Conversion of Meso to dl Form and Vice Versa in Bisphosphonates: Synthesis and Structures of New Meso, dl and (Meso + dl) Bisphosphonates Derived from Cyclic Phosphites and Dialkyl Acetylenedicarboxylates

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Received 11 August 2004

SYNTHESIS 2004, No. 18, pp 3037–3042
Advanced online publication: 02.11.2004
DOI: 10.1055/s-2004-834906; Art ID: P09504SS
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Abstract: The bisphosphonates [(OCH₂CR–CH₂O)P(O)CHC(O)OR’]₃, [R = R’ = Me (5), R = Me, R’ = Et (6), R = Et, R’ = Me (7), R = R’ = Et (8)], [CH₆(6-t-Bu-4-Me-C₆H₄)P(O)CHC(O)OR]₂, [R = Me (9), Et (10)] and [(OCH₂CMe₂–CH₂O)P(SCH₂C(O)OR)₂]₀, [R = Me (11), Et (12)] have been prepared by the reaction of the corresponding cyclic phosphites with dimethyl acetylenedicarboxylate or diethyl acetylenedicarboxylate in the presence of a base [Et₃N or n-BuLi]. The structures of dl-, meso- and (dl + meso) forms [6a, 6b and 6ab] of 6 as well as the meso form of 8 are determined from X-ray crystallography. By means of combined X-ray structural and ³¹P NMR spectroscopic investigations, it is shown that the meso form can be converted to the dl form and vice versa. A possible rationale invoking the intermediary of an enolic form is proposed for this observation.

Key words: bisphosphonates, epimerization, diastereomers, X-ray structures, ³¹P NMR

We have been interested in the synthesis and utility of organophosphonates, and in this paper, we report the synthesis of bisphosphonates (type IV) based on cyclic phosphites (OCH₂CR–CH₂O)P(O)H [R = Me (1), Et (2)], CH₆(6-t-Bu-4-Me-C₆H₄)P(O)H (3) and the thio-phosphate (OCH₂CMe₂–CH₂O)P(S)H (4) (Figure 1). More importantly, we demonstrate the thermal meso ↔ dl interconversion of the compounds thus prepared by means of a combined ³¹P NMR and X-ray structural investigations.

Figure 1

Synthesis of the bisphosphonates 5–12 is accomplished by treating 1–4 with dimethyl acetylenedicarboxylate or diethyl acetylene-dicarboxylate at room temperature (Scheme 1, Table 1). In the case of 5–8, 11 and 12, Et₃N was used as a base (catalyst) but for 9 and 10, n-BuLi was required to effect the reaction. In these reactions, bisphosphonates of type III were not observed (NMR evidence). The reaction using the thio-phosphate 4 was faster than the rest (TLC monitoring). The reaction mixture in all the cases showed two ³¹P NMR signals in significant quantities and we were able to isolate the compound (diastereomer) corresponding to the downfield signal in the case of 5, 6–10 and 12. An X-ray structure (see experimental section) of the downfield isomer of 8 reveals that it is the meso form and on this basis all the downfield signals are ascribed to the meso form.

Interestingly, while crystallizing 8, it was noticed that although the initial reaction mixture showed a 1:2 ratio of the two ³¹P NMR signals mentioned above, the mother-liquor after removal of subsequent batches of crystals still showed the downfield signal as a major component. This prompted us to look for the crystallizing of the second iso-mer also. We succeeded in the case of compound 6 which could be crystallized in three distinct forms from the same solvent system: (a) dl form [square blocks, orthorhombic space group, 6a] (b) meso form [needles, tetragonal space group; 6b], and (c) (meso + dl) form [thin plates, mono-

Racemization/epimerization of organic compounds containing chiral centers is an important process in organic chemistry. When a compound contains two chiral carbon atoms, the possible conversion of meso diastereomer to the dl form (or vice versa) is an interesting point for investigation. The reaction of dialkylphosphites (RO)₂P(O)H (I) with activated alkenes or acetylenes, in the presence of a suitable base/catalyst or upon heating, leads to a variety of very useful phosphonates, often with one or more chiral centers. For example, in the reaction of (RO)₂P(O)H (I) with R’C≡CR’, three types of products (RO)₂P(O)CR’=CHR’ (II), [(RO)₂P(O)]₂CR’CH₂R’ (III) and (RO)₂P(O)CHR’CH(R’P(O)(OR)₂ (IV), among which IV has two chiral centers, can be formed. Although there are a couple of reports on compounds of this type, no mention has been made of the diastereomer formation/isolation. Such addition of H–E bonds (E = heteroatom) across unsaturated carbon linkages is an important reaction from a synthetic viewpoint and the products containing heteroatom-to-carbon bonds are versatile intermediates in synthetic chemistry. In particular, organophosphonates that possess a C–P bond have been found to be versatile reagents, have a varied biological activity and are useful in material chemistry. 
clinic space group, 6ab). In general, the meso form was less soluble than the dl form. The X-ray structures of 6a and 6b along with the Newman projection along the C(H)–C(H) bond axis are shown in Figures 2 and 3 respectively.11 The relevant torsion angles are given in Table 2. The structure and dihedral angles in molecule-I (in the asymmetric unit) of 6ab are nearly the same as that in 6a while those in 8 and molecule-II of 6ab are essentially the same as that in 6b. It can be noticed that in the dl form the conformation is not perfectly staggered; we attribute this to the differing steric interactions of the substituents on C(6) and C(6¢). Although there are weak C–H···O intermolecular contacts [C···O distance 3.4–3.6 Å] present in these structures, it is unlikely that these are responsible for distorting the intramolecular torsion angles.

The presence of such diastereomers was not inferred in analogous bisphosphonates previously3 and hence we wanted to study this aspect further. Pure meso and dl forms are stable in CDCl3 solution at room temperature (31P NMR). But when 6a (dl form) was heated to its melting point, kept at this temperature for 3 min and cooled, the resulting solid showed a mixture of dl and meso diastereomers [Figures 4(a) and 4(b)] in nearly equal quantities. What is perhaps more interesting is that when meso-8 was heated to its melting point and cooled, the resulting solid also contained a mixture of dl and meso diastereomers [Figures 4(c) and 4(d)] in nearly equal quantities.

It is possible that the above interconversion takes place via the enol form (V, Figure 5) of the bisphosphonates, because of the lability of the hydrogen attached to the α-carbon.12 This enol form may be stabilized by intermolecular hydrogen bonding between O–H and the phosphoryl oxygen. Enolic hydrogen can go back to its original position through either of the sides and hence could lead to both the meso and dl forms. Although two doublets [JPP = 64 Hz] are also discernible in Figure 4(d), we are not able to obtain this material separated. The solid mixture showed a broad band at ca. 3450 cm–1 in the IR spectrum, but enolic OH could not be seen clearly in the 1H NMR spectrum.

As regards the identification of the dl and meso forms,13C NMR is also quite useful. Whereas the P-CH carbon

<table>
<thead>
<tr>
<th>Compd</th>
<th>Mp (°C)</th>
<th>Yield (%)</th>
<th>δ (P)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>206–208 (meso)d</td>
<td>70</td>
<td>10.1 (1)</td>
</tr>
<tr>
<td>6</td>
<td>170–172 (dl)</td>
<td>94</td>
<td>11.2 (1)d</td>
</tr>
<tr>
<td>7</td>
<td>150–154 (meso + dl)</td>
<td>84</td>
<td>10.3 (1)</td>
</tr>
<tr>
<td>8</td>
<td>146–148 (meso)d</td>
<td>86</td>
<td>11.4 (1)</td>
</tr>
<tr>
<td>9</td>
<td>260 (meso)d</td>
<td>56</td>
<td>9.3 (1)</td>
</tr>
<tr>
<td>10</td>
<td>250 (meso)d</td>
<td>48</td>
<td>10.8 (1)</td>
</tr>
<tr>
<td>11</td>
<td>202–206 (meso + dl)</td>
<td>80</td>
<td>80.9 (1)</td>
</tr>
<tr>
<td>12</td>
<td>164–166 (meso)d</td>
<td>70</td>
<td>79.8 (1)</td>
</tr>
</tbody>
</table>

Table 1 31P NMR Data for the Bisphosphonates 5–12 (cf Scheme 1)

* Chemical shifts (80 MHz or 160 MHz) are referenced to ext. 85%H3PO4.
* Meso + dl.
* Ratio of each isomer in the reaction mixture is given in parentheses.
* Pure diastereomer was isolated.

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shows a unique 5-line pattern for the meso form [A part of
AXX’ system; X = X’ = phosphorus], it shows up as a sim-
ple doublet for the dl form \[1 \mathbf{J}_{PC} = 118 \text{ Hz}\]. The C(O)OR
carbon for the meso form appears essentially as a singlet
\[\text{low}^{2,3} \mathbf{J}_{PC}\], but for the dl form it shows a multiplet [a dou-
blet of doublet due to higher \[2,3 \mathbf{J}_{PC}\] values].

In summary, we have presented here a well-characterized
bisphosphonate system for which the dl, meso and (dl +
meso) forms are isolated as crystalline solids. Conversion
of meso to dl form (and vice versa) is proven by means of
\[31P\] NMR spectroscopy. It is possible that the previously
reported analogous bisphosphonates also underwent this
epimerization process. Knowledge of this type of process
is deemed useful in practical resolution processes after
conversion of a meso compound to racemic mixture.

Chemicals were procured from Aldrich or local manufacturers; they
were purified when required. Solvents were purified according to
standard procedures.\(^\text{13}\) IR spectra were recorded on a JASCO FT/IR
5300 spectrometer using KBr pellets. \[1H, 13C\] and \[31P\] NMR spectra
were recorded on a Bruker 200 MHz or 400 MHz spectrometer with
chemical shifts (CDCl\(_3\)) measured against TMS (\[1H, 13C\]) or 85%
H\(_3\)PO\(_4\). The number of protons given under the \[1H\] NMR spectra for
all compounds except 9 and 10 is exactly half (since the other half
is symmetry-related). Elemental analyses were carried out on a
Thermo Finnigan EA1112 analyzer.

\[[(OCH_2CMe_2CH_2O)P(O)CHCOOEt]\] (6)
To a stirred solution of 1 (1.78 g, 11.8 mmol) and Et\(_3\)N (1.7 mL)
in anhyd CH\(_2\)Cl\(_2\) (30 mL) at 0 °C, diethyl acetylenedicarboxylate (1.01
g, 5.9 mmol) in CH\(_2\)Cl\(_2\) (10 mL) was added dropwise over a period
of 20 min. The reaction mixture was brought to r.t. and stirring con-
tinued for 8 h. The solvent was removed under reduced pressure and
the crude product was washed with EtOAc followed by crystalliza-
tion from CH\(_2\)Cl\(_2\)–hexane mixture (1:1) to give colorless crystals of
6. The crude material showed two peaks in the \[31P\] NMR spectrum
at \[\delta = 11.2\] and 12.9 (1:1 ratio). Yield (combined): 2.41 g (94%); mp
170–176 °C.

IR: 2982, 1736, 1285, 1057 cm\(^{-1}\).

\[1H\] NMR (400 MHz): \[\delta = 0.94, 1.01, 1.18, 1.30 \text{ (2 × s, 6 H, 2 ×}
C(CH\(_3\))\(_2\)), 1.31 \text{ (merged t,} \mathbf{J}_{HH} = 8.0 \text{ Hz, 3 H, CH}_3\text{CH}_3\), 4.02–4.36
(m, 7 H, 2 × OCH\(_2\) + P–CH + CH\(_2\)CH\(_3\)).

A small quantity (ca 10 mg, 6b) of the needle-shaped crystals was
first obtained from the reaction mixture (ca. 300 mg) using CH\(_3\)Cl\(_2–
hexane\) mixture (along with irregularly shaped crystals which were
not suitable for X-ray) and handpicked under the microscope. Further
crystallization of the rest of this material was done using
CH\(_3\)Cl\(_2–\)hexane (1:1) mixture at 35 °C. The first batch (ca. 3 h) of
crystals contained thin plates (ca. 100 mg, 6ab). From the mother-
lquor, the square block shaped crystals were obtained (ca. 100 mg,

\(\text{Table 2 Selected Torsion Angles in 6a and 6b}\)

<table>
<thead>
<tr>
<th>Torsion angle</th>
<th>Structure 6a</th>
<th>Structure 6b</th>
</tr>
</thead>
<tbody>
<tr>
<td>P–C6–C6′–P′</td>
<td>77.4 (2)</td>
<td>180.0</td>
</tr>
<tr>
<td>P–C6–C6′–C7′</td>
<td>−160.49 (12)</td>
<td>57.4 (2)</td>
</tr>
<tr>
<td>H6–C6–C6′–H6′</td>
<td>−158.8</td>
<td>180.0</td>
</tr>
<tr>
<td>C7–C6–C6′–C7′</td>
<td>−38.4 (3)</td>
<td>180.0</td>
</tr>
<tr>
<td>P–C6–C6′–H6′</td>
<td>−40.7</td>
<td>−61.6</td>
</tr>
<tr>
<td>H6–C6–C6′–C7′</td>
<td>81.4</td>
<td>−61.0</td>
</tr>
</tbody>
</table>
6a. ca. 12 h). The structures of all the three types of crystals were determined by X-ray crystallography.

6a

Mp 170–172 °C.

IR: 2973, 1736, 1289, 1057 cm⁻¹.

1H NMR (400 MHz): δ = 0.94, 1.28 [s, 6 H, C(CH₃)₃], 1.29 (merged t, 1JCH = 7.4 Hz, 3 H, CH₂CH₂), 3.99–4.28 (m, 6 H, 2 × OCH₂ + COOCH₂CH₂), 4.36–4.39 (d, 1JCH = 11.5 Hz, 1 H, P-CH).

13C NMR (50 MHz): δ = 13.8 (CH₃CH₂), 20.4, 22.0 [2 × s, C(CH₃)₃], 32.2 (s, CMe₂), 41.7 (d, 1JPC = 120.0 Hz, P-CH), 62.1 (s, CH₂CH₂), 78.0, 77.4 (2 × s) (or a d, 1JPC = 8.8 Hz, OCH₂), 166.9 (dd, 1JPC = 8.0 Hz, 1JPC = 20.0 Hz, COO).

31P NMR (160 MHz): δ = 11.2.

Anal. Calcd for C₁₈H₃₂O₁₀P₂: C, 45.96; H, 6.81. Found: C, 45.96; H, 6.78.

There was no conversion to the other diastereomer after 7 d in CDCl₃ solution (31P NMR).

6b

Mp 176–178 °C.

IR: 2980, 1736, 1285, 1055 cm⁻¹.

1H NMR (400 MHz): δ = 1.02, 1.19 [s, 6 H, C(CH₃)₃], 1.33 (t, 1JCH = 8.0 Hz, 3 H, COOCH₂CH₂), 4.07 (d, with virtual coupling, 1 H, P-CH), 4.10–4.40 (m, 6 H, 2 × OCH₂ + COOCH₂CH₂).

13C NMR (from the mixture, 50 MHz): δ = 13.8 (CH₃CH₂), 20.8, 21.6 [2 × s, C(CH₃)₃], 32.2, 32.3 (2 × d, 1JPC = 3.2 Hz, CMe₂), 40.3, 41.6, 42.8, 44.0, 44.7 (5 lines for P-CH), 62.2 (s, CH₂CH₂), 76.7, 77.0, 77.4 (three lines merged with others, OCH₂), 166.2 (s, COO).

31P NMR (160 MHz): δ = 13.3.

The NMR data for 6ab were the same as the reaction mixture; the data for the pure d and meso compounds are given above.

Compounds 5, 7, 8, 11 and 12 were prepared similarly; in the case of 5, MeCN was used for crystallization.

[(OCH₂CMe₂CH₂O)P(O)CHCOOMe]₂ (5)

The procedure was the same as that for 6 using 1 (4.45 g, 29.6 mmol) and dimethyl acetylenedicarboxylate (2.10 g, 14.8 mmol). The crude material showed two peaks in the 31P NMR spectrum at δ = 10.1, 11.9 (1:1 ratio). 31P NMR spectrum showed two sets of methyl signals: I set: δ = 0.98, 1.15; II set: δ = 0.92, 1.25. Two OCH₂ peaks at δ = 3.72, 3.77 were also observed. Other regions were complicated. In the 13C NMR spectrum, distinct peaks for the two isomers could not be observed. Repeated crystallization afforded the isomer with δ (P) = 11.9.

Yield (combined): 4.82 g (70%). Crystallization of the product from MeCN gave colorless crystals of 5 (meso form); mp 206–208 °C.

IR: 2980, 1736, 1285, 1055 cm⁻¹.

1H NMR (200 MHz): δ = 1.01, 1.18 (2 × s, 6 H, C(CH₃)₃), 3.81 (s, 3 H, COOCH₃), 4.05–4.12 (m, 5 H, 2 × OCH₂ + P-CH).

13C NMR (50 MHz): δ = 20.8, 21.7 [2 × s, C(CH₃)₃], 32.5 (CMe₂), 40.9, 41.7, 42.8, 44.0, 44.7 (5 lines for two P-CH), 53.1 (s, COOCH₃), 76.9 (d, 1JPC = 8.9 Hz, OCH₂), 166.7 (s, C=O).

31P NMR (80 MHz): δ = 11.9.

Anal. Calcd for C₁₉H₃₅O₅P₂; C, 43.44; H, 6.33. Found: C, 43.37; H, 6.39.

[(OCH₂CEt₂CH₂O)P(O)CHCOOMe]₂ (8)

The procedure was the same as that for 6 using same molar quantities.

Yield (combined): 84%; mp 150–154 °C.

IR: 2973, 1730, 1279, 986 cm⁻¹.

1H NMR (200 MHz): δ = 0.84, 0.85 (2 × merged t, 1JCH = 7.4 Hz, 6 H, CH₂CH₂), 1.37, 1.62 (merged 2 × q, 1JCH = 8.0 Hz, 4 H, CH₂CH₂), 3.81 (s, 3 H, COOCH₃), 4.05–4.14 (m, 5 H, 2 × OCH₂ + P-CH).

13C NMR (50 MHz): δ = 6.9 (s, CH₃), 22.6, 22.8 (2 × s, CH₂CH₂), 37.3 (s, CMe₂), 41.1, 41.7, 42.9, 44.1, 44.8, 45.9 (5 lines, d, 1JPC = 116.8 Hz for two types of P-CH), 52.9 (s, COOCH₂CH₂), 74.2, 74.8 (2 × s, OCH₂), 166.7 (s and four lines merged with others, C=O).

31P NMR (80 MHz): δ = 10.3, 12.3 (1:1 ratio). Pure isomer was not isolated in this case.

[(OCH₂CEt₂CH₂O)P(O)CHCOOMe]₂ (8)

The procedure was the same as that for 6 using same molar quantities; yield (combined): 86%.

The reaction mixture showed two 31P NMR signals at δ = 11.4 and 13.3 (1:2 ratio). In the 1H NMR, the reaction mixture showed complex spectrum due to which detailed assignment was difficult.

13C NMR (mixture): δ = 6.7, 6.8 (2 × s, CH₃CH₂), 13.6 (s, COOCH₂CH₂), 22.0, 22.2 (2 × s, CH₂CH₂), 37.2 (s, CMe₂), 42.3 (d, 1JPC = 116.0 Hz, P-CH), 62.0 (s, COOCH₂CH₂), 74.8, 75.4 (2 × s, OCH₂), 166.2 (four lines merged with others, C=O). Upon crystallization from CH₂Cl₂–hexane (1:1) the meso form of 8 with δ (P) = 13.3 could be isolated. An X-ray analysis was performed on this sample.
Mp 146–148 °C.

IR: 2969, 1738, 1302, 1073 cm⁻¹.

¹H NMR (200 MHz): δ = 0.85 (merged t, JFH₂ = 5.8 Hz, 6 H, CH₃(CH₂)), 1.32 (merged q, JFH₂ = 6.8 Hz, 4 H, 2 × CH₂CH₃), 1.52–1.56 (4 lines, JFH₂ = 7.6 Hz, 3 H, CH₂(CH₂COO), 3.92–4.24 (m, 7 H, 2 × OCH₂ + P-CH + COOC₂H₅).

¹³C NMR (50 MHz): δ = 6.7, 6.8 (2 × s, CH₂CH₃), 13.6 (s, COOCH₂), 22.4, 22.6 (2 × s, CH₂CH₃), 37.2 (s, CEl₂), 41.0, 41.7, 42.8, 44.0, 44.7 (5 lines for P-CH), 62.0 (s, COOCH₂CH₃), 73.9, 74.7 (2 × s, OCH₂), 166.1 (s, C=O).

³¹P NMR (80 MHz): δ = 13.3.


[(OCH₃C₂H₄O)(S)CHOOOMe]₂ (11)

The procedure was the same as that for 6. The reaction mixture showed two ³¹P NMR signals at δ = 80.99, 83.9 (1:1 ratio); yield (combined): 80%, mp 202–206 °C. IR: 2957, 1736, 1277, 992 cm⁻¹.

³¹P NMR (400 MHz): δ = 1.00, 1.27 (2 × s, H, 2 × CH₃), 3.79 (s, 3 H, COOCH₃), 4.03–4.54 (m, 5 H, 2 × OCH₂ + P-CH), 46.4, 47.8, 48.6, (five lines for P-CH), 53.0 (s, COOCH₂), 73.9, 74.7 (2 × s, OCH₂), 167.2, 167.3, (s, and four lines merged with others, C=O).

³¹P NMR (160 MHz): δ = 80.9, 83.9.

The compound was obtained as a mixture of *dl* and *meso* diastereomers.

[(OCH₃C₂H₄O)(S)CHOOEtt]₂ (12)

The procedure was similar to that for 6. The reaction mixture showed two ³¹P NMR signals at δ = 79.8, 83.3 (1:1 ratio). In the ¹H NMR, the reaction mixture showed signals at δ = 0.96, 1.09, 1.24–1.34 (m), 4.19–4.24 (m). ¹³C NMR (from the mixture): δ = 13.8 (C₂H₅CH₃), 20.8, 21.4 (2 × s, C(CH₃)₂), 32.2 (s, CMe₂), 47.3 (d, JCC = 11.8 Hz, PCH₂), 62.2 (CH₂C₂H₅), 77.5 (d, JPC = 10.6 Hz, OCH₂), 166.4 (dd, JPC = 6.0, 20.0 Hz, C=O).

Yield (combined): 70%; mp 164–166 °C. Pure *meso* isomer could be isolated.

IR: 2973, 1730, 1279, 1045, 985 cm⁻¹.

³¹P NMR (400 MHz): δ = 1.11, 1.12 (2 × s, 6 H, 2 × CH₃), 1.31 (t, JFH₂ = 7.2 Hz, 3 H, CH₂CH₃), 4.00–4.20 (m, 4 H, OCH₂), 4.26 (quat, JFH₂ = 7 Hz, 2 H, CH₂CH₃), 4.40 (ca d, with virtual coupling, 1 H, P-CH).

¹³C NMR (50 MHz): δ = 13.8 (CH₃C₂H₅), 21.6, 21.8 (2 × s, C(CH₃)₂), 32.8 (s, CMe₂), 47.3, 48.2, 49.1, 50.0, 50.9 (5 lines for P-CH₂), 62.2 (CH₂C₂H₅), 76.3 (d, JPC = 11.1 Hz, OCH₂), 165.8 (s, C=O).

³¹P NMR (160 MHz): δ = 83.3.

Anal. Calcd for C₁₈H₃₂O₁₀P₂: C, 74.01; H, 6.37; S, 12.78. Found: C, 74.20; H, 6.43; S, 12.30.

Crystal data for 6a: C₁₈H₃₂O₁₀P₂, M = 470.38, orthorhombic, space group Pccn, a = 10.97786(6) Å, b = 13.72417(4) Å, c = 15.9356(8) Å, V = 2400.992(1) Å³, Z = 4, m = 0.229 mm⁻², S = 1.044. Data/restraints/parameters: 2896/0/139. R indices [I > 2σ(I)]: R₁ = 0.0525, wR² (all data) = 0.1629. Max/min residual electron density [eÅ⁻³]: 0.48/–0.59.

Crystal data for 6b: C₁₈H₃₂O₁₀P₂, M = 470.38, tetragonal, space group P4₁nc, a = b = 16.3258(8) Å, c = 8.7906(6) Å, V = 2343.02(2) Å³, Z = 4, μ = 0.234 mm⁻¹, S = 1.055. Data/restraints/parameters: 2258/0/139. R indices (I > 2σ(I)): R₁ = 0.0442, wR² (all data) = 0.119. Max/min residual electron density [eÅ⁻³]: 0.22/–0.20.

Crystal data for 6c: C₁₈H₃₂O₁₀P₂, M = 470.38, monoclinic, space group C2/c, a = 18.7532(14) Å, b = 11.0501(8) Å, c = 23.8231(17) Å.
Å, β = 104.522(1), θ = 4779.0(6) Å, Z = 8, μ = 0.230 mm⁻¹, S = 1.033. Data/restraints/parameters: 5802/0/277. R indices (I > 2σ(I)): R1 = 0.0590, wR2 (all data) = 0.1880. Max/min residual electron density [eÅ⁻³]: 0.55/–0.32.

Crystal Data for

References

Acknowledgments

We thank Department of Science and Technology for financial support and for setting up of the National Single Crystal Diffractometer Facility at the University of Hyderabad. EB thanks CSIR (New Delhi) for a fellowship. We also thank UGC-UPE program for equipment.


(12) It can be noted that the proton attached to the carbon α to the phosphorus can be removed in the presence of a base (Horner–Wadsworth–Emmons reaction); in the present case it is suggested that the proton migrates due to thermal rearrangement.