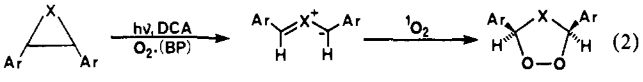
in the mother liquor after the fifth recrystallization showed enrichment (>90%) of **4b** exhibiting an absorption at δ 6.606. This material was further purified by preparative TLC and subsequently recrystallized from acetone to yield pure trans ozonide **4b** (Table I). Ozonation of *cis*- and *trans*-1-(1-naphthyl)-2-(2-naphthyl)ethene in pentane at −40 °C gave a complex mixture of peroxidic products. The NMR spectrum of the mixture showed absorptions for the four ozonides described above as well as absorptions expected for cis and trans ozonides **3c** and **4c**.

In our earlier study of the consensitized photooxygenation of *cis*- and *trans*-2,3-diphenyloxirane,[1c] we had compared the resulting photo-ozonide to authentic cis and trans ozonides prepared by ozonation of stilbene. The stereochemistry of these ozonides had been assigned by Criegee by chromatography over cellulose acetate.[9] The chiral trans ozonide was identified by its partial resolution on this stationary phase.[10] In order to establish the stereochemistry of the naphthyl-substituted ozonides, we have conducted similar experiments utilizing high-performance liquid chromatography over optically active (+)-poly(triphenylmethyl methacrylate).[12] As anticipated, **4b** obtained from ozonation of 2,3-bis(2-naphthyl)ethene was resolved by chromatography over this stationary phase (Figure 1A), confirming the trans dinaphthyl stereochemistry of this ozonide. Chromatography of the photo-ozonides **3a** and **3b** exhibited only one peak consistent with the proposed cis stereochemistry. The structure of ozonide **3b** has also been established by X-ray crystallography (Figure 1B).[13]

The results described herein demonstrate that the same stereochemical course is followed for DCA-sensitized photooxygenation of 2,3-dinaphthyloxiranes as for the DCA–BP-cosensitized reaction with 2,3-diphenyloxiranes. In a related study, we have found that the photooxygenation of *cis*- and *trans*-2,3-diphenylaziridine with DCA yields only the *cis*-1,2,4-dioxazolidine (eq 2).[1c,14b]



X = O, NH

These stereochemical observations are consistent with a mechanism involving ring-opened radical cation intermediates which may be formed either directly by substrate quenching of ^{1}DCA* or indirectly by electron transfer from the substrate to BP$^{+\cdot}$. As barriers to rotation in these species are quite low,[5,15] equilibration can occur to afford the most stable *E,E* conformation. Back electron transfer from $O_2^{-\cdot}$ or DCA$^{-\cdot}$ to the radical cations would yield the corresponding carbonyl or azomethine ylides (eq 2). Subsequent concerted addition of $^1O_2$ to the ylides would give the observed products. Foote[16] has shown that $^1O_2$ is formed in DCA-sensitized photooxygenations by energy transfer from singlet and triplet excited DCA to oxygen. Singlet oxygen may also be generated as a result of back electron transfer from $O_2^{-\cdot}$ to the radical cation.[17]

Although the proposed intermediacy of ylides in the photoxygenation of epoxides and aziridines is yet to be firmly established, this mechanism is, however, consistent with the extensive literature on trapping of photolytically and thermally genrated ylides.[5,15,18] Experiments are continuing in our laboratory on the mechanism of electron-transfer photooxygenation of epoxides, aziridines, and other substrates.

Acknowledgment. Support from the U.S. Army Research Office is gratefully acknowledged. We also thank Eduardo Palomino for assistance with determination of oxidation potentials by cyclic voltammetry.

Registry No. **1a**, 13528-49-9; **1b**, 81052-73-5; **1c**, 91879-84-4; **2a**, 13528-48-8; **2b**, 81052-72-4; **2c**, 91879-85-5; **3a**, 91879-88-8; **3b**, 91879-86-6; **3c**, 91879-90-2; **4b**, 91879-87-7; 4c, 91879-89-9; DCA, 1217-45-4; *cis*-1,2-bis(2′-naphthyl)ethene, 2633-08-1; *cis*-1-(1-naphthyl)-2-(2-naphthyl)ethene, 2633-12-7; *trans*-1-(1-naphthyl)-2-(2-naphthyl)ethene, 2633-11-6.

---

(9) Criegee, R.; Korber, H. *Chem. Ber.* **1971**, *104*, 1807.

(10) Murray and co-workers had earlier used kinetic resolution by brucine to identify the trans isomer of diisopropyl ozonide.[11]

(11) Murray, R. W.; Youssefyeh, R. D.; Story, P. R. *J. Am. Chem. Soc.* **1966**, *88*, 3655.

(12) (a) Okamoto, Y.; Honda, S.; Okamoto, I.; Yuki, H.; Murata, S.; Noyori, R.: Takaya, H. *J. Am. Chem. Soc.* **1981**, *103*, 6971. (b) Okamoto, Y.; Yashima, E.; Hatada, K.; Mislow, K. *J. Org. Chem.* **1984**, *49*, 557. (c) This HPLC column is commercially available under the trade name CHIRALPAK OT(+) from JASCO Inc., Easton, MD 21601.

(13) Details of the X-ray structure will accompany a full report.

(14) (a) Schaap, A. P.; Prasad, G.; Gagnon, S. D. *Tetrahedron Lett.* **1983**, 3047. (b) Schaap, A. P.; Prasad, G.; Siddiqui, S. *Ibid.* **1984**, 3035.

(15) (a) Albini, A.; Arnol, D. R. *Can. J. Chem.* **1978**, *56*, 2985. (b) Houk, K. N.; Rondan, N. G.; Santiago, C.; Gallo, C. J.; Gandour, R. W.; Griffin, G. W. *J. Am. Chem. Soc.* **1980**, *102*, 1504.

(16) Manring, L. E.; Gu, C.; Foote, C. S. *J. Phys. Chem.* **1983**, *87*, 40.

(17) Santamaria, J. *Tetrahedron Lett.* **1981**, 4511.

(18) (a) Lee, G. A. *J. Org. Chem.* **1978**, *43*, 4256. (b) Huisgen, R.; Mader, H. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 604. (c) Trozzolo, A. M.; Leslie, T. M.; Sarpotdar, A. S.; Small, R. D.; Ferraudi, G. J.; DoMinh, T.; Hartless, R. L. *Pure Appl. Chem.* **1979**, *51*, 261. (d) Clawson, P.; Lunn, P. M.; Whiting, D. A. *J. Chem. Soc., Chem. Commun.* **1984**, 134.

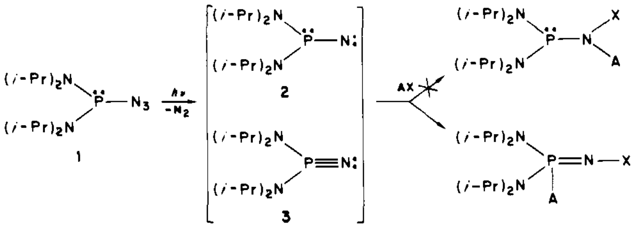
Synthesis and Structure of the First Cyclodiphosphazene. Dimerization of a Phosphonitrile $>P\equiv N$

Antoine Baceiredo,[†] Guy Bertrand,[*†] Jean-Pierre Majoral,[*‡] Ghislaine Sicard,[†] Joël Jaud,[§] and Jean Galy[§]

Laboratoire des Organométalliques
ERA 829, Université Paul Sabatier
31062 Toulouse Cedex, France
Laboratoire de Synthèse, Réactivité
et Structure de Molécules Phosphorées
ERA 926, Université Paul Sabatier
31062 Toulouse Cedex, France
G.I.T.E.R., Laboratoire de Chimie de Coordination
31400 Toulouse Cedex, France

Received June 12, 1984

Recently, ab initio calculations have proven that the structure of a singlet phosphinonitrene $>\ddot{P}-\ddot{N}:$ can be formulated to a certain extent as a phosphonitrile $>P\equiv N$, due to delocalization of the lone pairs $n_\pi(P) \rightarrow p_\pi(N)$ and $n_\pi(N) \rightarrow d_\pi(P)$.[1] Indeed, we have shown that the products obtained by photolysis of azidobis(diisopropylamino)phosphine (**1**), in the presence of various trapping agents, could be considered as adducts on a phosphorus–nitrogen triple bond.[2]



AX = MeOH, Me$_2$NH, Cl–SiMe$_3$, ···

Here we wish to report that photolysis of azide **1**, in the absence of any trapping agent, leads to the formation of the phosphonitrile dimer—the first stable cyclodiphosphazene—namely, 2,2,4,4-tetrakis(diisopropylamino)-1,3,2λ^5,4λ^5-diazadiphosphete (**4**). Although several hundred cyclo tri-, tetra-, and polyphosphazenes are known,[3] up to now no examples of cyclodiphosphazenes have

---

[†] Laboratoire des Organométalliques.

[‡] Laboratoire de Synthèse, Réactivité et Structure de Molécules Phosphorées.

[§] G.I.T.E.R.

(1) Trinquier, G. *J. Am. Chem. Soc.* **1982**, *104*, 6969.

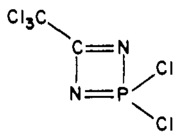
(2) Sicard, G.; Baceiredo, A.; Bertrand, G.; Majoral, J. P. *Angew Chem., Int. Ed. Engl.* **1984**, *23*, 459.

0002-7863/84/1506-6088$01.50/0

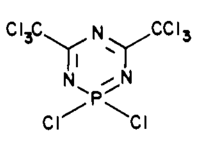
Table I. Pertinent Bond Lengths (Å) and Bond Angles (deg) for Cyclodiphosphazene 4

Bond Lengths			
P(1)-N(1)	1.651 (8)	N(2)-C(2)	1.624 (28)
P(1)-N′(1)	1.648 (8)	N(2)-C(3)	1.662 (41)
P(1)-N(2)	1.645 (8)	N(3)-C(7)	1.641 (33)
P(1)-N(3)	1.644 (9)	N(3)-C(8)	1.545 (35)
Bond Angles			
N(1)-P(1)-N′(1)	95.0 (6)	C(1)-N(2)-P(1)	117.5 (9)
P(1)-N(1)-P′(1)	85.0 (5)	C(1)-N(2)-C(2)	124.2 (11)
N(1)-P(1)-N(2)	113.6 (5)	P(1)-N(2)-C(2)	117.4 (10)
N(2)-P(1)-N(3)	105.2 (5)	C(7)-N(3)-P(1)	118.7 (12)
N′(1)-P(1)-N(3)	113.9 (8)	C(7)-N(3)-C(8)	117.3 (19)
N(1)-P(1)-N(3)	114.4 (4)	P(1)-N(3)-C(8)	122.4 (17)

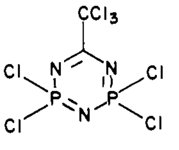
been reported. The nonexistence of these cyclic dimeric species has mainly been explained in terms of ring strain and contraction of the N–P–N bond angles below 115–120° which could cause serious interpenetration of the nitrogen van der Waals boundaries.[3a] Note that compound A claimed to be the first four-membered ring derivative possessing a phosphorus–nitrogen double bond[4] proved to be in fact a mixture of six-membered ring systems B and C.[5]



A

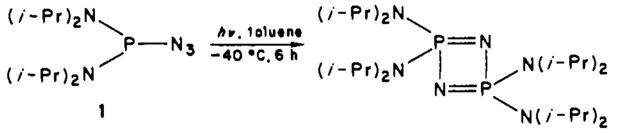


B



C

When the irradiation of azide 1[6] was carried out in toluene solution at 300 nm and −40 °C for 6 h, two products were detected by ^{31}P NMR spectroscopy. One of the signals ($\delta(^{31}P)$ +246, 10%) disappears after a few hours at room temperature. The product corresponding to the second signal ($\delta(^{31}P)$ +40) was isolated. From a chloroform solution, 4 recrystallizes, at room temperature,



1

4

with two molecules of chloroform as non-air-sensitive white crystals (mp 110 °C) in 42% yield.

The mass spectrum obtained for product 4 (M^+, 490, successive elimination of diisopropylamino groups) is consistent either with the linear product 5 (dimer of the phosphinonitrene 2) or with

$$((i\text{-Pr})_2N)_2P\text{-}N{=}N\text{-}P(N(i\text{-Pr})_2)_2$$

5

cyclic derivative 4 (dimer of the phosphonitrile 3). Note that the obtention of 5 would be in contradiction with the results observed during the photolytic reaction of 1 in the presence of trapping agents: no evidence for the formation of products arising from the phosphinonitrene structure 2 has yet been observed.[2]

Indeed, the following spectroscopic data strongly suggest structure 4. The ^{31}P chemical shift (+40 ppm) is in good agreement with a λ^5 phosphorus atom and not with a λ^3 which would give signals around +100 ppm.[8] Characteristic P=N and P—N vibrational frequencies were found in infrared spectroscopy: 1195 and 902, 890 cm^{-1}, respectively.[3a] ^{13}C and ^1H NMR spectra[9] also support such a structure (4).

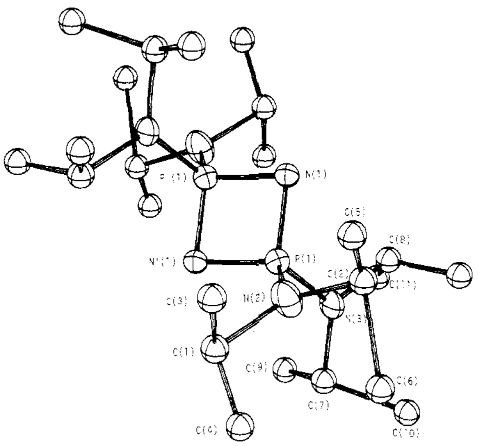


Figure 1. ORTEP view of cyclodiphosphazene 4 showing the atom numbering scheme.

The structure of 4 has been clearly established by a single-crystal X-ray diffraction study[10] and is illustrated in Figure 1 along with the atom numbering protocol. A summary of pertinent metric parameters appears in Table I. The four-membered ring is organized around a symmetry center implying the absolute planarity of the ring. The pinching of the ring around the nitrogen atoms, P(1)–N(1)–P′(1) = 85.0 (5)°, N(1)–P(1)–N′(1) = 95.0 (6)°, induces a N(1)–N′(1) distance (2.42 Å) notably longer than the P(1)–P′(1) one (2.22 Å).[11] Since all endo- and exocyclic phosphorus–nitrogen bond lengths are equal, P(1)–N(1) = 1.651 (8), P(1)–N′(1) = 1.648 (8), P(1)–N(2) = 1.645 (8), P(1)–N(3) = 1.644 (9) Å, and each nitrogen center is trigonal planar, within experimental error, it is clear that the unsaturation is strongly delocalized.

The surprising stability of the first isolated "heterocyclobutadiene" 4 is probably due to the high thermodynamic energy of the corresponding monomer[1] preventing dissociation and to steric factors which hinder polymerization. Finally, note that the formation of this cyclodiphosphazene is a novel proof for the transient existence of the phosphonitrile 3 ($\delta(^{31}P)$ +246?).

Further studies of the reactivity of phosphonitrile 3 and of its dimer 4 are in progress.

Acknowledgment. Thanks are due to Drs. G. Trinquier and P. Mazerolles for helpful discussions, to A. Jacquey for technical assistance, and to the C.N.R.S. (A.T.P. Concepts nouveaux de l'objectif Chimie Fine) for financial support.

Registry No. 1, 56183-64-3; 4, 91842-13-6.

---

(3) See, for examples: (a) Allcock, H. R. "Phosphorus-Nitrogen compounds"; Academic Press: New York, 1972. (b) Allcock, H. R.; Lavin, K. D.; Riding, G. H.; Suszko, P. R.; Whittle, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 2337. (c) Harris, P. J.; Williams, K. B.; Fisher, B. L. *J. Org. Chem.* **1984**, *49*, 406. (d) Ritchie, R. J.; Harris, P. J.; Allcock, H. R. *Inorg. Chem.* **1983**, *19*, 2483.

(4) Kukhar, V. P.; Kasheva, T. N.; Kozlov, E. S. *J. Gen. Chem. USSR (Engl. Transl.)* **1973**, *43*, 741.

(5) Schöning, G.; Glemser, O. *Chem. Ber.* **1976**, *109*, 2960.

(6) The stability of the bis(diisopropylamino)phosphine azide 1 is in marked contrast with those of most of the other phosphine azides which are extremely sensitive to mechanical shock.[7]

(7) Paciorek, K. L.; Kratzer, R. *Inorg. Chem.* **1964**, *3*, 594. Tesi, G.; Haber, C. P.; Douglas, C. M. *Proc. Chem. Soc.* **1960**, 219.

(8) For examples: 1, $\delta(^{31}P)$ +108; $[(i\text{-Pr})_2N]_2PNMe_2$, $\delta(^{31}P)$ +98.

(9) 4: ^1H NMR (250 MHz, C_6D_6) δ 1.47 [d, J_{HH} = 6.82 Hz, 48 H, Me(i-Pr)], 4.37 [m, J_{HH} = 6.82 Hz, 8 H, CH(i-Pr)]; $^{13}C\{^1H\}$(62.86 MHz, C_6D_6) δ 24.57 [s, Me(i-Pr)], 47.39 ([br s, CH(i-Pr)].

(10) A single crystal of 4·2$CHCl_3$ was grown from a chloroform solution, at room temperature. Some crystal data are as follows: monoclinic, a = 10.723 (2) Å, b = 17.850 (3) Å, c = 11.143 (2) Å; β = 112.2 (2)°; Z = 2 in space group $P2_1/n$. Diffractometer data (3140) were measured, at room temperature (due to syn crystallization with two molecules of chloroform, low-temperature measurements were impossible), on an ENRAF-NONIUS CAD-4, by $\theta/2\theta$ scan with Mo Kα radiation up to θ = 28° of which only 1587 were used [$I > \sigma I$] after correction of the large decrease in the standard intensity control reflections was applied. The structure was solved by using a MULTAN program and the structure determination package of ENRAF. Full-matrix least-squares refinement broke down only to R = 0.103, certainly because the high thermal agitation of the terminal groups did not allow us to localize the hydrogen atoms. However, the geometry around the phosphorus and nitrogen atoms was determined without any doubt. Tables of bond lengths, bond angles, atomic coordinates, thermal parameters, and structure factors are available on request from the authors.

(11) It is noteworthy that, in contrast, in the case of diazadiphosphetidine molecules, the N–P–N and P–N–P angles are in the ranges 82.5 – 85.5° and 95.2 – 97.5°, respectively.[12]

(12) Grapov, A. F.; Razvodovskaya, L. V.; Mel'Nikov, N. N. *Russ. Chem. Rev. (Engl. Transl.)* **1981**, *50*, 324.