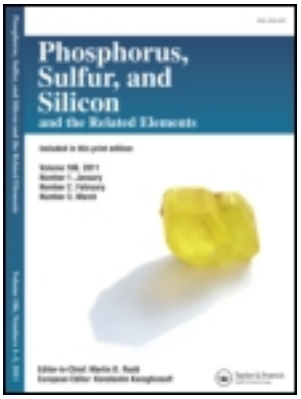

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gpss20

Intramolecular Diastereoselective Cascade Cyclization Reaction of N,N′-Bis(Salicylidene)Cyclohexanediimine with Phosphoryltrichloride to a Bis(Chlorophosphorylated) Decahydro-2,4-DI (2-Hydroxyphenyl)Benzo[d] [1,3,6]oxadiazepine

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Accepted author version posted online: 12 Aug 2013.Published online: 03 Dec 2013.

To cite this article: Hassan Hosseini-Monfared, Massomeh Ghorbanloo, Christoph Janiak & Peter Mayer (2014) Intramolecular Diastereoselective Cascade Cyclization Reaction of N,N′-Bis(Salicylidene)Cyclohexanediimine with Phosphoryltrichloride to a Bis(Chlorophosphorylated) Decahydro-2,4-DI (2-Hydroxyphenyl)Benzo[d][1,3,6]oxadiazepine, Phosphorus, Sulfur, and Silicon and the Related Elements, 189:2, 226-234, DOI: 10.1080/10426507.2013.818994

To link to this article: http://dx.doi.org/10.1080/10426507.2013.818994

Phosphorus, Sulfur, and Silicon, 189:226–234, 2014

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426507.2013.818994

INTRAMOLECULAR DIASTEREOSELECTIVE CASCADE CYCLIZATION REACTION OF *N,N'*-BIS(SALICYLIDENE)CYCLOHEXANEDIIMINE WITH PHOSPHORYLTRICHLORIDE TO A BIS(CHLOROPHOSPHORYLATED) DECAHYDRO-2,4-DI (2-HYDROXYPHENYL)BENZO[D][1,3,6]OXADIAZEPINE

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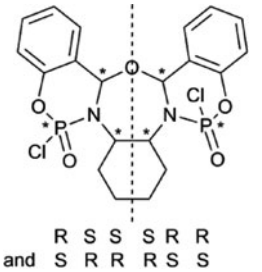
GRAPHICAL ABSTRACT



Abstract *A new type of cascade cyclization was observed in the phosphorylation reaction of (R,R)- or (S,S)-N,N′-bis(salicylidene)cyclohexanediimine with phosphoryltrichloride, which resulted in the formation of bis(chlorophosphorylated) decahydro-2,4-di(2-hydroxyphenyl)benzo[d][1,3,6]oxadiazepine with two new stereogenic phosphorus atoms and two new stereogenic carbon atoms in the oxadiazepine ring in the β-position to phosphorus. During the synthesis, the N atom attacks the phosphorodichloridate group with the formation of the P–N bond to give an asymmetric phosphorus atom and an iminium ion. This compound with six stereogenic centers crystallizes in the monoclinic centrosymmetric space group $P2_1/c$ and the crystal structure together with solution and solid-state MAS ^{13}C and ^{31}P NMR studies reveals a preferential formation of stereoisomers.*

Keywords Cyclization; chirality; diastereoselection; polycyclic phosphorus; X-ray diffraction

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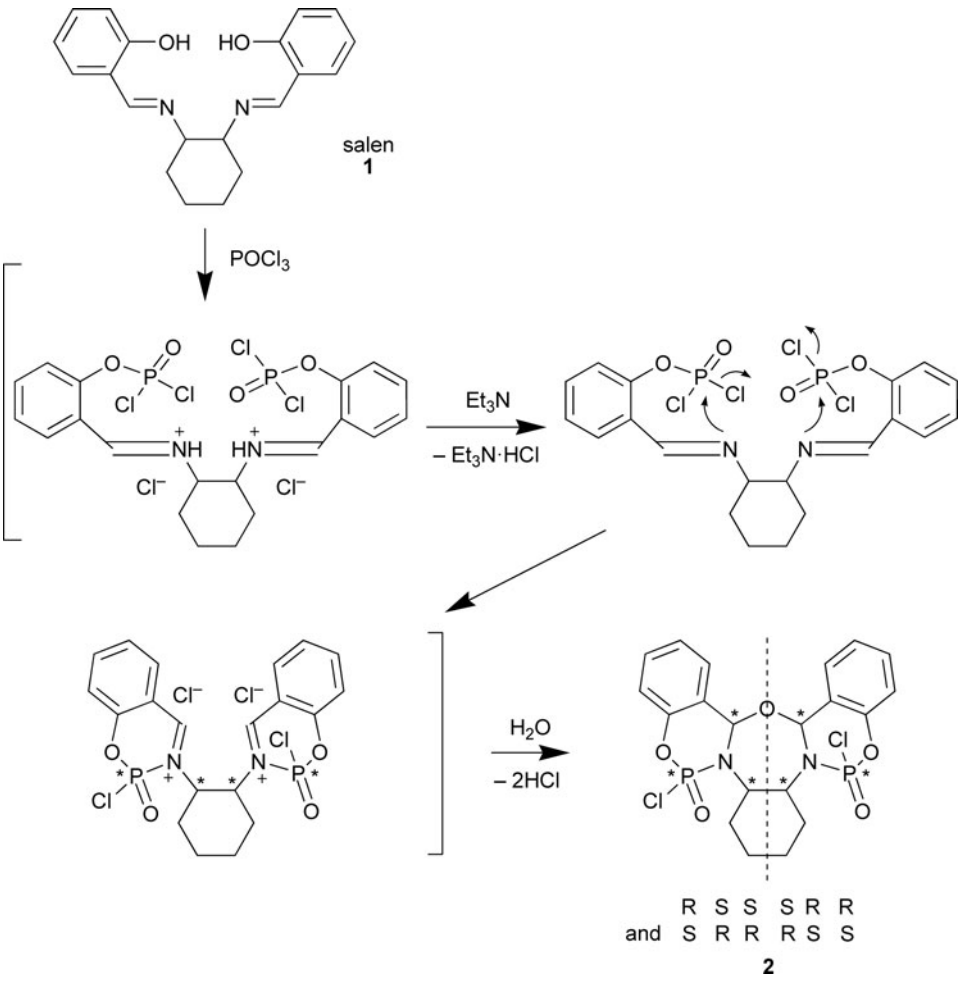
INTRODUCTION

Phosphorus is present in a multitude of forms in nature and is essential to life. Phosphorus-containing materials range from calcium phosphate in bone and teeth via the biochemical energy transfer agent adenosine triphosphate (ATP) to the essence of life itself in the form of the carriers of genetic information, the nucleic acids RNA and DNA.[1]

The development of new approaches to the synthesis of cyclic structures involving intramolecular transformations of polyfunctional three- and four-coordinated phosphorus derivatives has been a subject of interest.[2–4] Cyclization reactions resulting in the formation of an asymmetric center in the molecules of organophosphorus compounds proceed with high stereoselectivity and can be used in the synthesis of enantiopure substances.[5] The stereoselective synthesis of organophosphorus compounds is of considerable current interest because they exhibit biological activity. Enantiopure organophosphorus compounds are



Scheme 1 The synthesis of tricyclic tetracoordinated phosphorus (**2**) via intramolecular cascade cyclization reaction.

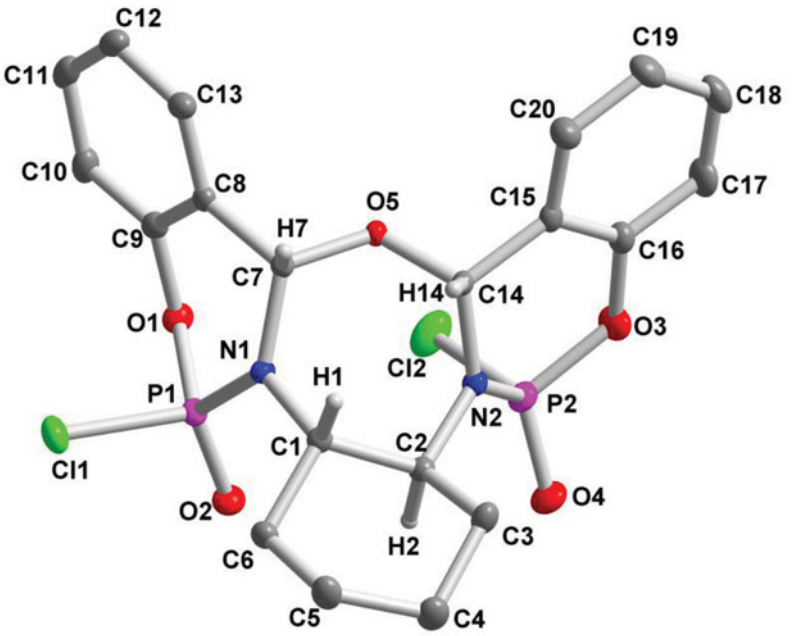


Figure 1 Molecular structure of **2**·$CHCl_3$. Non-hydrogen atom displacement ellipsoids are drawn at the 30% probability level; hydrogen atoms (except 4 of them) and $CHCl_3$ have been omitted for clarity. The stereoisomer with (*R*,*S*)(*S*,*S*)(*R*,*R*) configuration is shown here. (Color figure available online).

of interest as chiral drugs and ligands for the design of homogeneous or heterogeneous catalysts.[6,7]

On the other hand, phosphorus-containing heterocycles are of great interest as model compounds for fundamental investigations,[8,9] ligands in metal-complex catalysis,[10] and physiologically active compounds or precursors for their synthesis[11,12] and they are also used in other fields. However, in comparison to sulfur- and nitrogen-analogues, the structural diversity of numerous phosphorus-containing heterocycles remains highly limited to date,[13] because of significant limitations in the known methods of their synthesis. Therefore, the search for phosphorus analogues that are effective in the synthesis of other heterocycles is of theoretical and practical importance.

In this study, we have tested a new approach to obtain polycyclic phosphorus compound *via* the reaction of phosphoryltrichloride with *N*,*N*′-bis(salicylidene)cyclohexanediimine (salen, **1**).

RESULTS AND DISCUSSION

The salen **1** was synthesized from salicylaldehyde and trans-(±)-1,2-diaminocyclohexane in a 2:1 ratio. Phosphorylation of compound **1** with an equimolar amount of phosphorylchloride with a base resulted in the formation of product **2**. Compound **2** was characterized by ^{1}H, ^{13}C, and ^{31}P NMR experiments. It showed the phosphorus chemical shift $^{31}P\{^{1}H\}$ at 3.5 and 1.5 ppm characteristic of a tetracoordinated phosphorus atom. The structure **2** has six chiral centers; two phosphorus and four carbon atoms. The configuration at the *C*H–N carbon atoms of the cyclohexane ring is pre-set through the

Table 1 Selected bond lengths (Å) and angles (deg) for **2**

Cl1–P1	2.0239(9)
Cl2–P2	2.0188 (9)
P1–O1	1.5756 (17)
P1–O2	1.4504 (16)
P1–N1	1.6217 (18)
P2–O4	1.4464 (18)
P2–O3	1.5743 (19)
P2–N2	1.6229 (19)
O5–C14	1.436 (2)
O5–C7	1.429 (3)
N1–C1	1.478 (3)
N1–C7	1.469 (3)
N2–C2	1.485 (3)
N2–C14	1.458 (3)
C7–C8	1.496 (3)
C14–C15	1.499 (3)
Cl1–P1–N1	106.81 (7)
O1–P1–O2	113.63 (9)
O1–P1–N1	104.83 (9)
O2–P1–N1	117.74 (10)
Cl2–P2–O3	101.42 (8)
Cl2–P2–O4	110.45 (8)
Cl2–P2–N2	109.24 (7)
O3–P2–O4	113.18 (10)
O3–P2–N2	104.75 (9)
O4–P2–N2	116.62 (10)
C7–O5–C14	114.73 (15)
P1–N1–C7	122.55 (14)
C1–N1–C7	114.88 (16)
P2–N2–C14	119.87 (14)
C2–N2–C14	119.47 (17)
N1–C7–C8	113.06 (17)
N2–C14–C15	112.25 (17)

trans-(±)-1,2-diaminocyclohexane starting material. The additional configurations at the two phosphorus atoms and the two oxadiazepine N–*C*H–O atoms could give rise to a total of 20 stereoisomers as 10 enantiomeric pairs.

The crystal structure solution and refinement together with the NMR studies reveals that mainly one enantiomeric pair, that is, two stereoisomers are formed. Thus, the (*R*,*R*)- or *(S*,*S*)-configuration at the 1,2-diaminocyclohexane determines the configurations at the phosphorus and subsequently at the oxadiazapine carbon atoms during the cyclization process with high diastereoselectivity, *i.e.*, the cascade cyclization proceeds stereospecifically. The NMR spectra of **2** indicated the formation of mainly one diastereomeric product. From the (*R*,*R*)- or *(S*,*S*)-configuration of the 1,2-diaminocyclohexane starting material, this must exist as an enantiomeric pair. The single-crystal X-ray structure suggested that mainly two enantiomeric stereoisomers with (*R*,*S*)(*S*,*S*)(*R*,*R*) and (*S*,*R*)(*R*,*R*)(*S*,*S*) configurations in **2** (Scheme 1) are formed. Examples for diastereoselective reactions are construction of vicinal quaternary and tertiary carbon centers by the catalytic Michael reaction of α-substituted

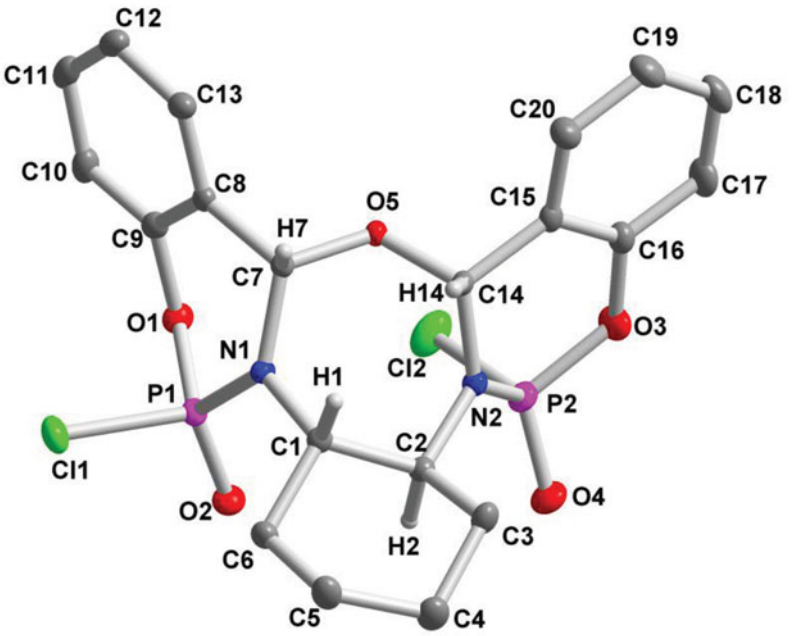


Figure 2 $\pi \cdots\pi$ and C–H$\cdots\pi$ interactions between phenyl rings in **2**, symmetry transformation i = 1–x, –y, –z; hydrogen atoms except H11 have been omitted for clarity. (Color figure available online).

β-keto esters to cyclic enones,[14] a Passerini reaction using p-toluenesulfonylmethyl isocyanide (TosMIC) as the isonitrile component[15] etc. To the best of our knowledge, there is no report on the diastereoselective oxadiazepines formation.

The mechanism of the formation of polycyclic product **2** has not been established experimentally. However, a possible explanation is proposed in Scheme 1. On the basis of the well-established chemistry of phosphorus oxychloride,[16] the reaction of the *o*–OH group of a salicylic fragment with $POCl_3$ produces an electrophilic iminium cation and phosphorodichloridate.[17] This reaction is facilitated in the presence of an HCl acceptor, namely an imine. The subsequent nucleophilic substitution on the phosphorus atom produces the P–N bond to give an asymmetric phosphorus atom and an iminium ion intermediate. The phosphorylated salen acquires a stereogenic center at the phosphorus atom upon the attack of N atom. Initially, this nitrogen–phosphorus bond formation will give a diastereomeric mixture of (*R*)- and (*S*)-configured phosphorus atoms in the iminium heterocycles. The final step in the synthesis of **2** is the stereospecific cyclization of oxadiazapine *via* an attack of H_2O at the carbon atoms of the iminium ion and elimination of HCl, which leads to new chiral centers at the imine carbon atoms; it is determined by the configuration of the chiral salen carbon atoms. The stereochemistry of these interactions most likely depends on the coordination of nitrogen to phosphorus already at the early steps, and it is clearly pronounced in product **2**.

Compound **2** crystallizes with one molecule of chloroform in the crystal lattice. The molecular structure of **2**·$CHCl_3$ and the atomic numbering adopted are depicted in Figure 1. Selected bond lengths and bond angles are collected in Table 1. The seven-membered oxadiazepine ring (C1-C2-N2-C14-O5-C7-N1) has chair conformation, the six-membered

Table 2 Crystal data and structure refinement parameters for **2**·$CHCl_3$

	$2{\cdot}CHCl_3$
Formula	$[C_{20}H_{20}Cl_2N_2O_5P_2]{\cdot}CHCl_3$
M_r/g mol^{-1}	620.613
Crystal size [mm^3]	0.41 × 0.28 × 0.23
Crystal system	Monoclinic
Space group	$P2_1/c$
a, Å	11.1561(3)
b, Å	15.5928(3)
c, Å	14.9075(3)
β, deg	90.372(2)
V, $Å^3$	2593.18(10)
Z	4
D_{calcd}, g cm^{-3} 1.58966(6)	
μ (MoK_α), mm^{-1}	0.720
Absorption correction	"Multi-scan"
Transmission factor range	0.95452–1.00000
Refls. measured	20247
R_{int}	0.0271
Mean $\sigma(I)/I$	0.0354
Theta Min–Max, deg	4.21–26.32
Observed refls.	0.0354
x, y (weighting scheme)	0.0602, 0
Hydrogen refinement	Constr.
Refls in refinement	5241
Parameters	316
Restraints	0
$R(F_{obs})$[a]	0.0385
$R_w(F^2)$[b]	0.1072
S	1.069
Shift/$error_{max}$0.001	
Max/min electron density, e $Å^{-3}$	0.650/−0.617

[a]$R1 = \|\|F_0\| - |F_c\|/\Sigma|F_o|$; $wR2 = [\Sigma w(F_0{}^2 - F_c{}^2)^2/\Sigma w(F_0{}^2)^2]^{1/2}$, $w = [\sigma^2(Fo^2) + (0.0602P)^2]^{-1}$, where P = (Max (Fo^2, 0) + $2Fc^2$)/3.

O1-P1-N1-C7-C8-C9 ring adopts a distorted $^{O1,C7}B$ boat conformation and the other six-membered ring O3-C16-C15-C14-N2-P2 adopts a distorted ^{N2}E envelope conformation. The cyclohexane ring is in a chair conformation with N1 and N2 in equatorial positions of the cyclohexane ring. The P1–N1 and P2–N2 bond distances are 1.6217(18) and 1.6229(19) Å, respectively, and N1 and N2 lie in a planar environment. This is due to the partial double bond character by the donation of nitrogen lone-pair electrons into the empty π orbitals on P(V). This shows the double bond nature of the N–P bonds. The P–N and P=O distances are in consistent with the reported studies.[18] The two aryl ring planes form an angle of 79.14(11)°. The molecule has neither C_2 nor mirror symmetry and the enantiomer depicted in Figure 1 shows *R* configuration on P1, P2 and C14 and *S*-configuration on C1, C2, and C7 (with the configuration on P set by the priority Cl > O=(P) > O–(P) > N). The other enantiomer (not shown) is generated by the crystallographic centrosymmetry in space group $P2_1/c$. Also, there are noteworthy reasonable π–π stacking and C–H···π interactions seen in **2**, that is, for π–π with centroid–centroid distances 3.728 Å between the exactly parallel ring planes (by symmetry) and a small angle between the centroid vector and the

normal to the plane of 19.06° which translates into a small slippage of 1.22 Å; for C–H···π, H···centroid 3.18 Å and C–H···centroid angle 163(1)°.[19,20]

CONCLUSIONS

A new type of cascade cyclization has been discovered, which yields a new polycyclic four-coordinated phosphorus compound. This cyclization results in the stereospecific formation of the P–N–C fragment with chiral carbon atoms in the β-position. The reaction can be used to synthesize enantiopure derivatives, which are of importance in bioorganic chemistry.[7]

EXPERIMENTAL DETAILS

Materials and Instrumentations

1,2-diaminocyclohexane ((*R*,*R*)- and (*S*,*S*)-racemate), salicylaldehyde, and phosphoryltrichloride were purchased from Merck and Fluka and used as received. Solvents were purified and dried according to the usual methods.[21] Solution ^{1}H NMR at 250 MHz, ^{13}C NMR at 63 MHz, and ^{31}P NMR at 101 MHz spectra were recorded by use of Bruker 250 MHz. Reference substances: TMS ext. (^{1}H); [D_6]$(CH_3)_2SO$ ext. (^{13}C); 85% H_3PO_4 ext. (^{31}P). FT-IR spectra were recorded using Perkin-Elmer 597. Microanalyses were carried out using a Heraeus CHN–O–Rapid analyzer. A thermospectronic model α, UV/Vis spectrometer with 1 cm quartz cells was used for recording and storage of UV/Vis absorbance spectra. Solid-state NMR spectra were recorded using 2.5 mm rotors on a Bruker Avance 500 solid-state NMR spectrometer (11.7 T) operating at a Lamor frequency of 202 MHz for ^{31}P. RF pulses were applied at a transverse B1 field of 125 kHz corresponding to a $\pi/2$ pulse width of 2 μs.

Synthesis of Salen (1) (*N*,*N*′-bis(salicylidene)cyclohexanediimine)

The salen was synthesized from racemic 1,2-diaminocyclohexane and salicylaldehyde following the reported procedure.[22] Yield: 80.6%, m.p. 100–104°C. Anal. for $C_{20}H_{22}N_2O_2$ (322.40): calc. C 74.51, H 6.88, N 8.69; found C 74.50, H 6.90, N 8.50. FT-IR (KBr): ν = 3446 (br, w) (OH), 3069 (w), 3015 (w), 2923 (s), 2854 (s), 2738 (w), 2661 (w), 1631 (vs) (C=N), 1500 (s), 1461 (m), 1423 (m), 1285 (s), 1215 (w), 1461 (s), 1100 (m), 1046 (m), 938 (w), 854 (s), 769 (vs), 661(m), 446 cm^{-1} (w). ^{1}H NMR (250.13 MHz, $CDCl_3$, 25°C): δ = 1.47–1.91 (m, 8 H, C*H*$_2$ groups of the cyclohexane ring), 3.30 (m, 2 H, C*H*–N cyclohexane ring, 6.77–7.32 (m, 8 H, aryl), 8.46 (s, 2 H, C*H*=N), 13.34 (s, 2 H, O*H*). –UV/Vis (CH_3OH): λ_{max} (lg ε_{max}) = 225^{sh} (6.83), 242 (4.90), 270 (4.76), 349 nm (4.27).

Synthesis of bis(chlorophosphorylated) Decahydro-2,4-di(2-hydroxyphenyl)benzo[d][1,3,6]oxadiazepine (2)

The salen **1** (0.64 g, 2 mmol) was dissolved in dry CCl_4 (10 mL) and cooled in an ice bath under a nitrogen atmosphere. A carbon tetrachloride solution (5 mL) of $POC1_3$ (0.61 g, 4 mmol) was added dropwise and regularly to the salen solution over a period of 30 min under continuous stirring and the resulting solution was neutralized with triethylamine

(about 8 mmol). Stirring was continued further for 2 h until the completion of the reaction. Then 20 mL water was added to the solution and stirring was continued for 30 min to dissolve the ammonium salt in water. The organic phase was removed and after addition of *n*-propanol (8 mL) the reaction mixture was stirred for 12 h and was then filtered. The filtrate was washed with CCl_4 and dried in air. It was further re-crystallized from $CHCl_3$ to give colorless single crystals of **2**·$CHCl_3$. Yield: 15% (186 mg). m.p. 240–244°C. The rest was unreacted material.

–$C_{20}H_{20}Cl_2N_2O_5P_2$·$CHCl_3$ (620.61): calc. C 40.64, H 3.41, N 4.51; found: C 40.63, H 4.48, N 4.53. FT-IR (KBr): ν = 3014 (m), 2953 (m), 2930 (m), 2867 (w), 1621 (m) (C═C), 1592 (m), 1493 (s), 1461 (s), 1287 (vs) (P═O), 1207 (vs)) (P═O), 1142 (vs), 1073 (s), 972 (vs) 915 (m), 849 (m), 754 (vs), 646 (s), 596 (s), 528 (vs), 501 cm^{-1} (m). ^{1}H NMR (250.13 MHz, DMSO-d_6, 25°C): δ = 1.29–2.34 (m, 8 H, CH_2 groups of the cyclohexane ring), 4.03 (m, 2H, C*H*–N groups of the cyclohexane ring), 6.08 (d, ^3J (HP) = 22.8 Hz, 1 H, N–C*H*-aryl), 6.66 (d, ^3J(HP) = 30.0 Hz, 1 H, N–C*H*-aryl), 7.10–7.57 (m, 8 H, aryls). ^{13}C-NMR (62.90 MHz, DMSO-d_6, 25°C): δ = 25.3 and 31.1 (*C*H_2 of cyclohexane), 62.1 (*C*H–N of the cyclohexane ring), 64.0 (*C*H-N of the cyclohexane ring), 82.8 (N–*C*-aryl), 90.2 (N–*C*-aryl), 118.6 (d, ^3J(CP) = 9.8 Hz, aryl), 119.3 (d, ^3J(CP) = 6.9 Hz, aryl), 121.6 (d, ^3J(CP) = 9.9 Hz, aryl), 122.4 (d, ^4J(CP) = 2.6 Hz, aryl), 123.8 (d, ^3J(CP) = 10.0 Hz, aryl), 125.1 (aryl), 125.7 (aryl), 126.8 (aryl), 127.8 (aryl), 129.8 (aryl), 147.5 (d, ^2J(CP) = 9.1 Hz, P-O-*C*(aryl), 148.28 (d, ^2J(CP) = 9.7 Hz, P-O-*C*(aryl). -^{31}P-NMR (101.25 MHz, DMSO-d_6, 25°C): δ = 1.5, 3.5. (202 MHz, MAS): δ = 6.4, 8.3.

The *R*, *S* configuration at the two oxadiazepine N–*C*H–O destroys the C_2-symmetry axis between the two molecular halves, thus, rendering the left and right side of the molecule diastereotopic. Hence, a separate chemical shift should be observed for H-, C-, and P-atoms on the left and right side of the molecule. These separate chemical shifts are resolved for the oxadiazepine-*C*- and –*H* including the *C*H-cyclohexane, for *C*-aryl and the P-atoms. –UV/Vis (CH_3OH): λ_{max} (lg ε_{max}) = 211 (4.35), 243 (4.04), 265 (4.06), 350 nm (3.30).

X-Ray Structure Determination

A colorless crystal of **2** (0.41 × 0.28 × 0.23 mm^3) was investigated at 200(2) K on an Oxford XCalibur diffractometer with monochromatized Mo$K\alpha$ radiation (λ = 0.71073 Å). The structure was solved by direct methods with SIR97,[23] and refined with full-matrix least-squares techniques on F^2 with SHELXL-97.[24] The crystal data and refinement parameters are presented in Table 2. The hydrogen atoms were calculated in idealized geometry riding on their parent atoms.

CCDC-759237 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

ACKNOWLEDGMENTS

The present work has been supported by the University of Zanjan and by the Fakultät für Chemie und Pharmazie, Ludwig-Maximilians-Universität, Munich. CJ thanks the DFG for grant Ja466/14-1 and Ja466/23-1 (initiation of bilateral cooperation HHM-CJ). We thank Mr. Alfred Hasenhindl from the University of Freiburg for the collection of the solid-state NMR spectra.

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