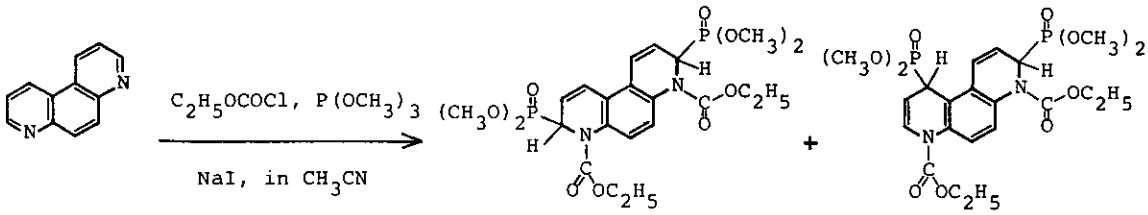
SYNTHESIS AND CRYSTAL STRUCTURE OF DIMETHYL N,N'-DIETHOXYCARBONYL-3,4,7,8-TETRAHYDRO-4,7-PHENANTHROLINE-3,8-DIPHOSPHONATE

Isao Takeuchi, Yasuhiro Shibata, and Yoshiki Hamada*
Faculty of Pharmacy, Meijo University,
Yagoto-Urayama, Tempaku-cho, Tempaku-ku, Nagoya 468, Japan
Masaru Kido
Laboratories of Natural Products Chemistry, Otsuka Pharmaceutical Co. Ltd., Kawauchi-cho, Tokushima 771-01, Japan

Abstract —— Reaction was performed of 4,7-phenanthroline with trimethyl phosphite and ethyl chlorocarbonate in the presence of sodium iodide in acetonitrile as a solvent, to yield dimethyl N,N'-diethoxycarbonyl-3,4,7,8-tetrahydro-4,7-phenanthroline-3,8-diphosphonate (3) and 3,10-diphosphonate (4). 3,8-Diphosphonate (3) was processed in the column chromatogram and was separated into isomers 3a and 3b whose structures were determined by X-ray analysis.

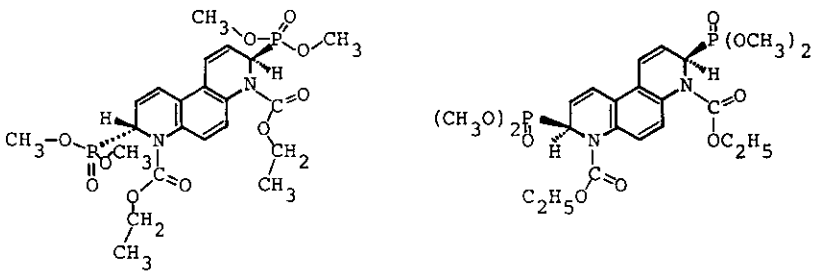
In recent practices, trialkyl phosphite is used in place of potassium cyanide in the Reissert type reactions.[1-3] The authors tried this method using benzo[*f*]quinoline and obtained α- and γ-phosphonates which are unobtainable through the Reissert reaction using potassium cyanide,[4] the findings of which were published.[5] The present study involves 1,10-phenanthroline (1) and 4,7-phenanthroline (2) which were brought into reaction in the same manner as reported previously.[5] The products of this reaction were subjected to an X-ray analysis.

First, compound 1 was put in contact with ethyl chlorocarbonate and trimethyl phosphite in the presence of sodium iodide and in acetonitrile as a solvent in compliance with the previous method,[5] only to recover the starting materials. Then, as shown in Chart 1, compound 2 was allowed to react with ethyl chlorocarbonate and trimethyl phosphite as previously described to yield compounds 3 and 4, in a yield of 70%, of which however 4 could not be isolated due to its small quantity obtained. Although compound 3 contained a small amount of impurity, its ^{1}H-NMR spectral data resulted in P-C-H (5.64δ) and P-C_2-H (6.17δ) which were in the proximity of P-C-H (5.76δ) and P-C_2-H (6.24δ), the spectra for α-phosphonate of N-ethoxycarbonylbenzo-



2 3 4

Chart 1



3a (*trans*) 3b (*cis*)

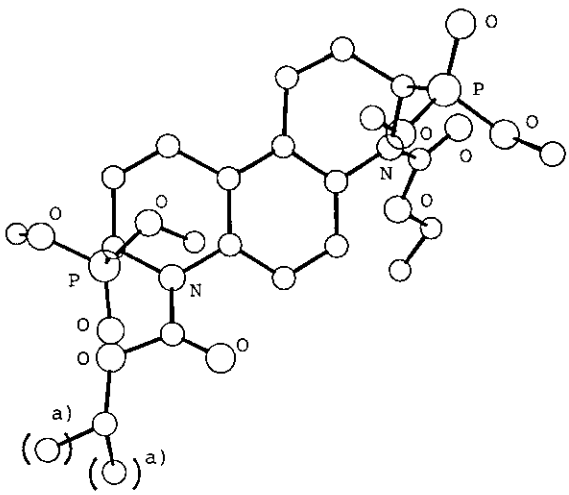


Fig. 1. The molecular structure of 3a

a) Probability: 1/2

*[f]*quinoline. *Compound* 3 *was therefore estimated to be the* α-*phosphonate.* Small amount of compound 4 was considered to be α,γ'-diphosphonate because the proton signal of α-phosphonate and γ-phosphonate were observed from its ^{1}H-NMR spectral data shown in Table I.

Compound 3 was further column-chromatographed, so that the proton signal of $H_{5,6}$ showed two peaks in spite of its must be appeared to one peak, and two substances were separately obtained. These were termed 3a and 3b from the elutions order and the ^{1}H-NMR spectral data are shown in Table I. These yields showed almost the same amount by the integral data in $H_{5,6}$ of the mixture. The physical data are mp 179-181°C for 3a and mp 137-139°C for 3b. The elemental analyses were C, 48.65; H, 5.50; N, 5.05 for 3a and C, 48.61; H, 5.41; N, 5.01 for 3b. The mass spectra obtained were identical and was m/z 544 (M^{+}). These brings about a conclusion that a formula $C_{22}H_{30}O_{10}P_2$ is relevant for both these compounds and that they are α,α'-diphosphonates. *Since melting point reduction was observed when they were mixed,* they are considered to be isomers, whose structures, as shown in Figure 1, can have either of the *cis* configuration where the phosphoryl group is on the same side as the phenanthroline plane and the *trans* configuration where they are located on the opposite sides. Thus, by using X-ray analysis, the structures for 3a and 3b were elucidated, 3a being determined as the *trans* and 3b therefore as the *cis* isomers. Crystal data: $C_{22}H_{30}N_2O_{10}P_2$, monoclinic, space group $P2_1/c$, a=8.118(4), b=22.270(7), c=15.032(3) Å, β=99.51(3)°, Dx=1.35 g/cm^3, z=4 and μ(MoKα)=2.2 cm^{-1}. The cell dimensions and intensities were measured on a Syntex R3 four-circle diffractometer with graphite-monochromated Mo Kα radiation with ω-scan mode within 2θ less than 40°. A total of 2505 independent reflections were collected, among which 2130 reflections ($I \geq 1.96\sigma(I)$) were stored as observed. The structure was solved by the direct method using MULTAN program.[6] The molecular structure is illustrated in Figure 1. A *block-diagonal least-squares method was applied to the refinement.* The final R-value was 0.057.

Table I. ^{1}H-NMR Spectral Data for Phosphonates (3a, 3b and 4) in $CDCl_3$ [a)]

Compd. No.	P-C-H	P-C_2-H	P-C_3-H	$POCH_3$	Other Protons
(3a)	5.64 (2H, dd) (J=21.2, 6.8)	6.17 (2H, m)	6.86 (2H, dd) (J=10.0, 6.0)	3.55 (6H, d, J=10.8) 3.63 (6H, d, J=10.8)	1.32 (6H, t, J=7.2) 4.27 (4H, q, J=7.2) 7.51 (2H, br s)
(3b)	5.66 (2H, dd) (J=21.2, 6.8)	6.14 (2H, m)	6.90 (2H, dd) (J=9.6, 5.6)	3.56 (6H, d, J=10.8) 3.64 (6H, d, J=10.8)	1.32 (6H, t, J=7.6) 4.28 (4H, q, J=7.6) 7.41 (2H, br s)
(4)	4.20 (1H, dd) (J= b), 6.8)	5.38 (1H, m)	6.76 (1H, dd) (J=10.0, 5.6)	3.52 (3H, d, J=10.8) 3.55 (3H, d, J=10.8) 3.64 (3H, d, J=10.8)	1.30 (3H, t, J=7.2) 1.36 (3H, t, J=7.2) 4.32 (4H, q, J=7.2)
	5.64 (1H, dd) (J=21.2, 6.8)	6.15 (1H, m)	7.05 (1H, t) (J=7.2)	3.67 (3H, d, J=10.8)	7.52 (1H, d, J=8.8) 7.81 (1H, d, J=8.8)

a) δ(ppm) from internal standerd TMS. Coupling constants are given in J=Hz.
b) Not observed: overlapped by other signals.

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Received, 11th October, 1985