Crystal and Molecular Structure of Ethylene-1-(diphenylphosphino)-1-(triphenylphosphonium)-2-(diphenylamino)-2-(phenylamide),[1a] $[(C_6H_5)_2P][(C_6H_5)_3P]CC[N(C_6H_5)_2][NC_6H_5]$. Phenyl Migration from Four-Coordinated Phosphorus to Two-Coordinated Nitrogen

Fred K. Ross,[1b] Ljubica Manojlovic-Muir,[1b] Walter C. Hamilton,*[1b]
Fausto Ramirez,[1c] and John F. Pilot[1c]

Contribution from the Departments of Chemistry, Brookhaven National Laboratory, Upton, New York 11973, and State University of New York at Stony Brook, Stony Brook, New York 11790. *Received February 25, 1972*

Abstract: The pyrolysis of ethylene-1,1-bis(triphenylphosphonium)-2,2-bis(phenylamide), $[(C_6H_5)_3P]_2CC(NC_6H_5)_2$, yields ethylene-1-(diphenylphosphino)-1-(triphenylphosphonium)-2-(diphenylamino)-2-(phenylamide), $[(C_6H_5)_2P]$-$[(C_6H_5)_3P]CC[N(C_6H_5)_2][NC_6H_5]$, in an unprecedented phenyl migration from four-coordinated P to two-coordinated N. The structure of the pyrolysis product has been determined by single-crystal X-ray diffraction. The crystals are monoclinic, space group $P2_1/c$, $a = 10.98$ (2), $b = 19.10$ (2), $c = 19.97$ (2) Å, $\beta = 105.87$ (8)°, $Z = 4$, $D_x = 1.21$ g cm^{-3}. Data (3656 independent) were collected on an automatic diffractometer. The structure was determined by direct methods and refined to a value of $R = 0.099$. The central C–C bond length is 1.426 (9) Å, and the central P–C and N–C bond lengths are 1.793 (7), 1.748 (6), 1.442 (8), and 1.291 (8) Å, respectively. Bonding about the two central carbon atoms is trigonal planar, about the four-coordinated phosphorus atom is tetrahedral, and about the three-coordinated phosphorus atom is pyramidal. Unexpectedly, the bonding about the three-coordinated nitrogen atom is perfectly trigonal planar.

Hexaphenylcarbodiphosphorane (**1**) was first reported[2] in 1961; its synthesis has been verified,[3] and its molecular structure has been established by X-ray crystallographic analysis.[4] The reaction of the carbodiphosphorane **1** with diphenylcarbodiimide **2** yields a crystalline 1:1 adduct,[5] ethylene-1,1-bis(triphenylphosphonium)-2,2-bis(phenylamide) (**3**). The molecular structure of adduct **3** is also known from X-ray crystallography.[6]

$$\underset{\mathbf{1}}{(C_6H_5)_3PCP(C_6H_5)_3} + \underset{\mathbf{2}}{C_6H_5NCNC_6H_5} \longrightarrow \underset{\mathbf{3}}{[(C_6H_5)_3P]_2C{=}C(NC_6H_5)_2}$$

The yellow adduct **3** is a relatively stable substance which, however, undergoes certain changes at temperatures approaching 185°. This paper describes the nature of these changes and the X-ray crystallographic analysis of the product of the pyrolysis.

Experimental Section

Pyrolysis of Ethylene-1,1-bis(triphenylphosphonium)-2,2-bis(phenylamide) (3). The adduct **3** was prepared as described;[5] it was characterized by its ^{31}P nmr signal in CH_2Cl_2 solution (*cf.* Table I) and by its ir spectrum in a KBr disk and in CH_2Cl_2 solution.[5] The adduct **3** was kept 1 hr at 184°. The ^{31}P nmr spectrum of the pyrolysis product, **4**, was observed in CH_2Cl_2 solution (*cf.* Table I). The ir spectrum of **4** in a KBr disk had these bands (cm^{-1}): 1599, 1586, 1573, 1539, 1493, 1436, 1311, 1271, 1230, 1200, 1184, 1167, 1097, 1068, 1041, 1021, 994–984; the spectrum was nearly identical in CH_2Cl_2 solution.

The pyrolysis product, **ethylene-1-(diphenylphosphino)-1-(triphenylphosphonium)-2-(diphenylamino)-2-(phenylamide) (4)**, was recrystallized from methylene chloride–anhydrous ethanol

Table I. ^{31}P Nmr Signals of Hexaphenylcarbodiphosphorane and Related Compounds

No.	Formula	$\delta(^{31}P)^a$	$J_{PCP}{}^a$
1	$[(C_6H_5)_3P]_2C$	+3.5	None
3	$\begin{array}{c}[(C_6H_5)_3P]_2C\\ \vert \\ (C_6H_5N)_2C\end{array}$	−10.2	None
4	$\begin{array}{c}(C_6H_5)_3PCP(C_6H_5)_2\\ \vert \\ C_6H_5NCN(C_6H_5)_2\end{array}$	−20.4 +7.1[b]	48
5	$\begin{array}{c}[(C_6H_5)_3P]_2C\\ \vert \\ (p\text{-}CH_3C_6H_4N)_2C\end{array}$	−8.6[c]	None
6	$\begin{array}{c}(C_6H_5)_3PCP(C_6H_5)_2\\ \vert \\ p\text{-}CH_3C_6H_4NCN(C_6H_5)(C_6H_4CH_3\text{-}p)\end{array}$	−20.2 +7.1[d]	48

[a] $\delta(^{31}P)$ in parts per million *vs.* $H_3PO_4 = 0$; coupling constant, *J*, in cps; measurements at 40.6 Mcps in CH_2Cl_2. [b] For $(C_6H_5)_2PCH_3$, $\delta(^{31}P) = +28$ ppm. [c] The two CH_3 groups give one ^1H nmr signal at τ 8.09 ppm *vs.* TMS = 10. [d] One CH_3 group gives a ^1H signal at τ 8.02 ppm; the other CH_3 group gives a signal at τ 7.77 ppm.

---

[1] (a) Research performed under the auspices of the U. S. Atomic Energy Commission (Brookhaven), and with the support of Grants CA-04769 from the Cancer Institute of the National Institutes of Health and GP-6690 from the National Science Foundation (Stony Brook); (b) Brookhaven National Laboratory; (c) State University of New York at Stony Brook.

[2] F. Ramirez, N. B. Desai, B. Hansen, and N. McKelvie, *J. Amer. Chem. Soc.*, **83**, 3539 (1961).

[3] (a) C. N. Matthews, J. S. Driscoll, J. E. Harris, and R. J. Wineman, *ibid.*, 84, 4349 (1962); (b) J. S. Driscoll, D. W. Grisley, J. V. Pristinger, J. E. Harris, and C. N. Matthews, *J. Org. Chem.*, **29**, 2427 (1964); (c) G. H. Birum and C. N. Matthews, *Accounts Chem. Res.*, **2**, 373 (1969).

[4] A. T. Vincent and P. J. Wheatley, *J. Chem. Soc.*, in press; *Chem. Commun.*, 582 (1971).

[5] F. Ramirez, J. F. Pilot, N. B. Desai, C. P. Smith, B. Hansen, and N. McKelvie, *J. Amer. Chem. Soc.*, **89**, 6273 (1967).

[6] F. K. Ross, W. C. Hamilton, and F. Ramirez, *Acta Crystallogr., Sect. B*, **27**, 2331 (1971).

(1:1.5) and had mp 234–236° dec and the same spectral characteristics as the original material before crystallization.

Anal. Calcd for $C_{50}H_{40}N_2P_2$: C, 82.2; H, 5.5; N, 3.8; P, 8.5; mol wt, 730. Found: C, 82.2; H, 5.6; N, 4.0; P, 8.4; mol wt, 679 (thermoelectric method in benzene).

Pyrolysis of Ethylene-1,1-bis(triphenylphosphonium)-2,2-bis(*p*-tolylamide) (5). The previously reported[5] methyl analog **5** (see Table I) was kept 1 hr at 184°, and the pyrolysis product, **6**, was investigated as described above. Ethylene-1-(diphenylphosphino)-1-(triphenylphosphonium)-2-(phenyl-*p*-tolylamino)-2-(*p*-tolylamide) (**6**) (Table I) had mp 229–230° (CH_2Cl_2–C_2H_5OH). The ir spectrum of **6** in CH_2Cl solution had these bands (cm^{-1}): 1612, 1595, 1538, 1511, 1496, 1439, 1321, 1237, 1202, 1102, 1040, 1027, 817.

Anal. Calcd for $C_{52}H_{44}N_2P_2$: C, 82.3; H, 5.8; N, 3.7; P, 8.2; mol wt, 758. Found: C, 82.2; H, 6.0; N, 3.5; P, 8.1; mol wt, 710 (thermoelectric method in benzene).

Crystal Data. Ethylene-1-(diphenylphosphino)-1-(triphenylphosphonium)-2-(diphenylamino)-2-(phenylamide) (**4**), $C_{50}H_{40}N_2P_2$, is monoclinic, space group $P2_1/c$, based on systematic absences ($0k0$), $k = 2n + 1$ and ($h0l$), $l = 2n + 1$; $a = 10.98\ (2)$ Å, $b = 19.10\ (2)$ Å, $c = 19.97\ (2)$ Å; $\beta = 105.87\ (8)°$; $V = 4028$ Å^3; $Z = 4$; $D_x = 1.21$ g cm^{-3} (measurement temperature 24 (1)°; radiation Mo Kα (Nb filter); λ 0.7107 Å); pale yellow prismatic crystals with poorly developed faces.

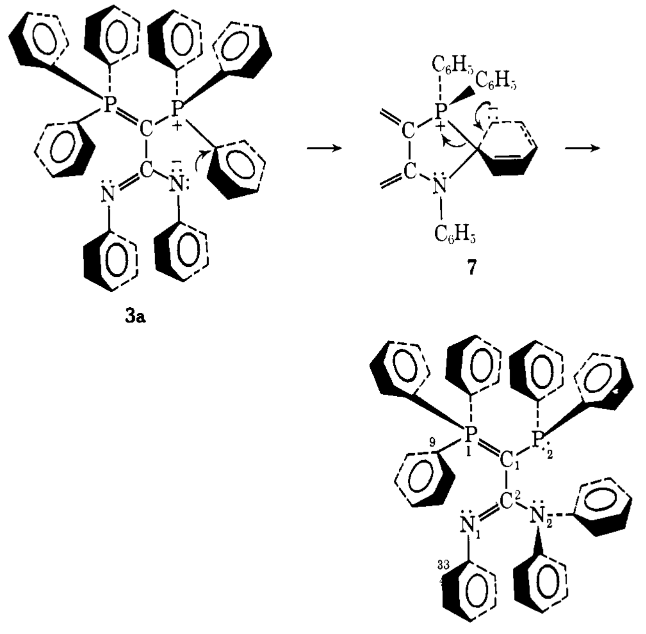
Intensity Measurements. A crystal grown from benzene solution was of approximate dimensions 0.6 × 0.5 × 0.4 mm. Diffraction data were obtained from θ–2θ step scans on an automatic diffractometer[7] equipped with a scintillation counter and pulse height and shape discriminator. The radiation used was Nb-filtered Mo Kα (λ 0.7107 Å). The intensities of 4965 independent reflections with $\sin\theta/\lambda < 0.55$ were measured. Of these, the 3656 with $I \geqslant 3\sigma(I)$, where $\sigma(I)$ is the estimated counting statistical error, were used in the structure solution and refinement. Several reflections were measured periodically during the data collection and suggested a linear decomposition of a total of about 10% during the period of data collection. The intensities of all reflections were scaled against these standards. No absorption correction (μ 0.14 mm^{-1}) was deemed necessary. Structure factors were derived by application of the usual Lorentz and polarization corrections.

Structure Determination and Refinement. Normalized structure factors[8] were used in a reiterative application of the Σ_2 relationship in a program written by Long[9] to obtain the signs for 242 E values whose magnitudes exceeded 1.7. The phosphorus atoms and several of the lighter atoms were found in the subsequent E map. Symbolic addition procedures[8] provided signs for 450 reflections, using the 242 originally determined signs as a starting set. The resulting E map and a subsequent difference Fourier resulted in the location of all atoms. A full-matrix least-squares refinement on the positional parameters of all atoms, anisotropic thermal parameter for all atoms except for those in the phenyl groups, and isotropic thermal parameters for these completed the structure determination. Hydrogen atoms were included at geometrically reasonable positions but were not refined; the expense of refining anisotropic thermal parameters (which would increase the number of parameters from 247 to 487) did not seem warranted. The function minimized in the least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$, with the weights being given by $w = 1/\sigma^2(F)$, $\sigma(F) = \sigma(F^2)/2F$, and $\sigma^2(F^2) = \sigma^2{}_{\text{count}} + (0.10\ F^2)^2$, with $\sigma^2{}_{\text{count}}$ being the variance due to the Poisson counting statistics. The final value of the residual $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ was 0.099. Scattering factors were standard values.[10] The small anomalous scattering contribution from phosphorus ($\Delta f = 0.1$, $\Delta f'' = 0.2$) was not included in the calculation. No correction was necessary for extinction. The observed and calculated structure amplitudes are presented in Table II.[11] Computer programs used have been described briefly by Schlemper, Hamilton, and La Placa.[12]

The final positional and thermal parameters are presented in Table III, and selected bond distances and angles are listed in Tables IV and V.[11]

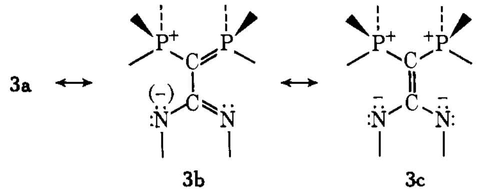
Discussion of Results

Mechanism of the Pyrolysis of Adduct 3. The X-ray data, which will be discussed in detail below, show that the pyrolysis of the carbodiphosphorane carbodiimide adduct causes the migration of a phenyl group from four-coordinated phosphorus to two-coordinated nitrogen: **3a** → **4a**. The reaction probably involves a cyclic intermediate **7** and the mechanism can be characterized as a nucleophilic aromatic substitution in which the amide nitrogen displaces a tertiary phosphine from the arylphosphonium cation. Probably, this reaction is facilitated by the overall structure of the molecule which brings the reactive centers relatively close to each other (see below). Moreover, the reaction might be facilitated by some interaction between the positive charge on the phosphorus and the negative charge on the phenyl carbon, as these develop in the transition state leading to intermediate **7**.



3a **7** **4a**

The best approximation to the molecular structure of the adduct **3** in the valence bond notation is that of a resonance hybrid of two equivalent dipolar forms **3a** ↔ **3b**, with a minor contribution from the tetrapolar form **3c**. The main feature of the structure is the predominant single bond character of the central C–C bond.



3b **3c**

The pyrolysis product **4** is best represented as a resonance hybrid of the imino phosphinemethylene form, **4a**, and the amide phosphonium ylide, **4b**, with minor contributions from dipolar and tetrapolar forms, **4c**

---

(7) D. R. Beaucage, M. A. Kelley, D. Ophir, S. Rankowitz, R. Spinrad, and R. van Norton, *Nucl. Instrum. Methods*, 40, 26 (1966).

(8) I. L. Karle and J. Karle, *Acta Crystallogr.*, **16**, 969 (1963).

(9) R. B. Long, Dissertation, University of California, Los Angeles, 1965.

(10) "International Tables for X-ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, Table 3.3.1A.

(11) These tables will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-72-8738. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche.

(12) E. O. Schlemper, W. C. Hamilton, and S. J. La Placa, *J. Chem. Phys.*, 54, 3990 (1971).

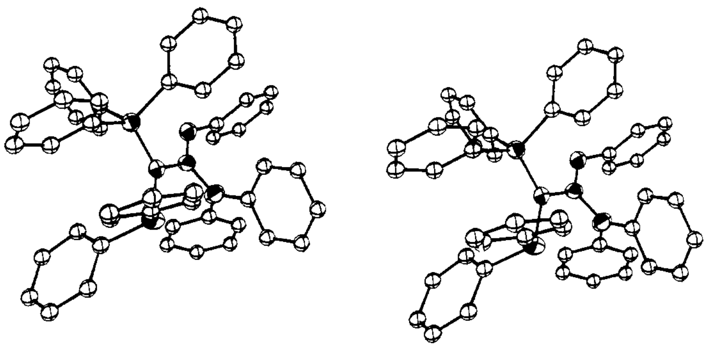
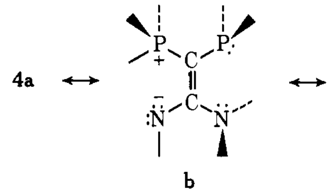
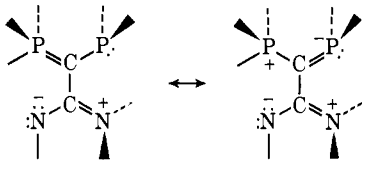


Figure 1. Stereo diagram of the molecular structure of ethylene-1-(diphenylphosphino)-1-(triphenylphosphonium)-2-(diphenylamino)-2-(phenylamide).

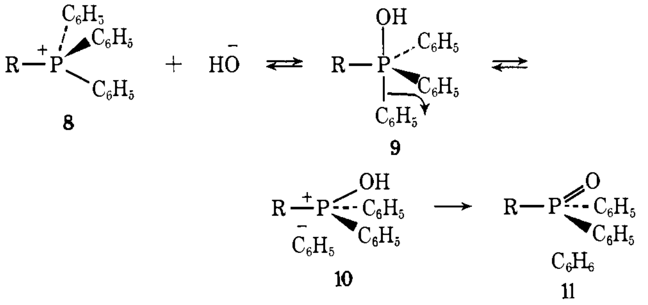
and **4d**, which generate positive charge on one nitrogen and negative charge on one phosphorus. The emphasis on the hybrid **4a** ↔ **4b** implies considerable double bond character of the central C–C bond.



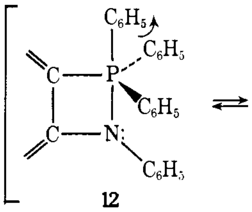


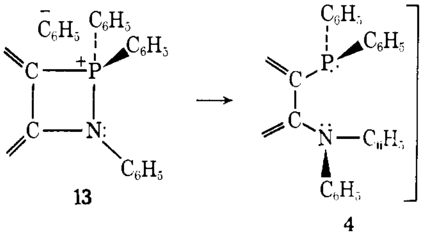
These resonance structures have the following additional implications.

(a) The positive charge on a given phosphorus atom of the adduct **3** is not as localized or "concentrated" as it is in the phosphorus of an ordinary quaternary phosphonium salt, $RP^+(C_6H_5)_3$. Consequently, the adduct P^+ is less electrophilic than the usual phosphonium P^+. (b) The pyrolysis product **4** has less p-d π bonding, *i.e.*, less phosphinemethylene character (**4a**) and more phosphonium ylide character (**4b**), than ordinary P ylides: $(C_6H_5)_3P{=}CR_2 \leftrightarrow (C_6H_5)_3P^+{-}CR_2^-$. These considerations account for the unusual behavior of the adduct **3**. In general, the cleavage of the $P{-}C_{Ph}$ bond in arylphosphonium salts, **8**, takes place in alkaline media and involves an intermediate oxyphosphorane, **9**, with trigonal-bipyramidal five-coordinated phosphorus.[13-19]



The operation of this type of mechanism in the reactions of the adduct **3** is disfavored by the relatively low electrophilicity of its phosphonium cation suggested above. If the mechanism is assumed to be intramolecular, the intermediate would be the four-membered cyclic azaphosphorane **12**. For several reasons, this pathway, **3** → **12** → **13** → **4**, to the observed product of the pyrolysis seems to us implausible.





Molecular Structure of the Pyrolysis Product, 4. (Figure 1) Table VI shows the main features of the molecular structures of carbodiphosphorane **1**, of its adduct with carbodiimide, **3**, and of the pyrolysis product, **4**, of the latter. Figure 1 also illustrates the three-dimensional structure of **4**.

The mean phosphorus to phenyl-carbon bond length, $P{-}C_{Ph}$, is not significantly different in the three compounds. To a very good approximation, the bonding of the phenyl groups to the phosphorus is invariant in these molecules and close to the value expected for a single P–C bond.[20-27]

---

(13) (a) G. W. Fenton and C. K. Ingold, *J. Chem. Soc.*, 2342 (1929); (b) K. Kumli, W. E. McEwen, and C. A. Van der Werf, Jr., *J. Amer. Chem. Soc.*, **81**, 3805 (1959); (c) W. E. McEwen, *Top. Phosphorus Chem.*, 2, 1 (1965).

(14) R. F. Hudson and M. Green, *Angew. Chem., Int. Ed. Engl.*, **2**, 11 (1963).

(15) L. Horner, *Pure Appl. Chem.*, **9**, 225 (1964).

(16) G. Kamai and G. M. Usacheva, *Russ. Chem. Rev.*, **35**, 601 (1966).

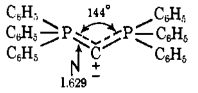
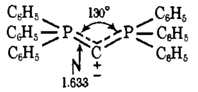
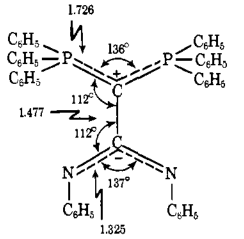
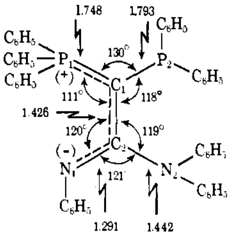
(17) K. Mislow, *Accounts Chem. Res.*, **3**, 321 (1970).

(18) P. Gillespie, F. Ramirez, I. Ugi, and D. Marquarding, *Angew. Chem.*, **85**, 1 (1973); *Angew. Chem., Int. Ed. Engl.*, in press.

(19) (a) F. Ramirez, *Accounts Chem. Res.*, **1**, 168 (1968); (b) *Bull. Soc. Chim. Fr.*, 3491 (1970); (c) F. Ramirez and I. Ugi, *Progr. Phys. Org. Chem.*, **9**, 25 (1971).

(20) The "normal" value for the single C–P bond length is said to be 1.82 Å; *cf.* ref 19. Previously given X-ray data show that $P{-}C_{Ph}$ bonds are indeed quite close to this value, for example, 1.78, 1.82, and 1.84 Å

Table VI. Mean Values of Selected Bond Angles and Bond Lengths in Hexaphenylcarbodiphosphorane and Related Compounds

No.	Structure	Mean values involving phenyl carbons Bond angles, deg	 Bond lengths, Å
1-I[a,b]		C–P–C_{Ph} 114.9 C_{Ph}–P–C_{Ph} 103.5	P–C_{Ph} 1.832
1-II[a,b]		C–P–C_{Ph} 114.5 C_{Ph}–P–C_{Ph} 104.0	P–C_{Ph} 1.837
3[c]		C–P–C_{Ph} 114.0 C_{Ph}–P–C_{Ph} 104.6 C–N–C_{Ph} 126.1	P–C_{Ph} 1.813 (8) N–C_{Ph} 1.379
4		C_1–P_1–C_{Ph} = 113.2 C_1–P_2–C_{Ph} = 108.2 C_{Ph}–P_1–C_{Ph} = 105.5 C_{Ph}–P_2–C_{Ph} = 103.4 C_2–N_1–C_{Ph} = 122.4 C_2–N_2–C_{Ph} = 118.3 C_{Ph}–N_2–C_{Ph} = 123.3	P–C_{Ph}[d] 1.821 N–C_{Ph}[e] 1.41

[a] Two crystallographically independent molecules in the unit cell. [b] Vincent and Wheatley, ref 4. [c] Ross, Hamilton, and Ramirez, ref 6. [d] The five phenyls on P are included in this mean value. [e] The three phenyls on N are included in this mean value.

The environment about the four-membered phosphorus (P_1) in the pyrolysis product **4** is tetrahedral; see Table VI for the mean values of the angles C_1–P_1–C_{Ph} and C_{Ph}–P_1–C_{Ph}. The environment about the three-coordinated phosphorus (P_2) is pyramidal, or tetrahedral with the unshared electron pair in the fourth position; *cf.* the values of angles C_1–P_2–C_{Ph} and C_{Ph}–P_2–C_{Ph}. The P atoms lie nearly in the plane of the phenyl ring in all cases, the P–C–C–C torsion angles being between 172 and 180°.

The central framework of the molecule **4**, $(P_1)(P_2)$-$C_1C_2(N_1)(N_2)$, is nearly planar as shown by the torsion angles P_1–C_1–C_2–N_1 (−11.1°), P_1–C_1–C_2–N_2 (169.3°), P_2–C_1–C_2–N_1 (174.5°), and P_2–C_1–C_2–N_2 (−5.1°). In the case of the adduct **3** the only independent torsion angle P_1–C_1–C_2–N_1 has the value 9.7°. Hence, there is little difference between the two compounds in this respect, and both frameworks are probably kept from strict planarity only by nonbonded repulsions. As reflected in the corresponding resonance structures **4a** $\leftrightarrow$ **4b** $\leftrightarrow$ **4c** $\leftrightarrow$ **4d**, and **3a** $\leftrightarrow$ **3b** $\leftrightarrow$ **3c**, there seems to be an extended π-bond system in the framework which does not however overlap significantly with the π-bond system of the phenyl groups.

The central C_1–C_2 bond length is significantly shorter in the pyrolysis product **4** than in the precursor adduct **3**. This suggests more double bond character in the former (*cf.* structure **4b**) than in the latter (*cf.* **3a** $\leftrightarrow$ **3b**). In fact, the C–C bond length of 1.477 Å for the adduct **3** is exactly that expected for two singly bonded trigonal carbon atoms,[28,29] $(sp^2)C$–$C(sp^2)$; this implies bond orders of 1.5 for the C–P[20–27] and C–N[30] bonds in this molecule **3**, in agreement with the observed values of 1.726 and 1.325 Å, respectively. Both C_1–P_1 and C_1–P_2 bonds in the pyrolysis product **4** are longer than the C–P bonds in the adduct **3**, indicating a decrease in the contribution of phosphorus to the π-bonding orbital in this region of the pyrolysis product **4a** $\leftrightarrow$ **4b** *vs.* **3a** $\leftrightarrow$ **3b**. As expected, C_1–P_2 is considerably longer than C_1–P_1 in **4**. The C_2–N_1 bond in **4** is a nearly perfect double bond, while C_2–N_2 is a reasonable single bond, in agreement with the weight ascribed to resonance structures **4a** and **4b**. It should be emphasized, however, that the near planarity of the central framework in both molecules must also be taken into account and this is done by invoking the participation of **4c** and **4d** as well.

---

for five-coordinated P, 1.828 and 1.83 Å for three-coordinated P, and 1.72–1.80 and 1.78 Å for four-coordinated P; *cf.* ref 22–27.

(21) D. W. Cruickshank, *J. Chem. Soc.*, 5486 (1961).

(22) M. Ul-Haque, C. N. Caughlan, F. Ramirez, J. F. Pilot, and C. P. Smith, *J. Amer. Chem. Soc.*, **93**, 5229 (1971).

(23) D. D. Swank, C. N. Caughlan, F. Ramirez, and J. F. Pilot, *ibid.*, **93**, 5236 (1971).

(24) P. J. Wheatley, *J. Chem. Soc.*, 2206 (1964).

(25) J. J. Daly, *ibid.*, 3799 (1964).

(26) J. C. J. Bart, *Acta Crystallogr. Sect. B*, **25**, 489 (1969).

(27) (a) C. Moret and L. M. Trefonas, *J. Amer. Chem. Soc.*, **91**, 2255 (1969); (b) C. J. Fritchie, *Acta Crystallogr.*, 20, 107 (1966).

(28) The length of the $(sp^2)C$—$C(sp^2)$ single bond of butadiene is 1.48 Å, and that of the $(sp^2)C{=}C(sp^2)$ double bond of ethylene is 1.34 Å; *cf.* ref 27.

(29) J. March "Advanced Organic Chemistry," McGraw-Hill, New York, N. Y., 1968, pp 22, 31.

(30) The following C—N bond lengths are relevant: $(sp^3)C$—N single bond (methylamine) = 1.47 Å; N—C_{Ph} (aniline) = 1.40 Å; $(sp^2)C$—N (formamide) = 1.36 Å; aromatic C=N (symmetric triazine) = 1.318 Å; $(sp^2)C{=}N$ (imines) = 1.28 Å. See ref 29.

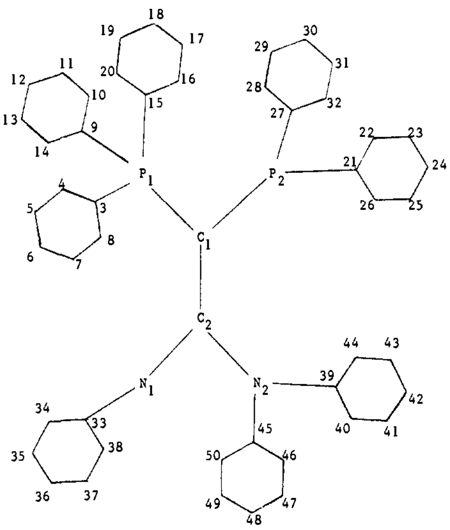
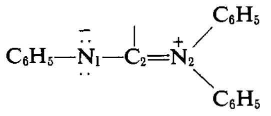


Figure 2. Atomic numbering used in this paper.

The P-C_{Ph} bond lengths were already discussed. The N-C_{Ph} bonds are longer in the pyrolysis product **4** than in the adduct **3** suggesting less bond shortening due to conjugation in the former than in the latter.

One of the most significant features in the structure of **4** is the planarity at the three-coordinated nitrogen (N_2). The angles around this atom (see Table VI) indicate almost perfect trigonal hybridization, which is in marked contrast to the pyramidal (or tetrahedral) environment of the three-coordinated phosphorus (P_2). Apparently, the "lone pair" of electrons on N_2 is somewhat involved in bonding to C_2, as implied by



$$C_6H_5-\overset{-}{\underset{..}{\ddot{N}}}_1-\overset{|}{C}_2=\overset{+}{N}_2(C_6H_5)_2$$

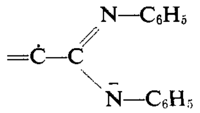
However, the C_2-N_2 bond is not particularly short,[30] and it should also be noted that the pertinent orbital on N_2 lies nearly in the plane of the central skeletal framework and thus cannot overlap with the orthogonal π-bond system of atoms $N_1C_2C_1P_1$ (see formula **4a**).[31] The interesting bonding problem posed by the planarity of N_2 in **4** (which is relatively close to the three-coordinated P_2) should be studied further.

Several close intramolecular contacts were noted in **4**. The N_1 is 2.77 Å from P_1, while the planar N_2 is 3.00 Å from the pyramidal P_2. The sum of the van der Waals radii is 3.4 Å. There are several 3.0-Å distances between a nitrogen atom and the α carbons of other phenyl groups; *i.e.*, the ring carbons connected to phosphorus. There is one H-H distance of 2.2 Å between one ring on P_2 and one ring on N_2 of the same molecule. There are a number of short C-H nonbonded distances in the range 2.5-2.7 Å. The molecule **4** is quite crowded as evidenced, for example, by the unequal P-C-C angles at the α carbons of the phenyl rings.

There are no unusually short intermolecular distances in the crystal structure of **4**. There are 10 C-H distances less than 3.0 Å: 2.78, 2.83, 2.85, 2.88, 2.89, 2.90, 2.92, 2.95, 2.96, and 2.99. There are 8 H-H distances less than 2.6 Å: 2.18, 2.45, 2.49, 2.54, 2.54, 2.57, 2.57, and 2.57.

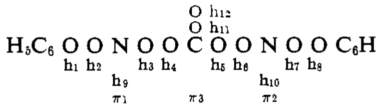
The benzene rings are planar, the largest deviation from the best least-squares planes being 0.035 (10) Å; the P and N atoms also lie in these planes.[32] The mean C-C distance in the rings is 1.380 (2) Å and the mean C-C-C bond angle is 120.0 (2) Å; there are some small but significant departures in both angles and distances of the rings from perfect sixfold symmetry; in particular, the mean value of the C-C-C angle at the carbon attached to phosphorus or nitrogen is 118.83 (24), a characteristic phenomenon in phenyl phosphorus and phenyl antimony compounds which we will discuss in a future paper. (It is possible in this case that inadequate treatment of the thermal motion of the phenyl groups may lead to apparent distortions and the shortening of the mean value below the normal value of 1.39 Å for the C-C distances.)

Molecular Orbital Description of the Adduct 3. The structure of **3** may also be described in terms of partially localized orbitals, which requires the utilization of five orbitals on each phosphorus atom. Consider first the "amidine anion" moiety



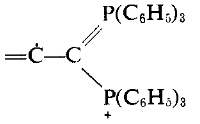
$$=\dot{C}-C\begin{matrix}\diagup\!\!\diagup N-C_6H_5\\ \diagdown \overset{-}{N}-C_6H_5\end{matrix}$$

one can write the following, with all hybrid orbitals (h) in the same plane



There are five σ orbitals which correspond to the bonding contribution of the hybrids h_1 through h_8, h_{11} and h_{12}. In addition, there is a π-bonding orbital ($\pi_1 + \pi_3 + \pi_2$), a π-nonbonding orbital ($\pi_1 - \pi_2$), and two σ-nonbonding orbitals ($h_9 + h_{10}$ and $h_9 - h_{10}$). Eighteen electrons are accommodated in these orbitals resulting in a net single negative charge on the amidine moiety. The three "lone pairs" of the valence bond description are accommodated in the three nonbonding orbitals.

A similar description may be used for the "geminal alkylidenediphosphorane cation" moiety



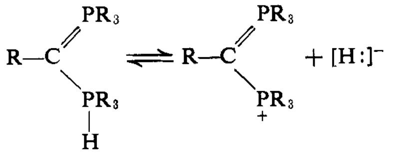
$$=\dot{C}-C\begin{matrix}\diagup\!\!\diagup P(C_6H_5)_3\\ \diagdown \underset{+}{P}(C_6H_5)_3\end{matrix}$$

with the important difference that now no nonbonding orbitals are occupied, the corresponding hybrids being used for bonding to additional phenyl groups. Thus, there are four single-bonding hybrids on each phosphorus and an additional hybrid involved in the delocalized P-C-P bond.

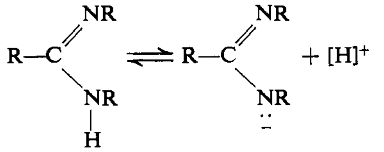
---

[31] The torsion angles C_1-C_2-H_2-C_{39} and C_1-C_2-N_2-C_{19} are 104.9 and −76.6°, respectively. There is a very small overlap of the orbital on N_2 with the two phenyl rings; the torsion angles with C_{39} and C_{45} (ring atoms attached to N_2) are −37 and −27°, respectively. The observed bond lengths are: C_{39}-N_2 = 1.415 Å; C_{45}-N_2 = 1.409.

[32] The P-C-C-C and N-C-C-C torsion angles are all greater than 170° with the exception of P_2-C_{21}-C_{22}-C_{23} 167.7°. The deviations of P_1, P_2, N_1 and N_2 from the mean planes of the phenyl groups identified by the α carbon atoms C(3), C(9), C(15), C(21), C(27), C(33), C(39), and C(45) are respectively 0.10, 0.09, 0.21, 0.29, 0.01, 0.05, 0.08, and 0.05 Å. The mean deviation is greater for phosphorus than for nitrogen.



14



15

These considerations lead to the formulation of a new function in phosphorus chemistry, the "geminal alkylidenediphosphorane" function **14**, analogous to the amidine function **15**.

The adduct **3** is merely the "zwitterion" of the conjugate acid and base forms of these two functions **14** and **15**, respectively. Further work based on this hypothesis is under way.

The description of the pyrolysis reaction **3** → **4** involves simply the migration of a formal phenonium ion $(C_6H_5)^+$ from the positive phosphorus to the negative nitrogen, forming a single bond using one of the sets of lone-pair electrons on nitrogen, with neutralization of the formal charges.

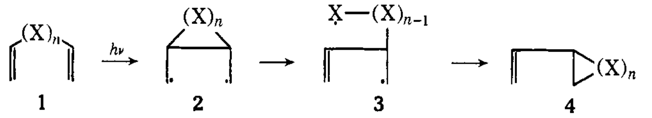
π-Interaction Photochemistry. Relationship between Photochemical Reaction in Tetraphenylalkanes and the Separation of Interacting π Systems[1]

Roger W. Binkley* and William C. Schumann

Contribution from the Department of Chemistry, Cleveland State University, Cleveland, Ohio 44115. *Received April 3, 1972*

Abstract: A general photochemical reaction type, named the π-interaction process, is described and discussed using examples to show the variety of photochemical processes which are understandable as π-interaction reactions. To explore the relationship between reactivity and separation of intereacting π systems in this reaction, a series of tetraphenylalkanes, 1,1,2,2-tetraphenylethane (**5**), 1,1,3,3-tetraphenylpropane (**6**), 1,1,4,4-tetraphenylbutane (**7**), and 1,1,5,5-tetraphenylpentane (**8**), were studied. Both **5** and **6** undergo π-interaction reaction (previously, **5** had been shown to participate in the process); however, **7** and **8** do not experience this photochemical change. For those systems which do react (**5** and **6**), the quantum yields were measured and a triplet assignment was made to the reactive excited state. The reason for the difference in reactivity among these compounds (**5–8**) and the significance of the nature of the excited state are discussed.

One of the problems facing organic photochemistry today is that the increase in the number of light-initiated reactions being discovered and investigated during the past few years is sufficiently great to make their proper assimilation and evaluation difficult. This situation creates a need for an organization of information in such a way that the importance of new reactions can be better assessed and the most desirable direction for further work more clearly understood. A possible solution to a portion of this organization problem is offered here in the form of a name and a definition for a type of photochemical process which brings together a wide variety of existing photochemical reactions under a common reaction type. This reaction type is called a π-interaction process and is defined as a photochemical reaction between nonconjugated π systems which passes through one or more of the following stages.



$X = CH_2, NH, O, \ldots$
$n = 1, 2, 3, \ldots$

There are basically four ways in which π-interaction reactions may differ from each other. The first of these is in the nature of the interacting π systems. The π systems shown in the definition are simple double bonds; however, a variety of other π systems are possible (aromatic rings, dienes, . .). A second potential difference arises from the fact that a molecule need not travel through the entire reaction pathway. It is possible for a reactant to be diverted into a new pathway at an intermediate stage (*i.e.*, **2** or **3**). The final two ways in which π-interaction reactions may differ from each other is that the number and nature of the atoms forming the bridging chain between the interacting π systems may vary; that is, n may assume different values and X may represent different atoms or groups of atoms.

The specific goal of the research described here is to investigate the π-interaction process between two aromatic rings to determine the effect on reactivity of systematically lengthening the bridging carbon chain. The four compounds selected for study are the four tetraphenylalkanes (**5–8**). The first of these, 1,1,2,2-tetraphenylethane (**5**), has previously been shown to undergo

---

[1] A preliminary communication of a portion of this work has appeared: R. W. Binkley and W. C. Schumann, *J. Amer. Chem. Soc.*, **94**, 1769 (1972).