REACTION OF N-BENZOYL-4,7-PHENANTHROLINIUM SALT WITH TRIMETHYL PHOSPHITE AND CRYSTAL STRUCTURE OF DIMETHYL N,N'-DIBENZOYL-3,4,7,8-TETRAHYDRO-4,7-PHENANTHROLINE-3,8-DIPHOSPHONATE

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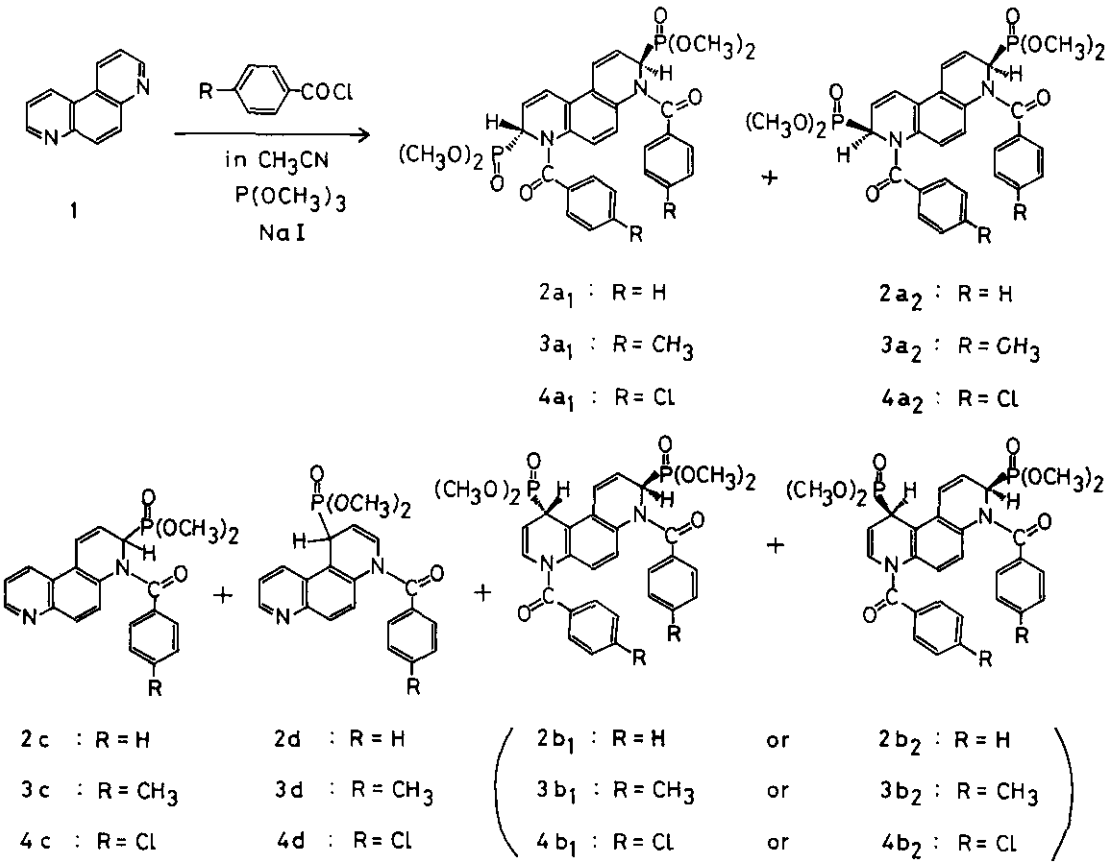
Abstruct ---- The reaction of 4,7-phenanthroline (1) with some substituted benzoyl chlorides and trimethyl phosphite in the presence of sodium iodide gave the corresponding α,α'-diphosphonates, α,γ'-diphosphonates, α-phosphonates, and γ-phosphonates respectively. 3,8-Diphosphonates (2a$_1$, 2a$_2$) were separated by thin layer chromatography and the crystal structure of 2a$_2$ was determined by X-ray analysis.

Recently, Akiba and his co-workers have reported the syntheses of α- and γ-phosphonates by the treatment of N-acyl salt of heteroaromatics with trialkyl phosphites and sodium iodide.[1]

The authors have hitherto conducted reactions between N-acyl derivatives of various nitrogen-containing heterocyclic compounds and phosphites to obtain a variety of phosphonates;[2] and have reported that, from 4,7-phenanthroline (p-phenanthroline), two kinds of diphosphonates were obtained via substitutions at α,α' positions of two ring nitrogens, and were found to be isomers with cis- and trans-forms against the plane of phenanthroline.[2b] As compared with the results, Reissert reaction of 4,7-phenanthroline with potassium cyanide gave mono-Reissert compound.[3] However treatment of 4,7-phenanthroline with trimethylsilyl cyanide afforded di-Reissert compound,[4] and the cis- or trans-isomer has not been separated as yet.

In the present study, we reexamined into the reaction of 4,7-phenanthroline with some substituted benzoyl chlorides and trimethyl phosphite in the presence of sodium iodide. 4,7-phenanthroline gave the corresponding α- and γ-phosphonates, and two kinds of α,α'-diphosphonates and α,γ'-diphosphonates which were separated into cis- and trans-isomers. (Scheme 1).



Scheme 1

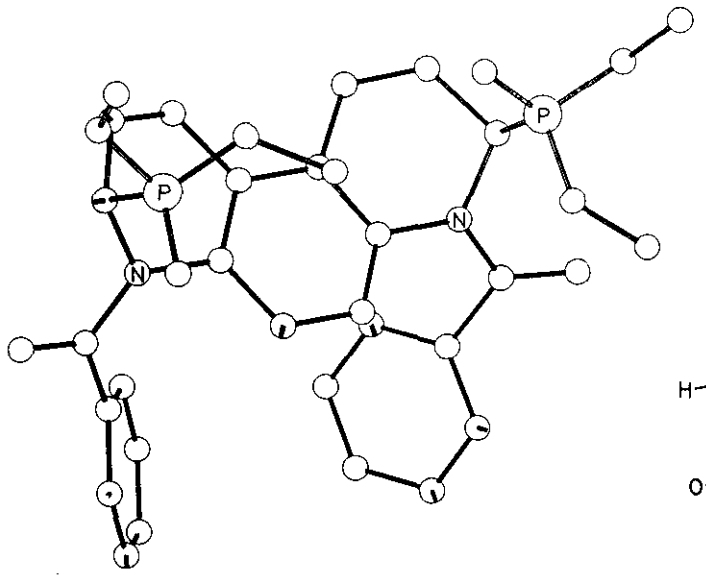


Figure 1A. Molecular structure of 2a$_2$

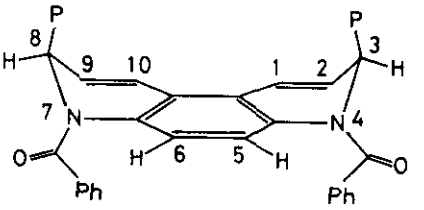


Figure 1B. Model illustration of 2a$_2$

The structures of these phosphonates were confirmed by ^{1}H-nmr spectroscopy, and that of $\underline{2a}_2$ by X-ray analysis. In the comparison between the cis- and trans-forms of α,α'-diphosphonate, the yields of the cis-forms were always higher. Because the cis-form has been sterically less favored. As to α,γ'-diphosphonate, its yield presumably decreased owing to the steric hindrance between the phosphonyl group at the γ-position and C_1-H.

X-RAY CRYSTAL STRUCTURE DETERMINATION OF $\underline{2a}_2$

The X-ray analysis confirmed the cis-form of $\underline{2a}_2$. (Figure 1A).
The phosphonyl group was found to be connected to the compound axially, with symmetry in bond lengths and bond angles of the compound. Figure 1B shows a model illustration of the cis-form viewed from an easy-to-understand direction.

^{1}H-NMR SPECTRUM

The protons, C_5-H and C_6-H, of $\underline{2a}_1$-$\underline{4a}_1$ and $\underline{2a}_2$-$\underline{4a}_2$ of α,α'-diphosphonate, gave singlets at 6.06-6.14 ppm, a higher field than for an ordinary proton. This is estimated to have been caused by the diamagnetic shift due to the adjacent phenyl group, as shown in the stereostructural formula derived by the X-ray analysis.
As $\underline{2a}_2$ of α,α'-diphosphonate was confirmed to be of a cis-form by the X-ray analysis, $\underline{2a}_1$, on the other hand, is estimated to be of a trans-form. ^{1}H-Nmr spectra of $\underline{2a}_1$ and $\underline{2a}_2$ were then compared. Generally they were much similar to each other, but the chemical shift of $POCH_3$ of $\underline{2a}_1$ (trans) appeared at a lower field by 0.04 ppm than that of $\underline{2a}_2$. The similar reaction was observed in the comparison between ($\underline{3a}_1$, $\underline{4a}_1$) and ($\underline{3a}_2$, $\underline{4a}_2$), both chemical shifts of $POCH_3$ of $\underline{3a}_1$ and $\underline{4a}_1$ being observed at lower fields by 0.05 ppm. Thus $\underline{3a}_1$ and $\underline{4a}_1$ are estimated to be a trans-form, and $\underline{3a}_2$ and $\underline{4a}_2$ of a cis-form. When the above relation with α,α'-di-phosphonate is assumed to be applicable to α,γ'-diphosphonate, the compounds, $\underline{2b}_2$-$\underline{4b}_2$, are estimated to be of a trans-form because the both signals standing for $POCH_3$ at the α position of them were observed at lower fields than that of $\underline{2b}_1$-$\underline{4b}_1$ by 0.03 ppm. Because no reliable standard material of α,γ'-diphosphonate is currently available, a structur analysis by other methods remains to be conducted.

The authors would like to add that they have previously reported that one of phosphonates revealed a weak muscle-relaxant activity,[2d] and we found that $\underline{2a}_2$ as a potential pesticide, at a concentration of 5000 ppm, exhibited a 90% or more of preventing effect against sheath blight.

EXPERIMENTAL

The ^{1}H-nmr spectra were recorded using a JEOL JNM GX-270 spectrometer. Chemical shifts are given in ppm from tetramethylsilane (TMS) as the internal standard, and coupling constants are given in Hz (s, singlet; d, doublet; dd, double doublet; m, multiplet). Mass spectra were taken with a Hitachi GC-MS M-80 spectrometer.

General Procedure for Synthesis of Phosphonates

Acyl chloride (10.6 mmol) was added to a solution of 4,7-phenanthroline (4.78 mmol) in acetonitrile (60 ml) at 0°C, and the mixture was stirred for 10 min. Then $P(OCH_3)_3$ (10.6 mmol) and NaI (14 mmol) were added to the reaction mixture at 0°C, and the mixture was warmed to 50°C with stirring for 10 min. The solvent was evaporated under reduced pressure, and 5% $NaHCO_3$ (50 ml) was added to the residue. The aqueous layer was extracted with CH_2Cl_2 and the extract was washed with water, and dried over anhydrous Na_2SO_4. Removal of the solvent afforded the crude phosphonate, which was purified by chromatography on silica gel with $CHCl_3$, and further more each fractions were separated using pre-coated tlc plates (Silica gel 60 F-254 20 X 20 cm, layer thickness 0.5 mm, MERCK) with EtOAc-EtOH (20:1) or MeCN, and recrystallized from EtOAc. The order of the developed in term of the magnitude of Rf value was as follows: starting material (1)(Rf=0.31) → γ-p.(2d-4d)(Rf=0.21, 0.25, 0.23) → α-p.(2c-4c)(Rf=0.13, 0.16, 0.15) → α,α'-p.($2a_1$-$4a_1$)(Rf=0.09, 0.12, 0.10) → α,γ'-p.($2b_1$-$4b_1$)(Rf=0.07, 0.09, 0.08) → α,γ'-p.($2b_2$-$4b_2$)(Rf=0.04, 0.07, 0.05) → α,α'-p.($2a_2$-$4a_2$)(Rf=0.02, 0.05, 0.03).

trans-Dimethyl N,N'-Dibenzoyl-3,4,7,8-tetrahydro-4,7-phenanthroline-3,8-diphsphonate ($2a_1$): Colorless prisms, mp 214-216°C (EtOAc)(lit.,[2c] mp 204-206°C), yield 1.4%. Nmr ($CDCl_3$) δ: 3.61, 3.74 (3H, d, J=10.8Hz, $POCH_3)_2$, 5.89 (2H, dd, J_{PCH}=21.9, 6.1Hz, $C_{3,8}$-H), 6.07 (2H, s, $C_{5,6}$-H), 6.38 (2H, m, $C_{2,9}$-H), 7.05 (2H, dd, J=9.4, 5.4 Hz, $C_{1,10}$-H), 7.12-7.35 (10H, m, Ph-H).

trans-Dimethyl N,N'-Di-p-toluoyl-3,4,7,8-tetrahydro-4,7-phenanthroline-3,8-diphosphonate ($3a_1$): Colorless prisms, mp 218-220°C (EtOAc), yield 0.3%. Ms m/z: 636 (M^+). Anal. Calcd for $C_{32}H_{34}N_2O_8P_2$: C, 60.38; H, 5.38; N, 4.40. Found: C, 60.64; H, 5.25; N, 4.82. Nmr ($CDCl_3$) δ: 2.27 (6H, s, $2CH_3$), 3.62 (3H, d, J=10.8 Hz, $POCH_3$), 3.74 (3H, d, J=11.1 Hz, $POCH_3$), 5.88 (2H, dd, J_{PCH}=21.5, 6.4 Hz, $C_{3,8}$-H), 6.12 (2H, s, $C_{5,6}$-H), 6.37 (2H, m, $C_{2,9}$-H), 6.96, 7.14 (4H, d, J=8.1 Hz, Ph-H), 7.05 (2H, dd, J=9.7, 5.4 Hz, $C_{1,10}$-H).

trans-Dimethyl N,N'-Di-p-chlorobenzoyl-3,4,7,8-tetarahydro-4,7-phenanthroline-3,8-diphosphonate ($4a_1$): Colorless prisms, mp 235-237°C (decomp.)(EtOAc), yield 0.2%. Anal.

Calcd for $C_{30}H_{28}N_2O_8Cl_2P_2$: C, 53.19; H, 4.17; N, 4.14. Found: C, 53.44; H, 4.11; N, 3.86. Nmr ($CDCl_3$) δ: 3.63, 3.77 (6H, d, J=10.8 Hz, $POCH_3)_2$, 5.84 (2H, dd, J_{PCH}=21.9, 6.7 Hz, $C_{3,8}$-H), 6.12 (2H, s, $H_{5,6}$-H), 6.37 (2H, m, $C_{2,9}$-H), 7.05 (2H, dd, J=9.8, 5.4 Hz, $C_{1,10}$-H), 7.17, 7.20 (4H, d, J=9.1 Hz, Ph-H)$_2$. Ms m/z: 676 (M^+).

cis-Dimethyl N,N'-Dibenzoyl-3,4,7,8-tetrahydro-4,7-phenanthroline-3,8-diphosphonate (2a$_2$): Colorless prisms, mp 208-210°C (lit.,[2c] 196-198°C)(EtOAc), yield 12%. Nmr ($CDCl_3$) δ: 3.57, 3.72 (3H, d, J=10.8 Hz, $POCH_3)_2$, 5.88 (2H, dd, J_{PCH}=21.5, 6.4 Hz, $C_{3,8}$-H), 6.06 (2H, s, $C_{5,6}$-H), 6.35 (2H, m, $C_{2,9}$-H), 7.04 (2H, dd, J=9.5, 5.4 Hz, $C_{1,10}$-H), 7.17-7.36 (10H, m, Ph-H).

cis-Dimethyl N,N'-Di-p-toluoyl-3,4,7,8,-tetrahydro-4,7-phenanthroline-3,8-diphosphonate (3a$_2$): Colorless prisms, mp 223-225°C(EtOAc), yield 8.2%. Anal. Calcd for $C_{32}H_{34}N_2O_8P_2$: C, 60.38; H, 5.38; N, 4.40. Found: C, 60.18; H, 5.35; N, 4.73. Nmr ($CDCl_3$) δ: 2.37 (6H, s, $2CH_3$), 3.57, 3.73 (3H, d, J=10.8 Hz, $POCH_3)_2$, 5.88 (2H, dd, J_{PCH}=21.5, 6.4 Hz, $C_{3,8}$-H), 6.14 (2H, s, $C_{5,6}$-H), 7.04 (2H, $C_{1,10}$-H)[6], 7.04, 7.22 (4H, d, J=8.1 Hz, Ph-H). Ms m/z: 636 (M^+).

cis-Dimethyl N,N'-Di-p-chlorobenzoyl-3,4,7,8-tetrahydro-4,7-phenanthroline-3,8-diphosnate (4a$_2$): Colorless prisms, mp 227-230°C (EtOAc), yield 3.7%. Ms m/z: 676 (M^+). Anal. Calcd for $C_{30}H_{28}N_2O_8Cl_2P_2$: C, 53.19; H, 4.17; N, 4.14. Found: C, 53.07; H, 4.42, N, 3.96. Nmr ($CDCl_3$) δ: 3.58 (3H, d, J=10.8 Hz, $POCH_3$), 3.73 (3H, d, J=11.1 Hz, $POCH_3$), 5.85(2H, dd, J_{PCH}=21.5, 6.4 Hz, $C_{3,8}$-H), 6.12 (2H, s, $C_{5,6}$-H), 6.37 (2H, m, $C_{2,9}$-H), 7.04 (2H, dd, J=9.8, 5.4 Hz, $C_{1,10}$-H), 7.25 (8H, s, Ph-H).

trans- or cis-Dimethyl N,N'-Dibenzoyl-3,4,7,10-tetrahydro-4,7-phenanthroline-3,10-diphosphonate (2b$_1$ or 2b$_2$)

2b$_1$: Gummy oil, yield 0.8%. Ms m/z: 608 (M^+). Nmr ($CDCl_3$) δ: 3.53 (3H, d, J=10.8 Hz, $POCH_3$), 3.68 (3H, d, J=11.1 Hz, $POCH_3$), 3.78, 3.83 (3H, d, J=10.4 Hz, $POCH_3)_2$, 4.31 (1H, dd, J_{PCH}=24.5, 6.7 Hz, C_{10}-H), 5.43 (1H, m, C_9-H), 5.88 (1H, dd, J_{PCH}=21.2, 6.7 Hz, C_3-H), 6.28 (1H, C_5-H)[6], 6.35 (1H, m, C_2-H), 6.38 (1H, t, J=7.1 Hz, C_8-H), 6.65 (1H, d, J=8.7 Hz, C_6-H), 7.16 (1H, dd, J=9.1, 5.4 Hz, C_1-H), 7.15-7.45 (8H, m, Ph-H), 7.61 (2H, m, Ph-H).

2b$_2$: Gummy oil, yield 1.2%. Ms m/z: 608 (M^+). Nmr ($CDCl_3$) δ: 3.56, 3.68, 3.75, 3.80 (3H, d, J=10.8 Hz, $POCH_3)_4$, 4.36 (1H, dd, J_{PCH}=25.2, 6.7 Hz, C_{10}-H), 5.53 (1H, m, C_9-H), 5.88 (1H, dd, J_{PCH}=21.5, 6.4 Hz, C_3-H), 6.28 (1H, C_5-H)[6], 6.34 (1H, m, C_2-H), 6.56 (1H, d, J=8.7 Hz, C_6-H), 6.91 (1H, dd, J=9.8, 5.0 Hz, C_1-H), 7.19-7.40 (8H, m, Ph-H), 7.46 (1H, t, J=7.1 Hz, C_8-H), 7.65 (2H, m, Ph-H).

trans- or cis-Dimethyl N,N'-Di-p-toluoyl-3,4,7,10tetrahydro-4,7-phenanthroline-3,10-diphosphonate (3b$_1$ or 3b$_2$)

3b$_1$: Gummy oil, yield 1.1%. Ms m/z: 636 (M^+). Nmr ($CDCl_3$) δ: 2.35, 2.37 (3H, s, CH_3)$_2$ 3.52, 3.67, 3.78 (3H, d, J=10.8 Hz, $POCH_3$)$_3$, 3.82 (3H, d, J=11.1 Hz, $POCH_3$), 4.31 (1H, dd, J_{PCH}=24.5, 6.7 Hz, C_{10}-H), 5.42 (1H, m, C_9-H), 5.88 (1H, dd, J_{PCH}=21.5, 6.7 Hz, C_3-H), 6.32 (1H, C_5-H)[6], 6.34 (1H, m, C_2-H), 6.64 (1H, d, J=8.7 Hz, C_6-H), 7.17 (1H, C_1-H)[6], 7/41 (1H, t, J=7.1 Hz, C_8-H), 7.03, 7.13, 7.19, 7.53 (2H, d, J=8.1 Hz)$_4$.

3b$_2$: Gummy oil, yield 2.0%. Ms m/z: 636 (M^+). Nmr ($CDCl_3$) δ: 2.28, 2.32 (3H, s, CH_3)$_2$ 3.55, 3.68, 3.78 (3H, d, J=10.8Hz, $POCH_3$)$_3$, 3.73 (3H, d, J=10.4 Hz, $POCH_3$), 4.36 (1H, dd, J_{PCH}=25.2, 6.7 Hz, C_{10}-H), 5.52 (1H, m, C_9-H), 5.87 (1H, dd, J_{PCH}=20.8, 6.4 Hz, C_3-H),6.29 (1H, C_5-H)[6], 6.53 (1H, d, J=9.1 Hz, C_6-H), 6.90 (1H, dd, J=9.8, 5.1 Hz, C_1-H), 7.51 (1H, t, J=7.1 Hz, C_8-H), 7.01, 7.05 (2H, d, J=8.4 Hz, Ph-H)$_2$, 7.15, 7.54 (2H, d, J=8.1 Hz, Ph-H)$_2$.

trans- or cis-Dimethyl N,N'-Di-p-chlorobenzoyl-3,4,7,10-tetrahydro-4,7-phenanthroline-3,10-diphosphonate (4b$_1$ or 4b$_2$)

4b$_1$: Gummy oil, yield 0.3%. Ms m/z: 676 (M^+). Nmr ($CDCl_3$) δ: 3.54, 3.68, 3.80, 3.83 (3H, d, J=10.8 Hz, $POCH_3$)$_4$, 4.31 (1H, dd, J_{PCH}=24.5, 6.7 Hz, C_{10}-H), 5.46 (1H, m, C_9-H), 5.83 (1H, dd, J_{PCH}=21.5, 6.7 Hz, C_3-H), 6.28 (1H, C_5-H)[6], 6.37 (1H, m, C_2-H), 6.57 (1H, d, J=8.7 Hz, C_6-H), 7.14 (1H, dd, J=9.7, 5.7 Hz, C_1-H),7.23 (4H, s, Ph-H), 7.33, 7.59 (2H, d, J=8.4 Hz, Ph-H)$_2$.

4b$_2$: Gummy oil, yield 0.8%. Ms m/z: 676 (M^+). Nmr ($CDCl_3$) δ: 3.57, 3.70, 3.72, 3.80 (3H, d, J=10.8 Hz, $POCH_3$)$_4$, 4.34 (1H, dd, J_{PCH}=25.5, 6.4 Hz, C_{10}-H), 5.53 (1H, m, C_9-H), 5.83 (1H, dd, J_{PCH}=20.8, 6.1 Hz, C_3-H), 6.32 (1H, C_5-H)[6], 6.33 (1H, m, C_2-H), 6.62 (1H, d, J=9.1 Hz, C_6-H), 6.90 (1H, dd, J=9.1, 5.4 Hz, C_1-H), 7.22 (4H, s, Ph-H), 7.42 (1H, t, J=7.1 Hz, C_8-H), 7.26, 7.66 (2H, d, J=8.4 Hz, Ph-H)$_2$.

Dimethyl N-Benzoyl-3,4-dihydro-4,7-phenanthroline-3-phosphonate (2c): Gummy oil, yield 1.5%. Ms m/z: 394 (M^+). Nmr ($CDCl_3$) δ: 3.45, 3.70 (3H, d, J=10.8 Hz, $POCH_3$)$_2$, 6.03 (1H, dd, J_{PCH}=21.2, 6.4 Hz, C_3-H), 6.46 (1H, m, C_2-H), 6.96 (1H, d, J=9.1 Hz, C_5-H), 7.22-7.40 (5H, m, Ph-H), 7.44 (1H, dd, J=8.7, 5.0 Hz, C_1-H), 7.48 (1H, dd, J=8.4, 4.4 Hz, C_9-H), 7.63 (1H, d, J=9.1 Hz, C_6-H), 8.44 (1H, dd, J=8.4, 1.7 Hz, C_{10}-H), 8.88 (1H, dd, J=4.4, 1.7 Hz, C_8-H).

Dimethyl N-p-Toluoyl-3,4-dihydro-4,7-phenanthroline-3-phosphonate (3c): Gummy oil, yield 2.0%. Ms m/z: 408 (M^+). Nmr ($CDCl_3$) δ: 2.32 (3H, s, CH_3), 3.45, 3.70 (3H, d, J=10.8 Hz, $POCH_3$)$_2$, 6.01 (1H, dd, J=21.5, 6.7 Hz, C_3-H), 6.45 (1H, m, C_2-H), 6.97 (1H, d, J=9.1 Hz, C_5-H), 7.04, 7.25 (2H, d, J=8.1 Hz, Ph-H)$_2$, 7.43 (1H, dd, J=9.4, 5.4 Hz, C_1-H), 7.47 (1H, dd, J=8.4, 4.4 Hz, C_9-H), 7.63 (1H, d, J=9.1 Hz, C_6-H), 8.43 (1H, d, J=8.4 Hz, C_{10}-H), 8.87 (1H, dd, J=4.4, 1.7 Hz, C_8-H).

Dimethyl N-p-Chlorobenzoyl-3,4-dihydro-4,7-phenanthroline-3-phosphonate (4c): Gummy

oil, yield 2.0%. Ms m/z: 440 (M^+). Nmr ($CDCl_3$) δ: 3.47, 3.68 (3H, d, J=10.8 Hz, $POCH_3$)$_2$, 5.98 (1H, dd, J_{PCH}=21.5, 6.4 Hz, C_3-H), 6.45 (1H, m, C_2-H), 6.95 (1H, d, J=9.1 Hz, C_5-H), 7.23, 7.31 (2H, d, J=8.7 Hz, Ph-H)$_2$, 7.43 (1H, dd, J=9.4, 5.4 Hz, C_1-H), 7.48 (1H, dd, J=8.4, 4.4 Hz, C_9-H), 7.67 (1H, d, J=9.1 Hz, C_6-H), 8.43 (1H, d, J=8.4 Hz, C_{10}-H), 8.89 (1H, dd, J=4.4, 1.7 Hz, C_8-H).

Dimethyl N-Benzoyl-1,4-dihydro-4,7-phenanthroline-1-phosphonate (2d): Colorless prisms, mp 200-202°C (EtOAc), yield 0.3%. Ms m/z: 394 (M^+). Anal. Calcd for $C_{21}H_{19}N_2O_4P$: C, 63.96; H, 4.86; N, 7.10. Found: C, 64.15; H, 4.80; N, 7.33. Nmr ($CDCl_3$) δ: 3.68 (3H, d, J=10.8 Hz, $POCH_3$), 3.72 (3H, d, J=10.4 Hz, $POCH_3$), 4.76 (1H, dd, J_{PCH}=24.5, 6.4 Hz, C_1-H), 5.58 (1H, m, C_2-H), 7.34-7.52 (3H, m, Ph-H), 7.39 (1H, C_5-H), 7.50 (1H, dd, J=8.7, 4.0 Hz, C_9-H), 7,58 (1H, t, J=7.1 Hz, C_3-H), 7.72 (2H, m, Ph-H), 7.80 (1H, d, J=9.4 Hz, C_6-H), 8.46 (1H, d, J=8.7 Hz, C_{10}-H), 8.90 (1H, dd, J=4.0, 1.4 Hz, C_8-H).

Dimethyl N-p-Toluoyl-1,4-dihydro-4,7-phenanthroline-1-phosphonate (3d): Colorless prisms, mp 189-191°C (decomp.)(EtOAc), yield 1.4%. Ms m/z: 408 (M^+). Anal. Calcd for $C_{22}H_{21}N_2O_4P$: C, 64.70; H, 5.18; N, 6.86. Found: C, 64.52; H, 5.27; N, 6.59. Nmr ($CDCl_3$) δ: 2.38 (3H, s, CH_3), 3.68 (3H, d, J=10.8 Hz, $POCH_3$), 3.72 (3H, d, J=10.4 Hz, $POCH_3$), 4.76 (1H, dd, J_{PCH}=24.5, 6.4 Hz, C_1-H), 5.57 (1H, m, C_2-H), 7.18, 7.62 (2H, d, J=8.4 Hz, Ph-H)$_2$, 7.35 (1H, d, J=9.4 Hz, C_5-H), 7.50 (1H, dd, J=8.4, 4.0 Hz, C_9-H), 7.61 (1H, t, J=7.1 Hz, C_3-H), 7.79 (1H, d, J=9.4 Hz, C_6-H), 8.46 (1H, d, J=8.4 Hz, C_{10}-H), 8.89 (1H, dd, J=4.0, 1.3 Hz, C_8-H).

Dimethyl N-p-Chlorobenzoyl-1,4-dihydro-4,7-phenanthroline-1-phosphonate (4d): Colorless prisms, mp 183-185°C (EtOAc), yield 0.2%. Ms m/z: 440 (M^+). Anal. Calcd for $C_{22}H_{18}ClN_2O_4P$: C, 59.94; H, 4.12; N, 6.35. Found: C, 60.05; H, 4.22; N, 6.49. Nmr ($CDCl_3$) δ: 3.68 (3H, d, J=10.8 Hz, $POCH_3$), 3.72 (3H, d, J=10.4 Hz, $POCH_3$), 4.75 (1H, dd, J_{PCH}=24.5, 6.4 Hz, C_1-H), 5.60 (1H, m, C_2-H), 7.33 (1H, C_5-H)[6], 7.36, 7.70 (2H, d, J=8.4 Hz, Ph-H)$_2$, 7.52 (1H, dd, J=8.7, 4.4 Hz, C_9-H), 7.57 (1H, t, J=7.1 Hz, C_3-H), 7.83 (1H, d, J=9.1 Hz, C_6-H), 8.45 (1H, d, J=8.7 Hz, C_{10}-H), 8.91 (1H, dd, J=4.4, 1.4 Hz, C_8-H).

X-Ray crystallography

Formula: $C_{30}H_{30}N_2O_8P_2$, Mw: 230.27

A crystal of colorless prisms with dimentions 0.4 x 0.4 x 0.3 mm^3 was mounted on a Rigaku AFC-6B four-circle diffractometer with graphite-monochromated Mo Kα radiation. The crystal data are: space group Pnma with z=2, a=12.123(6), b=12.091(5), c=12.893 (6)Å, α=106.17(4), β=116.94(3), γ=61.05(4)° . V=1468.9(1)$Å^3$. (Mo Kα)=2.08 cm^{-1}. Dx=1.376g/cm^3, F(000)=636. Within the range of 2θ<50°, 4146 indipendent reflections

with $|Fo|>3\sigma F$ were collected for backgraund, Lorenz, and polarization factors, but absorption correction was not applied. Positional parameters of all atoms were refined by the block-diagonal least-squares methods with the anisotropic thermal parameters. The hydrogen atom included on the structure factor calcurations were located from the difference map. $\Sigma w\Delta F^2$ minimized with $\omega=1.0$. The final R value was 0.068(Rw=0.0829). The atomic scattering factors were taken from the International Tables for X-Ray Crystallography.[5] Lists of the anisotropic thermal parameters and the final positional parameters, tables of the bond distances, angles, and a table of the observed and calculated structure factors are preserved by the HETEROCYCLES. The structure-analysis calculations were performed with a Rasa program (Rigaku) and X-STANP(Taira) using PANAFACOM U-1400 computer system.

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