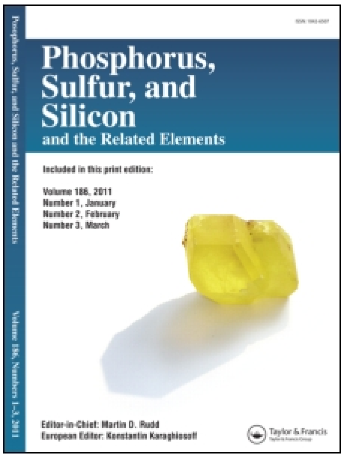


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

PHENYL N-BIS(2-CHLOROETHYL)-N'-PHENYLPHOSPHORODIAMIDATE (1): CRYSTAL STRUCTURE AND APPARENT ^{31}P-^{13}C COUPLING ANOMALIES

C. C. Orji[a]; J. H. Reibenspies[b]; E. A. Meyers[b]; A. G. Pinkus[a]
[a] Department of Chemistry, Baylor University, Waco, Texas, U.S.A. [b] Department of Chemistry, Texas A&M University College Station, Texas, U.S.A.

To cite this Article Orji, C. C. , Reibenspies, J. H. , Meyers, E. A. and Pinkus, A. G.(1994) 'PHENYL N-BIS(2-CHLOROETHYL)-N'-PHENYLPHOSPHORODIAMIDATE (1): CRYSTAL STRUCTURE AND APPARENT ^{31}P-^{13}C COUPLING ANOMALIES', Phosphorus, Sulfur, and Silicon and the Related Elements, 97: 1, 9 — 16

To link to this Article: DOI: 10.1080/10426509408020722

URL: http://dx.doi.org/10.1080/10426509408020722

Phosphorus, Sulfur, and Silicon, 1994, Vol. 97, pp. 9-16
Reprints available directly from the publisher
Photocopying permitted by license only

PHENYL N-BIS(2-CHLOROETHYL)-N'-PHENYLPHOSPHORODIAMIDATE (1): CRYSTAL STRUCTURE AND APPARENT ^{31}P-^{13}C COUPLING ANOMALIES*

C. C. ORJI,† J. H. REIBENSPIES,‡ E. A. MEYERS‡ and A. G. PINKUS†
†*Department of Chemistry, Baylor University, Waco, Texas, 76798, U.S.A.;*
‡*Department of Chemistry, Texas A&M University,*
College Station, Texas 77843, U.S.A.

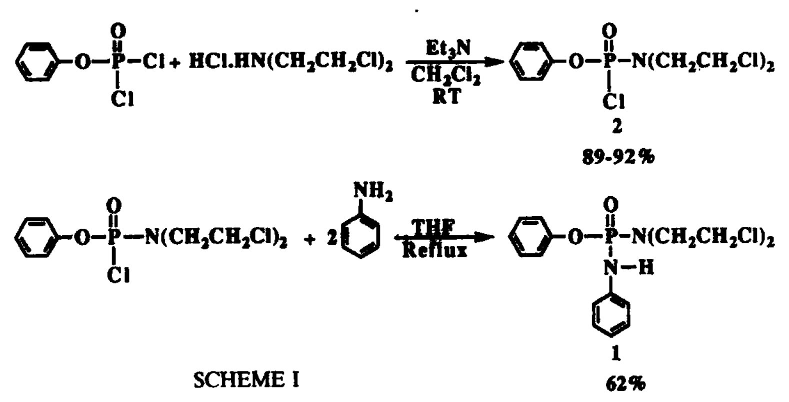
(Received April 28, 1994; in final form September 13, 1994)

The title compound (1) was synthesized by reacting phenyl phosphorodichloridate with bis(2-chlorethyl)amine hydrochloride to form 2 in 89–92% yield followed by reaction of 2 with aniline to form 1 in 62% yield. 1 crystallizes from benzene as a solvate with a ratio of 2 molecules of 1 to one of benzene. The solvate can be converted to the desolvated compound by heating in vacuo. Both the solvated and desolvated varieties of 1 were characterized by NMR, IR, MS, and elemental analyses. A single crystal x-ray structure determination of solvated 1 showed the position of benzene in the crystal lattice with respect to the rest of the molecule. The previously reported[1] 1 is a partially solvated substance. Anomalous features of ^{31}P-^{13}C coupling can be minimized by reducing the Hz/Pt ratio.

Key words: Syntheses, benzene solvate, x-ray crystal structure, IR, MS, NMR spectra, ^{31}P-^{13}C coupling.

INTRODUCTION

The only published example of a phenyl N-bis(2-chloroethyl)-N'-phenylphosphorodiamidate is the unsubstituted compound reported in 1963 by Rapp and Kuz'menko[1] who were synthesizing compounds to be examined for possible physiological activity. They prepared 1 by reacting phenol with phosphorus oxychloride to form phenyl phosphorodichloridate which was reacted first with aniline and then with bis(2-chloroethyl)amine (Scheme I). The nitrogen analysis of the title compound



SCHEME I

---

*Presented at 48th Southwest Region ACS Meeting, Lubbock, Texas, U.S.A., Oct. 21–24, 1992.

was low by 0.62% and no carbon and hydrogen analyses were given. Also no spectra of their compounds were reported. Since we were interested in obtaining derivatives of the title compound substituted in the N-phenyl moiety, synthesis of **1** by a route designed to introduce the N-Ar group in the final step (Scheme I) was undertaken. Conditions were developed so as to maximize the product yields in the two steps. In addition, better characterization of the identity of **1** was necessary.

RESULTS AND DISCUSSION

Syntheses

Yields in the first step of the reaction of phenyl phosphorodichloridate with bis(2-chloroethyl)amine hydrochloride to form the intermediate **2** were reasonably good, 89–92%. In this step, the more basic amine, triethylamine was used to react with the hydrogen chloride formed in order to conserve the less basic but more expensive bis(2-chloroethyl)amine hydrochloride. IR and NMR spectra are in accord with the expected structure.

In the second step the best procedure was to use an extra equivalent of the reagent, aniline to remove hydrogen chloride. The procedure above gives the best yield (62%) of recrystallized product **1**. In previous attempts to use other more basic tertiary amines such as 1,4-diazabicyclo[2.2.2]octane (DABCO) to react with hydrogen chloride, only low yields (11–17%) of product were obtained because of byproduct formation.

The melting point (104.0–105.5°C) of the product differed from that (87–88.5°C) reported by Rapp and Kuz'menko.[1] In addition, in the ^1H NMR spectrum, the integral for aromatic hydrogens was higher than that expected in comparison to eight for the CH_2CH_2 groups—10:8 expected vs. 13:8 observed. Since the solvent for recrystallization was benzene, on closer examination of the ^1H NMR spectrum, a peak at δ 7.35 was evident corresponding to benzene. Also a peak at δ 128.28 in the ^{13}C spectrum was additional confirmation of the presence of benzene as a solvate. The difference of three hydrogens between the observed and expected integrals for the aromatics (13-10) showed that benzene is incorporated into the crystal in a ratio of two molecules of nonsolvated **1** to one of benzene or 2 $C_{16}H_{19}Cl_2N_2O_2P$: C_6H_6. The elemental analysis (see Experimental Section) showed a good correspondence between calculated and experimental values in confirmation of the 2:1 solvated structure deduced from ^1H NMR spectral analysis. The position of benzene in the solvate crystal is shown in the crystal structure (see below). When a single crystal of the solvated compound was desolvated by heating below the melting point (at 80°C) to remove the benzene solvate, the crystal disintegrated into a powder. An x-ray powder diffraction determination on the desolvated compound showed that it was highly crystalline and that the diffraction pattern differed from one determined on a solvated sample. Powdering of the solvated material did not convert it into any of the desolvated variety since strong diffraction peaks of the desolvated material did not appear in the diffraction pattern of the solvated.

From the low melting point of 87.0–88.5°C reported by Rapp and Kuz'menko[1] as well as the discrepancy in the elemental analysis with the low value they obtained for % nitrogen, it is evident that they have a partially benzene-solvated product. The melting point they observed may be a eutectic temperature based on the relative proportions of benzene-solvated and unsolvated crystals.

NMR Spectra

Compound 2: The ^{13}C signals assigned were based on the following considerations. The higher field 41.08 δ singlet was assigned to the CH_2 (C-1) bound to the more electron-donating nitrogen and the more deshielded doublet at 49.20 δ to the CH_2 (C-2) attached to the more electronegative Cl. Based on this assignment, the more distant carbon is coupled to phosphorus ($^3J_{P-C2}$ = 4.8 Hz) whereas the closer carbon is not coupled to any observable extent. There is precedence in the literature for observations where ^3J values for P-C couplings have been demonstrated to be larger than ^2J values.[2-5]

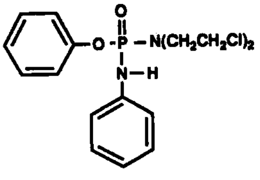
The aromatic carbon signals were assigned on the basis of relative intensities and coupling to phosphorus. The highly deshielded signal at 149.30 δ was assigned to the ipso COP carbon (C-16) on the basis of its having the lowest relative intensity of the four aromatic ^{13}C signals as well as its chemical shift position. The signal at 120.08 δ was assigned to the ortho carbons (C-11) on the basis of its coupling with phosphorus ($^3J_{POCC11}$ = 5.7 Hz) and its higher intensity as compared with the signal at 149.30 δ. The signals at 125.85 and 129.70 δ were tentatively assigned to C-13 (para) and C-12 (meta) carbons respectively on the basis of comparisons with some meta and para substituted derivatives of compound **1**.

Compound 1: The CH_2 carbon positions were assigned in the same way as for compound **2** with the 41.84 δ singlet and the 49.51 δ doublet ($^3J_{PNCC2}$ = 4.65 Hz) assigned to C1 and C2 respectively. The aromatic carbon signals were assigned on the same basis as for compound **2** as well the similarity of chemical shift position for the phenoxy carbons as compared with compound **2**. Thus for the phenoxy carbons the signals at 150.17 (d, $^2J_{POC16}$ = 6.56 Hz), 120.38 (d, $^3J_{POCC11}$ = 4.71 Hz), 125.08, and 129.72 δ were assigned to ipso (C-16), ortho (C-11 and C-15), para (C-13), and meta (C-12 and C-14) positions respectively. It should be noted that the ipso carbon (C-16) and ortho carbons (C-11 and C-15) are coupled to phosphorus by ^2J and ^3J coupling constants respectively and that ^2J is larger than ^3J.

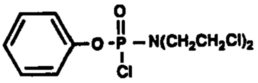
The aromatic ^{13}C shifts for the anilino group were assigned as follows. The signals at 139.15, 117.94, 129.30, and 122.19 δ were assigned to ipso (C-10), ortho (C-5 and C-9), meta (C-6 and C-8), and para (C-7) positions respectively. The ipso carbon (C-10) was assigned on the basis of its lowest intensity and its chemical shift being the most deshielded position at 139.15 δ. The signal at 120.38 δ was assigned to the ortho carbons because of the coupling. The meta and para carbons were assigned on the basis of comparisons with substituted derivatives.

^{31}P-^{13}C Coupling

The coupling constants for compounds **1** and **2** are listed in Tables I and II respectively as functions of digital resolution expressed as Hz/Pt (Pt = point). For



1



2

TABLE I

Variation of ^{31}P-^{13}C coupling constants with digital resolution for compound 1

Hz/Pt δ	0.060	0.238	0.477	0.954	1.907	3.815
41.8 (1)	s	s	s	s	s	s
49.5 (2)	4.7	4.8	4.8	4.8	3.8	s
118.0 (3)	7.2	7.2	7.6	6.7	7.6	7.6
120.3 (4)	4.7	4.8	4.8	4.8	3.8	s
122.3 (5)	s	s	s	s	s	s
125.0 (6)	s	s	s	s	s	s
129.3 (7)	s	s	s	s	s	s
129.7 (8)	s	s	s	s	s	s
139.1 (9)	1.9	1.9	1.4	1.9	s	s
150.1(10)	6.6	6.4	6.7	5.7	7.6	7.6

TABLE II

Variation of ^{31}P-^{13}C coupling constants with digital resolution for compound 2

Hz/Pt δ	0.076	0.238	0.477	0.954	1.907	3.815
41.2 (1)	2.4	2.4	2.4	1.9	3.8	s
49.3 (2)	4.3	4.1	4.3	3.8	5.7	s
120.1 (3)	5.5	5.5	5.2	5.7	5.7	s
126.0 (4)	1.7	1.7	1.4	s	s	s
129.8 (5)	1.1	1.2	1.0	s	s	s
149.4 (6)	8.2	8.3	8.6	7.6	7.6	11.4

compound **2** it can be noted that at the highest Hz/Pt value (3.815) all of the signals appear as singlets except for the ipso carbon (C-16 at 149.4 δ) for which the ^2J value is 11.4 Hz. As the Hz/Pt ratio is decreased to 1.907 this value changes to 7.6 Hz, the coupling constants for C-1 (CH_2N), C-2 (CH_2Cl) and C-11 (ortho) (at 41.2, 49.3, and 120.1 δ respectively) become 3.8, 5.7, and 5.7 respectively and the other two signals at 126.0 (meta C-12) and 129.8 (para C-13) remain as singlets. A further decrease in the Hz/Pt ratio to 0.954 changes the J values for the CH_2 signals whereas the values for the aromatic carbons remain the same. A further decrease in the Hz/Pt values of 0.477 results in different J values for all of the carbon signals. Further decreases in Hz/Pt ratios to 0.238 and 0.076 result in further changes for each carbon. It should be noted that the changes are relatively smaller and the J values appear to converge to within two significant figures ±0.1 to 0.2.

For compound **1** (Table I) similar observations can be made. It can be noted that the same J values appear as for compound **2**. At the highest Hz/Pt ratio of 3.815, J values of 7.6 Hz appear for the signals at 118.0 and 150.1 δ and singlets for the other eight peaks. When the ratio is reduced to 1.907, J values of 3.8 appear for signals at 49.5 and 120.3 δ in addition to the 7.6 Hz values. Further reductions in the Hz/Pt ratio result in further changes in the J values. It should be noted that the J values are all divisible by the value selected for Hz/Pt within the accuracy of J. The J values appear to level off to the values shown in Table I when the Hz/Pt ratio is reduced to 0.060.

Anomalous ^{31}P-^{13}C coupling phenomena were also observed for a variety of other organophosphorus compounds (including diphenyl phosphate, triphenylphosphine, and cyclophosphamide) at a Hz/Pt ratio of 0.954. Similar anomalous coupling was also observed with one other combination of nuclei, ^{19}F-^{13}C.

In summary, in order to obtain more accurate ^{31}P-^{13}C coupling constants, the Hz/Pt ratio should be kept as low as possible within any time limitations since in general longer periods of instrumental time are needed with lower Hz/Pt ratios. The lowest values in Tables I and II can be used as tentative guides.

Crystal Structure

Stereoviews of a molecule of compound **1** are shown in Figure 1. Relevant bond distances and bond angles are presented in Table III. The molecular structure of compound **1** is as anticipated. Bond distances, P-X, show considerable variations in length in different molecules,[6] but the coordination around P(1) in this structure is very similar to that reported earlier for an oxazaphosphorinane[7] which has the same atoms bonded to its phosphorus as were found here. None of the other bond angles or bond distances in the present molecule appear to be unusual. A hydrogen bond, O(1) . . .N′(2) = 2.78 Å, which is present between O(1), the atom doubly bonded to P(1), and N′(2), related by symmetry to N(2), is present. The center of this molecule is located on a center of symmetry in the crystal, thus accounting for the stoichiometric ratio of two moles of compound **1** to one mole of benzene in the solvated material. The average C-C distance in the benzene ring (1.35 Å), is considerably shorter than expected (1.396 Å), presumably because of the effect of large thermal amplitudes of motion[8] as indicated by the large temperature factors obtained for these carbon atoms.

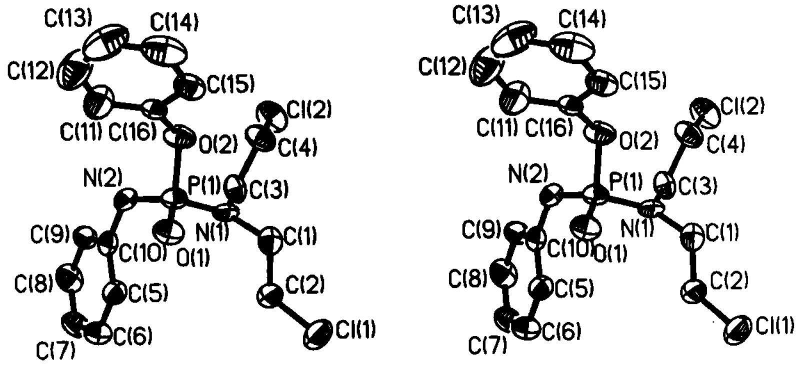


FIGURE 1 Labeled stereographic views of 1 with thermal ellipsoids shown at the 50% probability level. (Hydrogen atoms were omitted.)

TABLE III

Bond lengths (Å) and bond angles (°)

P(1)-O(1)	1.453 (6)	P(1)-O(2)	1.585 (5)
P(1)-N(1)	1.638 (6)	P(1)-N(2)	1.642 (6)
Cl(1)-C(2)	1.789 (10)	Cl(2)-C(4)	1.791 (10)
O(2)-C(16)	1.406 (8)	N(1)-C(1)	1.485 (10)
N(1)-C(3)	1.450 (10)	N(2)-C(10)	1.417 (9)
C(1)-C(2)	1.491 (11)	C(3)-C(4)	1.506 (11)
C(5)-C(6)	1.406 (10)	C(5)-C(10)	1.395 (12)
C(6)-C(7)	1.360 (13)	C(7)-C(8)	1.378 (14)
C(8)-C(9)	1.405 (12)	C(9)-C(10)	1.369 (11)
C(11)-C(12)	1.344 (15)	C(11)-C(16)	1.370 (11)
C(12)-C(13)	1.354 (17)	C(13)-C(14)	1.376 (18)
C(14)-C(15)	1.433 (13)	C(15)-C(16)	1.361 (10)
C(17)-C(18)	1.341 (32)	C(17)-C(19A)	1.334 (36)
C(18)-C(19)	1.369 (49)	C(19)-C(17A)	1.334 (36)
O(1)-P(1)-O(2)	114.2(3)	O(1)-P(1)-N(1)	111.7(3)
O(2)-P(1)-N(1)	103.8(3)	O(1)-P(1)-N(2)	116.5(3)
O(2)-P(1)-N(2)	101.9(3)	N(1)-P(1)-N(2)	107.6(3)
P(1)-O(2)-C(16)	124.3(5)	P(1)-N(1)-C(1)	119.0(5)
P(1)-N(1)-C(3)	121.8(5)	C(1)-N(1)-C(3)	117.8(6)
P(1)-N(2)-C(10)	124.0(5)	N(1)-C(1)-C(2)	109.4(6)
Cl(1)-C(2)-C(1)	109.2(6)	N(1)-C(3)-C(4)	112.2(6)
Cl(2)-C(4)-C(3)	109.3(6)	C(6)-C(5)-C(10)	118.7(7)
C(5)-C(6)-C(7)	120.8(8)	C(6)-C(7)-C(8)	120.4(8)
C(7)-C(8)-C(9)	119.6(8)	C(8)-C(9)-C(10)	120.2(8)
N(2)-C(10)-C(5)	121.2(7)	N(2)-C(10)-C(9)	118.5(7)
C(5)-C(10)-C(9)	120.2(7)	C(12)-C(11)-C(16)	119.0(9)
C(11)-C(12)-C(13)	121.0(11)	C(12)-C(13)-C(14)	121.1(10)
C(13)-C(14)-C(15)	118.9(9)	C(14)-C(15)-C(16)	116.5(8)
O(2)-C(16)-C(11)	121.5(7)	O(2)-C(16)-C(15)	115.0(6)
C(11)-C(16)-C(15)	123.4(7)	C(18)-C(17)-C(19A)	118.6(25)
C(17)-C(18)-C(19)	122.2(23)	C(18)-C(19)-C(17A)	119.2(20)

EXPERIMENTAL

Materials and Methods

^1H, ^{13}C, and ^{31}P NMR spectra were taken on a Bruker AMX 360 MHz spectrometer operated in the FT mode. Positive ^{31}P chemical shifts are in ppm downfield from 85% H_3PO_4. ^1H and ^{13}C chemical shifts are referenced to TMS. Coupling constants were determined by expansions of relevant peaks and measuring the coupling. Melting points were obtained on a Thomas Hoover Unimelt apparatus and are corrected. IR spectra were run on a Mattson FT-IR. Matched 0.1 mm sodium chloride cells were used for the solution spectra of a 5% solution of the solid in dry methylene chloride. Pure liquids were run as thin films between two sodium chloride plates. Mass spectra were run on a Finnigan 1020 mass spectrometer. Differential scanning calorimetry curves were run on a Perkin-Elmer Model DSC-1B instrument. Samples were sealed in aluminum capsules and run under a nitrogen atmosphere. The temperature was increased at a rate of 20°C/min. Aniline was freshly distilled over Zn dust; methylene chloride was distilled over P_2O_5; THF was distilled over potassium and benzophenone; benzene was distilled over sodium. Other reagents were used as supplied.

Preparation of Phenyl N-bis(2-Chloroethyl)phosphoramidochloridate (**2**)

Bis(2-chloroethyl)amine hydrochloride (51.5 g, 0.29 mol), dry methylene chloride (300 mL), and triethylamine (58.4 g, 0.58 mol) were placed in a 3-necked round-bottom flask protected from moisture with a calcium chloride tube. Phenyl phosphorodichloridate (60.8 g, 0.29 mol) dissolved in 73 mL of dry methylene chloride was added dropwise over 25 min and the mixture was stirred at ambient temperature overnight.

The precipitated triethylamine hydrochloride was removed by suction filtration. The filtrate was extracted with two 50 mL portions of 1M HCl. The organic layer was extracted with saturated sodium bicarbonate solution to remove excess acid and washed with distilled water until neutral to litmus. It was dried with anhydrous sodium sulfate and filtered to remove the sodium sulfate. The filtrate was evaporated to dryness using a rotary evaporator, and then subjected to a high vacuum until constant weight was obtained. The final product was an orange-brown oil, which was pure enough for the subsequent reaction but which can be decolorized with P_2O_5. Yield, 89–92% (lit.[9] 75%). ^{1}H NMR ($CDCl_3$) (δ ppm): 3.52–3.72 (m, CH_2CH_2, 8H), 7.22–7.36 (m, C_6H_5, 5H); ^{13}C NMR[§] ($CDCl_3$) (δ ppm): 41.08 (s, C_1), 49.20 (d, $^3J_{PNCC2}$ = 4.8 Hz, C_2), 120.08 (d, $^3J_{POCC11}$ = 5.7 Hz, C_{11}), 125.85 (s, C_{13}), 129.70 (s, C12), 149.30 (d, $^2J_{POC16}$ = 8.6 Hz, C_{16}); ^{31}P NMR ($CDCl_3$) (δ ppm) 11.3; IR (cm^{-1}): 945 (P—O—C), 1285(P=O), 1490(P—O—C).

Preparation of Phenyl N-bis(2-Chloroethyl)-N'-phenylphosphorodiamidate (**1**)

Solvated **1**. Aniline (3.77 g, 0.04 mol) was dissolved in 10 mL THF (~4 M solution) and placed in a 3-necked flask equipped with a condenser and an addition funnel and maintained at a positive argon pressure. While heated to 60°C and stirred, phenyl N-bis(2-chloroethyl)phosphoramidochloridate (**2**) (6.32 g, 0.020 mole in 4 mL THF ~ 5M) was added dropwise over 15 min. The reaction was maintained at this temperature for 16 h and then allowed to cool. The reaction mixture was diluted with 50 mL of water and then extracted with three 50 mL portions of methylene chloride. The resulting organic layer was washed once with water, dried with anhydrous sodium sulfate, filtered, and the filtrate evaporated to dryness using a rotary evaporator to yield an orange-yellow solid. The solid was recrystallized from benzene, yielding colorless crystals, mp 104.0–105.5°C; yield, 62%. ^{1}H NMR spectral evidence and elemental analysis revealed that two molecules of the compound crystallized with one molecule of benzene. ^{1}H NMR ($CDCl_3$) (δ ppm): 3.41–3.56 (m, CH_2CH_2, 8H), 6.06 (d, $^2J_{P-H}$ = 8.98 Hz, N—H, 1H), 6.98–7.35 (m, Ar, 13H). ^{13}C NMR ($CDCl_3$) (δ ppm): 41.84 (s, C_1), 49.51 (d, $^3J_{PNCC2}$ = 4.65 Hz, C_2), 117.94 (d, $^3J_{PNCC5}$ = 7.21 Hz, C_5), 120.38 (d, $^3J_{POCC11}$ = 4.71 Hz, C_{11}), 122.19 (s, C_7), 125.07 (s, C_{13}), 128.32 (s, benzene), 129.30 (s, C_6), 129.72 (s, C_{12}), 139.15 (d, $^2J_{PNC10}$ = 1.91 Hz, C10), 150.17 (d, $^2J_{POC16}$ = 6.56 Hz, C_{16}); ^{31}P NMR ($CDCl_3$) (δ, ppm) 5.60; IR (cm^{-1}): 3400 (NH), 1492 (P—O—C), 1202 (P=O), 923 (P—O—C arom); MS: M^+ 372 (41.3), 323 (100, M^+—CH_2Cl), 232 (M^+—NCH_2CH_2Cl). Anal.: Calcd. for $C_{19}H_{22}Cl_2N_2O_2P$: C, 55.35; H, 5.38; Cl, 17.20; N, 6.80; P, 7.51. Found: C,[¶] 55.17; H,[¶] 5.39; Cl,[¶] 17.08; N,[¶] 6.83; P, 7.93.

Differential scanning calorimetry curves showed two endotherms at 93°C and 113°C corresponding to melting of the benzene-solvated and unsolvated species, respectively. These endotherms differ somewhat from the melting points of the solvated and desolvated compounds probably because the DSC samples were measured in a sealed capsule from which the benzene solvate did not escape and would therefore act as an impurity to lower both of the endotherms as compared with the melting points observed in glass capillary tubes.

Desolvated **1**. Benzene was removed by subjecting a solvated sample to high vacuum at a temperature of 80°C using an Abderhalden drying apparatus. At the conclusion of the desolvation process the sample had mp = 117.0–118.0°C. The IR, NMR, and MS spectral data were the same as those listed above for the solvated sample except for the ^{1}H and ^{13}C signals for benzene which were absent. The following elemental analyses were obtained on the desolvated material. Anal.: Calcd. for $C_{16}H_{19}Cl_2N_2O_2P$: 51.49; H, 5.13; Cl, 19.00; N, 7.51; P, 8.30. Found: C, 51.51; H, 5.13; Cl, 19.25; N, 7.37; P, 8.70.

[§] In order to reduce confusion, the same numbering is used as for compound **1**.

[¶] Analyses by Atlantic Microlab Inc., Norcross, Georgia. Other analyses by Galbraith Laboratories Inc., Knoxville, Tennessee.

Crystal Diffraction

A single crystal for the x-ray diffraction study was obtained by slow evaporation of a dilute benzene solution. A colorless plate (0.12 × 0.28 × 0.36 mm) was mounted on a glass fiber with epoxy cement at room temperature and cooled to 193 K in a nitrogen cold stream. Preliminary examination and data collection ($\theta - 2\theta$ scan) were performed on a Nicolet R3m/V X-ray diffractometer (oriented graphite monochromator, MoKα radiation). Cell dimensions were obtained using 20 reflections ($20.1° < 2\theta < 32.3°$). Three standard reflections showed no significant change during data collection. After data collection was completed it was discovered that the monochromator required realignment and for this reason the intensity data have larger experimental errors than those customarily obtained with this instrumentation ($R_{int} = 0.07$). The structure was solved by direct methods and refined using SHELXTL-Plus programs.[10] The hydrogen atoms were placed in calculated positions and assigned the isotropic temperature factor U = 0.08 Å^2; all other atoms were refined anisotropically. The full matrix least squares refinement minimized $\Sigma w(|F_o| - |F_c|)^2$ with $w^{-1} = \sigma^2(F_o) + 0.002|F_o|)^2$.

Crystal data. $C_{22}H_{25}Cl_2N_2O_2P$. $M_r = 412.3$, monoclinic, $P2_1/n$ (non-standard setting of $P2_1/c$), a = 8.608(3), b = 10.017(4), c = 23.689(9) Å, $\beta = 90.80(3)°$, V = 2042(1) Å^3, Z = 4, $D_c = 1.341$ g cm^{-3}, λ(MoKα) = 0.71073, Å, $\mu = 4.09$ cm^{-1}, F(000) = 860. Temperature = 193 K; R = 0.077, $R_w = 0.063$, GoF = 1.52 for 1432 unique reflections with $I > 2.5\ \sigma(I)$ out of a total of 3126.2θ range 4–50°. The packing diagram and further information regarding the crystal structure may be obtained from E.A.M.

REFERENCES

1. L. B. Rapp and I. I. Kuz'menko, *J. Gen. Chem. U.S.S.R.*, **33,** 2219 (1963).
2. T. A. Albright, W. J. Freeman and E. Schweizer, *J. Org. Chem.*, **41,** 2716 (1976).
3. H. Fritz and C. D. Weis, *J. Org. Chem.*, **43,** 4900 (1989).
4. M. Pomerantz, D. S. Marynick, P. C. Y. Chen and T. Cain, *J. Org. Chem.*, **51,** 1223 (1986).
5. A. L. Llamas-Saiz, C. Foces-Foces, P. Molina, M. Alajarin, A. Vidal, R. M. Claramunt and J. Elguero, *J. Chem. Soc. Perkin Trans.*, **2,** 1025 (1991).
6. D. E. C. Corbridge, "The Structural Chemistry of Phosphorus," (Elsevier, 1974).
7. A. M. Brzozowski, A. Stepien, Z. Dauter and K. Misiura, *Acta Cryst.*, **C46,** 618 (1990).
8. D. W. J. Cruickshank, *Acta Cryst.*, **9,** 757 (1956).
9. O. M. Friedman and A. M. Seligman, *J. Am. Chem. Soc.*, **76,** 655 (1953).
10. G. M. Sheldrick (1990). Release 4.11/V for Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin.