Disproportionation of Tetrakis(anilinomethyl)phosphonium Chloride in Ethanol

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The product of the disproportionation of tetrakis(anilinomethyl)phosphonium chloride (1) or tris(anilinomethyl)phosphine (3) in ethanol has been identified as 1,1′-diphenyl-1,1′-diaza-3,3′-biphosphetidine (2). The proton NMR spectrum of 2 exhibits an ABX_2 splitting pattern with some unusual features.

The reactions of tetrakis(hydroxymethyl)phosphonium chloride (Thpc) with primary or secondary amines are of interest because they provide an insight into the chemistry of flame-retardant cotton finishes prepared from Thpc and polyfunctional nitrogen compounds such as ammonia, urea, or melamine.[2] The title compound (1), a product of the reaction of Thpc and aniline,[3] is a white, crystalline solid, mp 129–130 °C. With care, it can be recrystallized from organic solvents such as methanol, acetic acid, tetrahydrofuran, or chloroform, but upon attempted recrystallization from ethanol the product that separates is a high-melting white, crystalline solid (2), mp 170–171 °C. Recrystallization from methanol, if not performed rapidly, also yields 2 instead of 1. The isolation and characterization of 2 is the subject of this paper.

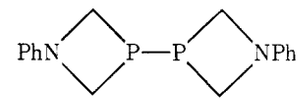
Elemental analysis of 2 establishes its empirical formula as C_8H_9NP. The IR spectrum shows aromatic C=C absorption but no NH. The proton NMR spectrum shows a well-separated pair of multiplets in the Ph and CH_2 regions in a ratio of 5 to 4. Together, these data suggest the composition $PhN(CH_2)_2P$.

The mass spectrum of 2 shows the fragmentation pattern characteristic of methyleneaniline derivatives,[4,5] with *m/e* 91 (PhN^+), 93 ($PhNH_2^{\cdot+}$), 104 ($PhN{\equiv}CH^+$), and 105 ($PhN{=}CH_2^{\cdot+}$) as abundant ions. In addition, strong lines appear at 119 [$PhN(CH_2)_2^+$], 120 [$PhNH(CH_2)_2^+$], and 300 {[$PhN(CH_2)_2P]_2^{\cdot+}$}. The strong parent ion at 300, coupled with a correct (P + 1)/P ratio,[6] establishes the compound to be a dimer of molecular formula $C_{16}H_{18}N_2P_2$ and probable composition $[PhN(CH_2)_2P]_2$.

The methylene multiplet in the 60-MHz NMR spectrum of 2 has the appearance of a singlet superimposed on an ABX octet (Figure 1). The singlet, however, shifts upfield toward the center of the multiplet when the field strength is increased from 60 to 100 MHz and is consequently not independent of the octet. By inspection, the separation of the singlet from the downfield AB quartet is found to be identical with the separation of the two AB quartets (7.25 Hz). The ratio of the intensities of the three subspectra approaches 1:2:1. These spacings and relative intensities are characteristic of ABX_2 spectra[7] and, in fact, analysis of the data using the appropriate equations for the ABX_2 system,[8] treating the singlet as an AB quartet of 0:2:2:0 intensity, provides a line spectrum that shows a good fit to the observed spectrum (Figure 1).

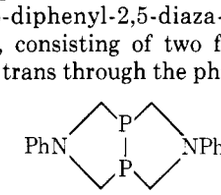
For confirmation, the NMR spectrum of 2 was examined at 100 MHz. This is a deceptively simple spectrum of five or possibly six lines (Figures 2 and 3). Calculation of the transition energies and relative intensities, using the 60-MHz data, provides a theoretical line spectrum that shows a good fit to the observed spectrum. The chemical shifts derived from this analysis are $\delta_A = 3.74$ and $\delta_B = 3.53$ ppm, and the coupling constants are $J_{AB} = 12.5$, $J_{AX} = 0.8$, and $J_{BX} = 13.7$ Hz. Details of the analysis are given in the supplementary section of this paper.

There are three possible structures that satisfy the composition $[PhN(CH_2)_2P]_2$. The first is 1,1′-diphenyl-1,1′-diaza-3,3′-biphosphetidine, consisting of two four-membered rings linked through the phosphorus atoms.



Tetramethylbiphosphine, a related acyclic compound, exhibits an A_3XX' spectrum whose parameters are $^2J_{PH} = 2.90$, $^3J_{PH} = 11.25$, and $J_{PP} = -179.7$ Hz.[9] 1,1′-Biphospholane is known[10] but not its NMR parameters. Assuming rapid nitrogen inversion and ring puckering but slow phosphorus inversion (assumptions valid for related six-membered ring systems),[3,11] the ring structure of the biphosphetidine imposes a constraint on the molecule such that the four outer-face hydrogen atoms are shielded constantly by the lone-pair electrons of the adjacent phosphorus atom. The four inner-face hydrogen atoms, owing to free rotation about the P–P bond, are shielded intermittently by the lone-pair electrons of the other phosphorus atom. The four outer-face hydrogen atoms (and, likewise, the four inner-face hydrogen atoms) are magnetically equivalent, since each has a counterpart in the other ring that is either identical to it or is a mirror image that is indistinguishable from it by NMR. A priori, the spectrum should exhibit an ABXX′ splitting pattern, where A and B are the outer- and inner-face hydrogen atoms, respectively, and X and X′ are the phosphorus atoms. The phosphorus atoms, though chemically equivalent, are not magnetically equivalent unless they are equally coupled to A and B.

The other two possible structures are the cis and trans isomers of 2,5-diphenyl-2,5-diaza-3a,6a-diphosphabicyclo[3.3.0]octane, consisting of two five-membered rings fused either cis or trans through the phosphorus atoms.



Very few ring systems of this type are known. Bicyclo[3.3.0]-octane itself exists in both cis and trans forms, the latter showing evidence of substantial strain.[12] Models of the two phosphorus compounds show severe distortion owing to the unequal P–P, P–C, and C–N bond lengths. It seems unlikely that either would possess sufficient symmetry to exhibit a simple ABXX′ splitting pattern.

This leaves the biphosphetidine structure as the only option. The criteria for obtaining ABX_2 spectra from compounds that contain nonequivalent X groups have been discussed by Riggs.[13] If the X groups have the same chemical shift as in the ABXX′ case, they need not be equally coupled to A and B provided that the sums of the coupling constants are identical.[14] In our case, this means that $^2J_{PH_A}$ and $^2J_{PH_B}$ are not necessarily equal to $^3J_{PH_A}$ and $^3J_{PH_B}$, respectively, provided that the sums are related as follows:

$$^2J_{PH_A} + {}^2J_{PH_B} = {}^3J_{PH_A} + {}^3J_{PH_B} = 14.50 \text{ Hz}$$

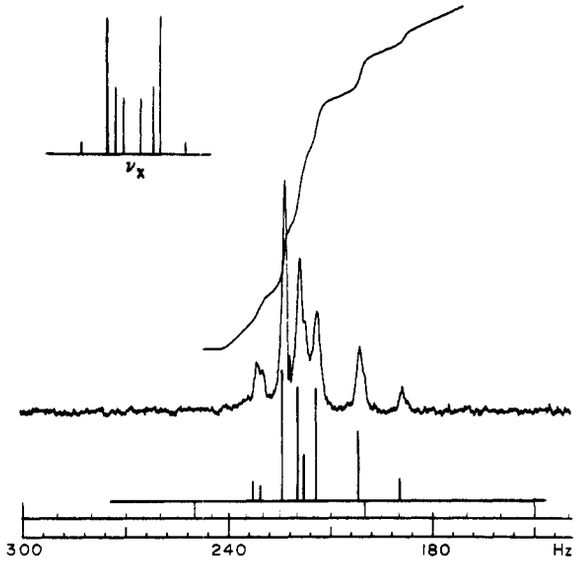


Figure 1. Methylene segment of the 60-MHz proton-NMR spectrum of **2** in $CDCl_3$. Scale: 1 cm = 10 Hz (h) or 0.80 H (v). Inset: Predicted ^{31}P-NMR spectrum.

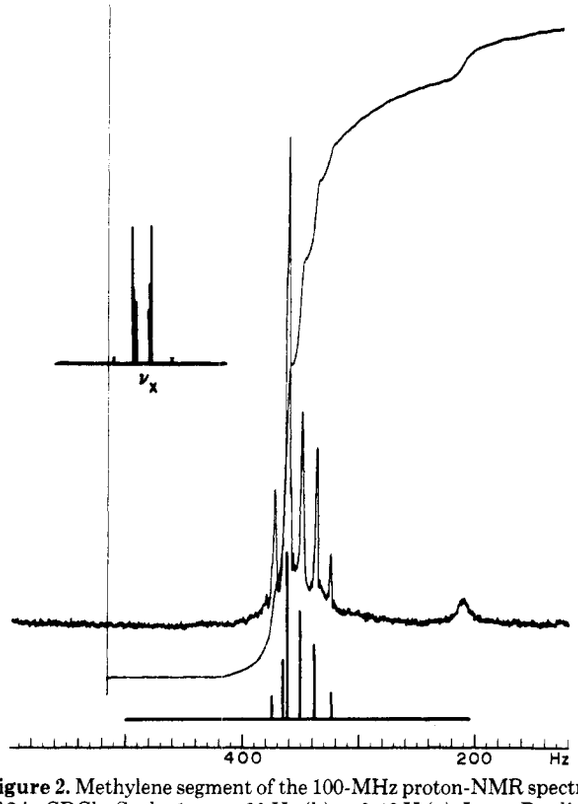


Figure 2. Methylene segment of the 100-MHz proton-NMR spectrum of **2** in $CDCl_3$. Scale: 1 cm = 30 Hz (h) or 0.46 H (v). Inset: Predicted ^{31}P-NMR spectrum.

The biphosphetidine structure is therefore compatible with the NMR spectrum of **2**, even though the phosphorus atoms do not appear to be magnetically equivalent.

The biphosphetidine **2** can also be prepared from tris(anilinomethyl)phosphine (**3**) but not from its methylene-bridged derivative, 5-anilinomethyl-1,3-diphenyl-1,3,5-diazaphosphorinane (**4**). Forcing conditions are required for **3**, and the yields are lower. Attempts to prepare oxide or sulfide derivatives of **2** were unsuccessful.

The disproportionation of **1** and **3** to substances richer and poorer in NH seems to be related to the disproportionation of *N,N'*-diphenylmethanediamine to aniline and hexahydro-1,3,5-triphenyl-*s*-triazine,[15] though obviously more deep-seated changes are involved. Equations 1 and 2, which satisfy the stoichiometry of the disproportionation, suggest that *N*-methylaniline and the triazine precursor, *N*-methyleneaniline, are formed in addition to **2** and aniline.

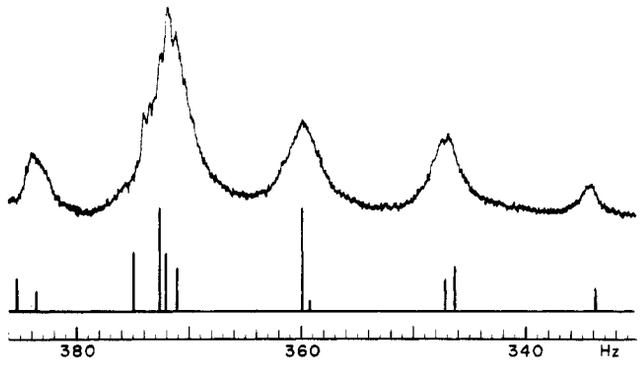
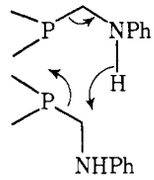


Figure 3. Methylene segment of Figure 2 expanded tenfold. Scale: 1 cm = 3 Hz (h) or 0.46 H (v).

$$2(PhNHCH_2)_4PCl \rightarrow \underset{\mathbf{1}}{} \underset{\mathbf{2}}{[PhN(CH_2)_2P]_2} + 3PhN{=}CH_2 + PhNHCH_3 + 2PhNH_2{\cdot}HCl \quad (1)$$

$$2(PhNHCH_2)_3P \rightarrow \underset{\mathbf{3}}{} \underset{\mathbf{2}}{[PhN(CH_2)_2P]_2} + PhN{=}CH_2 + PhNHCH_3 + 2PhNH_2 \quad (2)$$

These by-products could be formed as follows:



Further investigation is needed to identify the by-products and to determine to what extent, if any, the solvent participates in the disproportionation.

Experimental Section

Melting points are corrected. Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.[16] Infrared spectra (IR) were taken on a Perkin-Elmer 137B spectrophotometer with NaCl optics. Nuclear magnetic resonance spectra (^1H NMR) were taken on a Varian A-60 spectrometer at 60 MHz or a JEOLCO MH-100 spectrometer at 100 MHz, with tetramethylsilane as an internal standard. Mass spectra were taken on a CEC 21-110B spectrometer at 70 eV by direct probe insertion.

1,1'-Diphenyl-1,1'-diaza-3,3'-biphosphetidine (2). A. From 1. The phosphonium salt **1**[3] (2.00 g, 4.07 mmol) was slurried in ethanol (20 mL) and heated at reflux until it dissolved. The solution was allowed to cool and was filtered, giving 0.25 g (41.0 %) of **2**, mp 167–168 °C. After stripping, the filtrate yielded 1.35 g of pale yellow oil: $n^{20}D$ 1.6618; IR (neat) 3400 (vs, NH) cm^{-1}. One recrystallization of the solid from ethanol afforded pure **2**: mp 170–171 °C; IR (Nujol) 682 (s, Ph), 719 (w), 740 (m, sh), 749 (vs, Ph), 777 (w), 857 (m), 913 (w), 956 (w), 989 (w), 1030 (w), 1130 (w), 1165 (w), 1195 (s), 1250 (m, CN_{arom}), 1300 (vs, CN_{arom}), 1435 (vs), 1495 (vs, $C{=}C_{arom}$), 1560 (w), 1600 (vs, $C{=}C_{arom}$) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.1–3.8 (m, 4 H, CH_2) and 6.7–7.3 (m, 5 H, Ph); mass spectrum *m/e* (% rel abundance, ion fragment) 301 (10, P + 1), 300 (55, P), 223 (3), 208 (5), 207 (7), 195 (8, P − $PhN{=}CH_2$), 194 (9), 181 (3), 180 (4), 179 (3), 162 (8), 150 (5), 133 (7), 132 (16), 125 (4), 121 (10), 120 (83, $PhNH(CH_2)_2^+$), 119 (55, $PhN(CH_2)_2^+$), 118 (7), 107 (7), 106 (20, $PhNH{=}CH_2^+$), 105 (39, $PhN{=}CH_2^{\cdot+}$), 104 (31, $PhN{\equiv}CH^+$), 94 (4), 93 (56, $PhNH_2^{\cdot+}$), 92 (13, $PhNH^+$), 91 (100, PhN^+), 78 (7), 77 (37, Ph^+), 66 (13, $C_5H_6^+$), 65 (12, $C_5H_5^+$), 51 (15, $C_4H_3^+$). Anal. Calcd for C_8H_9NP: C, 64.00; H, 6.04; N, 9.33; P, 20.63; mol wt, 300 (dimer). Found: C, 63.99; H, 5.85; N, 9.02; P, 20.50; mol wt (osmometric, in $CHCl_3$), 346.

The biphosphetidine **2** is soluble in chloroform and acetone and insoluble in water. It dissolves in carbon disulfide without giving the

red color characteristic of tertiary phosphines[17] but decolorizes iodine instantly[18].

If the solvent for recrystallization is methanol, the outcome depends on the severity of the treatment. When the phosphonium salt 1 (10.00 g) was gently warmed with methanol (50 mL) until the solid just dissolved and the solution was cooled rapidly and filtered, part of 1 (3.20 g, 32.0%) was recovered unchanged (mp, IR). The filtrate, concentrated to half its volume, yielded 0.16 g (5.2%) of **2**. When 1 (3.00 g) was recrystallized from hot methanol (25 mL) as described above for ethanol, the first product to separate was **2** (0.15 g, 16.4%), none of 1 being recovered. When a solution of 1 in methanol was heated for 30 min at reflux prior to workup, neither substance could be isolated from the gummy mass that resulted.

B. From 3. The tertiary phosphine **3** (2.000 g, 5.15 mmol)[3] was heated in ethanol (50 mL) at reflux for 4 h under nitrogen. At first the **3** dissolved, but within 30 min white solids started to separate and were removed from time to time as the reaction proceeded, giving fractions of mp 95–97 °C dec (0.200 g), 128–148 °C (0.114 g), and 160–163 °C (0.058 g). The third fraction was identified (IR, NMR) as **2** (7.5%). The residue was a pale yellow oil: 1.260 g; n^{20}_D 1.6387; IR (neat) 3400 (vs, NH) cm^{-1}.

Pure **2**, free of solid by-products, was obtained in 2.1% yield by stirring a slurry of **3** (0.500 g, 1.29 mmol) in ethanol (20 mL) in a stoppered flask for 16 h at 25 °C. The yield of **2** was improved to 17.2% when the reaction was carried out in the presence of 0.039 g (1.29 mmol) of dissolved paraformaldehyde in an abortive attempt to prepare the methylene-bridged derivative **4**.

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Registry No.—**1**, 34885-67-1; **2**, 63731-20-4; **3**, 34885-71-7; ethanol, 64-17-5.

Supplementary Material Available: The ABX_2 analysis (5 pages). Ordering information is given on any current masthead page.

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Photosensitized Dimerization of Methylcytosine Derivatives

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Irradiation of cytosine and its 1-methyl, 4-methyl, 1,4-dimethyl, 4,4-dimethyl, and 1,4,4-trimethyl derivatives in acetone or acetone–water solutions with 313-nm light produces the corresponding derivatives of cyclobutyldicytosine (cytosine dimer, Cyt<>Cyt) with yields ranging from 14 to 86%. Under mild acid conditions, Cyt<>Cyt derivatives can be converted to the corresponding isomers of uracil dimer (Ura<>Ura) by deamination. This allows the stereoconfigurations of various Cyt<>Cyt to be determined by comparing with the corresponding isomers of Ura<>Ura and Me^1Ura<>Me^1Ura. Except for Cyt, which forms (t,a) Cyt<>Cyt in addition to the (t,s) isomer, the others yield only the (t,s) isomer. In F_3CCOOH, (t,a) Cyt<>Cyt is decomposed to Cyt, while syn dimers are stable. These Cyt<>Cyt derivatives display the AB or AA'BB' patterns in the NMR spectra, determined in F_3CCOOD at −2 °C. The mass spectra of these dimers resemble those of the corresponding monomer. N^4-unsubstituted dimers (U), Cyt<>Cyt and Me^1Cyt<>Me^1Cyt, have λ_{max} ~245 nm and ϵ_{max} ~10 000; N^4-monosubstituted dimers (M), Me^4Cyt<>Me^4Cyt and $Me_2{}^{1,4}$Cyt<>$Me_2{}^{1,4}$Cyt, have λ_{max} ~250 nm and ϵ_{max} ~15 000, and N^4-disubstituted dimers (D), $Me_2{}^{4,4}$Cyt<>$Me_2{}^{4,4}$Cyt and $Me_3{}^{1,4,4}$Cyt<>$Me_3{}^{1,4,4}$Cyt, have λ_{max} ~260 nm and ϵ_{max} ~20 000. These batho- and hyperchromic shifts indicate that the amino form is predominant in D and the imino form in U. In M both forms may be more evenly distributed. This assumption is further verified by the spectral characteristics of $Me_2{}^{1,3}$Cyt<>$Me_2{}^{1,3}$Cyt, which was synthesized because it could exist only in the imino form. IR and deuterated IR spectra were also studied (ν_{NH}/ν_{ND} = 1.33) in order to gather additional evidence for a possible amino–imino tautomerization for these Cyt<>Cyt derivatives in polar and nonpolar solvents. This information should be of importance to the photochemistry and photobiology of nucleic acids.

There is evidence to show that cyclobutane dipyrimidines containing cytosine [such as cytosine dimer (Cyt<>Cyt) or cytosine–thymine dimer (Cyt<>Thy)] are produced as photoproducts in DNA or polynucleotides by 280-nm irradiation[1] or possibly by photosensitized dimerization.[2] These Cyt-containing hetero- and homodimers were found[1] to be monomerized by shorter wavelength irradiation more easily than their corresponding Ura and Thy dimers and DNA