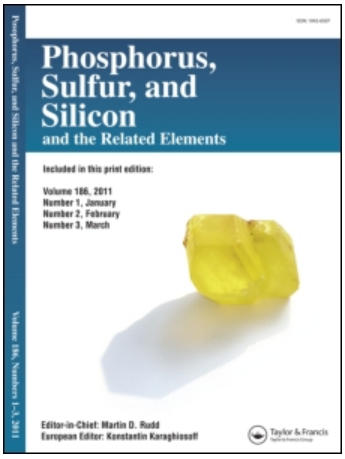

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The Stereochemical Behavior of Terephthalic Schiff Bases in Addition of Dialkyl or Diaryl Phosphites

Jarosław Lewkowski[a]
[a] Department of Organic Chemistry, University of Łódź, Narutowicza 68, 90-136, Łódź, Poland

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The Stereochemical Behavior of Terephthalic Schiff Bases in Addition of Dialkyl or Diaryl Phosphites

Jarosław Lewkowski
Department of Organic Chemistry, University of Łódź, Narutowicza 68, 90-136 Łódź, Poland

Addition of dialkyl (or diaryl) phosphites to N-alkyl terephthalic Schiff bases led exclusively to a meso*-form but addition to N-aryl terephthalic Schiff bases depended on the substituent of the aryl group. Semi-empirical calculations were involved to find the reason of this phenomenon.*

Keywords Addition of phosphites; imino-ester intermediates; *meso*-form formation; stereoselectivity; terephthalic Schiff bases

INTRODUCTION

About 10 years ago, Barycki *et al.*[1] and Gancarz[2] have reported that the addition of diethyl phosphite to N,N′-terephthalylidene-bis-benzylamine was stereoselective leading nearly exclusively to one diastereoisomeric form. This fact was also noted by Failla and Finocchiaro,[3–5] but they neither made attempts to determine which diastereoisomeric form occurred, nor gave any suggestion to explain the reason of this phenomenon. Some years ago, we reported several examples of this reaction with four N-alkyl (and alkylaryl) substituted[6] and with N-1-naphthyl[7] terephthallic Schiff bases. We noted that although in a case of N-alkyl (and alkylaryl) substituted terephthallic Schiff bases, the reaction led exclusively to one diastereoisomeric form but in a case of N-1-naphthyl derivative, it depended on the kind of the phosphite: the addition of dibenzyl and diphenyl ones led indeed to one product and the addition of diethyl phosphite led to two diastereomeric forms. We determined by the NMR experiments that the exclusively occurring product is the *meso* one.[6]

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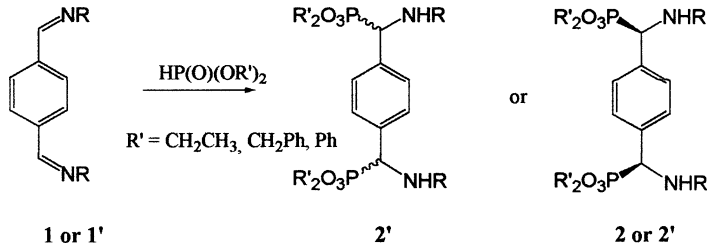
Address correspondence to Jarosław Lewkowski, Department of Organic Chemistry, University of Łódź, Narutowicza 68, 90-136 Łódź, Poland. E-mail: JLEWKOW@uni.lodz.pl

RESULTS AND DISCUSSION

For this study, the author performed the addition of three model phosphites—diethyl, dibenzyl, and diphenyl— to various N-alkyl (and alkylaryl) terephthallic Schiff bases **1a–f**, which led nearly exclusively (in 98–100%) to the one diastereoisomeric form, which was demonstrated to be the *meso*-form. (Scheme 1) The structure of diastereoisomers has been determined, as previously[6,7] by the NMR measurement, i.e., the NMR spectra of salts of esters **2** with (*R*)-mandelic acid. As salts gave one set of ^{1}H and ^{31}P NMR signals, I concluded that esters **2** had a *meso* configuration. The ^{31}P NMR data of esters **2aA–2fC** are summarized in the Table I.



1 or 1' **2'** **2 or 2'**

SCHEME 1

However, when the addition was performed to N-aryl substituted terephthalic Schiff bases **1′a–j**, results varied dependently on two factors: the kind of the substituent of the aryl group and the phosphite used. For example, the addition to N-phenyl substituted terephthalic Schiff base **1′a** led in the case of diethyl and dibenzyl phosphite to the mixture of both expected diastereoisomeric forms and in the case of diphenyl one—to the *meso*-form. The addition to the N-*p*-methoxyphenyl terephthalic Schiff base led to exclusive products

TABLE I ^{31}P NMR Data for Bis-N-alkyl (or Alkylaryl)-aminophosphonates 2aA–2fC

		^{31}P NMR data		
		R′ = CH_2CH_3 **(A)**	R′ = CH_2Ph **(B)**	R′ = Ph **(C)**
2a	R = CH_2Ph	24.05[6]	23.47[6]	15.47[6]
2b	R = CH_2Fur	23.67[6]	22.69[6]	15.48[6]
2c	R = $C(CH_3)_3$	20.67[6]	19.89[6]	15.41[6]
2d	R = $CHPh_2$	23.53	23.46	15.67
2e	R = CH_2CH_2(2-Pyr)	23.70[3]	23.54[3]	15.27[3]
2f	R = c-C_6H_{11}	24.66[3]	23.78[3]	15.65[3]

in the case of diethyl and diphenyl phosphites, but both diastereoisomeric forms occurred in the course of dibenzyl phosphite addition. The addition to N-*m*-methoxyphenyl terephthalic Schiff base was stereoselective in all three cases and the addition to N-*m*-methylphenyl terephthalic Schiff base led to both diastereoisomeric forms in all three cases. The addition to N-*m*-nitrophenyl and N-*p*-nitrophenyl Schiff bases led to both diastereoisomeric forms. The configuration of exclusive products was analysed as previously described. The ^{31}P NMR data of esters **2′aA–2′fC** are summarized in the Table II.

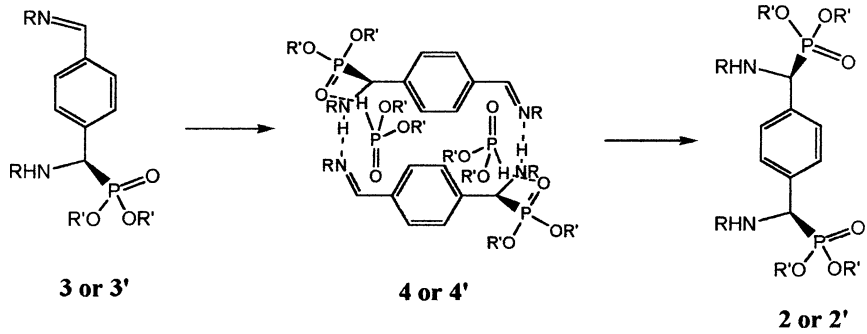
The syntheses of N-*p*-nitrophenyl derivatives **2′fA–2′fC** was troublesome as their conversion rates did not exceed 20%. Therefore they were not isolated and were characterized by means of ^{1}H and ^{31}P NMR spectroscopy and for all three cases signals of both diastereoisomeric forms of products and corresponding phosphites were observed. These data are included in Table II.

According to this author's observations, it depends on whether the substituent is an electron withdrawing group or an electron donating one. Previous papers,[6] have proposed the hypothetical reason of such a highly stereoselective reaction starting from completely achiral reagents. According to this hypothesis, the reaction is controlled kinetically and the key step is the formation of such an active complex **4** consisting of two molecules of iminoester **3** and two molecules of phosphite

TABLE II ^{31}P NMR Data for Bis-N-arylaminophosphonates 2′aA–2′jC

		^{31}P NMR data		
		R′ = CH_2CH_3 **(A)**	R′ ′ CH_2Ph **(B)**	R′ = Ph **(C)**
2′a	R = C_6H_5	22.47 and 22.42 (1:2)	23.08 and 23.00 (1:1)	14.95
2′b	R = *p*-C_6H_4-OCH_3	23.92[3]	24.54 and 24.46 (1:1)	16.42
2′c	R = *m*-C_6H_4-OCH_3	23.60	22.97	16.14
2′d	R = *p*-C_6H_4-CH_3	22.42	23.25 and 23.14 (3:2)	15.13
2′e	R = *m*-C_6H_4-CH_3	23.81 and 23.75 (1:1)	24.47 and 24.37 (1:1)	16.36 and 16.32 (1:1)
2′f	R = *p*-C_6H_4-NO_2	21.65 and 21.09 (1:1)	22.15 and 21.89 (1:1)	13.82 and 13.32 (5:2)
2′g	R = *m*-C_6H_4-NO_2	20.89 and 20.79 (1:1)	21.29 and 21.21 (1:1)	13.61 and 13.26 (1:1)
2′h	R = *p*-C_6H_4-COOH	21.84 and 18.33 (5:1)[4]	21.34 and 21.03 (3:1)	20.52
2′i	R = *m*-C_6H_4-COOH	21.87	23.12	16.01
2′j	R = α-naphthyl	21.73 and 21.64 (1:1)	22.48	12.51

linked to each other with hydrogen bonding (Scheme 2), which forced the attack of the phosphite molecule from strictly defined side. As it is generally known that the electron density on an azomethine nitrogen atom is less in a case of N-aryl derivatives and it depends on the substituent on the aryl ring. Thus the formation of such a complex is less probable in the case of N-aryl iminoeters **3′** and strongly depends on the kind of a substituent. Electron withdrawing substituents make the complex **4′** not to be formed, while electron-donating ones promote the formation of the complex **4′**. In a case of the N-*p*-nitrophenyl or N-*m*-nitrophenyl derivatives, the occurrence of two diastereoisomeric forms seems to support this theory, the same as the nearly exclusive formation of the *meso*-form in the case of N-*m*-methoxyphenyl derivative.



SCHEME 2

The formation of both diastereoisomeric forms of bis-aminophosphonate in the case of N,N′-terephthalylidene-bis-*m*-toluidine **1′e** was rather unexpected, the same as the exclusive formation of the *meso*-forms of **2′i** in the course of addition to N-*m*-carboxyphenyl terephthalic Schiff base for all three phosphites. But the preliminary semi-empirical AM1[8] Mulliken population analysis demonstrated that charge distribution in iminoesters **3′** on an azomethine nitrogen atom and on an amine group nitrogen and hydrogen atoms have values much less convenient for the hydrogen bonding (−0.14900e for =N, +0.204500e for H for **3′eA**) comparing to these values of the N-*m*-methoxyphenyl **3′cA** and carboxyphenyl derivatives **3′iA** (−0.15570e for =N, +0.21260e for H and −0.15740e for =N and +0.21570e for H) (Table III).

In the case of N-*p*-methylphenyl and N-*p*-methoxyphenyl Schiff bases **1′b** and **1′d** gave in the course of dibenzyl phosphite addition two diastereoisomeric forms. The preliminary AM1 results of

TABLE III Charges (Mulliken) of Iminoesters 3′aA–3′jC

		Charge distribution (Mulliken)					
		R′ = CH_2CH_3 **(A)**		R′ = CH_2Ph **(B)**		R′ = Ph **(C)**	
		HC=**N**	**H**—N	HC=**N**	**H**—N	HC=**N**	**H**—N
3′a	R = C_6H_5	−0.15090	+0.20400	−0.15250	+0.20910	−0.15510	+0.21480
3′b	R = *p*-C_6H_4-OCH_3	−0.15560	+0.20940	−0.15300	+0.20150	−0.15200	+0.20590
3′c	R = *m*-C_6H_4-OCH_3	−0.15570	+0.21260	−0.15580	+0.21330	−0.15610	+0.20930
3′d	R = *p*-C_6H_4-CH_3	−0.15770	+0.20160	−0.15490	+0.20060	−0.15640	+0.20840
3′e	R = *m*-C_6H_4-CH_3	−0.14900	+0.20450	−0.14870	+0.18960	−0.14400	+0.20190
3′f	R = *p*-C_6H_4-NO_2	−0.14760	+0.20120	−0.14770	+0.19060	−0.14510	+0.20090
3′g	R = *m*-C_6H_4-NO_2	−0.14210	+0.19090	−0.14680	+0.18750	−0.14380	+0.18790
3′h	R = *p*-C_6H_4-COOH	−0.15590	+0.21370	−0.16010	+0.21650	−0.16450	+0.22460
3′i	R = *m*-C_6H_4-COOH	−0.15740	+0.21570	−0.17430	+0.22760	−0.16260	+0.22530
3′j	R = α-naphthyl	−0.15090	+0.19900	−0.15650	+0.20910	−0.15510	+0.21480

Mulliken population analysis suggested that in case of benzyl iminoesters, the formation of the complex **4′b** and **4′d** would be less probable, as the values of charge distribution demonstrates too small acidity of hydrogen and too small basicity of an azomethine nitrogen atom (Table III).

Analysing data from Tables II and III, it is found that when charge distribution values suggest the lower basicity of an azomethine nitrogen and the lower acidity of an amine hydrogen (Table III), NMR data demonstrate the formation of both diastereoisomeric forms. Moreover the AM1 Mulliken population analysis of N-alkyl an N-alkylaryl iminoesters **3** demonstrated that, in all studied cases charge distribution values suggest a higher basicity of an azomethine nitrogen and a higher acidity of an amine hydrogen (Table IV). This indicates a higher possibility of the active complex **4** formation, and, in all these cases the

TABLE IV Charges (Mulliken) of Iminoesters 3aA–3fC

		Charge distribution (Mulliken)					
		R′ = CH_2CH_3 **(A)**		R′ = CH_2Ph **(B)**		R′ = Ph **(C)**	
		HC=**N**	**H**—N	HC=**N**	**H**—N	HC=**N**	**H**—N
2a	R = CH_2Ph	−0.18300	+0.17440	−0.18380	+0.17320	−0.18360	+0.17090
2b	R = CH_2Fur	−0.18040	+0.18040	−0.18100	+0.17880	−0.17940	+0.18310
2c	R = $C(CH_3)_3$	−0.17060	+0.17420	−0.17000	+0.17550	−0.16850	+0.17890
2d	R = $CHPh_2$	−0.17010	+0.17690	−0.17050	+0.17710	−0.16940	+0.17550
2e	R = CH_2CH_2(2-Pyr)	−0.17770	+0.16900	−0.17630	+0.16940	−0.17570	+0.16890
2f	R = c-C_6H_{11}	−0.17470	+0.18050	−0.17570	+0.17890	−0.17400	+0.18440

exclusive formation of *meso* forms of **2** was observed. So, our hypothesis concerning the formation of iminoesters first and then the formation of their active complexes **4** and **4′** seems to explain quite well the experimental data. But the explicit proof would be the isolation of iminoesters and studies on their physico-chemical properties (e.g., the IR study on hydrogen bonding) which have only recently been isolated.

EXPERIMENTAL

All solvents were routinely dried and distilled prior to use. Terephthalic aldehyde (Aldrich) as well as the three phosphites (Aldrich) and amines (Aldrich) were used as received. NMR measurements were recorded on a Varian Gemini 200 BB at 200 MHz (^{1}H NMR) and 81 MHz (^{31}P NMR) apparatus. Melting points were measured on a MeltTemp II apparatus and were not corrected. Elemental analyses were made in the Center for Molecular and Macromolecular Studies in Łódź, Poland.

All computations were performed on a PC with a Celeron® 1 GHz processor and 128 MB RAM. Minima of all hypothetical intermediates **3** or **3′** were searched by the use of Molecular Dynamics protocol in a MM2 packet included in the ChemOffice 7.0 Ultra pack with 10000 steps and 2 fs intervals. The generated conformational families were examined by the use of the MM2 force field packet included in the ChemOffice 7.0 Ultra pack. Geometries of resulting models with global minima were optimized by the use of the AM1 method and their geometries minimized and their charge distributions were computed. Semi-empirical RHF PM3 and AM1 computations were performed by the use of the GAMESS[8] for ChemOffice 7.0 pack. The tight convergence criteria have been used.

Synthesis of Terephthalic Schiff Bases—General Procedure

In a 250-ml round-bottom flask, 1.34 g (10 mmol) of terephthalic aldehyde was placed in 100 ml of benzene. To this solution was added 20 mmol of amine. Then it was stirred for 24 hours at room temperature. The precipitate was collected by filtration.

N,N′-Terephthalylidene-bis-diphenylmethylamine (1d)

Y = 3.22 g (70%); Mp = 197–200°C.

^{1}H NMR ($CDCl_3$, 200 MHz): δ 8.44 (s, CH=N, 2H); 7.87 (s, C_6H_4, 4H); 7.35 (m, ArH, 20H); 5.61 (s, $CHPh_2$, 2H).

Elemental analysis:

Calcd for $C_{34}H_{28}N_2$: C-87.90; H-6.07; N-6.03; Found: C-87.82; H-6.15; N-6.11.

N,N′-Terephthalylidene-bis-aniline (1′a)

Y = 1.70 g (60%); Mp = 163–165°C.

^{1}H NMR ($CDCl_3$, 200 MHz): δ 8.53 (s, CH=N, 2H); 8.02 (s, C_6H_4, 4H); 7.43 (dd, J = 7.4 and 7.5 Hz, CH_m, 4H); 7.32 (m, CH_p, 2H); 7.26 (d, J = 7.5 Hz, CH_o, 4H).

Elemental analysis:

Calcd for $C_{20}H_{16}N_2$: C-84.48-H, 5.67; N-9.85; Found: C-84.52; H-5.73; N-9.92.

N,N′-Terephthalylidene-bis-p-anisidine (1′b)

Y = 3.10 g (90%); Mp = 214–216°C

^{1}H NMR ($CDCl_3$, 200 MHz): δ 8.54 (s, CH=N, 2H); 7.99 (s, C_6H_4, 4H); 7.29 (d, J = 8.8 Hz, H_p, 4H); 6.95 (d, J = 8.8 Hz, H_p, 4H); 3.85 (s, OCH_3, 6H).

Elemental analysis:

Calcd for $C_{22}H_{20}N_2O_2$: C-76.72; H-5.85; N-8.13; Found: C-76.68; H-5.92; N-8.22.

N,N′-Terephthalylidene-bis-m-anisidine (1′c)

Y = 2.89 g (84%); Mp = 106–108°C

^{1}H NMR ($CDCl_3$, 200 MHz): δ 8.52 (s, CH=N, 2H); 8.01 (s, C_6H_4, 4H); 7.31 (t, J = 7.9 Hz, CH_m, 2H); 6.83 (m, CH_{arom}, 6H); 3.86 (s, OCH_3, 6H).

Elemental analysis:

Calcd for $C_{22}H_{20}N_2O_2$: C-76.72; H-5.85; N-8.13; Found: C-76.79; H-5.91; N-8.19.

N,N′-Terephthalylidene-bis-p-toluidine (1′d)

Y = 2.97 g (95%); Mp = 187–189°C; lit[9] = 195°C.

^{1}H NMR ($CDCl_3$, 200 MHz): δ 8.53 (s, CH=N, 2H); 8.00 (s, C_6H_4, 4H); 7.23 (d, J = 8.5 Hz, CH_p, 4H); 7.18 (d, J = 8.5 Hz, CH_p, 4H); 2.37 (s, CH_3, 6H).

N,N′-Terephthalylidene-bis-m-toluidine (1′e)

Y = 2.84 g (91%); Mp = 98–101°C; lit[10] = 98°C

^{1}H NMR ($CDCl_3$, 200 MHz): δ 8.52 (s, CH=N, 2H); 8.01 (s, C_6H_4, 4H); 7.30 (t, J = 8.0 Hz, CH_m, 2H); 7.08 (m, CH_{arom}, 6H); 2.41 (s, CH_3, 6H).

N,N′-Terephthalylidene-bis-p-nitroaniline (1′f)

Y = 2.43 g (65%); Mp = 278–280°C; lit[11] = 276.5–278.5°C.

^{1}H NMR ($CDCl_3$, 200 MHz): δ 8.58 (s, CH=N, 2H); 8.09 (d, J = 8.6 Hz, CH_p, 4H); 7.96 (s, C_6H_4, 4H); 7.78 (d, J = 8.5 Hz, CH_p, 4H).

N,N′-Terephthalylidene-bis-m-nitroaniline (1′g)

Y = 2.43 g (65%); Mp = 287–288°C.

^{1}H NMR ($CDCl_3$, 200 MHz): δ 8.59 (s, CH=N, 2H); 7.87 (s, C_6H_4, 4H); 8.12 (m, CH_{arom}, 2H); 7.60 (m, CH_{arom}, 2H); 7.27 (m, CH_{arom}, 2H); 7.17 (d, J = 6.8 Hz, CH_{arom}, 2H).

Elemental analysis:

Calcd for $C_{20}H_{14}N_4O_4$: C-64.17; H-3.77; N-14.97; Found: C-64.28; H-3.86; N-15.08.

N,N′-Terephthalylidene-bis-p-aminobenzoic acid (1′h)

Y = 3.13 g (84%); Mp = 386–389°C.

^{1}H NMR ($CDCl_3$, 200 MHz): δ 8.75 (s, CH=N, 2H); 8.12 (s, C_6H_4, 4H); 8.01 (d, J = 8.5 Hz, CH_p, 4H); 7.39 (d, J = 8.5 Hz, CH_p, 4H).

Elemental analysis:

Calcd for $C_{22}H_{16}N_2O_4$: C-70.96; H-4.33; N-7.52; Found: C-70.82; H-4.21; N-7.47.

N,N′-Terephthalylidene-bis-m-aminobenzoic acid (1′i)

Y = 3.61 g (97%); Mp = 320–323°C.

^{1}H NMR ($CDCl_3$, 200 MHz): δ 8.79 (s, CH=N, 2H); 8.12 (s, C_6H_4, 4H); 8.12 (m, CH_m, 2H); 7.86 (m, CH_m, 4H); 7.58 (d, J = 5.1 Hz, CH_p, 2H).

Elemental analysis:

Calcd for $C_{22}H_{16}N_2O_4$: C-70.96; H-4.33; N-7.52; Found: C-70.79; H-4.44; N-7.66.

Synthesis of 1,4-phenylene-bis-(N-alkyl (or N-aryl) aminomethane)-bis-phosphonates—General procedure

To a 250-ml round bottom flask equipped with a condenser was placed 10 mmol of the Schiff base and 20 mmol of dialkyl (diaryl) phosphite. Then it was heated for 0.5 h until melting, and the whole mixture was allowed to cool. Then 50 ml of toluene was added and stirred for 5 h at the boiling temperature. The precipitate was filtered, the filtrate concentrated, and the re-precipitated solid was collected by filtration.

Tetraethyl 1,4-phenylene-bis-(N-diphenylmethylaminomethane)-bis-phosphonate (2dA)

Y = 2.51 g (34%). Mp 181–184°C.

^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.34–7.20 (m, ArH, 24H); 4.66 (s, $CHPh_2$, 2H); 4.22 and 3.94 (2m, $\underline{CH_2}CH_3$, 8H); 3.95 (d, $^2J_{PH}$ = 22.0 Hz, CHP, 2H); 1.38 and 1.09 (2t, J = 7.1 Hz, $CH_2\underline{CH_3}$, 12H).

^{31}P NMR ($CDCl_3$, 81 MHz): δ 23.53.

Elemental analysis:

Calcd for $C_{42}H_{50}N_2O_6P_2$: C-68.10; H-6.80; N-3.78; Found: C-68.14; H-6.65; N-3.70.

Tetrabenzyl 1,4-phenylene-bis-(N-diphenylmethylaminomethane)-bis-phosphonate (2dB)

Y = 3.45 g (35%). Mp 149–152°C

^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.36 (s, C_6H_4, 4H); 7.20 (m, ArH, 40H); 5.15 (Część ukł. ABX, $^2J_{HH}$ = 11.8 Hz, $^3J_{PH}$ = 8.0 and 6.8 Hz, CH_2Ph, 4H); 4.74 (Część ukł. AMX, $^2J_{HH}$ = 11.8 Hz, $^3J_{PH}$ = 7.2 and 6.4 Hz, CH_2Ph, 4H); 4.65 (s, $CHPh_2$, 2H); 4.05 (d, $^2J_{PH}$ = 21.9 Hz, CHP, 2H); 2.63 (s, NH, 2H).

^{31}P NMR ($CDCl_3$, 81 MHz): δ 23.46.

Elemental analysis:

Calcd for $C_{62}H_{58}N_2O_6P_2$: C-75.29; H-5.91; N-2.83; Found: C-74.80; H-5.92; N-3.01.

Tetraphenyl 1,4-phenylene-bis-(N-diphenylmethylaminomethane)-bis-phosphonate (2dC)

Y = 2.85 g (30%). Mp 190–193°C

^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.46 (s, C_6H_4, 4H); 7.32–7.12 (m, ArH, 40H); 4.75 (s, $CHPh_2$, 2H); 4.34 (d, $^2J_{PH}$ = 22.2 Hz, CHP, 2H); 2.75 (s, NH, 2H).

^{31}P NMR ($CDCl_3$, 81 MHz): δ 15.67.

Elemental analysis:

Calcd for $C_{58}H_{50}N_2O_6P_2$: C-74.67; H-5.40; N-3.00; Found: C-74.58; H-5.38; N-2.90.

Tetraethyl 1,4-phenylene-bis-(N-anilinomethane)-bis-phosphonate (2′aA)

Y = 4.48 g (80%). Mp 162–165°C (benzen-heksan).

^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.44 (s, C_6H_4, 4H); 7.06 (dd, J = 7.8 and 7.6 Hz, CH_m, 4H); 6.67 (t, J = 7.6 Hz, CH_p, 2H); 6.54 (d, J = 7.8 Hz, CH_o, 4H); 4.73 (d, $^2J_{PH}$ = 23.3 Hz, CHP, 2H); 4.08 (m, O$\underline{CH_2}$$CH_3$, 4H); 3.83 and 3.54 (2m, O$\underline{CH_2}$$CH_3$, 2×2H); 2.17 (s, NH, 2H); 1.26 and 1.23 (2t, J = 6.9 Hz, $OCH_2\underline{CH_3}$, 6H); 1.04, 0.93 (2t, J = 7.1 Hz, $OCH_2\underline{CH_3}$, 6H).

^{31}P NMR ($CDCl_3$, 81 MHz): δ 22.47 and 22.42.

Elemental analysis:

Calcd for $C_{28}H_{38}N_2O_6P_2$: C-59.99; H-6.83; N-5.00; Found: C-60.18; H-6.98; N-4.82.

Tetrabenzyl 1,4-phenylene-bis-(N-anilinomethane)-bis-phosphonate (2′aB)

Y = 6.46 g (80%). Mp 143–145°C.

^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.42 (s, C_6H_4, 4H); 7.26–6.94 (m, ArH, 24H); 6.65 (m, ArH, 2H); 6.51 (m, ArH, 4H); 4.95–4.73 (m, O$\underline{CH_2}$Ph, 6H); 4.89 and 4.82 (2d, $^2J_{PH}$ = 23.1 Hz, CHP, 2H); 4.47 and 4.31 (Part of 2 AMX system, $^3J_{PH}$ = 8.0 Hz, $^2J_{HH}$ = 11.6 Hz; O$\underline{CH_2}$Ph, 4H).

^{31}P NMR ($CDCl_3$, 81 MHz): δ 23.08 and 23.00.

Elemental analysis:

Calcd for $C_{48}H_{46}N_2O_6P_2$: C-71.28; H-5.73; N-3.46; Found: C-71.42; H-5.89; N-3.58.

Tetraphenyl 1,4-phenylene-bis-(N-anilinomethane)-bis-phosphonate (2′aC)

Y = 6.01 g (80%). Mp 181–184°C.

^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.56 (s, C_6H_4, 4H); 7.25–7.02 (m, ArH, 20H); 6.74 (m, CH_{p+m}, 6H); 6.62 (d, J = 7.3 Hz, CH_o, 4H); 5.13 (d, $^2J_{PH}$ = 23.7 Hz, CHP, 2H); 5.05 (s, NH, 2H).

^{31}P NMR ($CDCl_3$, 81 MHz): δ 14.95.

Elemental analysis:

Calcd for $C_{44}H_{38}N_2O_6P_2$: C-70.21; H-5.09; N-3.72; Found: C-70.43; H-4.89; N-3.90.

Tetraethyl 1,4-phenylene-bis-(N-p-methoxyphenylaminomethane)-bis-phosphonate (2′bA)

Y = 2.48 g (40%); mp = 188–192°C.

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.41 (s, C_6H_4, 4H); 6.64 (d, J = 9.0 Hz, p-C_6H_4, 4H); 6.50 (d, J = 9.0 Hz, p-C_6H_4, 4H); 4.64 (d, $^2J_{PH}$ = 22.7 Hz, C$\underline{H}$P, 2H); 4.52 (large s, NH, 2H); 4.08 (m, O$\underline{CH_2}CH_3$, 4H); 3.80 (m, O$\underline{CH_2}CH_3$, 2H); 3.67 (s, OCH_3, 6H); 3.48 (m, O$\underline{CH_2}CH_3$, 2H); 1.26 (t, J = 7.0 Hz, $OCH_2\underline{CH_3}$, 6H); 0.95 (t, J = 7.0 Hz, $OCH_2\underline{CH_3}$, 6H). ^{31}P NMR (81 MHz, $CDCl_3$): δ 23.92.

Elemental analysis:

Calcd for $C_{30}H_{42}N_2O_8P_2$: C-58.06; H-6.82; N-4.51; Found: C-57.83; H-7.17; N-4.45.

Tetrabenzyl 1,4-phenylene-bis-(N-p-methoxyphenylaminomethane)-bis-phosphonate (2′bB)

Y = 7.91 g (92%); mp = 177–180°C.

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.42 (s, C_6H_4, 4H); 7.29–7.09 (m, C_6H_5, 20H); 6.59 and 6.58 (2d, J = 9.0 Hz, p-C_6H_4, 4H); 6.47 and 6.46 (2d, J = 9.0 Hz, p-C_6H_4, 4H); 4.98 and 4.74 (m, O$\underline{CH_2}$Ph, 8H); 4.47 and 4.32

(2d, $^2J_{PH}$ = 19.7 Hz, C<u>H</u>P, 2H); 4.30 (large s, NH, 2H); 3.60 and 3.57 (2s, OCH_3, 6H). ^{31}P NMR (81 MHz, $CDCl_3$): δ 24.54 and 24.46.

Elemental analysis:

Calcd for $C_{50}H_{50}N_2O_8P_2$: C-69.12; H-5.80; N-3.22; Found: C-69.31; H-5.95; N-3.20.

Tetraphenyl 1,4-phenylene-bis-(N-p-methoxyphenylaminomethane)-bis-phosphonate (2′bC)

Y = 5.85 g (72%); mp = 177–179°C.

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.55 (s, C_6H_4, 4H); 7.27–7.01 (m, C_6H_5, 20H); 6.67 (d, J = 8.9 Hz, p-C_6H_4, 4H); 6.57 (d, J = 8.9 Hz, p-C_6H_4, 4H); 5.05 (d, $^2J_{PH}$ = 23.2 Hz, C<u>H</u>P, 2H); 4.65 (large s, NH, 2H); 3.71 (s, OCH_3, 6H). ^{31}P NMR (81 MHz, $CDCl_3$): δ 16.42.

Elemental analysis:

Calcd for $C_{46}H_{42}N_2O_8P_2$: C-67.98; H-5.21; N-3.45; Found: C-68.07; H-5.32; N-3.18.

Tetraethyl 1,4-phenylene-bis-(N-m-methoxyphenylaminomethane)-bis-phosphonate (2′cA)

Y = 3.54 g (57%); mp = 166–170°C.

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.43 (s, C_6H_4, 4H); 6.69 (dd, J = 8.2 and 10.0 Hz, m-C_6H_4, 2H); 6.22 (dd, J = 8.1 and 2.2 Hz, m-C_6H_4, 2H); 6.17 (dd, J = 8.1 and 1.7 Hz, m-C_6H_4, 2H); 6.08 (t, J = 2.0 Hz, m-C_6H_4, 2H); 4.70 (d, $^2J_{PH}$ = 23.4 Hz, C<u>H</u>P, 2H); 4.82 (large s, NH, 2H); 4.08 (m, O<u>CH_2</u>CH_3, 4H); 3.82 (m, O<u>CH_2</u>CH_3, 2H); 3.66 (s, OCH_3, 6H); 3.48 (m, O<u>CH_2</u>CH_3, 2H); 1.26 (t, J = 7.1 Hz, OCH_2 <u>CH_3</u>, 6H); 0.96 (t, J = 7.1 Hz, OCH_2<u>CH_3</u>, 6H). ^{31}P NMR (81 MHz, $CDCl_3$): δ 23.60.

Elemental analysis:

Calcd for $C_{30}H_{42}N_2O_8P_2$: C-58.06; H-6.82; N-4.51; Found: C-57.88; H-6.64; N-4.62.

Tetrabenzyl 1,4-phenylene-bis-(N-m-methoxyphenylaminomethane)-bis-phosphonate (2′cB)

Y = 7.57 g (88%); mp = 117–120°C.

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.42 (s, C_6H_4, 4H); 7.39–7.07 (m, C_6H_5, 20H); 6.95 (m, m-C_6H_4, 2H); 6.17 (m, m-C_6H_4, 4H); 6.05 (m, m-C_6H_4, 2H); 4.99 (m, O<u>CH_2</u>Ph, 4H); 4.82 (m, O<u>CH_2</u>Ph, 2H); 4.79 (d, $^2J_{PH}$ = 24.9 Hz, C<u>H</u>P, 2H); 4.41 (m, O<u>CH_2</u>Ph, 2H); 3.57 (s, CH_3, 6H). ^{31}P NMR (81 MHz, $CDCl_3$): δ 22.97.

Elemental analysis:

Calcd for $C_{50}H_{50}N_2O_8P_2$: C-69.12; H-5.80; N-3.22; Found: C-69.33; H-5.63; N-3.34.

Tetraphenyl 1,4-phenylene-bis-(N-m-methoxyphenylaminomethane)-bis-phosphonate (2′cC)

Y = 3.48 g (56%); mp = 160–163°C.

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.78 (s, C_6H_4, 4H); 7.48–7.24 (m, C_6H_5, 20H); 6.98 (dd, J = 8.3 and 8.0 Hz, m-C_6H_4, 2H); 6.55 (d, J = 8.1 Hz, m-C_6H_4, 2H); 6.54 (d, J = 8.0 Hz, m-C_6H_4, 2H); 6.45 (t, J = 3.0 Hz, m-C_6H_4, 2H); 5.34 (d, $^2J_{PH}$ = 23.6 Hz, C<u>H</u>P, 2H); 5.15 (large s, NH, 2H); 3.82 (m, OCH_3, 6H). ^{31}P NMR (81 MHz, $CDCl_3$): δ 16.14.

Elemental analysis:

Calcd for $C_{46}H_{42}N_2O_8P_2$: C-67.98; H-5.21; N-3.45; Found: C-68.13; H-5.35; N-3.58.

Tetraethyl 1,4-phenylene-bis-(N-p-methylphenylaminomethane)-bis-phosphonate (2′dA)

Y = 5.41 g (92%); mp = 182–185°C.

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.42 (s, C_6H_4, 4H); 6.86 (d, J = 7.8 Hz, p-C_6H_4, 4H); 6.45 (d, J = 7.8 Hz, p-C_6H_4, 4H); 4.69 (d, $^2J_{PH}$ = 23.4 Hz, C<u>H</u>P, 2H); 4.07 (m, O<u>CH_2</u>CH_3, 4H); 3.86–3.41 (m, O <u>CH_2</u>CH_3, 4H); 2.16 (s, OCH_3, 6H); 1.25 and 1.23 (2t, J = 6.8 Hz, OCH_2<u>CH_3</u>, 6H); 1.04 and 0.94 (2t, J = 7.0 Hz, OCH_2<u>CH_3</u>, 6H). ^{31}P NMR (81 MHz, $CDCl_3$): δ 22.42.

Elemental analysis:

Calcd for $C_{30}H_{42}N_2O_6P_2$: C-61.22; H-7.19; N-4.76; Found: C-61.41; H-7.15; N-4.51.

Tetrabenzyl 1,4-phenylene-bis-(N-p-methylphenylaminomethane)-bis-phosphonate (2′dB)

Y = 7.45 g (90%); mp = 174–176°C.

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.41 and 7.40 (2s, C_6H_4, 4H); 7.31–7.08 (m, C_6H_5, 20H); 6.81 (d, J = 8.5 Hz, p-C_6H_4, 4H); 6.43 (d, J = 8.5 Hz, p-C_6H_4, 4H); 4.99–4.68 (m, O<u>CH_2</u>Ph, 6H); 4.81 (d, $^2J_{PH}$ = 22.4 Hz, C<u>H</u>P, 2H); 4.46 and 4.27 (2dd, $^3J_{PH}$ = 8.3 Hz, $^2J_{HH}$ = 11.8 Hz, O<u>CH_2</u>Ph, 2H); 2.11 and 2.08 (2s, CH_3, 6H). ^{31}P NMR (81 MHz, $CDCl_3$): δ 23.25 and 23.14 (3:2).

Elemental analysis:

Calcd for $C_{50}H_{50}N_2O_6P_2$: C-71.76; H-6.02; N-3.35; Found: C-71.49; H-5.82; N-3.07.

Tetraphenyl 1,4-phenylene-bis-(N-p-methylphenylaminomethane)-bis-phosphonate (2′dC)

Y = 7.18 g (92%); mp = 203–205°C.

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.53 (s, C_6H_4, 4H); 7.21–7.03 (m, C_6H_5, 16H); 6.93 (d, J = 8.2 Hz, p-C_6H_4, 4H); 6.74 (m, C_6H_5, 4H); 6.52

(d, J = 8.2 Hz, p-C_6H_4, 4H); 5.09 (d, $^2J_{PH}$ = 23.8 Hz, C<u>H</u>P, 2H); 3.86 (large s, NH, 2H); 2.20 (2s, CH_3, 6H). ^{31}P NMR (81 MHz, $CDCl_3$): δ 15.13.

Elemental analysis:

Calcd for $C_{46}H_{42}N_2O_6P_2$: C-70.76; H-5.42; N-3.59; Found: C-70.49; H-5.09; N-3.29.

Tetraethyl 1,4-phenylene-bis-(N-m-methylphenylaminomethane)-bis-phosphonate (2′eA)

Y = 5.17 g (88%); mp = 141–144°C.

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.44 (s, C_6H_4, 4H); 6.94 (ddd, $^3J_{HH}$ = 9.1 and 7.9 Hz, $^5J_{HH}$ = 1.4 Hz, m-C_6H_4, 2H); 6.49 (d, J = 9.1 Hz, m-C_6H_4, 2H); 6.38 (m, m-C_6H_4, 2H); 6.33 (d, J = 7.9 Hz, m-C_6H_4, 2H); 4.73 and 4.72 (2d, $^2J_{PH}$ = 23.2 Hz, C<u>H</u>P, 2H); 4.08 (m, O<u>CH_2</u>CH_3, 4H); 3.83 (m, O<u>CH_2</u>CH_3, 2H); 3.60 (m, O<u>CH_2</u>CH_3, 1H); 3.49 (m, O<u>CH_2</u>CH_3, 1H); 2.18 and 2.17 (2s, CH_3, 6H); 1.25 and 1.23 (2t, J = 7.1 Hz, OCH_2<u>CH_3</u>, 6H); 1.04 and 0.95 (2t, J = 7.0 Hz, OCH_2<u>CH_3</u>, 6H). ^{31}P NMR (81 MHz, $CDCl_3$): δ 23.81 and 23.75.

Elemental analysis:

Calcd for $C_{30}H_{42}N_2O_6P_2$: C-61.22; H-7.19; N-4.76; Found: C-61.43; H-7.28; N-4.91.

Tetrabenzyl 1,4-phenylene-bis-(N-m-methylphenylaminomethane)-bis-phosphonate (2′eB)

Y = 6.95 g (84%); mp = 123–125°C.

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.45 and 7.44 (2s, C_6H_4, 4H); 7.34–7.10 (m, C_6H_5, 20H); 6.91 (dd, $^3J_{HH}$ = 13.2 and 7.5 Hz, m-C_6H_4, 2H); 6.48 and 6.46 (2d, J = 7.5 Hz, m-C_6H_4, 2H); 6.37 and 6.36 (2m, m-C_6H_4, 2H); 6.33 and 6.32 (2d, J = 13.2 Hz, m-C_6H_4, 2H); 4.99 (m, O<u>CH_2</u>Ph, 4H); 4.80 (Part of ABX system, $^3J_{PH}$ = 7.2 and 7.5 Hz, $^2J_{HH}$ = 12.1 Hz, O<u>CH_2</u>Ph, 2H); 4.79 (d, $^2J_{PH}$ = 24.9 Hz, C<u>H</u>P, 2H); 4.42 (Part of AMX system, $^3J_{PH}$ = 7.8 and 8.1 Hz, $^2J_{HH}$ = 11.5 Hz, O<u>CH_2</u>Ph, 2H); 2.15 and 2.13 (2s, CH_3, 6H). ^{31}P NMR (81 MHz, $CDCl_3$): δ 24.47 and 24.37.

Elemental analysis:

Calcd for $C_{50}H_{50}N_2O_6P_2$: C-71.76; H-6.02; N-3.35; Found: C-71.91; H-6.22; N-3.51.

Tetraphenyl 1,4-phenylene-bis-(N-m-methylphenylaminomethane)-bis-phosphonate (2′eC)

Y = 6.72 g (86%); mp = 179–181°C.

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.57 and 7.56 (2s, C_6H_4, 4H); 7.21 (m, C_6H_5, 4H); 7.14–7.00 (m, C_6H_5, 16H); 6.76 (t, $^3J_{HH}$ = 8.2 Hz, m-C_6H_4, 2H); 6.58 (m, m-C_6H_4, 2H); 6.47 and 6.46 (2m, m-C_6H_4, 2H); 6.41 (d, J

= 8.2 Hz, m-C_6H_4, 2H); 5.13 (d, $^2J_{PH}$ = 23.6 Hz, C<u>H</u>P, 2H); 3.86 (large s, NH, 2H); 2.22 and 2.21 (2s, CH_3, 6H). ^{31}P NMR (81 MHz, $CDCl_3$): δ 16.36 and 16.32.

Elemental analysis:

Calcd for $C_{46}H_{42}N_2O_6P_2$: C-70.76; H-5.42; N-3.59; Found: C-70.91; H-5.56; N-3.70.

Tetraethyl 1,4-phenylene-bis-(N-meta-nitroanilinemethane)-bis-phosphonate (2′gA)

Y = 2.54 g (39%). Mp 198–201°C.

^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.62 and 7.33 (2m, CH_{arom}, 2H); 7.52 and 7.49 (2s, C_6H_4, 4H); 7.43 (d, J = 8.1 Hz, CH_{arom}, 2H); 7.18 and 7.17 (2d, J = 8.2 Hz, CH_{arom}, 2H); 6.88 (m, CH_{arom}, 2H); 4.84 and 4.78 (2d, $^2J_{PH}$ = 23.8 Hz, CHP, 2H); 4.26 and 3.59 (2m, <u>CH_2</u>CH_3, 8H); 1.97 (s, NH, 2H); 1.31, 1.27 and 1.06, 0.98 (4t, J = 6.6 Hz, CH_2 <u>CH_3</u>, 12H).

^{31}P NMR ($CDCl_3$, 81 MHz): δ 20.89 and 20.79.

Elemental analysis:

Calcd for $C_{28}H_{36}N_4O_{10}P_2$: C-51.70; H-5.58; N-8.61; Found: C-51.52; H-5.30; N-8.63.

Tetrabenzyl 1,4-phenylene-bis-(N-meta-nitroanilinomethane)-bis-phosphonate (2′gB)

Y = 4,05 g (45%). Mp 158–161°C.

^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.57 and 7.45 (2s, C_6H_4, 4H); 7.30–7.05 (m, CH_{arom}, 28H); 4.86 (2d, $^2J_{PH}$ = 22.6 Hz, CHP, 2H); 5.10–4.70 and 4.57–4.42 (2m, CH_2Ph, 8H); 3.10 (s, NH, 2H).

^{31}P NMR ($CDCl_3$, 81 MHz): δ 21.29 and 21.21.

Elemental analysis:

Calcd for $C_{48}H_{44}N_4O_{10}P_2$: C-64.14; H-4.93; N-6.23; Found: C-63.97; H-4.85; N-6.02.

Tetraphenyl 1,4-phenylene-bis-(N-meta-nitroanilinomethane)-bis-phosphonate (2′gC)

Y = 2,70 g (32%). Mp 201–203°C.

^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.58 (2s, C_6H_4, 4H); 7.35 and 7.24–6.61 (2m, CH_{arom}, 28H); 5.24 (d, $^2J_{PH}$ = 24.2 Hz, CHP, 2H); 1.97 (s, NH, 2H).

^{31}P NMR ($CDCl_3$, 81 MHz): δ 13.61 and 13.26.

Elemental analysis:

Calcd for $C_{44}H_{36}N_4O_{10}P_2$: C-62.71; H-4.31; N-6.65; Found: C-62.59; H-4.27; N-6.49.

Tetraethyl 1,4-phenylene-bis-(N-p-carboxyphenylaminomethane)-bis-phosphonate (2′hA)

Y = 2.91 g (45%); mp = 235–237°C (decomp).

^{1}H NMR (200 MHz, $CD_3S(O)CD_3$): δ 10.13 (c, COOH, 2H); 7.58 (d, J = 8.4 Hz, p-C_6H_4, 4H); 7.49 (s, C_6H_4, 4H); 6.81 (d, J = 8.4 Hz, p-C_6H_4, 4H); 5.15 and 5.10 (d, $^2J_{PH}$ = 23.7 Hz, C<u>H</u>P, 2H); 3.68 (m, O<u>CH_2</u>CH_3, 8H); 1.12 and 0.93 (2t, J = 7.0 Hz, OCH_2<u>CH_3</u>, 6H). ^{31}P NMR (81 MHz, $CD_3S(O)CD_3$): δ 21.84 and 18.33 (5:1).

Elemental analysis:

Calcd for $C_{30}H_{38}N_2O_{10}P_2$: C-55.56; H-5.91; N-4.32; Found: C-55.72; H-6.08; N-4.48.

Tetrabenzyl 1,4-phenylene-bis-(N-p-carboxyphenylaminomethane)-bis-phosphonate (2′hB)

Y = 7.88 g (88%); mp = 220–224°C (decomp).

^{1}H NMR (200 MHz, $CD_3S(O)CD_3$): δ 10.16 (s, COOH, 2H); 7.61 (d, J = 8.4 Hz, p-C_6H_4, 4H); 7.52 (s, C_6H_4, 4H); 6.86 (d, J = 8.4 Hz, p-C_6H_4, 4H); 4.99 (m, O<u>CH_2</u>Ph, 4H); 4.82 (m, O<u>CH_2</u>Ph, 2H); 4.41 (m, O<u>CH_2</u>Ph, 2H). ^{31}P NMR (81 MHz, $CD_3S(O)CD_3$): δ 21.34 and 21.03 (3:1).

Elemental analysis:

Calcd for $C_{50}H_{46}N_2O_{10}P_2$: C-66.96; H-5.17; N-3.12; Found: C-67.12; H-5.32; N-3.27.

Tetraphenyl 1,4-phenylene-bis-(N-p-carboxyphenylaminomethane)-bis-phosphonate (2′hC)

Y = 6.64 g (79%); mp = 215–217°C (decomp).

^{1}H NMR (200 MHz, $CD_3S(O)CD_3$): δ 10.14 (s, COOH, 2H); 7.75 (s, C_6H_4, 4H); 7.67 (d, J = 8.2 Hz, p-C_6H_4, 4H); 7.28–6.96 (m, C_6H_5, 16H); 6.72 (m, C_6H_5, 4H); 6.53 (d, J = 8.2 Hz, p-C_6H_4, 4H); 5.81 (d, $^2J_{PH}$ = 22.6 Hz, C<u>H</u>P, 2H); 3.86 (large s, NH, 2H). ^{31}P NMR (81 MHz, $CD_3S(O)CD_3$): δ 20.52.

Elemental analysis:

Calcd for $C_{46}H_{38}N_2O_{10}P_2$: C-65.71; H-4.56; N-3.33; Found: C-65.90; H-4.71; N-3.49.

Tetraethyl 1,4-phenylene-bis-(N-m-carboxyphenylaminomethane)-bis-phosphonate (2′iA)

Y = 3.30 g (51%); mp = 201–206°C (decomp).

^{1}H NMR (200 MHz, $CD_3S(O)CD_3$): δ 10.18 (s, COOH, 2H); 7.83 (m, m-C_6H_4, 2H); 7.76 (s, C_6H_4, 4H); 7.58 (m, m-C_6H_4, 2H); 6.71 (m, m-C_6H_4, 2H); 5.34 (d, $^2J_{PH}$ = 23.5 Hz, C<u>H</u>P, 2H); 4.09 (m, O<u>CH_2</u>CH_3, 4H); 3.66 (m, O<u>CH_2</u>CH_3, 4H); 1.26 and 1.24 (2t, J = 6.8 Hz, OCH_2<u>CH_3</u>, 6H); 1.07 and

0.98 (2t, J = 6.9 Hz, $OCH_2\underline{CH_3}$, 6H). ^{31}P NMR (81 MHz, $CD_3S(O)CD_3$): δ 21.87.

Elemental analysis:

Calcd for $C_{30}H_{38}N_2O_{10}P_2$: C-55.56; H-5.91; N-4.32; Found: C-55.72; H-6.21; N-4.51.

Tetrabenzyl 1,4-phenylene-bis-(N-m-carboxyphenylaminomethane)-bis-phosphonate (2′iB)

Y = 7.97 g (89%); mp = 209–210°C (decomp).

^1H NMR (200 MHz, $CD_3S(O)CD_3$): δ 10.09 (s, COOH, 2H); 7.79 (m, m-C_6H_4, 2H); 7.71 (s, C_6H_4, 4H); 7.53 (m, m-C_6H_4, 2H); 7.48–7.24 (m, C_6H_5, m-C_6H_4, 22H); 6.70 (m, m-C_6H_4, 2H); 5.34 (d, $^2J_{PH}$ = 23.8 Hz, C$\underline{H}$P, 2H); 4.99 (m, O$\underline{CH_2}$Ph, 4H); 4.82 (m, O$\underline{CH_2}$Ph, 2H); 4.41 (m, O$\underline{CH_2}$Ph, 2H). ^{31}P NMR (81 MHz, $CD_3S(O)CD_3$): δ 23.12.

Elemental analysis:

Calcd for $C_{50}H_{46}N_2O_{10}P_2$: C-66.96; H-5.17; N-3.12; Found: C-67.22; H-5.34; N-3.28.

Tetraphenyl 1,4-phenylene-bis-(N-m-carboxyphenylaminomethane)-bis-phosphonate (2′iC)

Y = 6.64 (79%); mp = 220–224°C (decomp).

^1H NMR (200 MHz, $CD_3S(O)CD_3$): δ 10.17 (s, COOH, 2H); 7.83 (m, m-C_6H_4, 2H); 7.74 (s, C_6H_4, 4H); 7.53 (m, m-C_6H_4, 2H); 7.48–7.24 (m, C_6H_5, m-C_6H_4, 22H); 6.70 (m, m-C_6H_4, 2H); 5.70 (d, $^2J_{PH}$ = 23.8 Hz, C$\underline{H}$P, 2H); 5.15 (large s, NH, 2H). ^{31}P NMR (81 MHz, $CDCl_3$): δ 16.01.

Elemental analysis:

Calcd for $C_{46}H_{38}N_2O_{10}P_2$: C-65.71; H-4.56; N-3.33; Found: C-65.94; H-4.71; N-3.17.

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