The Formation of 10,10′(5*H*,5′*H*)-Spirobiphenophosphazinium Chloride by the Interaction of Diphenylamine and Phosphorus Trichloride

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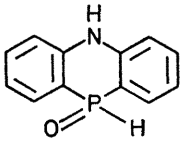
Summary The interaction of diphenylamine and phosphorus trichloride at 210° followed by treatment of the reaction mixture with water yields not only the known 5,10-dihydrophenophosphazine 10-oxide but also the novel compound, 10,10′(5*H*,5′*H*)-spirobiphenophosphazinium chloride.

IT is known that the reaction of diphenylamine with phosphorus trichloride at elevated temperatures followed by treatment of the reaction mixture with water yields the secondary phosphine oxide 5,10-dihydrophenophosphazine 10-oxide (**1**).[1] On attempting to repeat the reaction[1], we found that compound (**1**) was invariably admixed with a chlorine-containing compound with the empirical formula $C_{24}H_{18}ClN_2P$.† The i.r. spectrum of the latter substance showed that it did not contain a P–H bond; its lack of reactivity with hydrogen peroxide in acetic acid indicated that it was not a derivative of tervalent phosphorus and a base peak of *m/e* 364 suggested a loss of hydrogen chloride from $C_{24}H_{18}ClN_2P$; it was finally shown by *X*-ray diffraction to be 10,10′(5*H*,5′*H*)-spirobiphenophosphazinium chloride (2) (Figure). This is one of the few spirophosphonium compounds reported[2] and the first in which the phosphorus atom is a member of a ring containing a second heteroatom.


(1)

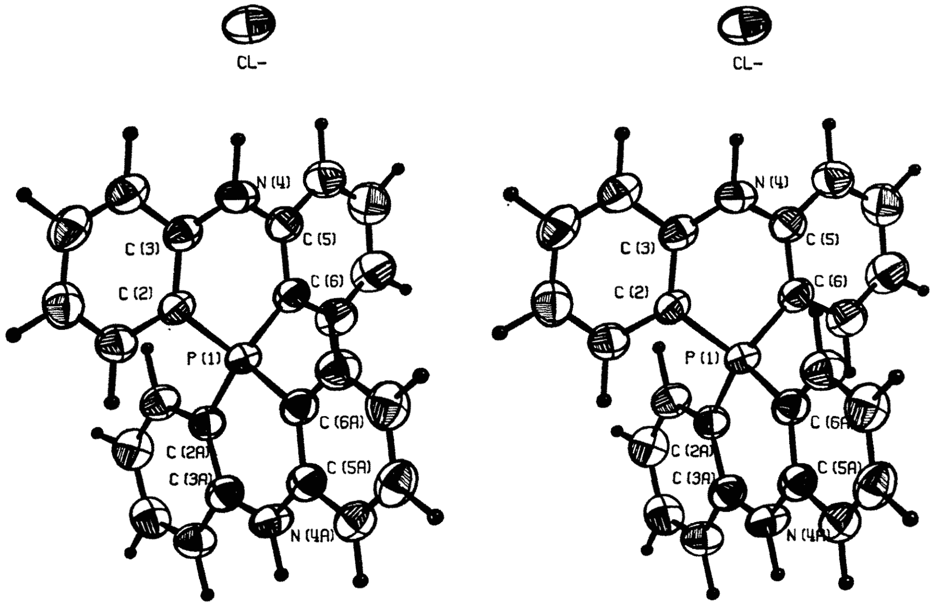
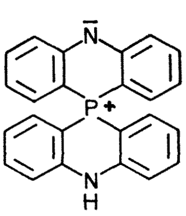
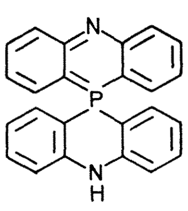


FIGURE *The stereoview of* 10,10′(5H,5′H)-*spirobiphenophosphazinium chloride* (2).

Treatment of an alcoholic solution of the chloride (**2**) (or the mixture of (**1**) and (**2**) obtained by Häring's[1] procedure) with aqueous NaOH yielded a fine yellow precipitate, which could not be purified by recrystallization since it was insoluble in water and in the common organic solvents (except for glacial acetic acid, which apparently converted it to an acetate). The yellow substance contained no chlorine, but its i.r. and mass spectra were virtually identical to the corresponding spectra of (**2**), and treatment with dilute HCl reconverted it into (**2**). It is possible that the yellow substance has the zwitterionic structure (3) and is resonance stabilized through canonical structures such as (**4**).


(3)


(4)

Compound (2) was crystallized from methanol and examined by a routine single crystal *X*-ray method. The

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† This compound gave satisfactory elemental analyses.

crystals were of space group $P2_1/c$ with $a = 12{\cdot}293$, $b = 13{\cdot}279$, $c = 17{\cdot}556$ Å, $\beta = 130{\cdot}43°$. One Angstrom intensity data (maximum sin θ/λ 0·5) was collected on a Syntex $P_{\bar{1}}$ diffractometer using copper radiation‡ and phased by the reiterative application of Sayre's equation.[3] A trial structure was obtained from the first E map, and refined to an R index of 0·06. The final cycle of refinement contained the co-ordinates for all nonhydrogen atoms, scale factor, and anisotropic temperature factors. The hydrogen positions were located by a difference Fourier technique. The hydrogen positions and isotropic temperature factors were added to the structure factor calculations, but these parameters were not refined.

Bond distances and angles of interest are given in the Table. Full details of the X-ray analysis will be published elsewhere.

Bond distances (Å) and bond angles (degrees)[a]

P(1)–C(2)	1·77	C(2)–P(1)–C(6)	104
P(1)–C(2A)	1·77	C(2A)–P(1)–C(6A)	104
P(1)–C(6)	1·77	C(2)–P(1)–C(2A)	114
P(1)–C(6A)	1·77	C(6)–P(1)–C(6A)	112
C(2)–C(3)	1·40	P(1)–C(2)–C(3)	120
C(2A)–C(3A)	1·40	P(1)–C(2A)–C(3A)	121
C(3)–N(4)	1·37	C(2)–C(3)–N(4)	124
C(3A)–N(4A)	1·38	C(2A)–C(3A)–N(4A)	123
N(4)–C(5)	1·38	C(3)–N(4)–C(5)	126
N(4A)–C(5A)	1·37	C(3A)–N(4A)–C(5A)	126
C(5)–C(6)	1·41	N(4)–C(5)–C(6)	123
C(5A)–C(6A)	1·40	N(4A)–C(5A)–C(6A)	121
		C(5)–C(6)–P(1)	121
		C(5A)–C(6A)–P(1)	121

[a] The uncertainties in the P, C, N bond distances are about 0·01 Å. Uncertainties in the bond angles are about 0·5°.

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‡ Monochromatic radiation was obtained by the use of a graphite monochromator.

[1] M. Häring, *Helv. Chim. Acta*, 1960, **43**, 1826.

[2] F. G. Mann, "The Heterocyclic Derivatives of Phosphorus, Arsenic, Antimony, and Bismuth", Wiley-Interscience, New York, N.Y., 1970, pp. 3—354.

[3] D. Sayre, *Acta Cryst.*, 1952, **5**, 60. The phasing process was facilitated by the use of a computer program written by R. E. Long, University of California at Los Angeles. Of the sixteen possible solutions generated by this program, the solution which converged in the fewest number of cycles (7) and had the highest consistency index (0·89932) proved to be the correct solution.