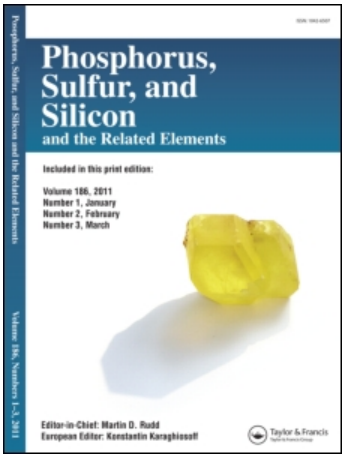

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STRUCTURAL INVESTIGATION ON 1-AMINO-ARYL-METHYLPHOSPHONATE ESTERS. X-RAY STRUCTURE OF *O,O*-DIETHYL-*N-N'*-ETHYLENE-BIS-PHENYLMETHYLPHOSPHONATE

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STRUCTURAL INVESTIGATION ON 1-AMINO-ARYL-METHYLPHOSPHONATE ESTERS. X-RAY STRUCTURE OF *O,O*-DIETHYL-*N*-*N'*-ETHYLENE-BIS-PHENYLMETHYLPHOSPHONATE

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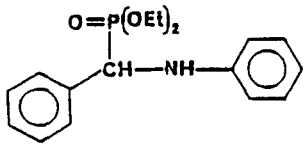
The crystal and molecular structure of the title compound has been determined by single crystal x-ray analysis. $C_{24}H_{38}N_2O_6P_2$ has a *meso* configuration, its crystal is triclinic, space group $P\bar{1}$, with a = 11.795(2), b = 8.616(2), c = 7.694(2), α = 112.72(2), β = 94.42(2), γ = 104.91(2), and Z = 1. The refinement had a R-value of 0.036 for 1580 reflections.

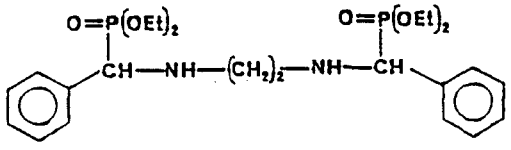
Key words: Amino-phosphonic esters; molecular configuration and geometry; stereospecific synthesis; *meso* form.

INTRODUCTION

Recently we described the preparation and the behaviour on chiral HPLC of 1-aminoaryl alkylphosphonate esters **1** and **2**.[1]



1



2

It was found that **1** could be resolved into its optical antipods, whereas the crystal product **2** isolated from the reaction mixture, was supposed to have a *meso* configuration, due to the impossibility of resolving it into its enantiomers by chiral HPLC.[1]

Therefore in order to gain more structural information on the configuration of **2** and on its geometry in the solid state we performed a crystal structure determination by x-ray diffraction methods.

Furthermore, 1-aminophosphonic esters and their acids, the latter being the analogues of α-aminocarboxylic acids, are of great interest owing to their action

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as enzyme regulators[2] and antifungal agents.[3] They can also be used in order to prepare phosphonodipeptides used as antibacterical agents[4] and for metal complexation studies.

Thus, considering that some peculiar properties of such compounds can be better interpreted by the knowledge of their conformation we felt that the crystal structure determination could be of interest to people working in such expanding area, providing structural details important for elucidating some biological properties. The x-ray structure of racemic **1** was already reported in literature[5]: both *D* and *L* forms are present in the structure and form centrosymmetric hydrogen-bond dimers.

RESULTS AND DISCUSSION

The molecular conformation of **2** and the atomic numbering scheme are illustrated in Figure 1. The atomic coordinates of **2** are reported in Table I; Tables II–IV shows bond distances, bond angles and torsion angles, respectively.

Inspection of Figure 1 clearly shows that the molecule has an inversion center and therefore its configuration is *meso* (the two identical chiral centers have opposite configuration). The crystal is not centrosymmetrical actually and for this reason we are reporting the coordinates for the full molecule. In this case the space group will be $P\underline{1}$. However, the only appreciable differences in the molecular geometry are evident in the conformation of the tail parts P-O2-C5-C10 (see Table IV) but, of course, in the limit of experimental errors the central part does look as centrosymmetrical, and therefore the space group can be described as $P\bar{1}$. This fact really confirms our previous results[1] using chiral HPLC columns which led us to propose, in absence of separation, a *meso* structure for the specimen of **2** used in the experiments and isolated from the reaction mixture. This finding nicely

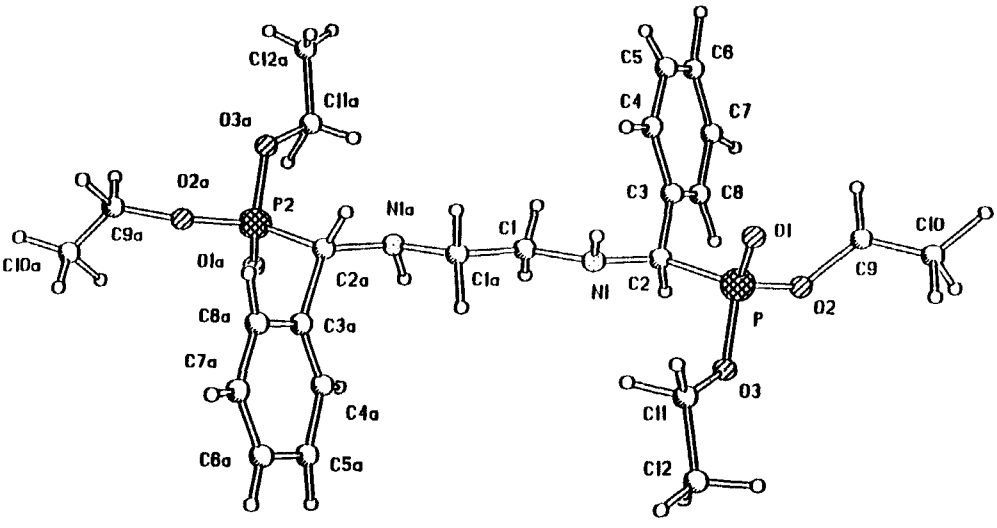

FIGURE 1 View of the phosphonate **2** with atom numbering scheme.

TABLE I

Atom coordinates ($\times 10^4$) and temperature factors ($Å^2 \times 10^3$) for **2** ($C_{24}H_{38}N_2O_6P_2$)

Atom	x	y	z	U
P	2650	4809	9280	47(1)*
O(1)	3570(6)	4986(8)	10825(8)	69(3)*
O(2)	1341(5)	3620(8)	9097(10)	64(3)*
O(3)	2427(5)	6598(8)	9432(9)	61(3)*
N(1)	4096(6)	4890(8)	6886(10)	51(3)*
C(1)	4432(7)	4381(10)	4991(10)	41(3)*
C(2)	2946(7)	3807(11)	6971(11)	45(4)*
C(3)	2791(7)	1871(11)	6287(11)	47(4)*
C(4)	3790(8)	1295(10)	6617(13)	58(4)*
C(5)	3647(8)	−431(15)	6112(15)	75(5)*
C(6)	2598(12)	−1785(14)	5089(14)	88(6)*
C(7)	1610(10)	−1252(12)	4722(15)	86(5)*
C(8)	1718(10)	561(14)	5270(15)	75(5)*
C(9)	1068(7)	2501(10)	10024(14)	97(4)*
C(10)	647(12)	3018(17)	11745(17)	123(6)*
C(11)	3416(9)	8277(12)	10222(17)	77(5)*
C(12)	2883(12)	9718(14)	10513(14)	104(6)*
P(2)	7350(1)	5190(2)	729(2)	48(1)*
O(1)a	6451(5)	4955(7)	−820(7)	52(3)*
O(2)a	8648(5)	6341(8)	908(8)	63(3)*
O(3)a	7604(5)	3464(8)	535(8)	57(3)*
N(1)a	5889(6)	5069(8)	3137(8)	43(3)*
C(1)a	5619(9)	5592(12)	5077(13)	62(4)*
C(2)a	7041(8)	6229(11)	3177(11)	48(3)*
C(3)a	7175(8)	8233(11)	3743(11)	49(4)*
C(4)a	6238(7)	8717(12)	3307(13)	63(5)*
C(5)a	6358(10)	10569(13)	4012(15)	80(5)*
C(6)a	7489(9)	11755(11)	4911(15)	76(5)*
C(7)a	8413(9)	11212(15)	5263(13)	79(5)*
C(8)a	8287(7)	9471(12)	4702(12)	56(4)*
C(9)a	9299(6)	6195(10)	−592(11)	84(3)*
C(10)a	9350(13)	7056(24)	−1618(20)	166(10)*
C(11)a	6694(10)	1799(14)	−209(15)	85(5)*
C(12)a	7176(9)	316(11)	−487(16)	82(5)*

*Equivalent isotropic U defined as one-third of the trace of the orthogonalised $U(i, j)$ tensor.

TABLE II

Bond lengths (Å) for **2**

P-O(1)	1.479(7)	P-O(2)	1.579(6)
P-O(3)	1.592(7)	P-C(2)	1.758(8)
O(2)-C(9)	1.40(1)	O(3)-C(11)	1.47(1)
N(1)-C(1)	1.47(1)	N(1)-C(2)	1.46(1)
C(1)-C(1)a	1.50(1)	C(2)-C(3)	1.50(1)
C(3)-C(4)	1.43(1)	C(3)-C(8)	1.38(1)
C(4)-C(5)	1.34(2)	C(5)-C(6)	1.38(1)
C(6)-C(7)	1.40(2)	C(7)-C(8)	1.42(2)
C(9)-C(10)	1.40(2)	C(11)-C(12)	1.48(2)
P(2)-O(1)a	1.448(6)	P(2)-O(2)a	1.558(6)
P(2)-O(3)a	1.545(8)	P(2)-C(2)a	1.859(8)
O(2)a-C(9)a	1.42(1)	O(3)a-C(11)a	1.42(1)
N(1)a-C(1)a	1.47(1)	N(1)a-C(2)a	1.45(1)
C(2)a-C(3)a	1.57(1)	C(3)a-C(4)a	1.34(2)
C(3)a-C(8)a	1.39(1)	C(4)a-C(5)a	1.44(2)
C(5)a-C(6)a	1.38(1)	C(6)a-C(7)a	1.34(2)
C(7)a-C(8)a	1.35(2)	C(9)a-C(10)a	1.27(2)
C(11)a-C(12)a	1.48(2)		

TABLE III

Bond angles (deg.) for **2**

O(1)-P-O(2)	115.9(4)	O(1)-P-O(3)	116.0(3)
O(2)-P-O(3)	101.6(4)	O(1)-P-C(2)	113.1(4)
O(2)-P-C(2)	102.7(3)	O(3)-P-C(2)	105.9(4)
P-O(2)-C(9)	123.8(6)	P-O(3)-C(11)	120.9(6)
C(1)-N(1)-C(2)	116.3(5)	N(1)-C(1)-C(1)a	111.6(5)
P-C(2)-N(1)	108.4(4)	P-C(2)-C(3)	114.4(7)
N(1)-C(2)-C(3)	115.6(7)	C(2)-C(3)-C(4)	120.1(6)
C(2)-C(3)-C(8)	123.2(9)	C(4)-C(3)-C(8)	116.7(9)
C(3)-C(4)-C(5)	120.6(7)	C(4)-C(5)-C(6)	124.5(12)
C(5)-C(6)-C(7)	115.7(11)	C(6)-C(7)-C(8)	121.4(9)
C(3)-C(8)-C(7)	120.8(11)	O(2)-C(9)-C(10)	121.5(9)
O(3)-C(11)-C(12)	107.4(9)	O(1)a-P(2)-O(2)a	116.9(4)
O(1)a-P(2)-O(3)a	114.0(3)	O(2)a-P(2)-O(3)a	99.0(3)
O(1)a-P(2)-C(2)a	114.9(4)	O(2)a-P(2)-C(2)a	103.1(3)
O(3)a-P(2)-C(20a	107.1(4)	P(2)-O(2)a-C(9)a	126.8(4)
P(2)-O(3)a-C(11)a	122.7(7)	C(1)a-N(1)a-C(2)a	110.5(5)
C(1)-C(1)a-N(1)a	109.3(6)	P(2)-C(2)a-N(1)a	104.9(4)
P(2)-C(2)a-C(3)a	110.4(6)	N(1)a-C(2)a-C(3)a	118.1(8)
C(2)a-C(3)a-C(4)a	120.5(7)	C(2)a-C(3)a-C(8)a	117.9(7)
C(4)a-C(3)a-C(8)a	121.6(9)	C(3)a-C(4)a-C(5)a	119.1(7)
C(4)a-C(5)a-C(6)a	117.1(11)	C(5)a-C(6)a-C(7)a	121.6(10)
C(6)a-C(7)a-C(8)a	121.3(8)	C(3)a-C(8)a-C(7)a	119.0(10)
O(2)a-C(9)a-C(10)a	126.2(11)	O(3)a-C(11)a-C(12)a	112.7(9)

TABLE IV

Torsion angles for **2**

O1	P	O2	C9	−12.6
O3	P	O2	C9	−139.3
C2	P	O2	C9	111.2
O1	P	O3	C11	34.0
O2	P	O3	C11	160.6
C2	P	O3	C11	−94.2
C2	N1	C1	C1A	179.5
O1	P	C2	N1	−59.9
O1	P	C2	C3	70.8
O2	P	C2	N1	174.5
O2	P	C2	C3	−54.9
O3	P	C2	N1	68.2
O3	P	C2	C3	−161.1
C1	N1	C2	P	−172.8
C1	N1	C2	C3	57.2
P	C2	C3	C4	−92.1
P	C2	C3	C3	90.1
N1	C2	C3	C4	34.9
N1	C2	C3	C3	−142.9
C2	C3	C4	C5	176.1
C3	C3	C4	C5	−6.0
C3	C4	C5	C6	6.8
C4	C5	C6	C7	−5.5
C5	C6	C7	C8	3.9
C2	C3	C8	C7	−177.5
C4	C3	C8	C7	4.6
C5	C7	C8	C3	−3.8
P	O2	C9	C10	98.3
P	O3	C11	C12	−169.3
O1A	P2	O2A	C9A	−48.4
O3A	P2	O2A	C9A	74.5

TABLE IV (*Continued*)

C2A	P2	O2A	C9A	−175.4
O1A	P2	O3A	C11A	−36.8
O2A	P2	O3A	C11A	−161.6
C2A	P2	O3A	C11A	91.5
N1	C1	C1A	N1A	−177.8
C2A	N1A	C1A	C1	179.9
O1A	P2	C2A	N1A	58.2
O1A	P2	C2A	C3A	−70.1
O2A	P2	C2A	N1A	−173.5
O2A	P2	C2A	C3A	58.2
O3A	P2	C2A	N1A	−69.6
O3A	P2	C2A	C3A	162.1
C1A	N1A	C2A	P2	171.5
C1A	N1A	C2A	C3A	−65.0
P2	C2A	C3A	C4A	88.9
P2	C2A	C3A	C3A	−91.1
N1A	C2A	C3A	C4A	−31.8
N1A	C2A	C3A	C8A	148.2
C2A	C3A	C4A	C5A	173.8
C8A	C3A	C4A	C5A	−6.2
C3A	C4A	C5A	C6A	7.8
C4A	C5A	C6A	C7A	−6.7
C5A	C6A	C7A	C8A	1.9
C2A	C3A	C8A	C7A	−177.8
C4A	C3A	C8A	C7A	2.2
C6A	C7A	C8A	C3A	0.1
P2	O2A	C9A	C10A	93.0
P2	O3A	C11A	C12A	172.6

supports our suggestion on the stereospecific addition of diethyl phosphite to the —C═N— group in aryldiimines.[1]

The solid-state molecular conformation of **2** shows a fully elongated trans-planar structure along the P—C—N—C—C—N—P skeleton; the phenyl rings are in *trans* position one to the other and lie almost perpendicular to the skeleton plane.

In **2** the two nitrogen atoms are pyramidal with angles C(1)-N(1)-C(2) of 116.3(5) and C(1a)-N(1a)-C(2a) of 110.5(5)°. The geometry around both phosphorus atoms is a distorted tetrahedron. All other bond lengths and angles are normal.

EXPERIMENTAL

The synthesis and characterization of compounds **1** and **2** were described elsewhere.[1]

Intensity data for **2** were collected using crystals of approximate dimensions 0.30 × 0.35 × 0.42 mm³ on Syntex P1 four-circle diffractometer using β-filtered Mo K_α radiation (λ = 0.71069 Å)—Crystal data are as folows: compound **2**, $C_{24}H_{38}N_2O_6P_2$, fw = 512.6, triclinic, $P\bar{1}$, a = 11.795(2) Å, b = 8.616(2) Å, c = 7.694(2) Å, α = 112.72(2)°, β = 94.42(2)°, γ = 104.91(2), Z = 1, D_X = 1.246 g/cm³, V = 683.2(0.7) Å³, T = 298 K, μ (Mo K_α) = 1.92 cm⁻¹.

Lattice parameters were determined by the least-square method from 14 reflections (20° < 2θ < 26°). 2300 reflections up to θ = 25° were measured in the θ–2θ scan mode. 1580 unique reflections had $I/\sigma(I) > 3.0$ and were used in the refinement.

The structure was solved by the direct method and refined with the anisotropic approximation for nonhydrogen atoms.

Weights of each reflection in the refinement (on F) were calculated from $w = 1/[\sigma^2(F_0 + 0.001252 F_0^2]$, $\sigma(F_0)$ being the esd, based on counting statistics of the observed structure factor. Scattering factors were taken from the *International Tables for X-ray Crystallography*.[6] All the H atoms included in the refinement were found from difference syntheses and were refined isotropically.

Refinement resulted in final values of $R = 0.036$, $R_w = 0.046$ and $S = 1.82$.

All calculations were performed on NOVA-3 computer using SHELXTL crystallographic computing system.[7]

REFERENCES

1. S. Caccamese, S. Failla, P. Finocchiaro, G. Hägele and G. Principato, *J. Chem. Res. (S)*, 242 (1992).
2. (a) R. I. Hildebrand, J. Curly-Joseph, H. J. Lubansky, T. O. Henderson, In *Topics in Phosphorus Chemistry*, eds. M. Grayson and E. J. Griffith, Interscience, New York, pp. 297–338 (1983); (b) I. van Assche, M. Soroka, A. Haemers, M. Hooper, D. Blanot and J. van Heijenoort, *Eur. J. Med. Chem.*, **26,** 505 (1991).
3. L. Maier and P. J. Diel, *Phosphorus, Sulphur, and Silicon*, **57,** 57 (1991).
4. (a) F. R. Atherton, C. H. Hassal and R. W. Lambert, *J. Med. Chem.*, **29,** 29 (1986); (b) B. Lejczak, P. Kafarshi, H. Sztajer and P. Mastarlerz, *J. Med. Chem.*, **29,** 2212 (1986); (c) Y. Okada, S. Iguchi, M. Mimura and M. Yagyui, *Chem. Pharm. Bull.*, **28,** 1320 (1980).
5. Z. Ruzic-Toros, B. Kojic-Prodic and M. Sljukic, *Acta Cryst.*, **B34,** 3110 (1978).
6. *International Tables for X-ray Crystallography*, Vol. IV, Birmingham: Kynoch Press (1974). Distributed by Kluwer Academic Publishers, Dordrecht.
7. G. M. Sheldrick, SHELXTL, Program for Crystal Structure Determination, University of Cambridge, Cambridge, England (1976).