Diastereoselective formation of 18-membered ring BINOL-hydrogen phosphonate dimers — Quasi-covalent hydrogen bonds?

Hossein A. Dabbagh, Nader Noroozi-Pesyan, Ali R. Najafi-Chermahini, Brian O. Patrick, and Brian R. James

Abstract: Diastereoselective syntheses of the unusual dimers, 4-heptyl-2-(2′-hydroxy-binaphthyl)hydrogen phosphonate (**5**) and the cyclohexyl analogue (**7**), are achieved by hydrolysis of 4-(3,5-dioxa-4-phosphacyclohepta[2,1-α;3,4-α′]-dinaphthalene-4-yloxy)heptane (**4**) and the cyclohexane analogue (**6**), respectively. Two out of eight possible pairs of monomers units are involved in the stereoselective formation of the dimer **5a** of configuration $BINOL_R$-P_S:$BINOL_R$-P_S; this is determined by X-ray crystallographic data, which reveal a centrosymmetric, 18-membered ring structure with C_i symmetry, consisting of two monomers strongly hydrogen-bonded between the oxygen of P=O units and hydroxyl hydrogen atoms. Mass spectrometric, melting point, and thermal decomposition point data, as well as NMR data, support the presence of strong, quasi-covalent hydrogen bonds. Computational analysis suggests that the diastereoselectivity is controlled by molecularly constrained geometry of the monomer. Compound **7**, although not characterized crystallographically, appears to be analogous to **5**.

Key words: 18-membered ring, phosphonate dimer, diastereoselectivity, hydrogen-bonds, computational analysis.

Résumé : On a réalisé les synthèses diastéréosélectives des dimères inhabituels du phosphonate acide de 4-heptyl-2-(2N-hydroxybinaphtyle) (**5**) et de son analogue cyclohexyle (**7**) par le biais de l'hydrolyse respectivement du 4-(3,5-dioxa-4-phosphacycloheptane[2.1-α;3,4-α′]dinaphtalène-4-yloxy)heptane (**4**) et de son analogue cyclohexane (**6**). Deux des huit paires possibles d'unités monomères sont impliquées dans la formation stéréosélective du dimère **5a** de configuration $BINOL_R$-P_S:$BINOL_S$-P_R; cette conclusion est basée sur des données de diffraction des rayons X qui mettent en évidence l'existence d'une structure cyclique centrosymétrique à 18 chaînons de symétrie C_i, formée de deux monomères reliés fortement par une liaison hydrogène entre l'oxygène des unités P=O et les atomes d'hydrogène des hydroxyles. Les données de spectrométrie de masse, de point de fusion et de point de décomposition thermique ainsi que les données de la RMN sont en accord avec la présence de liaisons hydrogènes fortes et de nature pratiquement covalentes. Une analyse par des calculs théoriques suggère que la diastéréosélectivité est contrôlée par la géométrie fixée d'une façon moléculaire du monomère. Même si le composé **7** n'a pasété caractérisé d'une façon cristallographique, il semble être analogue au composé **5**.

Mots-clés : cycle à 18 chaînons, dimère de phosphonate, diastéréosélectivité, liaisons hydrogènes, analyse par des calculs théoriques.

[Traduit par la Rédaction]

Introduction

During studies aimed at developing new chiral phosphine ligands based on the binaphthol backbone, we accidentally discovered a dimeric structure maintained by two exceptionally strong hydrogen bonds, and this work is described here.

Hydrogen bonding plays a key role in biology and chemistry and remains a topic of intense current interest, as judged by an enormous continuing amount of literature. A few selected recent articles exemplify the general scope of the topic, ranging from the role of H bonding in: weak interactions in the gas phase (1), supramolecular assemblies (2), helical structures (3), promoting catalytic enantioselective reactions (4), molecular rotors (5), through to measurement of H-bond acidity of organics (6). Important consequences of both inter- and intra-molecular H bonding have long been recognized in the physiochemical behavior of DNA and RNA (7), while H bonding within phosphorus systems, of

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Table 1. Classification of hydrogen bonds within P-containing systems.

Linkages	Bond distance [range, donor---H---acceptor] (Å)	Strength
P-O-H---O-P	2.39–2.50	Very strong
P-OH---O-P	2.50–2.70	Strong
P-O-H---O-C	2.41–2.82	Strong
P-H---OH_2	2.56–3.15	Moderate
P-O---H-N	2.65–3.10	Moderate
C-O-H---O=P[a]	2.70	Strong

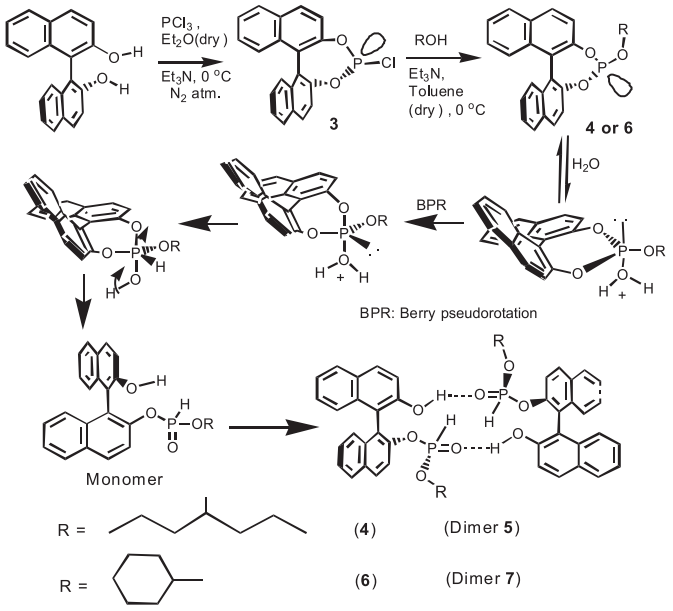
Note: Data taken from from refs. 8*a*, 10*b*, 10*f*, and 11*a*.
[a]Determined by an X-ray crystallographic study of **5a** (see Scheme 2 and Fig. 1).

relevance to our paper, is also well documented (8). Some contributions from our collaborative group have also demonstrated the importance of hydrogen bonding in determining the structure, conformation, energy, and reactivity properties of a molecule (9).

The factors determining the strength of a hydrogen bond, other than electronegativities of the donor and acceptor atoms, remain of interest. Homonuclear linear O---H---O bonds are well understood and display a practically continuous range of O---H---O distances from 2.36 to 3.69 Å: the upper value is the sum of the van der Waals radii and not a physical limit of the hydrogen-bond interaction that has been qualitatively defined as very strong (<2.50 Å), strong (2.41–2.82 Å), medium (2.56–3.15 Å), or weak (>3.15 Å); see Table 1 (8*a*, 10, 11). The strongest hydrogen bonds are seen in homonuclear linear or nearly linear systems with an O–H–O angle > 165°; the energies of bent O–H–O systems have been evaluated computationally and are 90%, 60%, and 10% of the linear system value for angles of 165°, 149°, and 110°, respectively (10*b*, 11*a*). A unified hydrogen bond theory has been presented in which O---H---O bonds are divided into five classes: negative charge-assisted $[–O---H---O–]^-$ (a strong H bond); positive charge-assisted $[=O---H---O=]^+$ (strong); resonance-assisted [-O–H---O=] (strong), where the two oxygens are connected by a π-conjugated system of variable length, including cases where the oxygens are attached to P or As atoms; polarization-assisted [---O(R)–H---O(R)H---] (moderate); and isolated H bonds [-O-H---O(R)(R)] (weak) (11*a*). Of note, a recently reported variable-temperature X-ray crystallographic and DFT computational study of the N-H---O/N---H-O tautomeric competition in 1-(arylazo)-2-naphthol has led to a transition-state hydrogen bond theory (12).

Our current work, based on designing chiral phosphines, prompted us to synthesize 4-(3,5-dioxa-4-phosphacyclohepta[2,1-α;3,4-α′]-dinaphthalene-4-yloxy)heptane (**4**) and the corresponding cyclohexane analogue (**6**) (see Scheme 1). During the attempted purification of **4** and **6**, we discovered their hydrolysis products, which proved to be the dimeric

Scheme 1. Formation of the dimeric phosphonates.



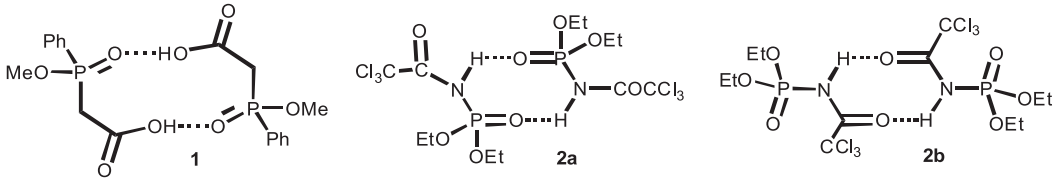
structures, 4-heptyl-2-(2′-hydroxybinaphthyl)hydrogen phosphonate (**5a**) and the cyclohexyl analogue (**7a**) (the "**a**" label refers to a particular stereoisomer of these dimers — see later). The 18-membered ring structure of these dimeric compounds is maintained by the presence of two strong hydrogen bonds, as discussed later (see Scheme 1).

Results and discussion

Prior to a discussion of compounds **5a** and **7a** and their unusual structures, it is best to introduce some general comments about H bonding in phosphorus compounds. The degree of such bonding, which is seen in the solid, liquid, and solution states, varies depending on the solvent, temperature, and the nature of the substituent group on the P atom. Most phosphorus acids form dimers with strong H bonds within a 6- to 10-membered ring (8*a*), although the esters $(RO)PO(OH)_2$ (R = 3-methylhexyl or *n*-octyl) are polymers containing intermolecular H bonding (8_a). Relevant to our paper, aryl H-phosphonates have been synthesized and characterized by ^{31}P NMR spectroscopy (13).

Dimeric centrosymmetric ring structures are quite common within phosphorus chemistry: **1** and **2** exemplify 12- and 8-membered ring structures, respectively (8*a*), and according to spectroscopic evidence, esters of (trichloroacetyl)amidophosphoric acid exist as **2a** rather than **2b**, which suggests that the H bond in N-H---O=P is more stable than that in N-H–O=C (8*a*).

Although lower oxy-acids of phosphorus were initially



thought to exist primarily in tautomeric forms in which the central atom was trivalent, it is now well-established that the majority of such compounds prefer structures that incorporate formally pentavalent phosphorus (8*a*, 14). A detailed analysis of bond and contact distances has suggested that when the O---O interaction is decreased from 2.80 to 2.40 Å, the H bond is transferred from a symmetrical O---H---O electrostatic interaction to a covalent unsymmetrical O–H---O bond (10*b*, 11*a*).

Synthesis of the BINOL phosphonates and solution NMR characterization (Scheme 1)

Hydrolysis of the phosphate esters 4-(3,5-dioxa-4-phosphacyclohepta[2,1-α;3,4-α′]-dinaphthalene-4-yloxy)heptane (**4**) and the cyclohexane analogue (**6**) produced what initially are the respective monomers, 4-heptyl-2-(2′-hydroxybinaphthyl)hydrogen phosphonate (**5m**) and the 4-cyclohexyl analogue (**7m**). The monomers, being chiral at phosphorus coupled with the axial chirality of the BINOL moiety, can exist theoretically in four possible configurations ($BINOL_R$-P_R, $BINOL_R$-P_S, $BINOL_S$-P_S, $BINOL_R$-P_S). Of interest, both precursor monomers appear to dimerize selectively with their mirror images to form the 18-membered ring dimers; certainly, the structurally characterized **5a** (see later) has the configuration $BINOL_R$-P_S:$BINOL_R$-P_S, maintained by two strong hydrogen bonds, while a second stereoisomer seen in solution (**5b**, see later) could be the $BINOL_R$-P_R:$BINOL_S$-P_S form. The analogous system based on **7** is considered from NMR data to behave similarly.

The necessary precursor reagent 4-chloro-3,5-dioxa-4-phosphacyclohepta[2,1-α;3,4-α′]-dinaphthalene (**3**) was prepared by reaction of PCl_3 with 2,2′-dihydroxy-1,1′-binaphthyl (BINOL) in dry Et_2O under an N_2 atmosphere, using procedures from the literature (15). This chloro compound was used without purification in the next step for the production of the phosphate esters **4** and **6** by treatment with the appropriate alcohol, 4-heptanol, or cyclohexanol, respectively. The esters were isolated in 70%–80% yields as yellow powders. The heptyl ester **4** was characterized in solution by ^1H NMR (with signals assigned for the methyl, methylene, and methyne protons of the heptyl group and the 12 binaphthyl protons) and a $^{31}P\{^1H\}$ singlet at δ 146. The corresponding cyclohexyl analogue **6** similarly showed three sets of ^1H signals for the 10 methylene protons, the single CH proton, and binaphthyl protons, as well as a $^{31}P\{^1H\}$ singlet at δ 150.

The remarkable hydrolysis products from **4** and **6** were accidentally synthesized by leaving acetone solutions of the esters in air at ambient temperatures for several days. After work-up procedures and purification by recrystallization, the respective yellow solid products 4-heptyl-2-(2′-hydroxybinaphthyl)hydrogen phosphonate (**5**) and the cyclohexyl analogue (**7**) were isolated as dimeric forms, based on NMR and MS data and an X-ray analysis of **5a**.

Analysis of crude samples of **5** by solution ^1H, $^1H\{^{31}P\}$, ^{31}P, and $^{31}P\{^1H\}$ NMR spectroscopy (see Experimental section) showed two major components **5a** and **5b**, two minor components **5c** and **5d**, and a trace amount of an unknown compound **5x** (Figs. S1–S8).[2] The ^{31}P NMR spectrum of pure **5a** (grown as a single crystal from a cyclohexane-CH_2Cl_2 solution of crude **5**) is a doublet of doublets centered at δ 3.80 because of coupling to two protons ($^1J_{PH}$ = 707, $^3J_{PH}$ = 10.7 Hz), as confirmed by a ^1H-decoupled spectrum that generates a $^{31}P\{^1H\}$ singlet; the $^1J_{PH}$ value is in the expected range (16). The ^1H NMR spectrum for **5a**, showing signals for the heptyl and binaphthyl protons, is consistent with the solid-state structure described later; the PH proton of **5a** is seen as a doublet at δ 6.65 ($^1J_{PH}$ = 703 Hz), which collapses to a singlet in the $^1H\{^{31}P\}$ spectrum. A $^{13}C\{^1H\}$ NMR spectrum of **5a** shows 27 signals corresponding to the number of binaphthyl and heptyl carbon atoms (20 and 7, respectively). Although **5a** was the only compound isolated in a pure state, it was not difficult (e.g., from the relative peak heights of the doublet of doublet patterns seen in the $^{31}P\{^1H\}$ spectra and relative intensities of the various ^1H resonances) to determine the NMR assignments (from data for mixtures) associated with what are possibly other stereoisomers (i.e., **5b**, **5c**, and **5d**, see later); similar reasoning allowed for the determination of resonances associated with each of **7a**–**7d**.

The NMR spectra of **5b** are similar to those of **5a**, and similar data are seen for **5c**, but for this species the ^{31}P shift is centered at δ 8.80; **5d** is characterized by just a doublet centered at δ 5.45 in the ^{31}P spectrum with a $^1J_{PH}$ value of 720 Hz. The structure of **5a** was elucidated by X-ray crystallography, while relevant EI and ES mass spectrometric data were also measured (see later).

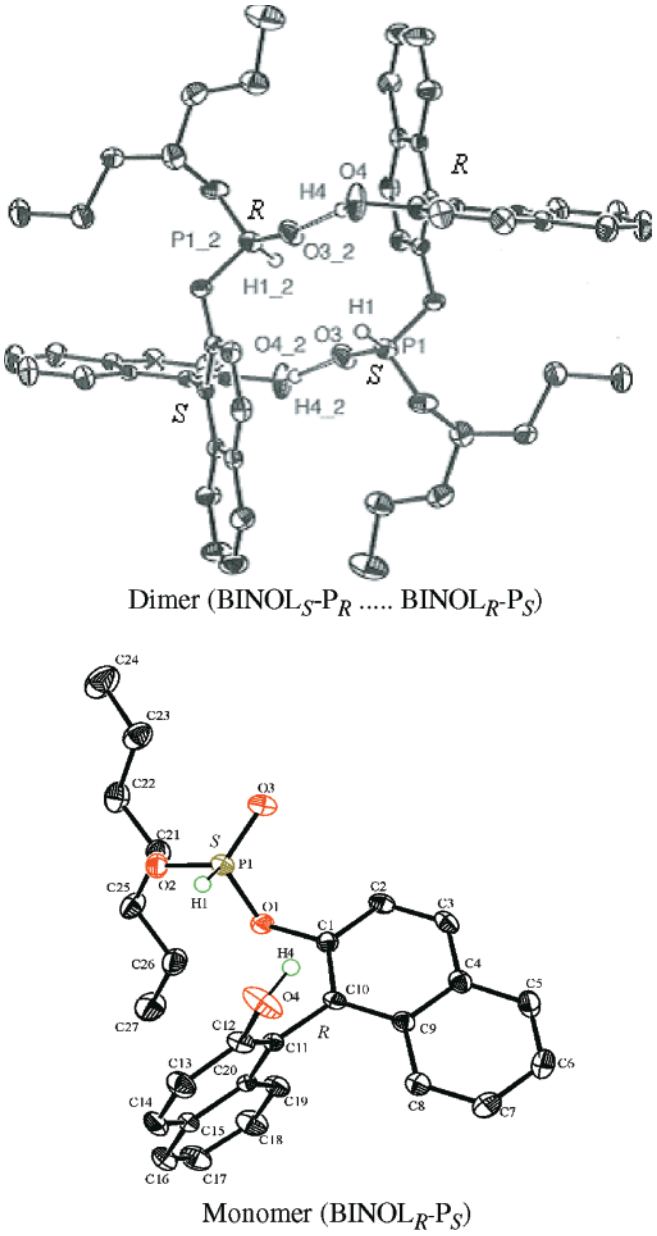
The cyclohexyl-2-(2′-hydroxybinaphthyl)hydrogen phosphonate (**7**), like **5**, was isolated as a pale yellow solid. ^{31}P, $^{31}P\{^1H\}$, ^1H, and $^1H\{^{31}P\}$ NMR analysis revealed again the presence of two major components, **7a** (40%) and **7b** (38%), and two minor components, **7c** (18%) and **7d** (4%); Figs. S9 and S10.[2] Unfortunately, we were unsuccessful in obtaining any crystals of **7** suitable for X-ray analysis. However, the NMR data correspond closely to those measured for the **5a**–**5d** mixture (after allowance for the replacing of the 4-heptyl by a cyclohexyl moiety), and the structure of **7a** is likely to be analogous to that of **5a** but with a different R group (Scheme 1).

X-ray structure of 5a

The X-ray crystallographic analysis of **5a** reveals the essential monomer structure **5m** shown in Fig. 1 (see also Scheme 1), while the unit cell reveals two such monomer units interacting strongly via two hydrogen bonds between phosphonate P=O moieties and the OH groups of the BINOL; an overall centrosymmetric dimer structure for **5a** is seen with an 18-membered ring with C_i symmetry (Fig. 1

[2] Supplementary data for this article are available on the journal Web site (http://canjchem.nrc.ca) or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0R6, Canada. DUD 5180. For more information on obtaining material refer to http://cisti-icist.nrc-cnrc.gc.ca/irm/unpub_e.shtml. CCDC 623091 contains the crystallographic data for this manuscript. These data can be obtained, free of charge, via http://www.ccdc.cam.ac.uk/conts/retrieving.html. Figs. S1–S13 include: $^{31}P\{^1H\}$, ^{31}P, ^1H, and $^1H\{^{31}P\}$ NMR spectra of **5a**, **5b**, **5c**, and **5d**; $^{31}P\{^1H\}$, ^{31}P, and ^1H NMR spectra of **7a**, **7b**, **7c**, and **7d**; computer-generated minimum configurations for the six pairs of **5m** monomers; and computer-generated minimum configuration for a **5b** dimer.

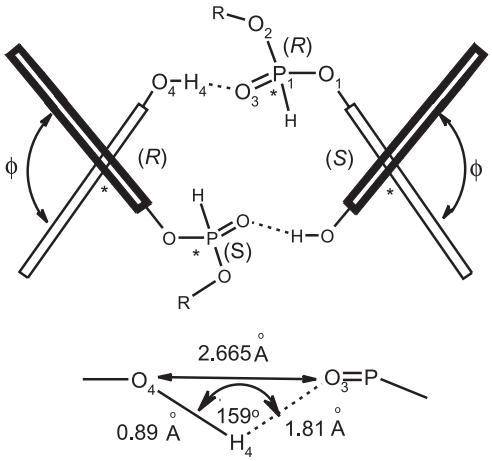
Fig. 1. Molecular structure of dimer **5a** (top) and monomer **5m** (bottom).



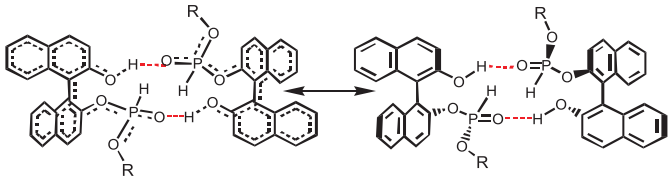
and Schemes 2 and 3). The torsion angles between the two BINOL rings are ~96°, favoring the *s*-transoid conformation. One of the BINOL units in the dimer structure necessarily has *R* axial symmetry and the other unit has *S* symmetry.

As expected, the P=O bond is some 0.1 Å shorter than the P–O bonds in the binaphthyl and heptyl groups, which are 1.58 and 1.55 Å, respectively. Within the hydrogen bonds, the distance between the hydroxyl-H and the acceptor-O atom is 1.81(2) Å, while the bond length for the hydroxyl group is 0.89(2) Å, and the O–H---O bond angle is 159°; the distance between the oxygens of the O---H-O moiety is ~2.70 Å, implying the presence of a strong hydrogen bond within this P=O---H-O-C system (Scheme 2 and Table 1). The strength of hydrogen bonding in the dimer may result from contributions of resonance-assisted and (or) polarization-assisted hydrogen bonds (see Introduction and Table 1),

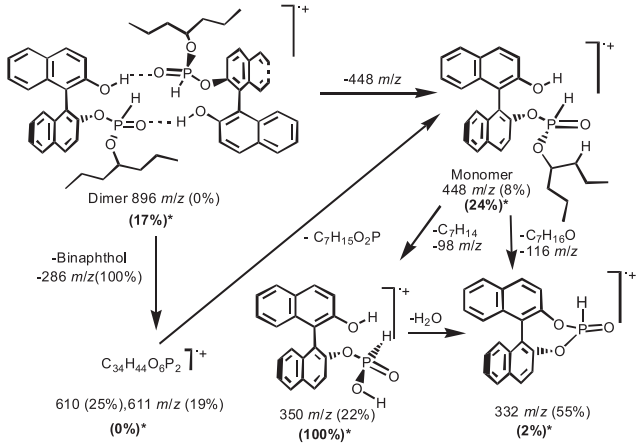
Scheme 2. Diagram showing hydrogen bonding within the dimer.



Scheme 3. Diagram showing resonance-assisted hydrogen bonding.



Scheme 4. Summary of the mass spectral data. Values in parentheses are the % base peak from EI. Values in boldface marked with asterisks (*) are the % base peak from TOF MS Electron Spray (ES$^+$).

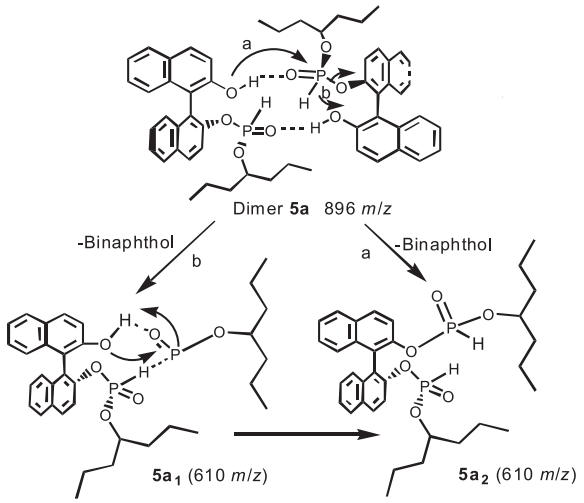


while the deviation from linearity of the O–H---O angle likely allows for a decrease in strain energy of the dimer structure (Scheme 3). More information supporting the presence of strong hydrogen bonds in **5a** was gleaned from mass spectrometric data.

Mass spectroscopic analysis

Positive ion electrospray mass spectral data for a solution of **5a** in CH_3OH–$CHCl_3$ showed molecular ions of *m/z* values around 897 corresponding to the dimer formulation M_2^+, 449 corresponding to the monomer M^+, and a 100% base peak at 350 corresponding to [BINOL + PO_2H]. Electron

Scheme 5. Plausible pathways for fragmentation of dimer 5a.

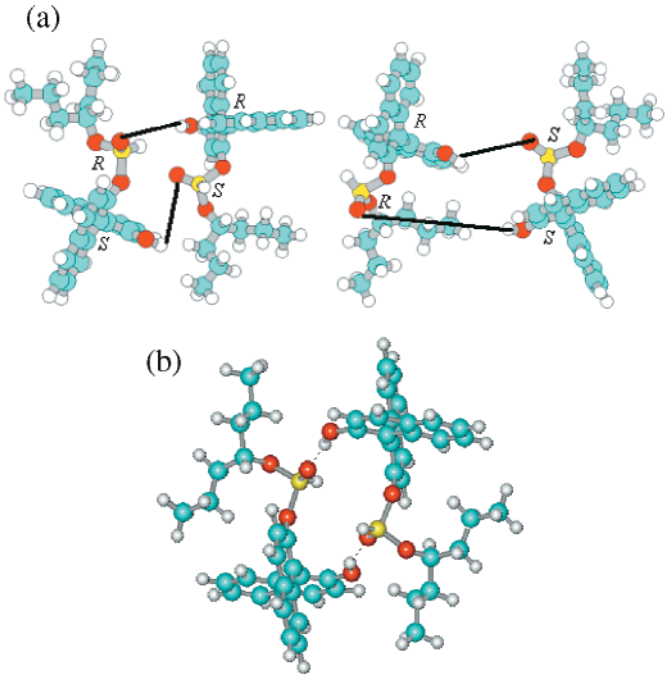


impact MS data did not show M_2^+ and instead revealed a 610/611 fragment (not detected by the ES analysis), a peak for M^+, the 350 peak, a peak at 332, and a 100% base peak at 286 for binaphthol. Scheme 4 summarizes these MS data and the formulations that correspond to the *m/z* values.

The percent abundance in the EI spectrum of the M^+ 448 peak is only about a fifth that of the 610/611 fragment, implying that cleavage of one P–O_{BINOL} bond and one [O–H---O] H-bond to form the 610/611 fragment takes preference over cleavage of the two H bonds to form the monomer; this suggests that the hydrogen bonding is strong (as indicated by the O---H---O structural data) and indeed even implies strength comparable to that of a P–O bond (at least under the EI conditions!). The reverse situation pertains to ES conditions where the monomer is formed exclusively (with the 350/332 fragments) from the dimer with respect to the 610/611 fragment; presumably, methanol breaks down most of the dimer structure by hydrogen-bond formation and prevents the intramolecular rearrangement required to produce the 610 fragment (Scheme 4).

Plausible mechanisms for the conversion of dimer **5a** to fragment 610 *m/z* (depicted by structures **5a$_1$** and **5a$_2$**) are outlined in Scheme 5 and involve direct loss of binaphthol from the dimer to give **5a$_1$** (step b), rearrangement of **5a$_1$** to **5a$_2$**, or direct nucleophilic attack by a binaphthol oxygen of one monomer at the phosphorus of the second monomer to give **5a$_2$** again with loss of binaphthol (step a). The facts that (*i*) the 610 fragment is not seen in the ES-MS, (*ii*) the polar methanol solvent does not break up completely the hydrogen bonds of the dimer, and (*iii*) judging by the sharp melting point at 144 to 145 °C (the hydrogen bonds likely remain intact at this temperature) are all consistent with the [O---H---O=P] hydrogen bond of the dimer being as strong as the P-O_{BINOL} bond. The loss of BINOL would then release strain to give **5a$_1$**, which could rearrange to **5a$_2$**. Justification of the direct rearrangement of the dimer **5a$_1$** to **5a$_2$** rearrangement is less obvious: a direct intramolecular nucleophilic attack by an oxygen of a BINOL hydroxyl group is unlikely because methanol is a better nucleophile and should interact more readily with the dimer to breakup the H bonds. However, the strength of H bonds between methanol and

Fig. 2. (*a*) Computer-generated minimum configuration of monomers **5m** using the HF/STO-3G program. Black lines (——) indicate hypothetical points of interactions to form dimers **5a** (left) and **5b** (right). (*b*) Computer-generated minimum configuration of dimer **5a** ($BINOL_R$-P_S---$BINOL_S$-P_R). Dotted lines show computed H bonds.

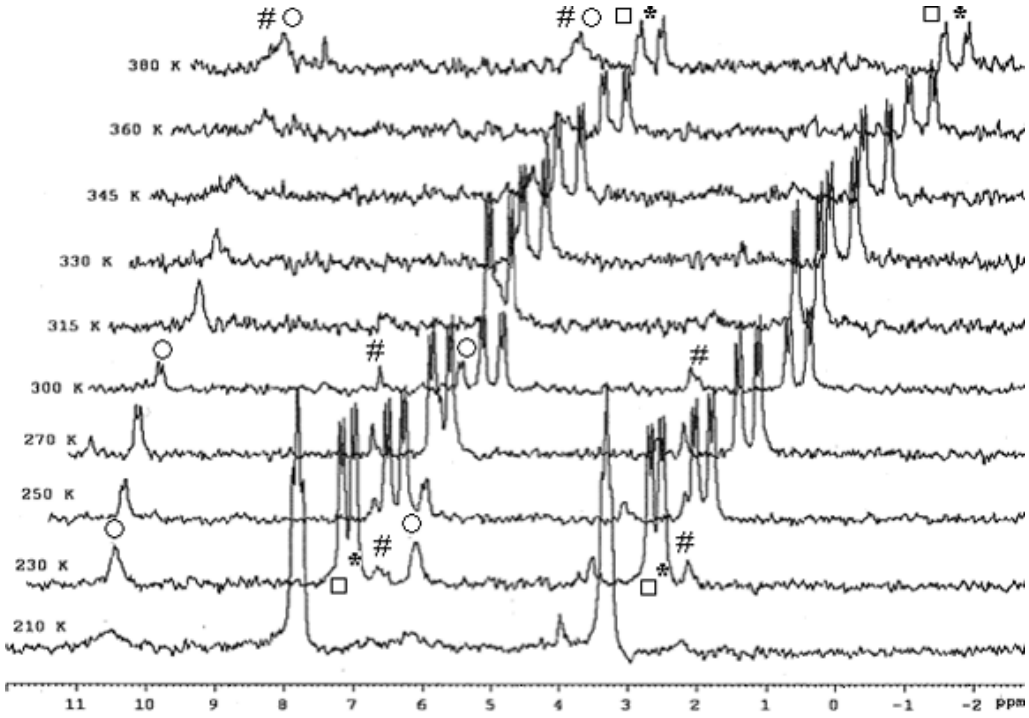


monomer is considered to be less than that of the H bonding in the dimer (judging by the observation of the M_2^+ ion). As evidenced by the high melting point, the boiling point (~180 °C in air), and thermal stability up to 250 °C (clear liquid at boiling point temperature with no color change), the stability of the dimer that results from the strong ("quasi-covalent") H bonds is remarkable. Liquid dimer, when cooled to room temperature (RT), re-melts again at 144 to 145 °C; when the dimer is placed under vacuum in a sealed capillary tube, decomposition becomes apparent at ~260 °C, with darkening of the color. A $CDCl_3$ solution of the dimer slowly decomposes in air (likely via hydrolysis) at RT to an unknown mixture as shown by ^{31}P NMR spectroscopy (Fig. S11).[2]

Diastereoselectivity of the dimer formation

Monomer **5m** has a chiral P center and axial chirality within the BINOL unit, while the dimer correspondingly has twice as many chiral moieties. The X-ray data of **5a** show the presence of the diastereomers $BINOL_S$-P_R:$BINOL_R$-P_S (meso form), and the NMR data of the crystal dissolved in $CDCl_3$ are consistent with the same structure. The solution NMR spectra of the crude sample show that the major component corresponds to **5a**; seen also are very similar resonances for the other major component (**5b**) and those of two minor ones (**5c** and **5d**), which have the same ^1H and ^{31}P NMR patterns as **5a** and **5b**, but as noted earlier the ^{31}P shifts are about 4 and 1 ppm downfield, respectively, from those of **5a** and **5b** (Figs. S1-S5).[2]

Fig. 3. Variable temperature ^{31}P NMR spectra of crude mixture of 4-n-heptyl-2-(2′-hydroxybinaphthyl)hydrogen phosphonate **5a** (*), **5b** (□), **5c** (○), and **5d** (#) in $CDCl_3$.



Computational analysis of the molecular geometry of the monomers predicts that only two enantiomeric pairs of these, with configurations $BINOL_R$-P_S:$BINOL_R$-P_S and $BINOL_R$-P_R:$BINOL_S$-P_S, have the appropriate geometry to interact and form the dimers (see Figs. 2, S12 and S13).[2] The first combination ($BINOL_R$-P_S:$BINOL_R$-P_S) is that found experimentally for **5a**, while the non-isolated **5b** is most likely of the $BINOL_R$-P_R:$BINOL_S$-P_S configuration. Other double combinations of monomers via hydrogen bonding to form the six other diastereomers are not possible because the monomers do not have the appropriate configurations, as seen in Fig. S12.[2]

Variable temperature ^{31}P NMR data from 210–380 K (Fig. 3) indicate that the chemical shifts of the major components (**5a** and **5b**) do not vary much with temperature, while those of the minor components (**5c** and **5d**) do. The NMR behavior is reversible, and the original ratio of isomers was seen on cooling the solution to 230 K; the data are qualitatively consistent with reversible conversion of dimers to monomers with increasing temperature, and so speculatively **5c** and **5d** might be monomeric diastereomers.

NMR and MS data on the mixture of major species **7a** and **7b** and minor species **7c** and **7d**, in which the 4-heptyl group of **5** has been replaced by cyclohexyl, suggest behavior similar to that found for the 4-heptyl system.

Conclusions

The dimer 4-heptyl-2-(2′-hydroxybinaphthyl)hydrogen phosphonate, accidentally synthesized by hydrolysis of 4-(3,5-dioxa-4-phosphacyclohepta[2,1-α;3,4-α′]-dinaphthalene-4-yloxy)heptane at RT, is a centrosymmetric 18-membered ring structure consisting of monomers, strongly hydrogen bonded via two P=O---H–O moieties; a corresponding cyclohexyl analogue appears to behave similarly. Racemic BINOL was used as a precursor reagent, but only two out of the eight possible diastereomeric dimers are formed from the racemic mixture of monomers. The diastereoselective formation of the H-bonded dimers is controlled by molecularly constrained geometry of the monomer.

Experimental

The various NMR spectra were recorded at RT (~20 °C) in $CDCl_3$ solution (unless stated otherwise) on Varian 90 MHz or Bruker AV 300 or 400 MHz instruments; singlet (s), doublet (d), triplet (t), multiplet (m), quintet (quin), broad (br); *J* values are given in Hz. FT-IR spectra (KBr, reported in cm^{-1}) were obtained on a Shimadzu IR-470 instrument. MS data (stated as *m*/*z* values) were acquired on Kratos Concept IIHQ LSIMS or Bruker Esquire ESI instruments. The computational analyses were performed using HyperChem pro 6.0, with PM3 calculations optimized by Polak-Ribiere algorithms. The PM3 optimized geometries were then taken for further optimization with the HF/STO-3G basis set. Racemic 1,1′-bi-2-naphthol (BINOL) was either purchased or prepared by a reported method (17).

X-ray crystallographic analysis of 5a

Measurements were made at –100 °C on a Rigaku ADSC CCD area detector with graphite monochromated Mo Kα radiation (λ = 0.710 60 Å). The final unit-cell parameters were based on 7004 reflections with 2θ = 4.2°–55.7°. The data were collected and processed using the d*TREK program (18). The structure was solved by direct methods (19) and

Table 2. Crystal data for **5a**.

Emprical formula	$C_{27}H_{29}O_4P$
Formula weight	448.50
Crystal size (mm^3)	0.20 × 0.20 × 0.20
Crystal system	Triclinic
Space group	$P\bar{1}$ (#2)
a (Å)	1.6440(2)
b (Å)	11.3196(3)
c (Å)	11.4692(2)
α (°)	67.535(9)
β (°)	86.23(1)
γ (°)	67.544(8)
Volume ($Å^3$)	1175.0(1)
Z	2
D_{calcd} (mg m^{-3})	1.268
F(000)	476
μ cm^{-1}	1.48
Reflections collected	10 620
Unique reflections	4785 (*R*(int) = 0.032)
No. of observations	($I > 2\sigma(I)$) 3759
Data, parameters	4785, 335
Goodness-of-fit (all data)	1.00
Final *R* indices	($I > 2\sigma(I)$) $R_1 = 0.040$, $wR_2 = 0.103$
R indices (all data)	$R_1 = 0.055$, $wR_2 = 0.109$

Table 3. Selected bond lengths of **5a** (esds in parentheses).

Bond[a]	Length (Å)
P(1)—O(3)	1.4578(11)
P(1)—O(2)	1.5544(12)
P(1)—O(1)	1.5865(11)
P(1)—H(1)	1.295(16)
O(1)—C(1)	1.4073(17)
O(2)—C(21)	1.5006(19)
O(4)—C(12)	1.3634(18)
O(4)—H(4)	0.89(2)
O(3)—H(4)	1.81(2)
C(10)—C(11)	1.4942(19)

[a]Atom numbers correspond to those shown in Fig. 1.

expanded using Fourier techniques (20). The non H atoms were refined anisotropically, while the H atoms were included but not refined. Some of the crystallographic data are given in Table 2, while selected bond lengths and angles are given in Tables 3 and 4, respectively.

4-Chloro-3,5-dioxa-4-phosphacyclohepta-[2,1-α;3,4-α′]-dinaphthalene (3)

In a 250 mL, two-necked flask, maintained at ~0 °C and equipped with a magnetic stirrer, freshly redistilled PCl_3 (1.5 mL, 17.2 mmol) was dissolved in 50 mL of dry Et_2O under N_2. To this solution was added BINOL (3.67 g, 13 mmol) in 100 mL of dry Et_2O, followed by Et_3N (4.3 mL, 14.9 mmol) dropwise, and the solution was stirred for 20 h at ~0 °C. The reaction mixture was then filtered, and the residue was washed with 5 mL of dry Et_2O; solvent was evaporated under vacuum from the filtrate to yield a yellow solid. IR: 3500 (m), 3100 (m), 1620 (s), 1590 (s), 1500 (s), 1210 (s), 960 (s), 820 (s), 750 (s). ^{1}H NMR (CCl_4) δ: 7.3–7.7 (m, 8H), 8.0–8.3 (m, 4H). ^{31}P NMR ($CDCl_3$) δ: (s, 178.8). Compound **3** was used without further purification for the synthesis of **4**.

Table 4. Selected bond angles of **5a** (esds in parentheses).

Bond[a]	Angle (°)
O(4)–H(4)–O(3)	159(2)
O(3)–P(1)–O(2)	118.32(7)
O(3)–P(1)–O(1)	113.50(7)
O(2)–P(1)–O(1)	102.16(6)
O(3)–P(1)–H(1)	112.7(7)
O(2)–P(1)–H(1)	103.9(7)
O(1)–P(1)–H(1)	104.7(8)
C(1)–O(1)–P(1)	122.24(9)
C(21)–O(2)–P(1)	122.27(10)
C(12)–O(4)–H(4)	114.4(14)
C(10)–C(1)–C(2)	123.47(14)
C(10)–C(1)–O(1)	117.78(13)
C(2)–C(1)–O(1)	118.66(13)
C(9)–C(10)–C(11)	120.98(12)
O(4)–C(12)–C(11)	124.08(14)
O(4)–C(12)–C(13)	114.68(13)
O(2)–C(21)–C(22)	107.92(12)
O(2)–C(21)–C(25)	111.86(18)
C(22)–C(21)–C(25)	108.84(18)
O(2)–C(21)–H(21)	109.4
C(22)–C(21)–H(21)	109.4
C(25)–C(21)–H(21)	109.4

[a]Atom numbers correspond to those shown in Fig. 1.

4-(3,5-Dioxa-4-phosphacyclohepta[2,1-α;3,4-α′]-dinaphthalene-4-yloxy)heptane (4)

Under conditions used for the preceding synthesis, to compound **3** (1.50 g, 4.3 mmol) dissolved in 20 mL dry toluene was added 4-heptanol (0.50 g, 4.3 mmol). To this solution at 0 °C, Et_3N (2.5 mL, 8.6 mmol) was added dropwise, and the mixture was stirred for 48 h, with the reaction progress being monitored by TLC. The white solid $[Et_3NH]^+Cl^-$ was removed by filtration, and the filtrate evaporated to dryness to give a light yellow solid, which was then washed through a silica gel column using cyclohexane – ethyl acetate (9:1); the fraction containing **4** was evaporated to dryness and the solid residue was recrystallized from the same solvent mixture to yield pure **4** in 80% yield. Melting point 124–126 °C. IR: 3050 (w), 2900 (m), 2850 (m), 1620, (m), 1580 (s), 1500 (s), 1375 (s), 1320 (s), 1060 (m), 950 (s), 930 (s), 820 (s), 750 (s), 695 (m), 640 (m), 550 (m). ^{1}H NMR δ: 0.8–1.7 (m, 6H, C*H*$_3$; and 8H, C*H*$_2$), 4.1–4.5 (m, 1H, C*H*), 7.2–8.2 (m, 12H, binaphthyl). ^{31}P{^{1}H} δ: (s, 146.0).

4-*n*-Heptyl-2-(2′-hydroxybinaphthyl)-hydrogen-phosphonate (5)

The compound was prepared by allowing compound **4** to stand in air at ambient temperature for days, either in the solid state or in acetone solution. A mixture of species is formed but one, labeled **5a**, was isolated as pale yellow crys-

tals (mp 144 to 145 °C, bp. ~180 °C), which were grown by slow evaporation of solvent at RT from a 9:1 mixture of cyclohexane–CH_2Cl_2 solution of the crude isolated product. Characterization data of **5a** were as follows. ^{1}H NMR $\delta_{binaphthyl}$: 8.08 (d, 1H, J = 9), 8.02 (d, 1H, J = 8.98), 7.97 (d, 1H, J = 8.91), 7.89 (d, 1H, J = 7.42), 7.69 (dd, 1H, J = 8.94, J = 1.0), 7.47 (t, 1H, J = 8.0), 7.39 (d, 1H, J = 8.90), 7.30 (m, 4H, one due to O*H*?), 7.25 (d, 1H, J = 8.3), δ: 7.20 (d, 1H, J = 9.0), 6.65 (d, 1H, $^1J_{HP}$ = 703, O=P-*H*; seen as a singlet in the ^{1}H{^{31}P} spectrum), 3.64 (m, 1H, C*H*), 1.27–1.07 (m, 8H, CH_2), 0.60 (t, 3H, J = 7.30, CH_3), 0.72 (t, 3H, J = 7.30, CH_3); Fig. S6. ^{31}P NMR δ: 3.80 (dd, $^1J_{PH}$ = 707, $^3J_{PH}$ 10.7); Fig. S7. ^{31}P{^{1}H} NMR δ: 3.80 (s); Fig. S7. ^{13}C{^{1}H} NMR (1:1 CD_3COCD_3–$CDCl_3$) δ: 18.08, 18.34, 28.50, 37.36, 37.40, 37,44, 77.50, 114.6, 118.7, 121.5, 121.5, 123.5, 124.8, 125.9, 126.2, 126.9, 127.2, 128.3, 128.5, 130.2, 130.4, 132.0, 134.2, 134.4, 146.5, 146.6, 153.1. MS (EI): dimer M^+ = 896 (0%); M – 286 = 610 (25%), 611 (19%); monomer M^+ 448 (8%), 350 (22%), 332 (55%), 286 (100%), 268 (40%), 239 (40%). Low-resolution ESI MS (CH_3OH–$CHCl_3$): dimer M^+ 897.3 (17%), 898.3 (6.5%), 899.3 (1.1%), 610 (0%); monomer M^+ = 449.1 (24%), 450.1 (4.2%), 352.0 (10.8%), 351.0 (100%), 333.0 (2%), 338.3 (2.2%), 287.1 (2%), 269.1 (1.86%).[2]

Species present in the crude product were **5a** (45%), **5b** (36%), **5c** (13%), **5d** (5%), and **5x** (2%). NMR data for the other species were as follows: ^{1}H NMR δ: 8.0–6.98 (m, binaphthyl) 6.65 (d, ^1J = 703), 6.58 (d, ^1J = 703), 6.575 (d, $^1J_{HP}$ = 705), 6.21 (d, $^1J_{HP}$ = 706); δ: 4.32 (m), at 3.95 (m), at 3.65 (m), and 3.53 (m), 1.60–0.40 (m, CH_3 and CH_2); Figs. S3, S5, and S8. ^{31}P NMR (**5b**) δ: 4.20 (dd, $^1J_{PH}$ = 720, $^3J_{PH}$ = 8.4); (**5c**) δ: 8.80 (dd, $^1J_{PH}$ = 704, $^3J_{PH}$ = 9.0); (**5d**) δ: 5.45 (d, br, $^1J_{PH}$ = 720); and an unknown (**5x**) δ: 3.35 (d, br); Figs. S2. ^{31}P{^{1}H} NMR δ: 4.20 (s, **5b**), 8.80 (s, **5c**), 5.45 (s, **5d**), and unknown compound at δ 3.35 (s, **5x**); Fig. S1. ^{1}H{^{31}P} NMR δ: 8.05–6.97 (m), 6.63 (s), 6.59 (s), 6.57 (s), and 6.62 (s), 4.40 (quin), 4.10 (quin), 3.65 (quin), 3.45 (quin), 1.60– 0.40 (m, CH_3 and CH_2); Fig. S8. Recrystallization of the crude solid from Et_2O–cyclohexane (1:9) gave mainly the two major components (**5a** and **5b**); Figs. S4 and S5.[2]

3,5-Dioxa-4-phosphacyclohepta[2,1-α;3,4-α′]-dinaphthalene-4-yloxy)cyclohexane (6)

The synthesis of **6** was identical to that used for the synthesis of **4** except that cyclohexanol (0.43 g, 4.3 mmol) was used. The crystallization produced **6** in 70% yield, mp 64–66 °C. IR: 3100 (w), 2900 (s), 2800 (m), 1720, (s), 1620 (m), 1590 (s), 1510 (s), 1460 (s), 1370 (m), 1330 (s), 1230 (s), 1080 (m), 980 (s), 940 (s), 820 (s), 750 (s), 690 (s), 600 (s). ^{1}H NMR δ: 1.0–1.90 (m, 10H), 4.1– 4.5 (m, 1H), 7.5–8.3 (m, 12H). ^{31}P{^{1}H} NMR δ: (s, 150.0).

Cyclohexyl-2-(2′-hydroxybinaphthyl)-hydrogen phosphonate (7)

The compound was prepared by allowing compound **6** to stand at ambient temperature for several days in the solid state or in solution. Crystallization of the isolated crude residue from a 19:1 mixture of cyclohexane–acetone solution produced a pale yellow solid. ^{1}H NMR (for mixture) δ: 8.00–6.94(m), 6.91 (d, $^1J_{HP}$ = 720), 6.55 (d, $^1J_{HP}$ = 705), 6.43 (d, $^1J_{HP}$ = 720), 4.31 (m), 4.02 (m), 3.78 (m), 3.42 (m) and 1.70–0.70 (m); Fig. S10. ^{31}P{^{1}H} NMR analysis showed components at δ: 3.94 (**7a**, 40%), 4.23 (**7b**, 38%), 8.55 (**7c**, 18%), 5.50 (**7d**, 4%), and a trace amount of an unknown component; Fig. S9. ^{31}P NMR for **7a**–**7d**, respectively, δ: 3.95 (dd, $^1J_{PH}$ = 720, $^3J_{PH}$ = 9.9); 4.29 (dd, $^1J_{PH}$ = 720, $^3J_{PH}$ = 9.3); 8.60 (dd, $^1J_{PH}$ = 704, $^3J_{PH}$ = 9.0); 5.50 (br d, $^1J_{PH}$ = 725); Fig. S9. Low-resolution ESI MS (CH_3OH–$CHCl_3$): dimer M^+ 866.1 (10%), 865.3 (26%), 863.0 (8.8%), 795.3 (3%), 770.3 (3.8%), 707.3 (6.6%), 693.3 (6.6%), 619.3 (8.6%), 605.3 (1.16%), 561.2 (12.9%), 534.1 (26.5%), 532.1 (23%), 517.2 (10.1%); monomer M^+ = 433.1 (32.99%), 351 (40.74%), 311 (8.68%), 237 (100%).

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