=15.6 Hz), 7.72–7.61 (m, 10H), 7.44 (d, 2H, J=15.6 Hz), 4.02 (s, 6H), 3.99 (s, 6H); Anal. Calcd For $C_{42}H_{32}N_{10}O_8$: C, 62.68; H, 4.01; N, 17.40; found C, 62.41; H, 4.10; N, 17.28%; ^{13}C NMR not recorded on account of low solubility, even on heating.

18a: Yield: 0.109 g (85%), white solid, mp: 120–124 °C (dec.); IR 1732, 1502, 1269, 1134, 774, 696 cm^{-1}; ^1H NMR: 8.63 (2H, s), 8.24 (1H, br s), 8.08 (4H, d, J=7.9 Hz), 7.98 (2H, dd, J=7.5, 1.5 Hz), 7.87 (2H, d, J=16.0 Hz), 7.80 (2H, d, J=16.0 Hz), 7.75 (1H, t, J=7.5 Hz), 7.58 (4H, t, J=7.8 Hz), 7.48 (2H, t, J=7.9 Hz), 3.97 (6H, s), 3.92 (6H, s); ^{13}C NMR: 165.5, 164.5, 152.7, 151.9, 147.8, 143.4, 139.5, 136.1, 133.6, 130.9, 130.6, 129.4, 128.8, 126.9, 125.6, 125.2, 121.5, 119.6, 54.2, 54.0; Anal. Calcd For $C_{42}H_{32}N_{10}O_8$: C, 62.68; H, 4.01; N, 17.40; found C, 62.55; H, 3.95; N, 17.76%.

18b: Yield: 0.116 g (90%), white solid, mp: 174–176 °C (dec.); IR 1729, 1505, 1262, 1141, 777, 695 cm^{-1}; ^1H NMR: 8.38 (2H, s), 8.14 (4H, d, J=7.7 Hz), 8.00 (2H, d, J=16.2 Hz), 7.85 (4H, s), 7.50 (2H, d, J=16.2 Hz), 7.47 (4H, t, J=7.7 Hz), 7.35 (2H, t, J=7.7 Hz), 4.02 (6H, s), 4.01 (6H, s); ^{13}C NMR: 165.3, 164.9, 152.4, 151.9, 147.2, 142.7, 139.8, 136.7, 131.2, 129.8, 129.6, 128.7, 126.4, 125.3, 124.4, 119.6, 54.1, 54.0; Anal. Calcd For $C_{42}H_{32}N_{10}O_8$: C, 62.68; H, 4.01; N, 17.40; found C, 62.80; H, 4.09; N, 17.01%.

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