Available online at www.sciencedirect.com
ScienceDirect
Dyes and Pigments 77 (2008) 103–110
DYES and PIGMENTS
www.elsevier.com/locate/dyepig

Synthesis, spectral, and thermal properties of some phosphorus-containing 9,10-anthraquininoid, thermally stable dyes

Issa Yavari*, Elaheh Kowsari

Chemistry Department, Tarbiat Modarres University, P.O. Box 14115-175, Tehran, Iran

Received 5 December 2006; received in revised form 15 March 2007; accepted 17 March 2007
Available online 27 April 2007

Abstract

The multi-component, one-step reaction of dialkyl acetylenedicarboxylates with 1-amino-9,10-anthraquinone in the presence of triphenyl phosphite or trialkyl phosphites, produces 9,10-anthraquinone derivatives containing dialkyl(aryl) phosphoryl groups as novel, thermally stable dyes in fairly good yields. The structural characterization and some physical properties of these dyes are reported.

Keywords: Triphenyl phosphite; Trialkyl phosphites; Thermally stable dyes; 1-Aminoanthraquinone; Disperse dyes

1. Introduction

Aminoanthraquinones are the basic structural units of disperse dyes [1–6], which are an important class of dye, characterized by good fastness properties and brightness on hydrophobic fibres, such as poly(ethylene terephthalate), on which they provide mostly bright red to blue hues; also are included acylamino-anthraquinones which furnish mainly yellow and orange dyes. In addition, anthraquinones have become recently very important due to their application in high technology electronics. Some aminoanthraquinone derivatives are used in transfer printing toners and others are used in thermal printing [7,8]. The P═O group has often been incorporated into the compounds to enhance their thermal/oxidative stability and ignition resistance [9].

In a continuation of our current interest in the development of new routes to 9,10-anthraquinones [10,11], herein we report a simple, one-pot synthesis of some thermally stable anthraquinone derivatives containing dialkyl(aryl) phosphoryl moieties.

2. Results and discussion

2.1. Structural characterization of dyes

The reaction of dialkyl acetylenedicarboxylates (**2**) with 1-aminoanthraquinone (**3**) in the presence of trialkyl(aryl) phosphites (**1**) in toluene, under reflux, leads to dialkyl 2-{bis[alkyl(aryl)oxy]-phosphoryl}-3-[(9,10-dioxo-9,10-dihydro-1-anthracenyl)amino]-butanedioates (**4**) in 70–90% yield (Scheme 1).

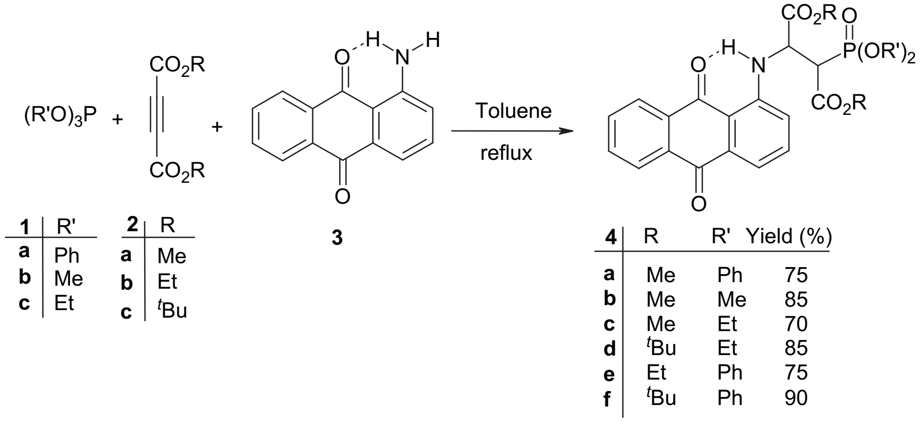
The structures of **4a**–**4f** were deduced from their elemental analyses and high-field ^{1}H, ^{13}C, and ^{31}P NMR spectra, IR spectra and UV–vis absorption spectral data. The mass spectra of these compounds exhibited molecular ion peaks at the appropriate *m*/*z* values.

The ^{1}H NMR spectrum of **4a** in $CDCl_3$ shows two singlets at $\delta = 3.71$ and 3.99 ppm for the methoxy protons, a double doublet at $\delta = 4.30$ ($^2J_{PH} = 25.3$, $^3J_{HH} = 4.0$ Hz) and a broad peak at 5.21 (ddd, $^3J_{HH} = 10.5$, $^3J_{HP} = 7.8$, $^3J_{HH} = 4.0$) for the methine protons. The NH proton appears as a doublet ($^3J_{HH} = 10.5$ Hz) at $\delta = 10.70$ ppm, as a result of strong intramolecular hydrogen bonding. Although the presence of the ^{31}P nucleus complicates both the ^{1}H and ^{13}C NMR spectra of **4a**–**4f**, it helps in the assignment of the signals by

---

* Corresponding author. Tel.: +98 21 88006631; fax: +98 21 88006544.
E-mail addresses: yavarisa@modares.ac.ir, isayavar@yahoo.com (I. Yavari).

0143-7208/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2007.03.013



1	R'
a	Ph
b	Me
c	Et

2	R
a	Me
b	Et
c	^{t}Bu

4	R	R'	Yield (%)
a	Me	Ph	75
b	Me	Me	85
c	Me	Et	70
d	^{t}Bu	Et	85
e	Et	Ph	75
f	^{t}Bu	Ph	90

Scheme 1. Reaction condition for the preparation of compounds **4a**–**4f**.

long-range coupling with ^{1}H and ^{13}C nuclei (see Section 4). The ^{1}H, ^{13}C, and ^{31}P NMR spectra of **4a** and **4b**, are shown in Figs. 1–5.

Observation of $^3J_{HH}$ 3.5–4.6 Hz for the vicinal methine protons in **4a**–**4f** indicates the dominance of the *gauche* arrangement. Since compound **4** possesses two stereogenic centers, two diastereomers with *gauche* HCCH arrangements are possible (Scheme 2). Observation of $^3J_{CP}$ 20–24 Hz for the *C*O$_2$Me group is in agreement with the (2*R*,3*S*) or (2*S*,3*R*) diastereoisomer as the major isomer (60–99%). Hence, the minor diastereoisomer (1–40%) is (2*S*,3*S*) or (2*R*,3*R*) and the reaction is diastereoselective. Selected ^{1}H, ^{13}C, and ^{31}P NMR chemical shifts and coupling constant for **4a**–**4f** (major and minor isomers) are shown in Table 1.

Characteristic ester carbonyl resonances for the major diastereoisomer of **4a** appeared at $\delta = 168.0$ (d, $^3J_{PC} = 5.0$ Hz) and 171.4 (d, $^2J_{PC} = 17.7$ Hz), whereas the carbon atom of the P–CH moiety appeared at $\delta = 47.6$ (d, $^1J_{PC} = 136.3$ Hz). The presence of three electronegative oxo substituents on the phosphorus atom increases the $^1J_{CP}$ value. The UV–vis absorption spectrum of **4a** showed absorption bands at 480 and 310 nm; the UV–vis absorption spectra of compounds **4a**–**4f** are shown in Fig. 6.

The IR spectrum of **4a** and **4d** are shown in Fig. 7. The P=O stretching absorption bands appeared at about 1180–1195 cm^{-1} and the N–H stretching at 3300–3500 cm^{-1}. The P=O stretching band was shifted from 1220 to 1180–1195 cm^{-1} due to the electron-donating effect of the amine group.

Although the mechanistic details of the reaction are not clearly known, a plausible rationale may be advanced to explain the product formation. Presumably, the zwitterionic intermediate [12] **5** formed from (R′O)$_3$P and the dialkyl acetylenedicarboxylate was protonated by 1-aminoanthraquinone to furnish the intermediate **6**, which was then attacked by the conjugate base **7** to produce **8**; this intermediate was protonated to furnish **9**, which was converted to the final product by loss of R′OH (Scheme 3).

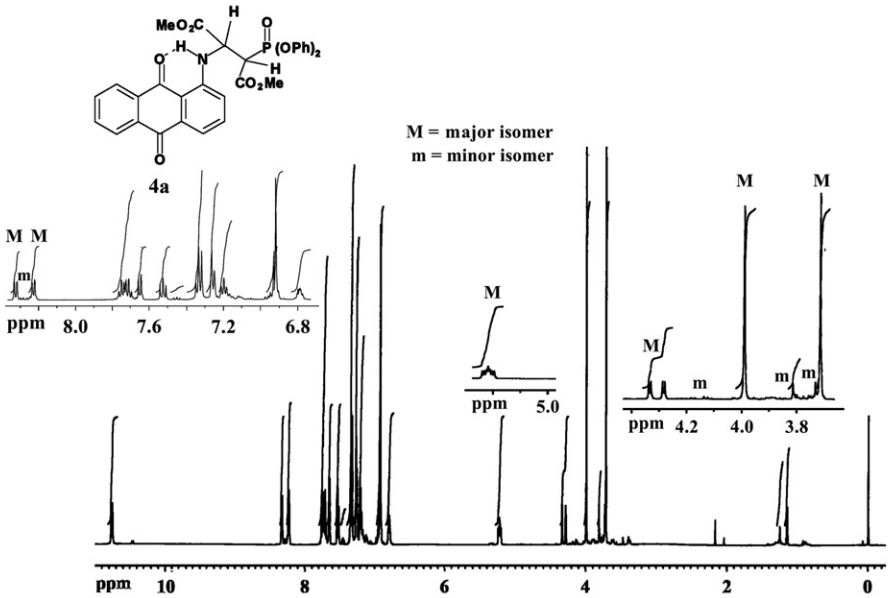


Fig. 1. ^{1}H NMR spectrum (500.1 MHz) of **4a** in acetone-d_6.

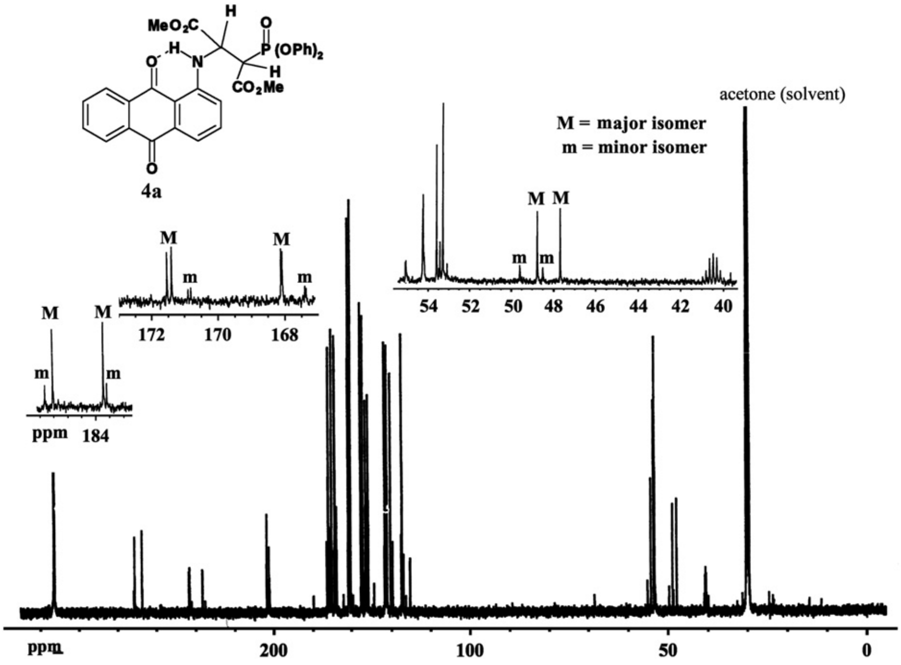


Fig. 2. ^{13}C NMR spectrum (125.8 MHz) of **4a** in acetone-d_6.

2.2. Thermal properties of dyes *4a–4f*

The thermal properties of **4a** were studied by means of TGA and DSC at a heating rate of 10 °C min^{-1} under a nitrogen atmosphere (see Fig. 8). The TGA–DSC diagram of 1-methylamino-9,10-anthraquinone (**10**), measured under similar conditions, is shown in Fig. 9. The thermal data and char yields for **4a**, **4b**, **4d**, **4e**, **4f** and **10** are listed in Table 2.

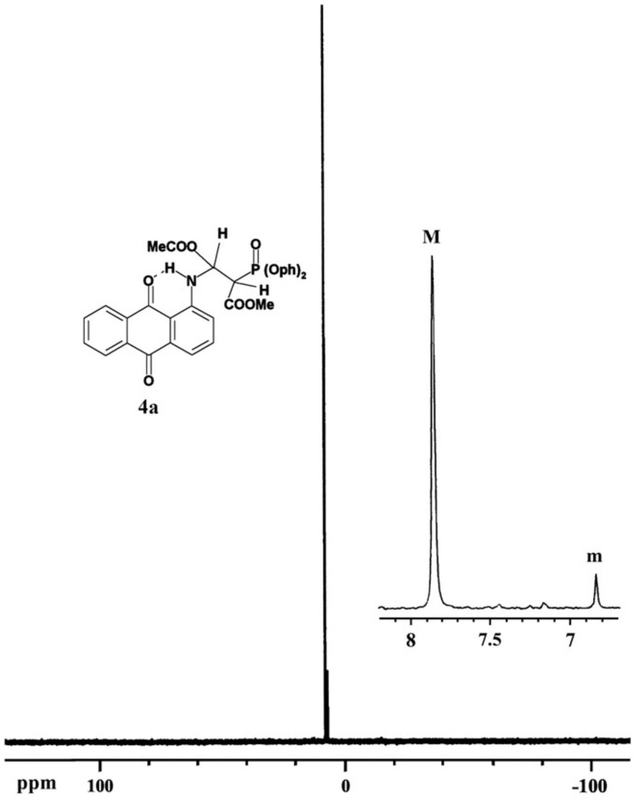


Fig. 3. ^{31}P NMR spectrum (202.4 MHz) of **4a** in acetone-d_6.

Several thermal regions were selected on the TGA curves for comparison of the relative thermal stabilities of **4a**, **4b**, **4d**, **4e**, **4f**, and **10** (Figs. 8–10). These were T_0, T_5, and T_{10}, which refer to the initial decomposition temperature and the temperature at which 5 and 10% loss of mass occurred, respectively.

The temperature of initial decomposition of **4a** at the first stage was about 240 °C. Compound **4a** possessed higher thermal stability (10% mass loss occurring around 280 °C and char yield >40%, at 500 °C) compared with **10** (10% mass loss occurring around 184 °C and char yield <5%, at 500 °C). The TGA measurements showed a distinct variation in thermal stability between **4a** and **10**. The incorporation of a dialkyl(aryl) phosphoryl group in **4**, enhanced its thermal stability and increased its T_i value. Comparing the results shown in Table 2 for the five dialkyl(aryl) phosphoryl pigments (**4a**, **4b**, **4d**, **4e**, **4f**) shows that, in general, the dialkyl(aryl) phosphoryl pigment containing phenyl groups had higher thermal stability.

The DSC curve of **4a** is presented in Fig. 8; it shows an endotherm at 135 °C due to melting and a second endothermic at 450 °C, which corresponds to the mass loss in TGA.

3. Conclusions

The reaction of 1-aminoanthraquinone with dialkyl acetylenedicarboxylates in the presence of trialkyl(aryl) phosphites leads to the efficient synthesis of thermally stable anthraquinone derivatives containing dialkyl(aryl) phosphoryl moieties. All of the pigments were fully characterized by ^{1}H NMR, ^{13}C

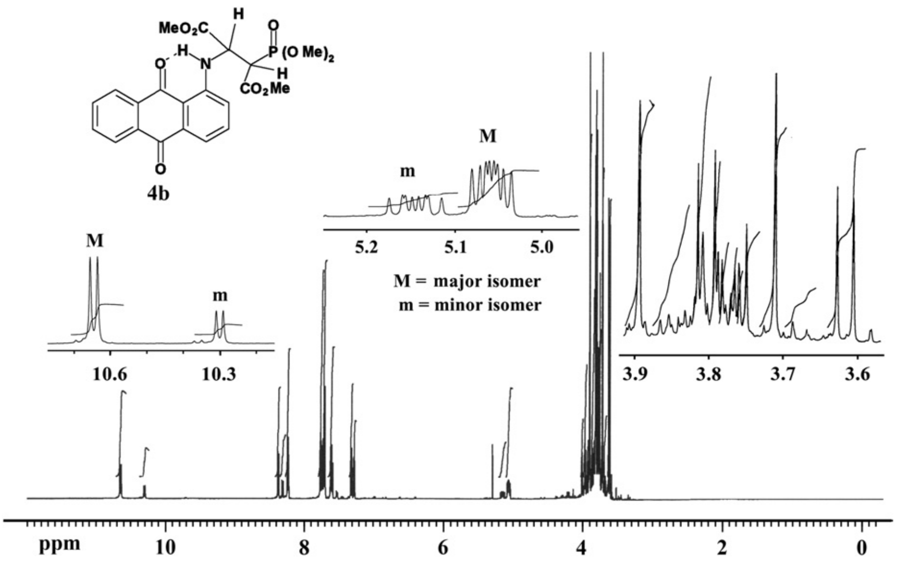


Fig. 4. ^{1}H NMR spectrum (500.1 MHz) of **4b** in $CDCl_3$.

NMR, ^{31}P NMR, IR, and UV−vis absorption spectra, mass spectra and TGA−DSC measurements. Some structural characterization and physical properties of the dyes are reported.

4. Experimental

4.1. General

Compounds **1**−**3** were obtained from Fluka and were used without further purification. M.p.: Electrothermal-9100 apparatus; uncorrected. IR spectra: Shimadzu IR-460 spectrometer. ^{1}H, ^{13}C, and ^{31}P NMR spectra: Bruker DRX-500 Avance instrument; in $CDCl_3$ at 500.1, 125.8, and 202.4 MHz, respectively; δ in parts per million, J in hertz. EI-MS (70 eV): Finnigan-MAT-8430 mass spectrometer, in *m*/*z*. Elemental analyses (C, H, N) were performed with a Heraeus CHN−O-Rapid analyzer. UV spectra were taken on a Shimadzu UV-160A spectrometer. TGA−DSC analysis was performed with an STA-1200 instrument. ^{1}H, ^{13}C, and ^{31}P NMR spectra were obtained for solutions in $CDCl_3$ using TMS as internal standard or 85% H_3PO_4 as external standard. All the chemicals used in this work were purchased from Fluka (Buchs, Switzerland) and were used without further purification.

4.2. General procedure for the preparation of compounds *4*

To a stirred solution of **2** (2 mmol) and **3** (0.45 g, 2 mmol) in 8 cm^3 toluene was added a mixture of **1** (2 mmol) in 2 cm^3 toluene. The reaction mixture was heated for 6 h. The solvent was removed under reduced pressure to give a red solid. The products were separated by silica gel column chromatography (Merck 230−400 mesh) using *n*-hexane−EtOAc (8:1) as eluent. The solvent was removed under reduced pressure to afford pure compounds.

4.2.1. Dimethyl 2-[bis(phenyloxy)-phosphoryl]-3-[(9,10-dioxo-9,10-dihydro-1-anthracenyl)amino]-butanedioate (*4a*)

Yield: 0.89 g (75%). Red crystals. M.p.: 136-137 °C. IR (KBr): 1625, 1657 (2C=O), 1733 (C=O, ester), 3430 (N−H). UV (CH_2Cl_2): 375, 309, 244 nm. EI-MS: 599 (M^+, 5), 520 (8), 485 (10), 223 (98), 195 (26), 167 (64), 149 (100), 139

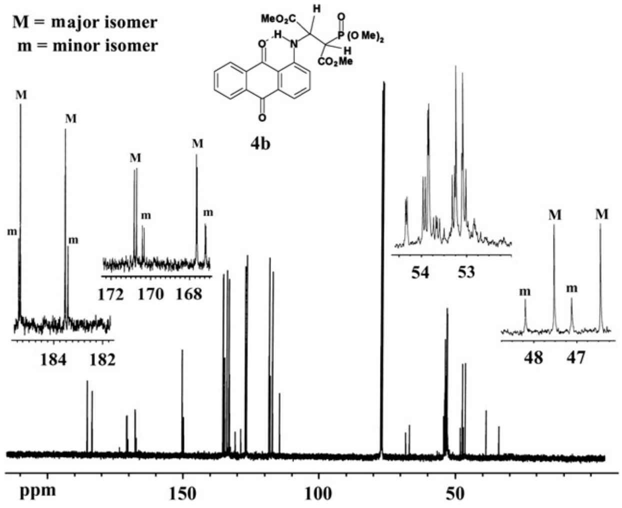
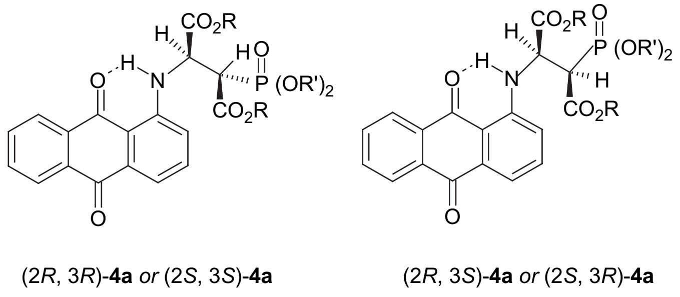


Fig. 5. ^{13}C NMR spectrum (125.8 MHz) of **4b** in $CDCl_3$.



Scheme 2. The diastereoisomers of compounds **4a**−**4f**.

Table 1
Selected ^{1}H, ^{13}C, and ^{31}P NMR chemical shifts (in ppm) and coupling constants (in Hz) for major (M) and minor (m) diastereoisomers of **4a–4f**

Compound	Isomer (%)	^{1}H NMR		^{13}C NMR			^{31}P NMR
		H-2 ($^{2}J_{PH}$)	NH ($^{3}J_{HH}$)	C=O ($^{2}J_{PC}$)	C=O ($^{3}J_{PC}$)	C-2 ($^{1}J_{PC}$)	
4a	M (92)	4.30 (25.3)	10.74 (10.5)	171.4 (17.7)	168.0 (5.0)	47.6 (136.3)	7.85
4a	m (8)	–	–	170.8 (10)	167.4 (5.0)	48.5 (135.6)	6.83
4b	M (55)	3.88 (20.1)	10.63 (10.1)	170.7 (16)	167.6 (4.7)	46.4(135.0)	22.45
4b	m (45)	3.90 (20.0)	10.29 (9.4)	170.3 (12)	167.1 (4.6)	47.1 (135.0)	22.10
4c	M (60)	3.83 (m)	10.60 (10.0)	170.8 (15)	167.7 (3.8)	47.0 (134.8)	19.61
4c	m (40)	3.84 (m)	10.26 (9.4)	170.4 (13)	167.4 (3.7)	47.9 (134.7)	19.59
4d	M (60)	3.83 (25.2)	10.51(10.0)	169 (15)	165.8 (5)	47.8 (132.9)	21.17
4d	m (40)	3.85 (25.2)	10.21 (10.0)	170 (20)	165.7 (6)	48.6 (134.1)	20.94
4e	M (60)	4.29 (25.3)	10.72 (10.3)	170.2 (17)	166.4 (5)	47.6 (136.9)	13.19
4e	m (40)	4.29 (25.3)	10.45 (11.0)	169.4 (11)	165.9 (6.2)	48.1 (135.8)	12.85
4f	M (99)	4.22 (25.8)	10.7 (10.2)	169.6 (19)	166.3 (5)	48.9 (135.5)	14.39
4f	m (1)	–	–	–	–	–	13.76

(26), 113 (20), 71 (18), 57 (42), 43 (28). Anal. calc. for $C_{32}H_{26}NO_9P$ (599.20): C, 64.11; H, 4.37; N, 2.34%; found: 64.15; H, 4.40; N, 2.35%. NMR data for the major isomer (92%). ^{1}H NMR: 3.71 (s, OMe), 3.99 (s, OMe), 4.30 (dd, $^{2}J_{HP} = 25.3$, $^{3}J_{HH} = 4.0$, CH), 5.21 (ddd, $^{3}J_{HH} = 10.5$, $^{3}J_{HP} = 7.8$, $^{3}J_{HH} = 4.0$, CH), 6.78–6.79 (m, CH), 6.90–6.91 (m, 3CH), 7.18–7.19 (m, 2CH), 7.18–7.19 (m, 2CH), 7.32–7.34 (m, 3CH), 7.51–7.52 (m, CH), 7.64–7.65 (m, CH), 7.72–7.74 (m, 2CH), 8.23 (dd, $^{3}J_{HH} = 7.7$, $^{4}J_{HH} = 1.5$, CH), 8.30 (dd, $^{3}J_{HH} = 7.4$, $^{4}J_{HH} = 1.3$, CH), 10.70 (d, $^{3}J_{HH} = 10.5$, NH). ^{13}C NMR: 47.6 (d, $^{1}J_{PC} = 136.3$, CH), 53.3 (OMe), 53.6 (OMe), 54.3 (d, $^{2}J_{PC} = 3.1$, CH), 115.1 (CH), 116.1 (CH), 116.7 (CH), 117.1 (CH), 120.1 (CH), 120.9 (CH), 121.0 (d, $^{3}J_{PC} = 4.6$, CH), 121.5 (d, $^{3}J_{PC} = 4.5$, CH), 125.7 (CH), 126.4 (CH), 127.0 (CH), 127.2 (CH), 127.4 (CH), 127.6 (C), 130.1 (CH), 130.5 (CH), 130.7 (C), 133.7 (C), 134.2 (C), 135.0 (CH), 135.8 (C), 151.0 (C), 151.2 (C), 151.7 (N–C), 168.0 (d, $^{3}J_{PC} = 5.0$, C=O), 171.4 (d, $^{2}J_{PC} = 17.7$, C=O), 183.7 (C=O), 185.5 (C=O). ^{31}P NMR: 7.8. NMR data for the minor isomer (8%). ^{1}H NMR: 3.73 (s, OMe), 3.81 (s, OMe), 4.10 (CH), 5.10 (CH), 6.93–6.94 (m, CH), 6.90–6.91 (m, 3CH), 7.18–7.19 (m, 2CH), 7.18–7.19 (m, 2CH), 7.25–7.26 (m, 3CH), 7.51–7.52 (m, CH), 7.64–7.65 (m, CH), 7.72–7.74 (m, 2CH), 8.23 (dd, $^{3}J_{HH} = 7.7$, $^{4}J_{HH} = 1.5$, CH), 8.30 (dd, $^{3}J_{HH} = 7.4$, $^{4}J_{HH} = 1.3$, CH), 10.40 (d, $^{3}J_{HH} = 10.5$, NH). ^{13}C NMR: 48.5 (d, $^{1}J_{PC} = 135.6$, CH), 53.1 (OMe), 53.4 (OMe), 55.1 (d, $^{3}J_{PC} = 3.6$, CH), 115.2 (CH), 116.1 (CH), 116.7 (CH), 117.3 (CH), 119.5 (CH), 119.8 (CH), 121.3 (d, $^{3}J_{PC} = 4.9$, CH), 121.4 (d, $^{3}J_{PC} = 4.0$, CH), 126.1 (CH), 126.6 (CH), 127.2 (CH), 127.3 (CH), 127.4 (C), 129.6 (CH), 130.5 (CH), 130.8 (CH), 134.0 (CH), 134.3 (C), 135.2 (C), 135.3 (CH), 136.2 (C), 150.9 (C), 151.0 (C), 151.5 (N–C), 167.4 (d, $^{3}J_{PC} = 5.0$, C=O), 170.8 (d, $^{2}J_{PC} = 10.0$, C=O), 183.6 (C=O), 185.9 (C=O). ^{31}P NMR: 6.8.

The procedure for preparation of other products was similar to that for **4a**.

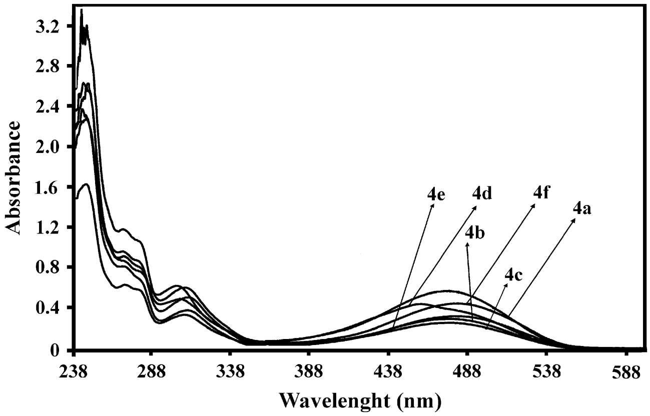


Fig. 6. UV–vis absorption spectra of **4a–4f**, measured in CH_2Cl_2 at a concentration of 0.08 mmol dm^{-1}.

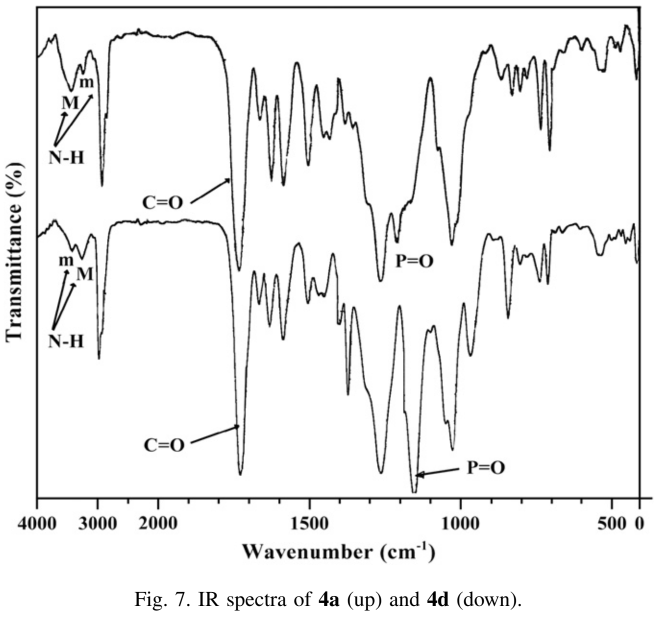
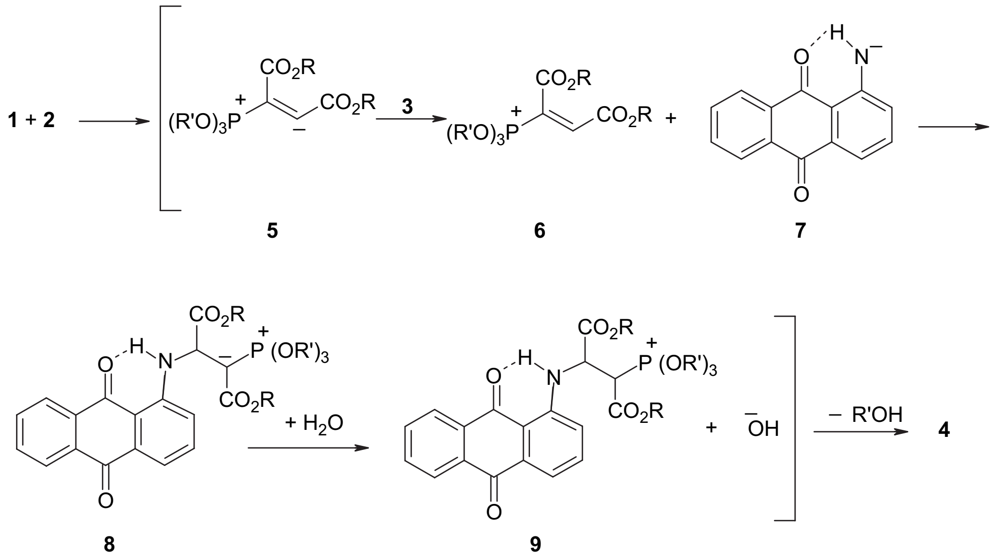


Fig. 7. IR spectra of **4a** (up) and **4d** (down).



Scheme 3. Plausible mechanism for the formation of compound **4**.

*4.2.2. Dimethyl 2-[bis(methoxy)-phosphoryl]-3-[(9,10-dioxo-9,10-dihydro-1-anthracenyl)amino]-butanedioate (**4b**)*

Yield: 0.80 g (85%). Red powder. M.p.: 129.0–130.0 °C. IR (KBr): 1623 and 1661 (2C═O), 1731 (C═O, ester), 3449 (N–H). UV (CH_2Cl_2): 477, 308, 244 nm. EI-MS: 475 (M^+, 3), 460 (9), 232 (24), 223 (48), 224 (12), 167 (8), 132 (6), 109 (5), 57 (20), 31 (55). Anal. calc. for $C_{22}H_{22}NO_9P$ (475.38): C, 55.58; H, 4.66; N, 2.99%; found: C, 55.60; H, 4.68; N, 3.01%. NMR data for the major isomer (60%). ^1H NMR: 3.60 (d, $^3J_{HP} = 11.5$, OMe), 3.71 (s, OMe), 3.79 (d, $^3J_{HP} = 11.3$, OMe), 3.89 (s, OMe), 3.88 (dd, $^2J_{HP} = 20.1$, $^3J_{HH} = 4.6$, CH), 5.0 (ddd, $^3J_{HH} = 10.1$, $^3J_{HP} = 8.0$, $^3J_{HH} = 4.6$, CH), 7.29–7.31 (m, CH), 7.51–7.69 (m, 2CH), 7.69–7.76 (m, 2CH), 8.22 (dd, $^3J_{HH} = 6.0$, $^4J_{HH} = 1.5$, CH), 8.35 (dd, $^3J_{HH} = 6.5$, $^4J_{HH} = 1.0$, CH), 10.63 (d, $^3J_{HH} = 10.1$, NH). ^{13}C NMR: 46.4 (d, $^1J_{PC} = 135.0$, CH), 53.2 (OMe), 53.3 (d, $^3J_{PC} = 3.7$, CH), 53.7 (d, $^3J_{PC} = 6.8$, OMe), 53.8 (OMe), 53.8 (d, $^3J_{PC} = 6.8$, OMe), 114.6 (CH), 117.2 (CH), 118.5 (CH) 126.6 (CH), 127.2 (CH), 128.8 (C), 132.9 (C), 133.2 (CH), 133.9 (CH), 134.7 (C), 135.3 (C), 150.3 (N–C), 167.6 (d, $^3J_{PC} = 4.7$, C═O), 170.7 (d, $^2J_{PC} = 16.0$, C═O), 183.5 and 185.3 (2C═O). ^{31}P NMR: 22.4. NMR data for the minor isomer (40%). ^1H NMR: 3.75 (d, $^3J_{HP} = 10.2$, OMe), 3.76 (s, OMe), 3.78 (d, $^3J_{HP} = 10.1$, OMe), 3.80 (s, OMe), 3.90 (dd, $^2J_{HP} = 20.0$, $^3J_{HH} = 4.3$, CH), 5.14 (ddd, $^3J_{HH} = 9.4$, $^3J_{HP} = 7.6$, $^3J_{HH} = 4.3$CH), 7.25–7.26 (m, CH), 7.60–7.62 (m, 2CH), 7.69–7.70 (m, 2CH), 8.22 (dd, $^3J_{HH} = 6.0$, $^4J_{HH} = 1.5$, CH), 8.31 (dd, $^3J_{HH} = 7.4$, $^4J_{HH} = 1.3$, CH), 10.29 (d, $^3J_{HH} = 9.4$, NH). ^{13}C NMR: 47.1 (d, $^1J_{PC} = 135.0$, CH), 53.0 (OMe), 53.1 (d, $^3J_{PC} = 2.7$, CH), 53.2 (OMe), 53.9 (d, $^3J_{PC} = 6.8$, OMe), 54.3 (d, $^3J_{PC} = 6.7$, OMe), 114.5 (CH), 117.1 (CH), 118.1 (CH) 126.7 (CH), 127.0 (C), 132.4 (C), 132.9 (CH), 133.2 (C), 133.9 (CH), 134.8 (C), 135.4 (C), 150.3 (N–C), 167.1 (d, $^2J_{PC} = 4.6$, C═O), 170.3 (d, $^3J_{PC} = 12.0$, C═O), 183.4 and 185.4 (2C═O). ^{31}P NMR: 22.1.

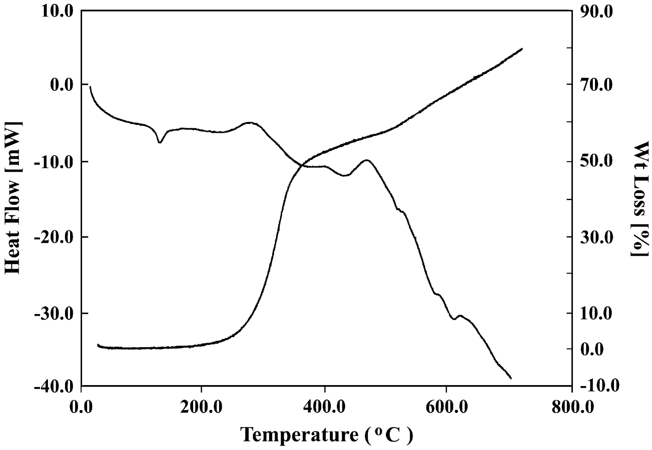


Fig. 8. TGA–DSC of **4a** with a heating rate of 10 °C/min in nitrogen atmosphere.

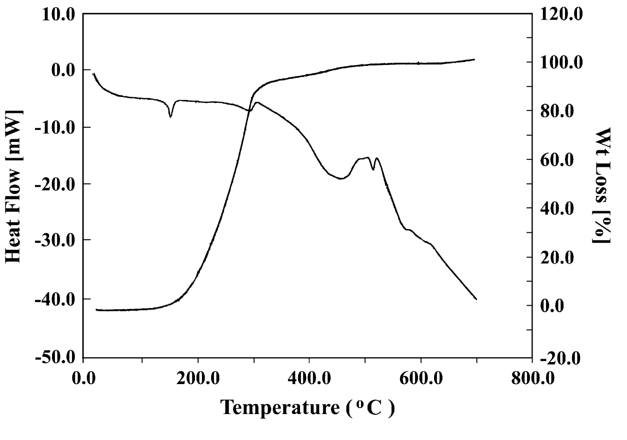


Fig. 9. TGA–DSC of **10** with a heating rate of 10 °C/min in nitrogen atmosphere.

Table 2
Comparison of thermal properties of **4a**, **4b**, **4d**, **4e**, **4f**, and 1-methylamino-9,10-anthraquinone (**10**)

Compound	T_0[a] (°C)	T_5[b] (°C)	T_{10}[c] (°C)	Char yield[d] (%)
4a	240	260	280	42
4b	177	189	215	10
4d	153	177	208	12
4e	210	231	251	11
4f	207	215	223	13
10	140	172	184	5

[a] The initial decomposition temperature by TGA at a heating rate of 10 °C/min in nitrogen atmosphere.

[b] Temperature at which 5% weight loss was recorded by TGA at a heating rate of 10 °C/min in nitrogen atmosphere.

[c] Temperature at which 10% weight loss was recorded by TGA at a heating rate of 10 °C/min in nitrogen atmosphere.

[d] Percentage weight of material left undecomposed after TGA analysis at the maximum temperature of 500 °C at heating rate of 10 °C/min in nitrogen atmosphere.

*4.2.3. Dimethyl 2-[bis(ethoxy)-phosphoryl]-3-[(9,10-dioxo-9,10-dihydro-1-anthracenyl)amino]-butanedioate (**4c**)*

Yield: 0.70 g (70%). Red powder. M.p.: 144–146 °C. IR (KBr): 1626 and 1679 (2C=O), 1730 (C=O, ester), 3445 (N–H). UV (CH_2Cl_2): 476, 302, 246 nm. EI-MS: 503 (2, M^+), 474 (14), 458 (16), 224 (25), 223 (65), 137 (16), 45 (87), 29 (65). Anal. calc. for $C_{24}H_{26}NO_9P$ (503.44): C, 57.26; H, 5.21; N, 2.78%; found: C, 57.28; H, 5.23; N, 2.80%. NMR data for the major isomer (60%). ^{1}H NMR: 1.10 (t, $^3J_{HH} = 7.2$, Me), 1.29 (t, $^3J_{HH} = 7.2$, Me), 3.65 (s, OMe), 3.73–3.74 [m, P(OCH_2CH$_3$)$_2$], 3.83–3.84 (m, CH), 3.85 (s, OMe), 4.1 (ddd, $^3J_{HH} = 10.3$, $^3J_{HP} = 7.0$, $^3J_{HH} = 4.5$, CH), 7.26–7.28 (m, CH), 7.54–7.57 (m, 2CH), 7.71–7.74 (m, 2CH), 8.19 (dd, $^3J_{HH} = 7.6$, $^4J_{HH} = 1.1$, CH), 8.32 (dd, $^3J_{HH} = 7.6$, $^4J_{HH} = 1.0$, CH), 10.60 (d, $^3J_{HH} = 10.3$, NH). ^{13}C NMR: 15.9 (Me), 16.0 (Me), 47.0 (d, $^1J_{PC} = 134.8$, CH), 53.0 (OMe), 53.5 (OMe), 53.8 (d, $^3J_{PC} = 2.6$, CH), 63.6 (d, $^3J_{PH} = 5.8$, OCH$_2$), 66.7 (d, $^3J_{PH} = 6.4$, OCH$_2$), 114.4 (CH), 117.0 (CH), 118.4 (CH), 126.6 (C), 127.1 (CH), 128.7 (CH), 130.8 (CH), 133.1 (C), 133.9 (CH), 134.0 (C), 135.2 (C), 150.4 (N–C), 167.7 (d, $^3J_{PC} = 3.8$, C=O), 170.8 (d, $^2J_{PC} = 15.0$, C=O), 183.6 and 185.2 (2C=O). ^{31}P NMR: 19.6. NMR data for the minor isomer (40%). ^{1}H NMR: 1.31 (t, $^3J_{HH} = 7.2$, Me), 1.34 (t, $^3J_{HH} = 7.2$, Me), 3.70 (s, OMe), 3.72–3.73 [m, P(OCH_2CH$_3$)$_2$], 3.83–3.88 (m, CH), 3.80 (s, OMe), 4.1 (ddd, $^3J_{HH} = 10.0$, $^3J_{HP} = 7.0$, $^3J_{HH} = 4.0$, CH), 7.26–7.28 (m, CH), 7.48–7.65 (m, 2CH), 7.66–7.74 (m, 2CH), 8.19 (dd, $^3J_{HH} = 7.6$, $^4J_{HH} = 1.1$, CH), 8.25 (dd, $^3J_{HH} = 8.0$, $^4J_{HH} = 1.2$, CH), 10.26 (d, $^3J_{HH} = 10.0$, NH). ^{13}C NMR: 15.8 (Me), 15.9 (Me), 47.9 (d, $^1J_{PC} = 134.7$, CH), 50.8 (OMe), 51.1 (OMe), 54.3 (d, $^3J_{PC} = 2.6$, CH), 63.4 (d, $^3J_{PH} = 6.0$, OCH$_2$), 66.6 (d, $^3J_{PH} = 6.3$, OCH$_2$), 114.4 (CH), 117.1 (CH), 118.2 (CH), 126.6 (C), 126.9 (CH), 127.6 (C), 128.7 (CH), 132.4 (CH), 133.2 (C), 134.0 (CH), 134.7 (C), 134.8 (CH), 135.3 (C), 149.9 (N–C), 165.9 (d, $^3J_{PC} = 5.0$, C=O), 169 (d, $^2J_{PC} = 16.0$, C=O), 183.4 and 185.3 (2C=O). ^{31}P NMR: 19.6.

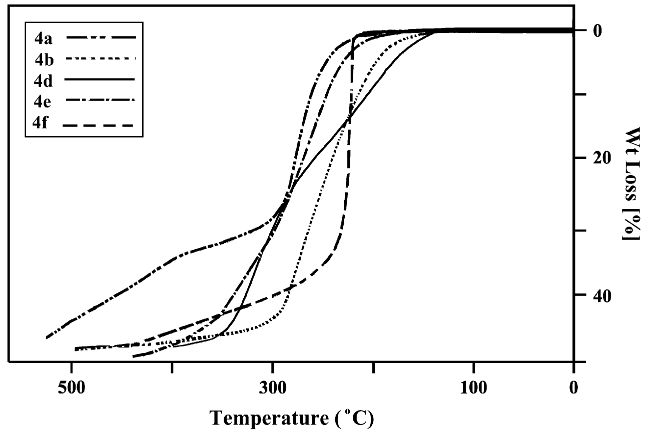


Fig. 10. Comparison of the TGA profiles of **4a**, **4b**, **4d**, **4e**, and **4f**, obtained with a heating rate of 10 °C/min in nitrogen atmosphere.

*4.2.4. Di-tert-butyl-2-[bis(ethoxy)-phosphoryl]-3-[(9,10-dioxo-9,10-dihydro-1-anthracenyl)amino]-butanedioate (**4d**)*

Yield: 1.0 g (85%). Orange powder. M.p.: 128–130 °C, IR (KBr): 1627 and 1662 (2C=O), 1722 (C=O, ester), 3415 (N–H). UV (CH_2Cl_2): 456, 304, 246 nm. EI-MS: 587 (4, M^+), 569 (42), 530 (18), 232 (28), 223 (15), 137 (18), 57 (100), 43(10), 41 (10). Anal. calc. for $C_{30}H_{38}NO_9P$ (587.60): C, 61.32; H, 6.52; N, 2.38%; found: C, 61.34; H, 6.54; N, 2.40%. NMR data for the major isomer (60%). ^{1}H NMR: 0.90 (t, $^3J_{HH} = 7.0$, Me), 1.14 (t, $^3J_{HH} = 7.0$, Me), 1.41 (s, CMe_3), 1.58 (s, CMe_3), 3.83 (dd, $^2J_{HP} = 25.2$, $^3J_{HH} = 4.5$, CH), 4.10–4.20 [m, P(OCH_2CH$_3$)$_2$], 4.86–4.87 (ddd, $^3J_{HH} = 10.0$, $^3J_{HP} = 7.7$, $^3J_{HH} = 4.5$, CH), 7.28–7.30 (d, $^3J_{HH} = 8.5$, CH), 7.51–7.53 (m, 2CH), 7.66–7.68 (m, 2CH), 8.23 (dd, $^3J_{HH} = 7.5$, $^4J_{HH} = 0.8$, CH), 8.35 (dd, $^3J_{HH} = 7.5$, $^4J_{HH} = 0.8$, CH), 10.51 (d, $^3J_{HH} = 10.0$, NH). ^{13}C NMR: 16.3 (Me), 16.4 (Me), 27.8 (CMe_3), 27.9 (CMe_3), 47.8 (d, $^1J_{PC} = 132.9$, CH), 55.4 (d, $^3J_{PC} = 3.1$, CH), 62.6 (OCH$_2$), 63.2 (OCH$_2$), 82.7 (CMe$_3$), 83.5 (CMe$_3$), 114.3 (CH), 116.9 (CH), 118.9 (CH) 126.5 (CH), 126.9 (C), 127.1 (CH), 128.8 (CH), 130.8 (C), 132.9 (CH), 133.8 (C), 135.1 (C), 150.9 (N–C), 165.8 (d, $^3J_{PC} = 5.0$, C=O), 169.0 (d, $^2J_{PC} = 15.0$, C=O), 183.8 and 184.8 (2C=O). ^{31}P NMR: 21.2. NMR data for the minor isomer (40%). ^{1}H NMR: 0.9 (t, $^3J_{HH} = 7.0$, Me), 1.43 (s, CMe_3), 1.44 (t, $^3J_{HH} = 7.0$, Me), 1.50 (s, CMe_3), 3.83 (dd, $^2J_{HP} = 25.2$, $^3J_{HH} = 4.4$, CH), 3.9–4.0 [m, P(OCH_2CH$_3$)$_2$], 4.88 (ddd, $^3J_{HH} = 10.0$, $^3J_{HP} = 7.6$, $^3J_{HH} = 4.4$, CH), 7.37–7.39 (d, $^3J_{HH} = 8.5$, CH), 7.54–7.57 (m, 2CH), 7.76–7.78 (m, 2CH), 8.23 (dd, $^3J_{HH} = 7.5$, $^4J_{HH} = 0.8$, CH), 8.35 (dd, $^3J_{HH} = 7.3$, $^4J_{HH} = 0.9$, CH), 10.21 (d, $^3J_{HH} = 10.0$, NH). ^{13}C NMR: 16.1 (Me), 16.2 (Me), 27.8 (CMe_3), 28.0 (CMe_3), 48.6 (d, $^1J_{PC} = 134.1$, CH), 55.5 (d, $^3J_{PC} = 3.0$, CH), 62.7 (OCH$_2$), 62.8 (OCH$_2$), 81.9 (CMe$_3$), 83.5 (CMe$_3$), 114.3 (CH), 116.9 (CH), 118.9 (CH) 126.6 (CH), 126.7 (C), 127.1 (CH), 128.8 (CH), 130.8 (C), 132.4 (CH), 133.9 (C), 134.6 (C), 150.2 (N–C), 165.7 (d, $^3J_{PC} = 6.0$, C=O), 170.0 (d, $^2J_{PC} = 20.0$, C=O), 183.6 and 185.0 (2C=O). ^{31}P NMR: 20.9.

4.2.5. Diethyl 2-[bis(phenyloxy)-phosphoryl]-3-[(9,10-dioxo-9,10-dihydro-1-anthracenyl)amino]-butanedioate (**4e**)

Yield: 0.94 g (75%). Red powder. M.p.: 175.0–176.0 °C. IR (KBr): 1628 and 1668 (2C=O), 1730 (C=O, ester), 3428 (N–H). UV (CH_2Cl_2): 476, 310, 240 nm. EI-MS: 627 (6, M^+), 485 (10), 223 (100), 167 (40), 139 (36), 113 (20), 71 (16), 57 (20), 43 (25). Anal. calc. for $C_{34}H_{30}NO_9P$ (627.58): C, 65.06; H, 4.82; N, 2.23%; found: C, 65.08; H, 4.85; N, 2.27%. NMR data for the major isomer (65%). ^{1}H NMR: 1.16 (t, $^{3}J_{HH} = 7.0$, Me), 1.42 (t, $^{3}J_{HH} = 7.0$, Me), 4.16 (q, $^{3}J_{HH} = 7.0$, CH_2O), 4.29 (dd, $^{2}J_{HP} = 25.3$, $^{3}J_{HH} = 4.0$, CH), 4.33 (q, $^{3}J_{HH} = 7.0$, CH_2), 5.19 (ddd, $^{3}J_{HH} = 10.3$, $^{3}J_{HP} = 7.6$, $^{3}J_{HH} = 4.0$, CH), 6.77–6.78 (m, CH), 6.92–6.93 (m, 4CH), 7.10–7.12 (m, CH), 7.22–7.25 (m, CH), 7.26–7.35 (m, 4CH), 7.49–7.53 (m, CH), 7.63–7.67 (m, CH), 7.70–7.74 (m, 2CH), 8.20–8.24 (m, CH), 8.31 (dd, $^{3}J_{HH} = 7.7$, $^{4}J_{HH} = 1.1$, CH), 10.72 (d, $^{3}J_{HH} = 10.3$, NH). ^{13}C NMR: 13.9 (Me), 14.1 (Me), 47.0 (d, $^{1}J_{PC} = 136.9$, CH), 53.8 (d, $^{3}J_{PC} = 2.3$, CH), 62.3 (d, $^{3}J_{PC} = 5.0$, OCH_2), 62.5 (d, $^{3}J_{PC} = 5.0$, OCH_2), 114.6 (CH), 115.3 (CH), 117.0 (CH), 118.7 (CH), 120.0 (d, $^{3}J_{PC} = 3.5$, CH), 120.4 (CH), 120.7 (d, $^{3}J_{PC} = 4.4$, CH), 124.8 (CH), 125.5 (CH), 125.6 (CH), 126.6 (CH), 127.1 (CH), 129.2 (CH), 129.4 (CH), 129.6 (C), 129.9 (CH), 133.0 (CH), 133.7 (CH), 134.4 (C), 134.6 (CH), 134.7 (C), 134.9 (C), 149.6 (C), 149.8 (C), 150.0 (N–C), 166.4 (d, $^{3}J_{PC} = 5.0$, C=O), 170.2 (d, $^{2}J_{PC} = 17.0$, C=O), 183.6 and 184.9 (2C=O). ^{31}P NMR: 13.2. NMR data for the minor isomer (35%). ^{1}H NMR: 1.22 (t, $^{3}J_{HH} = 7.0$, Me), 1.29 (t, $^{3}J_{HH} = 7.0$, Me), 4.18 (q, $^{3}J_{HH} = 7.0$, CH_2O), 4.29 (dd, $^{2}J_{HP} = 25.3$, $^{3}J_{HH} = 3.5$, CH), 4.40 (q, $^{3}J_{HH} = 7.0$, CH_2), 5.32 (ddd, $^{3}J_{HH} = 9.5$, $^{3}J_{HP} = 6.0$, $^{3}J_{HH} = 3.5$, CH), 6.78–6.79 (m, CH), 6.92–6.93 (m, 4CH), 7.10–7.12 (m, CH), 7.22–7.25 (m, CH), 7.26–7.35 (m, 4CH), 7.49–7.53 (m, CH), 7.63–7.67 (m, CH), 7.70–7.74 (m, 2CH), 8.20–8.24 (m, CH), 8.31 (dd, $^{3}J_{HH} = 7.7$, $^{4}J_{HH} = 1.1$, CH), 10.45 (d, $^{3}J_{HH} = 9.5$, NH). ^{13}C NMR: 13.9 (Me), 14.0 (Me), 48.10 (d, $^{1}J_{PC} = 135.8$, CH), 54.4 (d, $^{3}J_{PC} = 2.9$, CH), 62.3 (d, $^{3}J_{PC} = 4.0$, OCH_2), 62.4 (d, $^{3}J_{PC} = 5.0$, OCH_2), 114.6 (CH), 115.3 (CH), 117.0 (CH), 118.7 (CH), 120.0 (d, $^{3}J_{PC} = 4.7$, CH), 120.4 (CH), 120.7 (d, $^{3}J_{PC} = 4.4$, CH), 124.8 (CH), 125.5 (CH), 125.6 (CH), 126.6 (CH), 127.1 (CH), 129.2 (CH), 129.6 (C), 129.9 (CH), 133.0 (CH), 133.7 (CH), 134.4 (C), 134.6 (CH), 134.7 (C), 134.9 (C), 149.9 (C), 150.0 (C), 150.1 (N–C), 165.9 (d, $^{3}J_{PC} = 6.2$, C=O), 169.4 (d, $^{2}J_{PC} = 11.0$, C=O), 183.4 and 185.2 (2C=O). ^{31}P NMR: 12.8.

4.2.6. Di-tert-butyl-2-[bis(phenyloxy)-phosphoryl]-3-[(9,10-dioxo-9,10-dihydro-1-anthracenyl)amino]-butanedioate (**4f**)

Yield: 1.20 g (90%). Red-violet powder. M.p.: 154.0–154.2 °C, IR (KBr): 1629 and 1662 (2C=O), 1728 (C=O, ester), 3435 (N–H). UV (CH_2Cl_2): 485, 311, 243 nm. EI-MS: 683 (2, M^+), 581 (8), 482 (5), 294 (6), 232 (36), 223 (10), 167 (8), 132 (6), 57 (100), 41 (10). Anal. calc. for $C_{38}H_{38}NO_9P$ (683.69): C, 66.76; H, 5.60; N, 2.05%; found: C, 66.78; H, 5.70; N, 2.05%. NMR data for the major isomer (99%). ^{1}H NMR: 1.41 (s, CMe_3), 1.63 (s, CMe_3), 4.22 (dd, $^{2}J_{HP} = 25.8$ Hz, $^{3}J_{HH} = 4.1$, CH), 5.23–5.27 (ddd, $^{3}J_{HH} = 10.2$, $^{3}J_{HP} = 6.9$, $^{3}J_{HH} = 4.1$, CH), 6.83–6.85 (m, CH), 7.00–7.04 (m, 4CH), 7.21–7.23 (m, CH), 7.28–7.30 (m, 2CH), 7.37–7.40 (m, CH), 7.51–7.61 (m, 3CH), 7.81–7.84 (m, 2CH), 8.18 (dd, $^{3}J_{HH} = 7.3$, $^{4}J_{HH} = 1.0$, CH), 8.24–8.26 (m, CH), 10.7 (d, $^{3}J_{HH} = 10.2$, NH). ^{13}C NMR: 28.0 (CMe_3), 28.2 (CMe_3), 49.7 (d, $^{1}J_{PC} = 134.5$, CH), 55.0 (d, $^{3}J_{PC} = 4.0$,CH), 82.7 (CMe_3), 82.9 (CMe_3), 114.5 (CH), 115.3 (CH), 117.0 (CH), 120.4 (CH), 120.9 (CH), 121.0 (d, $^{3}J_{PC} = 4.9$, CH), 121.6 (d, $^{3}J_{PC} = 4.4$, CH), 125.5 (CH), 126.1 (CH), 126.3 (CH) 127.0 (C), 127.14 (CH), 127.5 (CH), 130.1 (CH), 130.5 (C), 130.7 (CH), 133.7 (CH), 134.0 (CH), 134.9 (CH), 135.7(C), 136.1 (C), 150.2 (C), 151.2 (C), 152.2 (N–C), 166.3 (d, $^{3}J_{PC} = 5.0$, C=O), 169.6 (d, $^{2}J_{PC} = 19.0$, C=O), 183.8 and 185.3 (2C=O). ^{31}P NMR: 14.4. NMR data for the minor isomer (1%). ^{31}P NMR: 13.7.

References

[1] Herbst W, Hunger K, editors. Industrial organic pigments. Wiley-VCH; 2004.

[2] Hunger K, editor. Industrial dyes. Wiley-VCH; 2003.

[3] Smith HM, editor. High performance pigments. Wiley-VCH; 2003.

[4] Patai S, Rappaport Z, editors. The chemistry of quinonoid compounds, vols. 1 and 2. New York: Wiley-Interscience; 1988.

[5] Patai S, editor. The chemistry of quinonoid compounds, vols. 1 and 2. New York: Wiley-Interscience; 1974.

[6] Thomsom RH. Naturally occurring quinones. New York: Academic Press; 1971.

[7] Miki S, Noda R, Fukunishi K. Photo- and electro-chromism of a 1,4-anthraquinone derivative. A multi-mode responsive molecule. J Chem Soc Chem Commun 1997;925–6.

[8] Boldt P, Zippel S, Haucke G. 1-Amino-4-(4-hydroxyalkylphenyl)- and 1-amino-4-(ω-hydroxyalkoxy)-9,10-anthraquinones for photochromic methacrylate polymers. J Chem Res Synop 1997;386–7.

[9] Babb DA, Boone HW, Smith DW, Rudolf PW. Perfluorocyclobutane aromatic ether polymers. Synthesis and thermal stability of a thermoset polymer containing triphenylphosphine oxide. J Appl Polym Sci 1998;69:2005–12.

[10] Yavari I, Alborzi A, Dehghan Sh, Nourmohammadian F. Synthesis of dialkyl-1-(9,10-dioxo-9,10-dihydro-1-anthracenyl)-4-ethoxy-5-oxo-4,5-dihydro-1*H*-pyrrole-2,3-dicarboxylates. Phosphorus, Sulfur, Silicon Relat Elem 2005;180:625–31.

[11] Yavari I, Alborzi AR, Mohtat B. Synthesis of highly functionalized 9,10-anthraquinones. Dyes Pigments 2006;68:85–8.

[12] Nair VJ, Rajesh C, Vinod AU, Bindu S, Sreekanth AR, Mathess JS, et al. Strategies for heterocyclic construction via novel multicomponent reactions based on isocyanides and nucleophilic carbenes. Acc Chem Res 2003;36:899–909.