Organophosphorus Chemistry. Part VIII.[1] Four-membered Phosphorus–Nitrogen Ring Compounds

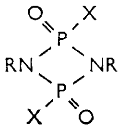
By M. Green, R. N. Haszeldine, and G. S. A. Hopkins

NN'-Dialkyl- or -diaryl-2,2,2,4,4,4-hexachloro-1,3,2,4-diazadiphosphetidines react with liquid sulphur dioxide to provide a convenient route to the corresponding 2,4-dichloro-1,3,2,4-diazadiphosphetidine 2,4-dioxides, which are readily converted into the 2,4-bisdimethylamino- or 2,4-bisthiomethyl derivatives. The n.m.r. spectra of these compounds are discussed in the light of d_π–p_π bonding, and virtual coupling.

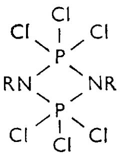
A CONVENIENT synthetic route to derivatives of *NN'*-dialkyl-1,3,2,4-diazadiphosphetidine 2,4-dioxides was required. It was reported that heating triamides of the type $(RNH)_3PO$ gave either the phosphine imides (I; R = Pr^n, Bu^i, or pentyl;[2] X = alkylamino) or the diazadiphosphetidine (II; R = Ph,[3] X = phenylamino), but a recent study[4] of the thermal decomposition of the compounds $(RNH)_3P{:}Z$ (R = Bu^i, Z = O; R = Pr^n or Bu^i, Z = S) has now shown that the products are dimers of type (II; X = NHR) rather than phosphine imides. The reaction apparently follows a different course when the methylamino-triamide $(MeNH)_3PO$ is heated, since the product has the formula $(MeN)_3P_2O_2$; the t-butylamino-triamide gave no characterisable product when heated.[5] *NN'*-Diaryl-2,4-dialkyl-1,3,2,4-diazadiphosphetidine 2,4-dioxides (II; R = aryl, X = alkyl) have also been prepared in relatively low yields by heating the corresponding alkyl-phosphonamides.[6]

$RN{:}P(O)X$

(I)



(II)



(III)

2,4-Dichloro-*NN'*-diphenyl-1,3,2,4-diazadiphosphetidine 2,4-dioxide (II; R = Ph, X = Cl) was reported to have been prepared by the reaction of aniline hydrochloride with phosphorus oxychloride;[2] the reaction apparently cannot be extended to alkylamine hydrochlorides.

Compounds of type (II) are precursors of related compounds of interest for spectroscopy, and may be regarded as difunctional monomers of interest in the synthesis of inorganic polymers. Other routes to them were therefore sought, particularly for those where R = alkyl. It has now been found that the readily available *NN'*-dialkyl- or *NN'*-diaryl-2,2,2,4,4,4-hexachloro-1,3,2,4-diazadiphosphetidines (III; R = alkyl or aryl)[7,8] react with sulphur dioxide to provide a con-

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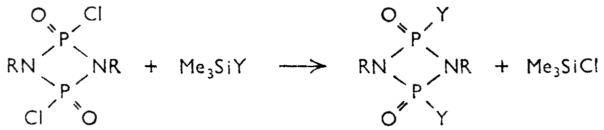
venient route to the *NN*′-dialkyl- or *NN*′-diaryl-2,4-dichloro-1,3,2,4-diazadiphosphetidine 2,4-dioxides (II; X = Cl). Removal of the excess of sulphur dioxide used as solvent, and of the thionyl chloride also produced, is easy and the products (II) are obtained as thermally stable compounds which can be sublimed. A similar result for the alkyl compound (II; R = Me, X = Cl) has been reported since completion of this work.[9] It had been previously reported that the compound (III; R = Ph) did not react with sulphur dioxide[7] and that reaction with moist sulphur dioxide gave a ring-opened product.[10]

In the original preparation of the compound (II; R = Ph, X = Cl) by Michaelis,[2] the mixture was treated with boiling water, implying a low hydrolytic reactivity. This is at variance with the ready reaction with water observed for all the 2,4-dichloro-1,3,2,4-diazadiphosphetidine 2,4-dioxides, including the *NN*′-diphenyl derivative, prepared by the new sulphur dioxide reaction.

The chlorine atoms in (II) can be replaced by dimethylamino or thiomethyl as in Scheme 1. This is in sharp contrast to the closely related bisdiethylaminophosphorochloridate which is unreactive towards diethylaminotrimethylsilane.[11]



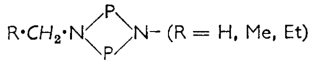
R = Me, Et, Prⁿ, Y = NMe₂, or R = Me, Y = SMe

Scheme 1

The structures of the new ring compounds (II) were established by elemental analyses, molecular weights in solution, infrared and mass spectroscopy (appearance of parent ion), and n.m.r. measurements. The infrared spectra of (II; R = Me, Et, Prⁿ, or Ph, X = Cl) contained bands at 1290 cm.$^{-1}$ (P:O) and 850 cm.$^{-1}$ (P–N), but the band in the 2760—2820 cm.$^{-1}$ region, which would be expected[12] if the nitrogen atom retained its lone-pair of electrons, is very weak, implying that dipolar d_π–p_π bonding may be important.

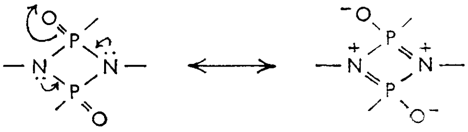
The ^{1}H n.m.r. spectra of the 2,4-dichloro-1,3,2,4-diazadiphosphetidine 2,4-dioxides (II; R = Me, Et, or Prⁿ; X = Cl) showed that the group (R·CH_2N) coupled with the equivalent ^{31}P nuclei thus demonstrating the presence of the arrangement N.P.N.P. The ^{31}P n.m.r. spectra showed the presence of two isomers, each containing the N.P.N.P. system; these may be *cis* and *trans* isomers with the chlorines on the same and opposite sides of the ring, respectively.

Virtual Coupling and Dipolar d_π–p_π *Bonding in the Ring.*—The magnitude of the coupling constant $|J_{HP}|$ in the ring-system (IV) depends on the bond order



(IV)

of the ring phosphorus–nitrogen bonds, and since donation of the nitrogen lone-pairs into vacant phosphorus *d*-orbitals of the type shown in Scheme 2 has been postulated[8,13] to be of importance in such ring systems, the magnitudes of $|J_{HP}|$ for a series of 1,3,2,4-diazadiphosphetidines (II) and (III) are compared in the Table. The importance of dipolar d_π–p_π bonding is clearly closely dependent on the nature of the substituents attached to phosphorus. Dipolar structures are of greatest importance in the hexachloro-1,3,2,4-diazadiphosphetidines (III) and of least importance with the corresponding fluoro-compounds,[14] in agreement with the indications from the infrared spectra in the 2760—2820 cm.$^{-1}$ region of the fluoro-compounds.[14] The chloro-1,3,2,4-diazadiphosphetidine 2,4-dioxides (II) and their derivatives clearly fall between these two extremes, and some delocalisation of the nitrogen lone-pair electrons is implied both by the infrared and n.m.r. spectra.



Scheme 2

The ^{1}H n.m.r. spectra of the dimethylamino- and thiomethyl-*NN*′-dialkyl-1,3,2,4-diazadiphosphetidine 2,4-dioxides show interesting deviations from the spectra predicted by a simple first-order treatment, *i.e.*, a doublet for the ^{1}H spectrum of the Me_2N and MeS groups. The thiomethyl groups attached to phosphorus have the X-pattern of an $X_3AA^1X_3{}^1$ system. From the ^{1}H n.m.r. spectrum of *NN*′-dimethyl-2,4-bisthiomethyl-1,3,2,4-diazadiphosphetidine 2,4-dioxide (II; R = Me, X = SMe) the coupling constants $J_{CH_3S,P} = 18{\cdot}2$ c./sec., $J_{CH_3S,P^1} = 0{\cdot}2$ c./sec., and $J_{PP^1} = 31{\cdot}5$ c./sec. were derived by Harris method.[15] In the spectrum of 2,4-bisdimethylamino-*NN*′-dimethyl-1,3,2,4-diazadiphosphetidine 2,4-dioxide the Me_2N-groups have the X-pattern of an $X_6AA^1X_6{}^1$ system; although the fine structure of the broad central band can be seen, the separation of the lines could not be measured sufficiently accurately to allow calculation of the "true" coupling constants. A related example of virtual coupling has recently been observed[16] in the ^{1}H n.m.r. spectra of some ethoxycyclotriphosphazatrienes.

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N.m.r. spectra of 1,3,2,4-diazadiphosphetidines

	^{1}H Spectra		^{31}P Spectra	
Diazadiphosphetidine	τ	$\lvert J_{HP}\rvert$ (c./sec.)	(from 85% H_3PO_4) p.p.m.	$\lvert J_{HP}\rvert$ c/sec.
$(MeN{\cdot}PCl_3)_2$	7·00	20·0	+77·5	20·0
$(CH_3{\cdot}CH_2{\cdot}N{\cdot}PCl_3)_2$ (*b*) (*a*)	(*a*) 6·50 (*b*) 8·59	30·0	+79·0	30·0
$(CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}N{\cdot}PCl_3)_2$ (*a*) (*b*) (*a*)	(*a*) 6·68 (*b*) 8·05 (*c*) 9·10	28·5	+79·0	29·0
$(MeN{\cdot}PPhF_2)_2$	7·54	12·5 [14]		
$[MeN{\cdot}P(O)Cl]_2$	7·07	16·2	1st isomer +3·0 2nd isomer 0·0	16·0
$[CH_3{\cdot}CH_2{\cdot}N{\cdot}P(O)Cl]_2$ (*b*) (*a*)	(*a*) 6·63 (*b*) 8·57	16·3	1st isomer +5·7 2nd isomer +3·1	16·3 16·7
$[CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}N{\cdot}P(O)Cl]_2$ (*c*) (*b*) (*a*)	(*a*) 6·68 (*b*) 8·20 (*c*) 8·90	Complex	1st isomer +2·4 2nd isomer +1·1	17·0 17·0
$[CH_3{\cdot}N{\cdot}P(O)N(CH_3)_2]_2$ (*a*) (*b*)	(*a*) 7·40 (*b*) 7·16	$\lvert J_{H_aP}\rvert = 13{\cdot}0$ $\lvert J_{H_bP}\rvert = 10{\cdot}7$ (apparent)	−7·0	Complex
$[CH_3{\cdot}N{\cdot}P(O)S{\cdot}CH_3]_2$ (*a*) (*b*)	(*a*) 7·22 (*b*) 7·71	$\lvert J_{H_aP}\rvert = 14{\cdot}0$ $\lvert J_{H_bP}\rvert = 18{\cdot}2$		

EXPERIMENTAL

The NN′-dialkyl(and diphenyl)-2,2,2,4,4,4-hexachlorodiazadiphosphetidines were prepared by published methods,[7,8] and characterised by their m. p.s, elemental analyses, molecular weights in solution, infrared and n.m.r. spectra. The n.m.r. spectra were measured on a Perkin-Elmer R10 instrument operating at 14·09kœ and 35°; ^{1}H spectra were measured as saturated solutions in deuteriochloroform, and ^{31}P spectra were measured in methylene chloride solution.

2,4-*Dichloro*-NN′-*dimethyl*-1,3,2,4-*diazadiphosphetidine* 2,4-*Dioxide*.—Dry sulphur dioxide (106 g., 1·66 mole) was condensed *in vacuo* into a 200 ml. Pyrex tube containing powdered 2,2,2,4,4,4-hexachloro-*NN′*-dimethyl-1,3,2,4-diazadiphosphetidine (31·6 g., 0·09 mole). The tube was sealed and the contents allowed to warm to room temperature. The solid dissolved after 4—5 hr. of intermittent shaking. After 12 hr. the volatile contents of the tube were fractionated *in vacuo* to give unchanged sulphur dioxide and thionyl chloride (115 g.; total volatile material, 97%) identified by infrared spectroscopy. The solid residue was washed with carbon tetrachloride and sublimed *in vacuo* at 60° to give the *dioxide* (18·4 g., 0·08 mole, 90%) (Found: C, 10·7; H, 2·6; Cl, 31·6; N, 12·5; P, 28·0%; *M* (mass-spectroscopy), 222. $C_2H_6Cl_2N_2O_2P_2$ requires C, 10·8; H, 2·7; Cl, 31·8; N, 12·6; P, 27·8%; *M*, 222), m. p. 100—102°, $\nu_{max.}$ 3279w, 2900w, 2841vw, 1460m, 1389m, 1316shs, 1290vs, 1181vs, 1050s, 913s, 852s, 679s, 654m, 597m, 588m, 563w, 535m, 491w, 465w cm.$^{-1}$.

2,4-*Dichloro*-NN′-*diethyl*-1,3,2,4-*diazadiphosphetidine* 2,4-*Dioxide*.—Dry sulphur dioxide (24·5 g., 0·38 mole) and *NN′*-diethyl-2,2,2,4,4,4-hexachloro-1,3,2,4-diazadiphosphetidine (3·77 g., 0·01 mole), gave an homogeneous solution in a 100 ml. tube 10 min. after reaching room temperature. After 12 hr., fractionation gave unchanged sulphur dioxide and thionyl chloride (25·6 g., total volatile material, 99%). The solid residue was washed with light petroleum (b. p. 40—60°) and sublimed *in vacuo* at 40° to give the *dioxide* (2·60 g., 0·01 mole, 100%) (Found: C, 19·1; H, 4·1; Cl, 28·6; N, 11·5; P, 25·0%; *M* (mass-spectroscopy), 250. $C_4H_{10}Cl_2N_2O_2P_2$ requires C, 19·1; H, 4·0; Cl, 28·3; N, 11·2; P, 24·7%; *M*, 250), m. p. 65—68°, $\nu_{max.}$ 3257vw, 2967shw, 2933w, 2890w, 2849shvw, 1468m, 1449m, 1389m, 1366m, 1361shm, 1309vs, 1282vs, 1261shs, 1160vs, 1093m, 1031m, 967m, 917m, 886s, 780m, 674s, 571vs, 560m, 529vs, 505m cm.$^{-1}$.

2,4-*Dichloro*-NN′-*di-n-propyl*-1,3,2,4-*diazadiphosphetidine* 2,4-*Dioxide*.—2,2,2,4,4,4-Hexachloro-NN′-di-n-propyl-1,3,2,4-diazadiphosphetidine (12·7 g., 0·032 mole) similarly reacted with sulphur dioxide (81·4 g., 1·3 mole) (12 hr.) to give the *dioxide* (7·12 g., 0·025 mole, 80%) (Found: C, 25·6; H, 4·7; Cl, 25·2; N, 10·3; P, 22·4%; *M* (mass-spectroscopy), 278. $C_6H_{14}Cl_2N_2O_2P_2$ requires C, 25·8; H, 5·0; Cl, 25·6; N, 10·0; P, 22·2%; *M*, 278), b. p. 110°/0·1 mm., $\nu_{max.}$ 3226vw, 2900m, 2833w, 1449m, 1370w, 1351vw, 1337vw, 1290vs, 1253m, 1149vs, 1087m, 1031m, 961w, 926s, 844m, 806w, 746w, 704w, 676s cm.$^{-1}$.

2,4-*Dichloro*-NN′-*diphenyl*-1,3,2,4-*diazadiphosphetidine* 2,4-*Dioxide*.—2,2,2,4,4,4-Hexachloro-NN′-diphenyl-1,3,2,4-diazadiphosphetidine (10·1 g., 0·02 mole) and sulphur dioxide (30·0 g., 0·47 mole) (4 days) gave the dioxide (7·7 g., 0·02 mole, 100%) [Found: C, 41·5; H, 3·1; Cl, 20·2; N, 8·1; P, 18·1%; *M*($CHCl_3$), 361. Calc. for $C_{12}H_{10}Cl_2N_2O_2P_2$: C, 41·5; H, 2·9; Cl, 20·5; N, 18·1; P, 17·9%; *M*, 347], m. p. 144·5—145°, purified by sublimation *in vacuo* at 100°, $\nu_{max.}$ 4032vw, 3356w, 3215m, 3067w, 2890vw, 2801vw, 2604vw, 1949vw, 1876vw, 1779vw, 1597s, 1497s, 1490shs, 1453w, 1403m, 1383m, 1290vs, 1242s, 1218s, 1190s, 1172m, 1101m, 1073s, 1029s, 1005m, 980vs, 949vs, 904m, 893m, 797w, 683m, 633w, 629m, 617w, 610w, 591s, 580w, 541m, 524w, 521w, 511w, 505w, 455w, 446w cm.$^{-1}$.

2,4-*Bisdimethylamino*-NN′-*dimethyl*-1,3,2,4-*diazadiphosphetidine* 2,4-*Dioxide*.—Dimethylaminotrimethylsilane (7·9 g., 0·068 mole) was condensed into a 100 ml. Pyrex tube containing 2,4-dichloro-*NN′*-dimethyl-1,3,2,4-diazadiphosphetidine 2,4-dioxide (5·2 g., 0·023 mole). A vigorous reaction occurred on attainment of room temperature to give chlorotrimethylsilane, unchanged dimethylaminotrimethylsilane, and a solid, sublimed *in vacuo* at 160° to give the *dioxide* (5·5 g., 0·023 mole, 96%) [Found: C, 30·2; H, 7·8; N, 23·0; P, 26·0%; *M*($CH_2Cl{\cdot}CH_2Cl$), 242. $C_6H_{18}N_4O_2P_2$ requires C, 30·2; H, 7·5; N, 23·3; P, 25·8%;

M, 240], m. p. 172—173°, $\nu_{max.}$ 2941shm, 2907m, 2874shm, 2817shw, 2786shw, 2762shw, 1481m, 1460m, 1307s, 1239s, 1185s, 1068m, 990s, 871s, 683w, 521w, 456w cm.$^{-1}$.

2,4-*Bisdimethylamino*-NN′-*diethyl*-1,3,2,4-*diazadiphosphetidine* 2,4-*Dioxide*.—Dimethylaminotrimethylsilane (4·0 g., 0·034 mole) and 2,4-dichloro-*NN*′-diethyl-1,3,2,4-diazadiphosphetidine 2,4-dioxide (4·0 g., 0·016 mole) similarly gave chlorotrimethylsilane and a solid, which on sublimation at *ca*. 40° gave the *dioxide* (4·18 g., 0·016 mole, 97%) [Found: C, 35·8; H, 8·2; N, 20·6; P, 23·0%; *M* (benzene), 256, (mass spectroscopy) 268. $C_8H_{22}N_4O_2P_2$ requires C, 35·8; H, 8·2; N, 20·9; P, 23·1%; *M*, 268], m. p. 73—75°, $\nu_{max.}$ 3030m, 2959s, 2924s, 2874s, 2849m, 2801m, 2532vs, 2315vw, 1754vw, 1704vw, 1486s, 1460s, 1439s, 1418w, 1383s, 1357w, 1365vs, 1238vs, 1176vs, 1093m, 1074m, 997vs, 968vs, 910vs, 788m, 685w, 549w, 521m, 510m, 502w, 459s cm.$^{-1}$.

2,4-*Bisdimethylamino*-NN′-*di*-*n*-*propyl*-1,3,2,4-*diazadiphosphetidine* 2,4-*Dioxide*.—Dimethylaminotrimethylsilane (4·1 g., 0·035 mole) and 2,4-dichloro-*NN*′-di-*n*-propyl-1,3,2,4-diazadiphosphetidine 2,4-dioxide (3·5 g., 0·012 mole) gave chlorotrimethylsilane and a solid, sublimed *in vacuo* to give the *dioxide* (3·4 g., 0·011 mole, 96%) [Found: C, 40·5; H, 8·5; N, 19·0%; *M* (benzene), 299. $C_{10}H_{26}N_4O_2P_2$ requires C, 40·5; H, 8·8; N, 18·9%; *M*, 296], m. p. 54—55°, $\nu_{max.}$ 3704vw, 3049w, 2985s, 2941s, 2890s, 2817w, 2864vw, 2451vw, 2347vw, 1570vw, 1493s, 1466s, 1425w, 1389w, 1370vw, 1351vw, 1304vs, 1235vs, 1196s, 1163vs, 1093m, 1072m, 1036s, 1013vs, 995vs, 941vs, 912m, 897m, 851s, 806m, 687w, 525m, 521m, 517m, 459m, 418w cm.$^{-1}$.

NN′-*Dimethyl*-2,4-*bisthiomethyl*-1,3,2,4-*diazadiphosphetidine* 2,4-*Dioxide*.—Thiomethyltrimethylsilane (2·45 g., 0·021 mole) was condensed into a 100 ml. tube containing 2,4-dichloro-*NN*′-dimethyl-1,3,2,4-diazadiphosphetidine 2,4-dioxide (2·3 g., 0·01 mole). The tube was warmed to room temperature overnight and then heated at 60° for 10 min. to give chlorotrimethylsilane and a solid, sublimed *in vacuo*, to give the *dioxide* (2·4 g., 0·01 mole, 99%) [Found: C, 19·7; H, 5·0; N, 11·2; S, 26·0%; *M* (mass-spectroscopy), 246. $C_4H_{12}N_2O_2P_2S_2$ requires C, 19·5; H, 4·9; N, 11·4; S, 26·0%; *M*, 246], m. p. 176—178°, $\nu_{max.}$ 2950m, 2841w, 1464m, 1429m, 1389w, 1319m, 1282s, 1235s, 1183s, 1087m, 1053m, 1020m, 971m, 901m, 855m, 847s cm.$^{-1}$.

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[6/727 *Received, June* 13*th*, 1966]