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PHOSPHORUS HETEROCYCLE SYNTHESIS BY RPX_2. AlX_3 ADDITION TO [1,*n*] DIENES—VIII

THE SYNTHESIS AND STRUCTURE OF 3,9-DIOXA-2, 4-DIPHOSPHABICYCLO [3.3.1] NONANES.

A. Rudi, D. Reichman, I. Goldberg* and Y. Kashman*
Department of Chemistry, Tel-Aviv University, 69978 Ramat Aviv, Israel

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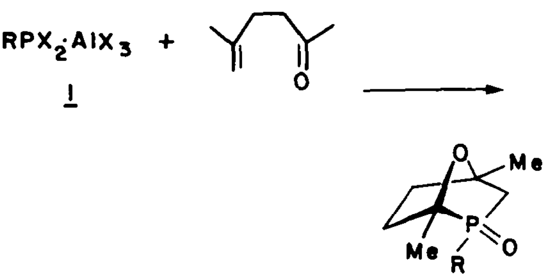
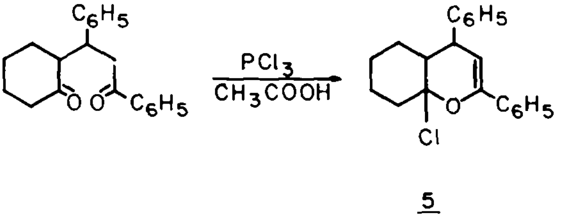
Abstract—3,9-Dioxa-2, 4-diphosphabicyclo [3.3.1] nonanes were synthesized by the reaction of methyl dihalophosphane with 1,5-diphenylpentan-1,5-dione in acetic acid. The structures of two (2 to 1) addition products (2 and 3) were established by X-ray diffraction analysis. The ^1H and ^{13}C NMR spectra of the new compounds are discussed.

The use of the $RPX_2.AlX_3$ complex (**1**) for the synthesis of new phosphaheterocycles starting from 1,*n*-dienes has been described in previous reports and summarized in a recent paper.[1] Furthermore, it could be shown that $\beta\gamma$- and $\gamma\delta$-unsaturated ketones and imines also react with **1**.[2] The $\gamma\delta$-unsaturated compounds react in a similar manner to the corresponding dienes to give the 7-oxa and 7 aza-2-phosphabicyclo [2.2.1] heptanes, e.g.



The above reaction led to the examination of the reaction between complex **1** and 1,*n* diketones. Among the first examined diketones were the 1, 5 diones. Unfortunately, under usual reaction conditions (CH_2Cl_2, 0–10°) no low molecular compound could be isolated. The literature revealed the reaction of Vyzotskii between 2-(α-phenacylbenzyl)cyclohexanone and PCl_3 which led to a mixture of three products.[3]

The reaction of $MePX_2$ and 1, 5-diphenylpentan-1, 5-dione afforded two isomeric crystalline compounds, **2** and **3**. Under similar conditions, 1,*n*-dienes and unsaturated ketones failed to give any pure products. Thus, Vyzotskii's reaction seems to be specific for 1, 5 diketones, as can be expected from the mechanism[3] (The following Scheme indicates compounds **5** and **6** to be intermediates of **7**).



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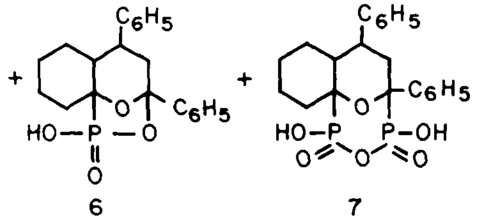

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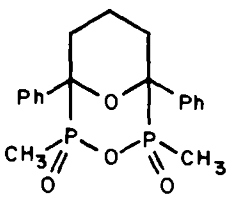
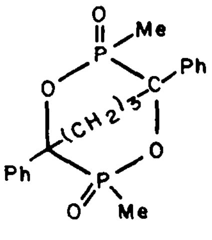
Both **2** and **3** are structural isomers, $C_{19}H_{22}O_4P_2$ (mass spectra and elemental analysis). The ^1H and ^{13}C NMR spectra of **2** and **3** (Table 1 and Experimental) clearly show the following moieties: 2 phenyls and a $-(CH_2)_3-$ chain (as could be expected starting from a 1, 5-diphenylpentadione), 2-MeP(O)O– groups and 2 quaternary C atoms α to O and P atoms. Characteristic for the MeP(O)OC– moiety are the relative large J_{pc}-values (e.g. 81 and 87 Hz in **2**). Compound **3** exhibiting a single P–Me resonance line, is of higher symmetry than **2** which shows two signals for the P–Me groups.

According to the spectral data, more than a single bicyclic structure could be suggested for **2** and **3** (Structures I and II).

All chemical efforts to distinguish between I and II as either one can give more than a single stereoisomer failed. Thus, we turned to an X-ray diffraction analysis.



I



II

An *ORTEP* view of the molecular structures of **2** and **3** is shown in Fig. 1. The structure of **3** is in agreement with the proposed model I (see above), having an approximate mirror (C_s) symmetry. The less symmetric product **2** has an isomeric structure, in which there is a different arrangement of substituents on one of the P atoms. However, in both molecules the bicyclic frame-

Table 1. ^1H NMR data of compounds 2–4

	2		3	4
$H_{6\alpha}, H_{8\alpha}$	3.08 bd $J_{6\alpha6\beta} = 14$ $^3J_{6\alpha P} = 2.5$ $J_{6\alpha7\alpha} = 3.8$	2.66m	3.07 bd $J_{6\alpha6\beta} = 14$ $^3J_{6\alpha P} = 2$ $J_{6\alpha7\alpha} = 3.4$ $J_{6\alpha7\beta} = 2.5$	3.02 bd $J_{6\alpha6\beta} = 14$ $^3J_{6\alpha P} = 2$ $J_{6\alpha7\alpha} = 3.2$
$H_{6\beta}H_{8\beta}$	1.78d quintet $^3J_{6\beta P} = 28$ $J_{6\beta7\alpha} = 14$ $J_{6\alpha6\beta} = 14$ $J_{6\beta7\beta} = 5$	2.05m $^3J_{8\beta P} = 22$	1.77d quintet $^3J_{6\beta P} = 28$ $J_{6\beta7\alpha} = 14$ $J_{6\beta6\alpha} = 14$ $J_{6\beta7\beta} = 4.6$	1.88 quintet $^3J_{6\beta P} = 28$ $J_{6\beta7\alpha} = 14$ $J_{6\alpha6\beta} = 14$
$H_{7\alpha}$	2.41 tquartet $J_{7\alpha7\beta} = 14$ $J_{7\alpha6\beta} = 14$ $J_{7\alpha6\alpha} = 3.8$		2.48 tquartet $J_{7\alpha7\beta} = 14$ $J_{7\alpha6\beta} = 14$ $J_{7\alpha6\alpha} = 3.4$	3.77 tt. [a] $J_{7\alpha6\beta} = 14$ $J_{7\alpha6\alpha} = 3.2$
$H_{7\beta}$	2.14 dd $J_{7\beta7\alpha} = 14$ $J_{7\beta6\beta} = 5$		2.00 bd $J_{7\beta7\alpha} = 14$ $J_{7\beta6\beta} = 4.6$ $J_{7\beta6\alpha} = 2.5$	
$P\text{-}CH_3$	1.48d $J_{PH} = 14$	1.79dd $J_{PH} = 14$ $J_{HH} = 1$	1.245 bd $J_{PH} = 13$	1.270 bd $J_{PH} = 13.5$

Note: (a) observed separately from the OMe signal when recording the spectrum in C_5D_5N

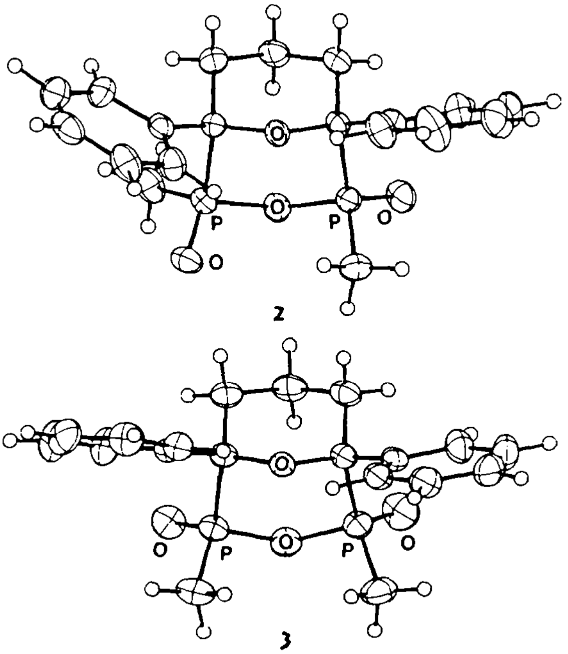


Fig. 1. ORTEP view of compounds 2 and 3.

work is the same. The difference between the relative orientations of the phenyl substituents could be attributed to the different nature of the 1, 2 phenyl-to-methyl and phenyl-to-phosphoryl steric interactions.

Details of the molecular geometries in the two compounds, which characterize covalent bonding in the diphosphabicyclo [3.3.1] nonane framework are compared in Table 2. They reveal the distribution of conformational strain within this system. For example the covalent bonds involving the quaternary C atoms are consistently longer than C(sp^3)–C(sp^3) and C(sp^3)–P bonds in other parts of the molecule, or than C(sp^3)–O bonds in ethers.

Interestingly, 2 crystallizes as a dihydrate, each water molecule being associated with one of the P=O groups. The observed P=O...O_w distances are 2.80 and 2.83 Å. In the crystal the H_2O molecules are located close to the inversion centers, allowing H-bonding interactions (at O_w...O_w distances of 2.83–2.84 Å) between the centro-symmetrically related entities. Consequently, there is a network of H-bonds extending throughout the crystal and stabilizing the structure.

After the structure determination of 2 and 3 by X-ray analysis, the interpretation of the NMR spectra could be undertaken. Among the spectra of 2 and 3, elucidation of

Table 2. Bond distances (Å) and bond angles (°) in the 3,9-dioxa-2, 4-diphosphabicyclo[3.3.1]nonanes. (The crystallographic numbering of atoms is shown in the Experimental)

	(3)	(2)		(3)	(2)
P(1) - C(7)	1.840(2)	1.060(2)	C(5) - C(6)	1.384(4)	1.394(5)
P(1) - C(19)	1.776(3)	1.769(2)	C(7) - C(8)	1.535(3)	1.531(2)
P(1) - O(3)	1.602(2)	1.622(2)	C(7) - O(1)	1.448(3)	1.450(2)
P(1) - O(4)	1.464(2)	1.473(1)	C(8) - C(9)	1.518(3)	1.519(4)
P(2) - C(11)	1.854(2)	1.843(2)	C(9) - C(10)	1.512(4)	1.512(3)
P(2) - C(18)	1.772(3)	1.774(2)	C(10)- C(11)	1.531(3)	1.532(2)
P(2) - O(2)	1.458(2)	1.472(2)	C(11)- C(12)	1.524(4)	1.517(3)
P(2) - O(3)	1.618(2)	1.607(2)	C(11)- O(1)	1.444(3)	1.444(3)
C(1) - C(2)	1.386(4)	1.387(2)	C(12)- C(13)	1.390(3)	1.379(3)
C(1) - C(6)	1.388(4)	1.390(4)	C(12)- C(17)	1.391(4)	1.396(4)
C(1) - C(7)	1.515(3)	1.521(3)	C(13)- C(14)	1.387(4)	1.385(3)
C(2) - C(3)	1.384(3)	1.383(4)	C(14)- C(15)	1.377(4)	1.380(5)
C(3) - C(4)	1.361(4)	1.374(5)	C(15)- C(16)	1.372(5)	1.365(4)
C(4) - C(5)	1.370(5)	1.367(3)	C(16)- C(17)	1.375(4)	1.386(3)
C(7) -P(1) -C(19)	108.5(1)	111.4(1)	C(1) -C(7) -C(8)	109.6(1)	113.3(2)
O(3) -P(1) -C(7)	102.8(1)	101.8(1)	C(1) -C(7) -O(1)	106.9(2)	104.8(1)
O(3) -P(1) -C(19)	104.8(1)	103.3(1)	O(1) -C(7) -C(8)	112.4(2)	110.6(2)
O(4) -P(1) -C(7)	114.6(1)	113.1(1)	C(7) -C(8) -C(9)	113.7(2)	113.0(2)
O(4) -P(1) -C(19)	114.1(1)	114.6(1)	C(8) -C(9) -C(10)	109.3(2)	110.1(2)
O(4) -P(1) -O(3)	111.1(1)	111.5(1)	C(9) -C(10)-C(11)	112.1(1)	113.4(2)
C(11)-P(2) -C(18)	109.0(1)	108.0(1)	P(2) -C(11)-C(12)	107.4(1)	108.1(2)
O(2) -P(2) -C(11)	114.2(1)	115.1(1)	P(2) -C(11)-O(1)	108.8(2)	105.7(1)
O(2) -P(2) -C(18)	115.2(1)	114.5(1)	C(10)-C(11)-P(2)	110.7(2)	112.3(1)
O(3) -P(2) -C(11)	103.0(1)	102.3(1)	C(10)-C(11)-C(12)	112.8(2)	111.7(2)
O(3) -P(2) -C(18)	103.7(1)	105.5(1)	C(10)-C(11)-O(1)	111.2(1)	112.3(2)
O(3) -P(2) -O(2)	110.7(1)	110.5(1)	O(1) -C(11)-C(12)	105.9(2)	106.4(2)
C(6) -C(1) -C(2)	118.4(2)	118.5(2)	C(11)-C(12)-C(13)	121.4(2)	121.9(2)
C(7) -C(1) -C(2)	122.0(2)	120.1(2)	C(11)-C(12)-C(17)	120.1(2)	119.5(2)
C(7) -C(1) -C(6)	119.6(2)	121.1(4)	C(17)-C(12)-C(13)	118.4(2)	118.6(2)
C(1) -C(2) -C(3)	120.2(2)	120.6(3)	C(12)-C(13)-C(14)	120.7(2)	120.5(3)
C(2) -C(3) -C(4)	121.0(3)	120.6(2)	C(13)-C(14)-C(15)	119.8(3)	120.5(2)
C(3) -C(4) -C(5)	119.6(3)	119.4(3)	C(14)-C(15)-C(16)	119.9(3)	119.4(2)
C(4) -C(5) -C(6)	120.3(3)	120.9(3)	C(15)-C(16)-C(17)	120.6(3)	120.8(3)
C(5) -C(6) -C(1)	120.5(2)	120.0(2)	C(16)-C(17)-C(12)	120.6(3)	120.2(2)
P(1) -C(7) -C(8)	112.3(2)	113.4(1)	C(11)-O(1) -C(7)	118.1(2)	118.8(1)
P(1) -C(7) -O(1)	106.3(1)	106.2(1)	P(2) -O(3) -P(1)	135.2(1)	128.4(1)
C(1) -C(7) -P(1)	109.1(1)	107.9(1)			

those belonging to the less symmetrical 2, was straight forward (Table 1 and Experimental).

The ^1H and ^{13}C NMR spectra of 3, on the other hand, require some explanations. Both spectra contain second-order resonance line systems. The most unusual 2 Me's signal of the $CH_3P(O)$–O–$P(O)CH_3$ moiety (Fig. 2) might well find its rationale assuming the Me to be part of a $[AXn]_2$ spin system. Our results are in good agreement with the spectra of molecules of type $[R_2P(X)]_2Y$ which were analyzed by Hagele *et al.* on the basis of a $[AXn]_2$

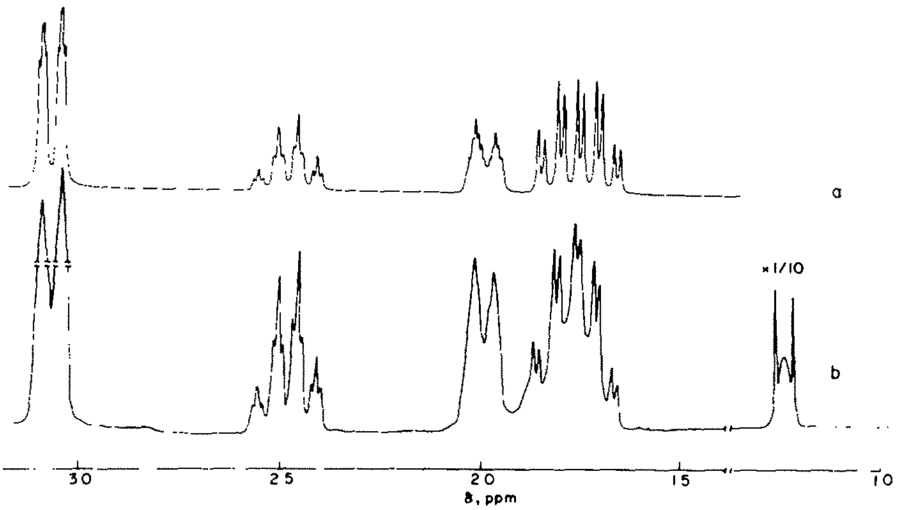


Fig. 2. Partial ^1H NMR spectrum of compound 3. (a) Calculated with the Bruker PANIC program, (b) observed.

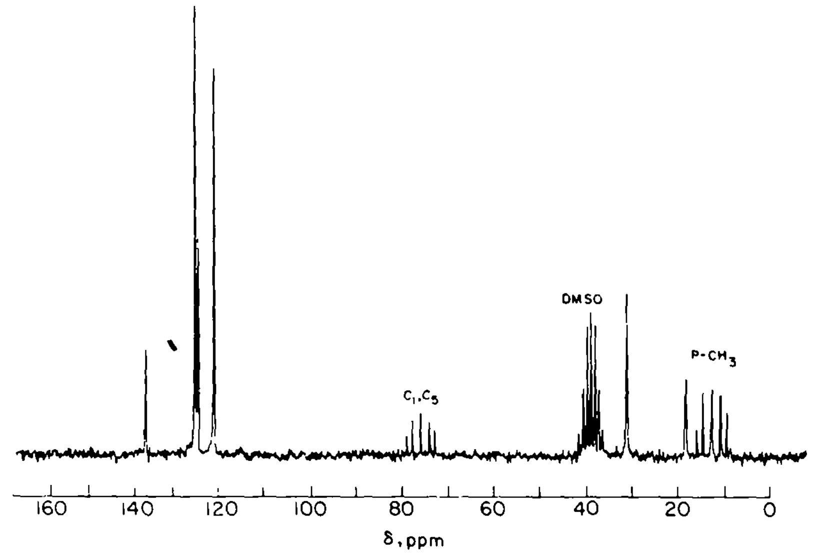


Fig. 3. ^{13}C NMR of compound **3**.

spin system and were simulated by computer programs.[4] Simulation of the ^1H-spectrum of **3** (Fig. 2)* gave good agreement with the observed spectrum.

In the ^{13}C NMR spectrum of **3**, the $C_{1(5)}$ and the two P–CH_3 signals are outstanding; both giving rise to 5 line multiplets centered at 77.0 and 11.6 ppm respectively (Fig. 3).

When there are two additional (to the ^{13}C and ^1H) spin-1/2 nuclei present in a compound and they are strongly coupled among themselves, the ^{13}C spectrum may be second-order.[5] Such a situation is common for compounds containing two P-atoms, since, as is well-known J_{PP} can be quite large. In particular ^{13}C spectrum will in general be second-order when the P nuclei are in equivalent chemical positions. The ^{13}C spectrum will then be the X region of an ABX system. Since isotopic chemical shifts induced by ^{13}C in ^{31}P resonance are likely to be small (relative to J_{PP}) the value of $\Delta\nu_{AB}$ will also be small; moreover, a 5-line pattern will result for the ^{13}C spectrum rather than the more general 6-line X spectrum expected from an ABX system.[6,7] Five-line patterns were observed for example in 1,6-diphosphatriptycene,[8] diphosphanes, dithioxo^5-λ diphosphanes and other compounds.[9] A full interpretation of the $[AXn]_2$ system (A=P) of the latter and similar compounds requires the knowledge of the J_{PC}-values. These coupling constant are sometimes available from the observation of the ^{13}C satellites in the ^{31}P spectrum. However, there are cases, as was found for **3**, where such data are not available.[8] Jakobsen has shown that the ^{13}C-^{31}P and ^{31}P-^{31}P coupling constants may also be determined solely from an analysis based on line position and intensities of the PND ^{13}C NMR spectrum.[8] Using this approach the spectrum of **3** could be rationalized and a good agreement was found between the calculated (based on the J values given in Table 3) and measured spectra.

Reacting 3-*p*-methoxyphenyl-1, 5-diphenylpentan-1, 5-dione with $MePCl_2$ afforded a single compound, **4**. The proton NMR spectrum of H-7 of **4** (possessing an axial–axial coupling constant of 14 Hz, Table 1) establishes the equatorial position of the *p*-methoxyphenyl substituent.

Supplementary material available. Tables of atomic coordinates and thermal parameters for **2** and **3** (4 pages) have been deposited with the British Library Lending Division.

EXPERIMENTAL

M.ps were taken on a Unimelt Thomas and Hoover's capillary m.p. apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer Infracord model 337 Spectrophotometer. NMR spectra were taken on a Bruker WH-300 or a Jeol JNM-C-60HL spectrometer (equipped with a P-decoupler) on 5–10% soln in $CDCl_3$ containing 1% TMS. ^{13}C-NMR spectra were taken on a Bruker WH-90 (22.63 MHz) instrument in $CDCl_3$; all chemical shifts are reported with respect to TMS (δo). Mass spectra were recorded on a DuPont 21–491B spectrometer.

General procedure. In the course of 5 min with stirring, 0.05 mol of the 1, 5-diketone was added in small portions to 0.01 mol of CH_3PCl_2 at 60°. Then, at the same temp 3mL of HOAc (gla) was added. The mixture was kept for 2 hr at 60°, then cooled down to r.t. and stirred for additional 16 hr. The mixture was then poured onto ice, extracted with $CHCl_3$ (3 × 30 mL), washed with $NaHCO_3$ aq, dried over $MgSO_4$, evaporated and finally submitted to a silica-gel column for chromatography.

Compound **2**. M.p. (Acetone) 214°, $\nu_{max}^{CHCl_3}$ 1490, 1450, 1310, 1050, 990, 940, 760 and 700 cm^{-1}, ^{13}C NMR, δ (d_6-DMSO): 12.6 dq (J_{pc} = 81 Hz), 13.0 dq (J_{pc} = 87 Hz), 17.4 t, 31.0 t, 30.5 t, 77.6 d (J_{pc} = 91 Hz), and 77.9 d (J_{pc} = 95 Hz), mass spectrum (*m*/*e*, %); 376 (M^+, 70), 296(30), 270(65), 244(45), 243 (100) and 235(80), for ^1H NMR see Table 1.

Compound **3**. M.p. (acetone) 230°, $\nu_{max}^{CHCl_3}$ 1505, 1450, 1430, 1310, 1305, 1250, 1210, 1100, 1050, 990, 950, 930, 910, 890, 880 790, 760, 710, 680 and 660 cm^{-1}, ^{13}C NMR, δ(d_6-DMSO): 11.63 (5 lines see Table 3), 22.55 t, 35.87 t(×2), 77.01 (5 lines, see Table 3), mass spectrum (*m*/*e*, %): 376 (M^+, 3), 297(10), 296(18), 282(35), 243(100), 235(30) and 182(43), for ^1H NMR see Table 1.

Compound **4**. M.p. (acetone) 193°, $\nu_{max}^{CHCl_3}$ 1600, 1510, 1450, 1310, 1250, 1210, 1180, 1100, 1030, 1010, 950, 890, 760, and 770 cm^{-1}, ^{13}C NMR, δ ($CDCl_3$) 13.06 (5 lines, see Table 3), 34.6d, 39.6 t (×2), 55.1 q (OCH_3), 79.3 (5 lines, see Table 3), mass spectrum (*m*/*e* %) 482 (M^+, 40), 402(67), 388(50) and 340(100) for ^1H NMR see Table 1.

Crystal structure analyses. X-ray diffraction data were measured on an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator, employing MoKα radiation ($\bar{\lambda}$ = 0.71069 Å). For both compounds the unit-cell dimensions were determined from 2θ measurements of 25 carefully centered

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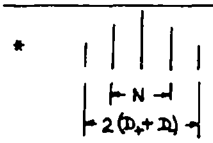
*The assignment of the spectrum was verified by calculated simulation with the Bruker PANIC program.

Table 3. ^{13}C NMR data of compounds 3 and 4[6,7]

	N*	2(D++D-)*	J (calculated)
3 P-CH_3	88.8	144	$J_{pp} = 56$, $J_{PCH_3} = 89.5$, $^3J_{PCH_3} = 0.9$
3 P-C-	93.6	143	$J_{pp} = 56$, $J_{PC_2} = 92$, $^3J_{PC_2} = 2.$
4 P-CH_3	91	145	$J_{pp} = 56$, $J_{PCH_3} = 91.5$, $^3J_{PCH_3} = -0.6$
4 P - C	98	150	$J_{pp} = 56$, $J_{PC_2} = 98.5$, $^3J_{PC_2} = -0.5$

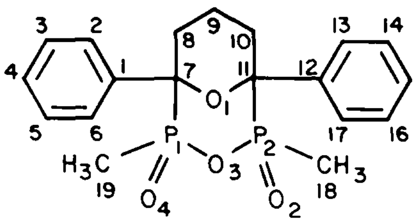


reflections and refined by the method of least-squares. Intensity data were collected in the ω-2θ mode with a scan width of $0.9 + 0.35 \tan\theta$ out to $2\theta = 50°$. The scan rate varied according to the detected intensity between 1.0 and 4.0° min^{-1}. Intensity-control reflections, monitored frequently, showed no decay of the crystals. The intensities were corrected for Lorentz and polarization effects and variable measuring time but not for absorption or secondary extinction. Because of the small size of the crystals absorption corrections were not considered necessary. Compound **2** was found to cocrystallize with two mol of water.

Crystal data of **2**. $C_{19}H_{22}O_4P_2.2H_2O$, $M_r = 412.4$, triclinic, $a = 10.185(1)$ Å, $b = 10.566(2)$ Å, $c = 11.117(2)$ Å, $\alpha = 87.08(1)°$, $\beta = 108.13(1)°$, $\gamma = 116.02\ (1)°$, $V = 1016.5$ Å^3, $Z = 2$, $d_c = 1.347$ g cm^{-3}, F(000) = 436, space group $P\bar{1}$.

Crystal data of **3**. $C_{19}H_{22}O_4P_2$, $M_r = 376.3$, triclinic $a = 8.687\ (2)$ Å, $b = 11.017\ (2)$ Å, $c = 11.441\ (2)$ Å, $\alpha = 113.66\ (1)°$, $\beta = 105.16\ (1)°$, $\gamma = 95.48\ (1)°$, $V = 942.8$ Å^3, $Z = 2$, $d_c = 1.325$ g. cm^{-3}, F(000) = 396, space groups $P\bar{1}$.

Both structures were solved by direct methods using the MULTAN system of computer programs. Refinement was carried out by full-matrix least-squares calculations, including the atomic coordinates of all atoms, anisotropic thermal parameters of the non H-atoms, and isotropic thermal parameters of the hydrogens. All hydrogen atom positions could be found from the corresponding difference maps. The final discrepancy indices at the end of the refinement were $R = 0.033$ for 2929 observations above threshold of 3σ of the intensity in **2**, and $R = 0.032$ for 2466 unique observations above threshold in **3**. Positional and thermal atomic parameters are available as supplementary material; the crystallographic numbers shown below, differ from the systematic ones as there is no continuity in the latter.



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