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# The Crystal Structures of Two Bicyclophosphazenes: $[(C_6H_5)_4CH_3(PN)_3]_2$ and $[(C_6H_5)_4CH_3S(PN)_3]_2Ni$*

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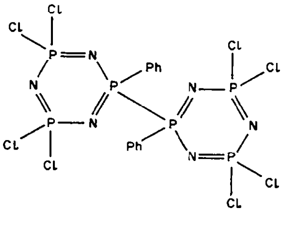
Crystals of the title compounds are triclinic, $P\bar{1}$, with $Z=1$. The first compound, $C_{50}H_{46}N_6P_6$, has $a=10{\cdot}925$ (3), $b=13{\cdot}609$ (3), $c=8{\cdot}274$ (3) Å, $\alpha=86{\cdot}55$ (5), $\beta=94{\cdot}28$ (5), $\gamma=106{\cdot}24$ (5)°. Its structure has been determined by the direct method, and refined by least squares to $R=0{\cdot}038$ and $R_w=0{\cdot}040$ for 3937 observed reflexions. The second, $C_{50}H_{46}N_6P_6S_2Ni$, has $a=11{\cdot}142$ (2), $b=12{\cdot}598$ (3), $c=9{\cdot}620$ (4) Å, $\alpha=110{\cdot}82$ (2), $\beta=77{\cdot}84$ (7), $\gamma=102{\cdot}58$ (2)°. Its structure has been determined by the heavy-atom method, and refined similarly to $R=0{\cdot}041$ and $R_w=0{\cdot}040$ for 3452 observed reflexions. In both compounds, the molecule has a centre of symmetry, with its pair of cyclotriphosphazene rings in a slight boat conformation. In the first compound, P–N = 1·595–1·607 (3) Å, P–N–P = 120·5–121·7 (2)°, N–P–N = 116·6–117·7 (2)°, and P–P′ = 2·210 (2) Å, while in the second, P–N = 1·581–1·649 (4) Å, P–N–P = 123·0–125·4 (3)°, N–P–N = 114·2–117·3 (2)°, P–S = 2·005 (2), S–Ni = 2·229 (2), and Ni–N = 1·944 (4) Å. The Ni atom in the latter has a planar coordination, and the four-membered chelate ring is bent across its S···N diagonal at a 25·4° dihedral angle.

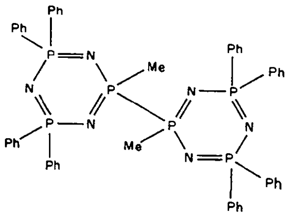
## Introduction

The first compound with a two-ring assembly phosphazene, (I), was synthesized by Biddlestone & Shaw (1968, 1971), and its crystal structure determined by Zoer & Wagner (1972). The second, (II), with the same double-ring assembly but with different substituents was synthesized by Högel & Schmidpeter. Its chemical synthesis and a brief summary of its crystal structure have been reported by Schmidpeter, Högel & Ahmed (1976). The third bicyclophosphazene, (III), which was also synthesized by Schmidpeter and co-workers, has the two phosphazene rings linked together through two four-membered chelate rings. The detailed crystal structure analyses of (II) and (III) are reported in this paper. These studies are intended to elucidate the mechanism of bond formation in P compounds which occur widely in biological systems.



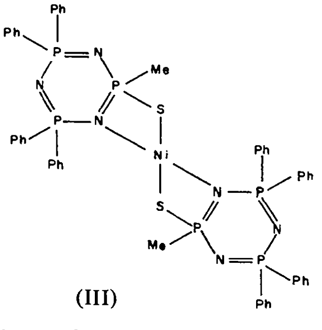
Ph = $C_6H_5$

(I)



Me = $CH_3$

(II)



(III)

## Experimental

### *Crystal and intensity data*

A summary of the crystal and intensity data of (II) and (III) is given in Table 1. The X-ray measurements were carried out on a four-circle diffractometer with Cu radiation for the cell parameters, and Mo radiation with Nb filters for the intensities. The integrated intensities were measured by the $\theta$–$2\theta$ scan method, and the background was recorded separately for each reflexion. Two reflexions were monitored for each compound at regular intervals for scaling of the intensities. Lorentz and polarization corrections were applied to both data sets, but an absorption correction was applied only to (III). The densities were measured by flotation in aqueous KI solution at about 23°C.

### *Structure determination*

The structure of (II) was derived by the symbolic addition procedure (Karle & Karle, 1963). The $|E|$ distribution statistics were strongly in favour of a centrosymmetric structure (space group $P\bar{1}$) with half a molecule in the asymmetric unit. The map which included the 894 reflexions with $|E|\geq 1{\cdot}4$ gave all the non-H atoms, as well as a few spurious peaks as high as those of the N atoms. The additional peaks were attributed to the effect of finite summation since all but one of the included reflexions were correctly signed.

The structure of (III) was obtained by the heavy-

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Table 1. *Crystal and intensity data of compounds* (II) *and* (III)

| | (II) | (III) |
|---|---|---|
| Formula | $C_{50}H_{46}N_6P_6$ | $C_{50}H_{46}N_6P_6S_2Ni$ |
| M.W. | 916·80 | 1039·63 |
| Space group | $P\bar{1}$ | $P\bar{1}$ |
| $a$ | 10·925 (3) Å | 11·142 (2) Å |
| $b$ | 13·609 (3) | 12·598 (3) |
| $c$ | 8·274 (3) | 9·620 (4) |
| $\alpha$ | 86·55 (5)° | 110·82 (2)° |
| $\beta$ | 94·28 (5) | 77·84 (7) |
| $\gamma$ | 106·24 (5) | 102·58 (2) |
| $V$ | 1176·89 Å$^3$ | 1218·60 Å$^3$ |
| $Z$ | 1 | 1 |
| $D_x$ | 1·293 g cm$^{-3}$ | 1·416 g cm$^{-3}$ |
| $D_m$ | 1·290 | 1·415 |
| $\mu$(Cu) | 24·24 cm$^{-1}$ | 34·84 cm$^{-1}$ |
| $\mu$(Mo) | 2·73 | 7·20 |
| $F$(000) | 478 | 538 |
| $2\theta_{\max}$ | 54° | 50° |
| *hkl* scanned | 5109 | 4131 |
| *hkl* observed | 3937 | 3452 |
| Observations/ parameters | 10·6 | 8·9 |

atom method from a sharpened Patterson map and a Fourier map. In both structures the H atoms were located from a difference map after partial refinement of the parameters of the other atoms.

The atomic parameters were refined by cycles of block-diagonal least squares, minimizing $\sum w(\Delta F)^2$, with weights $w = 1/\{1 + [(|F_o| - p_1)/p_2]^4\}$, where $p_1$ and $p_2$ were 22 and 18 for (II), and 25 and 30 for (III) respectively. The observed structure amplitudes were in the range $1{\cdot}7 \le |F_o| \le 107{\cdot}1$ for (II), and $2{\cdot}2 \le |F_o| \le 130{\cdot}2$ for (III). Only the observed reflexions were included in the refinement, but the unobserved reflexions were calculated at the end and showed no bad discrepancies. The final refinement indicators are listed in Table 2. The *f* curves were those of Hanson, Herman, Lea & Skillman (1964) for C, N, P, S, Ni; and of Stewart, Davidson & Simpson (1965) for H.

## Results

Two orthogonal views of (II) are presented in Fig. 1, and a view of (III) is given in Fig. 2. In each case the molecule consists of two identical halves related to each other by inversion through a crystallographic centre of symmetry. The refined atomic parameters of the asymmetric halves, and their estimated standard deviations are listed in Tables 3 and 4.* The bond lengths and angles, uncorrected for thermal vibration, are listed in Tables 5 and 6. Their estimated standard deviations have been increased by 50% to allow for the exclusion of the parameters' covariance from the calculations (Rollett, 1970). The C–H lengths are in the range 0·91–1·01 Å (mean = 0·96 Å) for (II), and 0·77–1·02 Å (mean = 0·92 Å) for (III).

Table 2. *Final refinement indicators*

| | (II) | (III) |
|---|---|---|
| $R$ (for observed data) | 0·038 | 0·041 |
| $R_w$ (for observed data) | 0·040 | 0·040 |
| Average (shift/e.s.d.) | 0·15 | 0·10 |
| Maximum (shift/e.s.d.) | 0·63 | 0·71 |
| $[\sum w(\Delta F)^2/(m-n)]^{1/2}$ | 0·6 | 0·7 |

## Discussion

### *Bond lengths and valency angles*

A summary of the main bond lengths and angles in the three bicyclophosphazene structures is given in Table 7. The corresponding values of the P–P′ bond

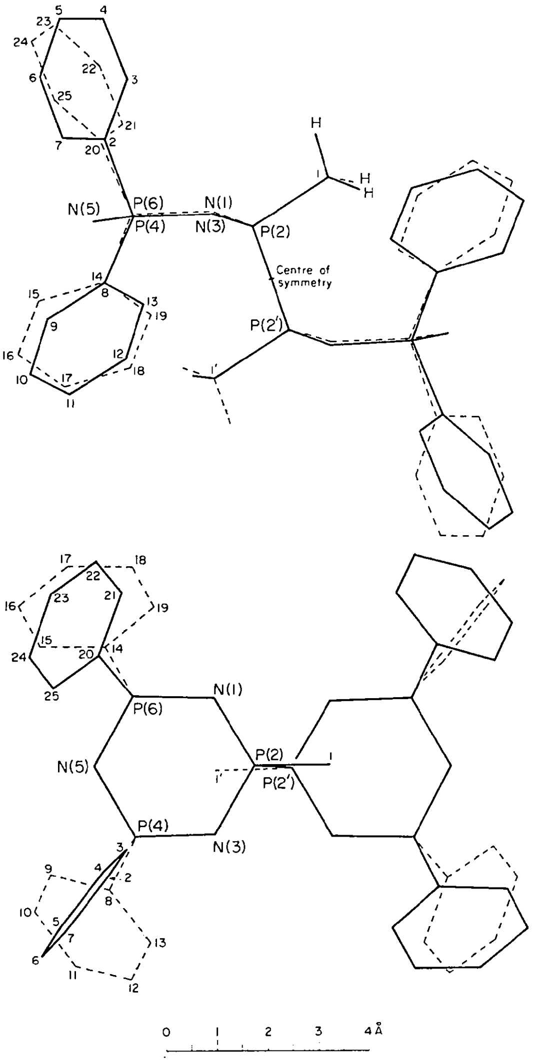

Fig. 1. Two orthogonal views of the molecular structure of $C_{50}H_{46}N_6P_6$.

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* The lists of structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31884 (39 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

and its associated C–P–P′ angle in (I) and (II) are nearly identical. The mean values of the other bond lengths and angles of these two compounds are consistent with their expected values, as derived from the graphs of bonds and angles *versus* electronegativity of substituents (Ahmed, Singh & Barnes, 1969). The only discrepancies are the mean P–N–P angle of (II) (observed value = 121·0, expected value = 122·2°), and in one of the C–P–C angles of (II) [observed as 107·2 (2)° while its expected value is 104·2°]. The latter discrepancy, however, appears to be a direct result of the abnormal orientation of one of the phenyl rings as will be discussed later.

The presence of the Ni–N(1) bond in (III) has made

Table 3. *Fractional coordinates and anisotropic thermal parameters* (Å$^2$) *of compound* (II)

$T = \exp[-2\pi^2(U_{11}a^{*2}h^2 + \ldots + 2U_{23}b^*c^*kl + \ldots)]$. All quantities × 10$^4$. The isotropic $B$ values are in Å$^2$.

| | X | Y | Z | U11 | U22 | U33 | 2U23 | 2U13 | 2U12 |
|---|---|---|---|---|---|---|---|---|---|
| N(1) | -1307(2) | 1002(1) | 4551(2) | 331(9) | 350(9) | 438(10) | -110(16) | 0(16) | 276(16) |
| P(2) | -105(1) | 623(1) | 4127(1) | 344(3) | 282(3) | 281(2) | -56(4) | 15(4) | 282(4) |
| N(3) | 1244(2) | 1474(1) | 4098(2) | 380(10) | 360(9) | 449(11) | -90(16) | 196(17) | 274(16) |
| P(4) | 1505(1) | 2496(1) | 5072(1) | 299(3) | 297(3) | 341(3) | 13(4) | 82(4) | 201(4) |
| N(5) | 327(2) | 2695(1) | 5911(2) | 346(9) | 362(9) | 411(10) | -127(16) | 104(16) | 240(16) |
| P(6) | -1103(1) | 2005(1) | 5560(1) | 298(3) | 296(3) | 301(3) | -10(4) | 63(4) | 272(4) |
| C(1) | -453(2) | 27(2) | 2216(3) | 572(15) | 511(14) | 330(12) | -130(20) | -78(21) | 544(24) |
| C(2) | 2120(2) | 3562(2) | 3658(3) | 374(12) | 350(11) | 390(12) | 40(18) | 156(18) | 256(19) |
| C(3) | 1357(3) | 3632(2) | 2256(3) | 502(16) | 582(16) | 478(14) | 206(24) | -38(24) | 146(26) |
| C(4) | 1708(3) | 4471(2) | 1185(3) | 686(19) | 747(20) | 471(15) | 345(28) | -39(27) | 426(32) |
| C(5) | 2820(3) | 5226(2) | 1489(4) | 726(19) | 507(16) | 579(17) | 370(26) | 315(29) | 300(28) |
| C(6) | 3584(3) | 5142(2) | 2841(4) | 655(19) | 501(16) | 660(19) | 245(28) | 31(30) | -71(28) |
| C(7) | 3234(2) | 4315(2) | 3935(3) | 486(14) | 458(14) | 494(14) | 181(23) | -36(23) | 114(23) |
| C(8) | 2746(2) | 2517(2) | 6651(3) | 334(11) | 337(11) | 419(12) | 134(19) | 90(18) | 169(18) |
| C(9) | 2713(3) | 2924(2) | 8129(3) | 594(17) | 588(16) | 496(15) | -188(24) | -168(24) | 611(27) |
| C(10) | 3626(3) | 2879(2) | 9368(3) | 719(20) | 739(20) | 479(15) | -159(28) | -218(27) | 623(32) |
| C(11) | 4560(3) | 2420(2) | 9133(3) | 487(16) | 605(17) | 551(16) | 215(26) | -152(24) | 298(26) |
| C(12) | 4602(3) | 2016(2) | 7684(4) | 439(15) | 788(20) | 661(18) | 216(30) | 84(26) | 642(28) |
| C(13) | 3696(2) | 2055(2) | 6440(3) | 455(14) | 725(18) | 461(14) | 14(26) | 133(23) | 544(27) |
| C(14) | -1837(2) | 1636(2) | 7470(3) | 320(11) | 446(12) | 350(11) | 96(19) | 74(17) | 367(19) |
| C(15) | -1625(3) | 2341(2) | 8681(3) | 508(15) | 637(16) | 400(13) | -94(23) | 150(22) | 387(26) |
| C(16) | -2174(3) | 2056(3) | 10159(3) | 632(18) | 1021(24) | 375(14) | -75(29) | 149(25) | 754(35) |
| C(17) | -2924(3) | 1079(3) | 10430(3) | 623(18) | 1024(25) | 463(15) | 492(31) | 413(27) | 842(35) |
| C(18) | -3154(3) | 383(2) | 9241(4) | 604(18) | 691(19) | 712(19) | 599(32) | 441(30) | 401(30) |
| C(19) | -2607(2) | 656(2) | 7753(3) | 461(14) | 483(15) | 532(15) | 156(23) | 189(23) | 256(23) |
| C(20) | -2017(2) | 2807(2) | 4530(3) | 454(13) | 442(12) | 300(11) | 0(19) | 110(18) | 509(21) |
| C(21) | -3314(2) | 2414(2) | 4142(3) | 450(14) | 711(17) | 400(13) | 75(24) | 87(21) | 576(26) |
| C(22) | -3981(3) | 3043(3) | 3317(3) | 567(17) | 1078(25) | 448(15) | -27(30) | 14(25) | 957(35) |
| C(23) | -3380(3) | 4033(3) | 2876(3) | 1064(26) | 1000(25) | 486(16) | 284(32) | 154(32) | 1597(45) |
| C(24) | -2104(3) | 4429(2) | 3279(4) | 1029(25) | 596(18) | 630(18) | 262(29) | 227(34) | 1030(37) |
| C(25) | -1419(3) | 3817(2) | 4113(3) | 689(18) | 426(14) | 518(15) | 79(23) | 120(25) | 591(26) |

| | X | Y | Z | B | | X | Y | Z | F |
|---|---|---|---|---|---|---|---|---|---|
| H(1,1) | 135(30) | -341(24) | 1970(38) | 6.6(0.8) | H(13) | 3700(23) | 1743(18) | 5444(29) | 3.6(0.5) |
| H(1,2) | -442(24) | 546(20) | 1448(30) | 4.2(0.6) | H(15) | -1056(26) | 3025(22) | 8504(33) | 4.9(0.7) |
| H(1,3) | -1275(30) | -476(25) | 2187(38) | 6.6(0.8) | H(16) | -1989(30) | 2541(23) | 10992(37) | 6.2(0.8) |
| H(3) | 593(29) | 3059(24) | 2031(37) | 6.1(0.8) | H(17) | -3303(30) | 840(24) | 11512(38) | 6.4(0.8) |
| H(4) | 1153(26) | 4565(21) | 243(33) | 4.7(0.6) | H(18) | -3621(32) | -305(26) | 9389(40) | 7.5(0.9) |
| H(5) | 3065(27) | 5806(22) | 752(34) | 5.5(0.7) | H(19) | -2781(24) | 196(20) | 6936(30) | 4.1(0.6) |
| H(6) | 4374(30) | 5649(24) | 3073(38) | 6.3(0.8) | H(21) | -3748(25) | 1673(20) | 4399(32) | 4.4(0.6) |
| H(7) | 3792(26) | 4277(21) | 4908(32) | 4.8(0.6) | H(22) | -4836(28) | 2753(22) | 3111(35) | 5.5(0.7) |
| H(9) | 2038(26) | 3219(21) | 8326(32) | 4.7(0.6) | H(23) | -3873(31) | 4481(26) | 2342(39) | 7.2(0.8) |
| H(10) | 3577(35) | 3161(29) | 10375(45) | 8.6(1.0) | H(24) | -1687(33) | 5166(27) | 2974(42) | 7.6(0.9) |
| H(11) | 5204(27) | 2374(22) | 10053(34) | 5.6(0.7) | H(25) | -474(29) | 4110(24) | 4381(37) | 6.7(0.8) |
| H(12) | 5191(27) | 1680(22) | 7531(35) | 5.4(0.7) | | | | | |

Table 4. *Fractional coordinates and anisotropic thermal parameters* (Å$^2$) *of compound* (III)

$T = \exp[-2\pi^2(U_{11}a^{*2}h^2 + \ldots + 2U_{23}b^*c^*kl + \ldots)]$. All quantities × 10$^4$. The isotropic $B$ values are in Å$^2$.

| | X | Y | Z | U11 | U22 | U33 | 2U23 | 2U13 | 2U12 |
|---|---|---|---|---|---|---|---|---|---|
| NI | 0(0) | 5000(0) | 5000(0) | 330(3) | 299(3) | 496(4) | 68(5) | 103(5) | 120(4) |
| S | 1934(1) | 5937(1) | 4751(1) | 359(5) | 341(5) | 1128(9) | 245(10) | 206(10) | 102(7) |
| N(1) | 842(2) | 3666(2) | 4329(3) | 345(13) | 338(14) | 543(16) | 109(24) | 104(24) | 195(22) |
| P(2) | 2217(1) | 4406(1) | 4707(1) | 382(5) | 345(4) | 457(5) | -26(7) | -29(7) | 99(7) |
| N(3) | 3385(2) | 3901(2) | 3628(3) | 352(14) | 430(15) | 672(19) | -106(27) | -167(26) | 141(23) |
| P(4) | 3283(1) | 2713(1) | 2289(1) | 294(4) | 341(4) | 442(5) | 53(7) | -51(7) | 185(6) |
| N(5) | 1925(2) | 2034(2) | 2019(3) | 341(13) | 375(14) | 533(17) | -40(25) | -3(24) | 172(22) |
| P(6) | 662(1) | 2473(1) | 2919(1) | 290(4) | 312(4) | 442(5) | 158(7) | -1(7) | 143(6) |
| C(1) | 2344(5) | 4520(5) | 6577(5) | 871(33) | 1271(43) | 619(29) | 316(57) | -336(49) | 132(61) |
| C(2) | 4074(3) | 2952(3) | 567(4) | 379(17) | 396(17) | 562(20) | 310(30) | -94(29) | 278(27) |
| C(3) | 5233(3) | 3638(3) | 535(5) | 503(22) | 707(25) | 766(27) | 659(44) | -286(38) | -56(37) |
| C(4) | 5821(4) | 3845(4) | -794(6) | 590(25) | 765(29) | 1135(38) | 1025(56) | 40(48) | -101(43) |
| C(5) | 5264(4) | 3396(4) | -2051(5) | 826(30) | 852(30) | 716(28) | 815(49) | 199(46) | 536(49) |
| C(6) | 4143(4) | 2707(4) | -2036(5) | 758(28) | 834(29) | 612(26) | 554(45) | -77(42) | 366(46) |
| C(7) | 3552(3) | 2490(3) | -734(4) | 477(20) | 636(23) | 576(23) | 353(37) | -35(34) | 232(35) |
| C(8) | 4146(3) | 1792(3) | 2613(3) | 316(15) | 459(17) | 383(17) | 251(28) | 87(26) | 222(27) |
| C(9) | 4982(3) | 2219(3) | 3624(4) | 522(21) | 481(20) | 595(23) | 271(34) | -321(34) | 98(32) |
| C(10) | 5633(4) | 1498(3) | 3860(5) | 594(23) | 678(25) | 728(27) | 477(42) | -508(40) | 180(39) |
| C(11) | 5458(3) | 352(3) | 3094(5) | 563(22) | 640(23) | 740(26) | 604(41) | -166(38) | 380(37) |
| C(12) | 4641(4) | -88(3) | 2069(5) | 657(24) | 468(21) | 783(27) | 265(38) | -236(41) | 379(36) |
| C(13) | 3981(3) | 617(3) | 1827(4) | 553(21) | 499(20) | 558(22) | 104(34) | -283(34) | 335(33) |
| C(14) | -391(3) | 1363(3) | 3599(4) | 359(16) | 380(16) | 529(20) | 312(29) | -180(29) | 101(27) |
| C(15) | -373(3) | 230(3) | 2663(4) | 576(22) | 429(19) | 597(23) | 230(34) | -196(35) | 110(32) |
| C(16) | -1090(4) | -633(3) | 3184(5) | 791(28) | 339(19) | 934(31) | 299(39) | -596(47) | -32(35) |
| C(17) | -1733(4) | -379(3) | 4609(5) | 684(26) | 628(24) | 902(31) | 896(46) | -259(45) | -252(40) |
| C(18) | -1660(4) | 729(4) | 5526(5) | 760(28) | 708(26) | 679(26) | 713(44) | -31(43) | 47(43) |
| C(19) | -939(3) | 1606(3) | 5034(4) | 618(22) | 465(20) | 583(22) | 432(35) | -52(35) | 89(34) |
| C(20) | -158(3) | 2662(3) | 1622(4) | 495(19) | 434(18) | 459(19) | 230(30) | 85(30) | 406(30) |
| C(21) | -1358(4) | 2128(3) | 1410(5) | 717(26) | 580(23) | 737(27) | 330(40) | -594(42) | 267(39) |
| C(22) | -1933(5) | 2288(4) | 372(6) | 1129(39) | 792(31) | 989(37) | 20(53) | -1239(63) | 644(56) |
| C(23) | -1316(6) | 2960(5) | -463(5) | 1733(55) | 1184(41) | 542(27) | 195(53) | -524(61) | 1799(80) |
| C(24) | -133(5) | 3492(5) | -263(5) | 1462(47) | 1286(43) | 786(33) | 1327(65) | 765(64) | 1707(77) |
| C(25) | 449(4) | 3360(4) | 784(5) | 722(27) | 872(30) | 836(30) | 1001(51) | 321(46) | 685(47) |

| | X | Y | Z | B | | X | Y | Z | B |
|---|---|---|---|---|---|---|---|---|---|
| H(1,1) | 166(5) | 482(4) | 717(6) | 10.0(1.4) | H(13) | 339(3) | 34(3) | 111(4) | 4.9(0.8) |
| H(1,2) | 225(5) | 370(4) | 661(6) | 11.2(1.6) | H(15) | 10(3) | 4(2) | 169(3) | 3.1(0.6) |
| H(1,3) | 394(4) | 487(4) | 680(5) | 9.5(1.3) | H(16) | -109(3) | -131(3) | 258(3) | 4.0(0.7) |
| H(3) | 560(3) | 393(3) | 145(4) | 4.5(0.8) | H(17) | -218(3) | -94(3) | 496(4) | 5.2(0.8) |
| H(4) | 653(4) | 431(3) | -70(5) | 7.0(1.0) | H(18) | -204(4) | 85(3) | 652(4) | 7.1(1.1) |
| H(5) | 563(4) | 354(3) | -297(5) | 7.1(1.1) | H(19) | -83(3) | 239(3) | 568(4) | 4.9(0.8) |
| H(6) | 381(3) | 239(3) | -303(4) | 6.3(1.0) | H(21) | -174(3) | 165(3) | 194(4) | 5.3(0.9) |
| H(7) | 282(3) | 207(3) | -70(4) | 5.0(0.8) | H(22) | -274(4) | 198(4) | 31(5) | 9.0(1.3) |
| H(9) | 507(3) | 299(3) | 416(4) | 5.1(0.8) | H(23) | -169(4) | 306(4) | -121(5) | 7.5(1.1) |
| H(10) | 618(3) | 178(3) | 462(4) | 5.5(0.9) | H(24) | 20(4) | 384(4) | -79(5) | 9.3(1.3) |
| H(11) | 599(3) | -17(3) | 323(4) | 5.4(0.9) | H(25) | 120(4) | 368(3) | 90(4) | 6.5(1.0) |
| H(12) | 451(3) | -84(3) | 162(4) | 6.0(0.9) | | | | | |

the mean values of the bond lengths and angles inconsistent with the graphs of Ahmed *et al.* (1969). In this molecule, the two adjoining bonds N(1)–P(2) and N(1)–P(6) are considerably longer (1·649 and 1·635 Å) than the other four P–N bonds (1·581–1·591 Å). There are also significant changes in the mean endocyclic angles N–P–N and P–N–P of (II) and (III). Their values are 117·3 and 121·0° in (II), and 116·0 and 124·0° in (III) respectively. For detailed comparison of the bonds and angles of these two compounds, see Tables 5 and 6.

Table 5. *Bond lengths* (Å) *and valency angles* (°) *of compound* (II)

The standard deviations have been increased by 50% to allow for the parameters' covariance.

| | | | |
|---|---|---|---|
| P(2)–P(2′) | 2·210 (2) | C(8)—C(9) | 1·379 (5) |
| N(1)–P(2) | 1·607 (3) | C(9)—C(10) | 1·387 (6) |
| P(2)–N(3) | 1·601 (3) | C(10)–C(11) | 1·367 (7) |
| N(3)–P(4) | 1·595 (3) | C(11)–C(12) | 1·357 (6) |
| P(4)–N(5) | 1·600 (3) | C(12)–C(13) | 1·383 (6) |
| N(5)–P(6) | 1·597 (3) | C(13)–C(8) | 1·381 (6) |
| P(6)–N(1) | 1·597 (3) | C(14)–C(15) | 1·390 (5) |
| P(2)–C(1) | 1·787 (3) | C(15)–C(16) | 1·389 (6) |
| P(4)–C(2) | 1·814 (3) | C(16)–C(17) | 1·367 (7) |
| P(4)–C(8) | 1·807 (4) | C(17)–C(18) | 1·367 (7) |
| P(6)–C(14) | 1·806 (3) | C(18)–C(19) | 1·394 (6) |
| P(6)–C(20) | 1·813 (4) | C(19)–C(14) | 1·381 (5) |
| C(2)–C(3) | 1·391 (5) | C(20)–C(21) | 1·388 (6) |
| C(3)–C(4) | 1·386 (6) | C(21)–C(22) | 1·391 (6) |
| C(4)–C(5) | 1·373 (7) | C(22)–C(23) | 1·364 (8) |
| C(5)–C(6) | 1·364 (7) | C(23)–C(24) | 1·370 (8) |
| C(6)–C(7) | 1·386 (6) | C(24)–C(25) | 1·390 (7) |
| C(7)–C(2) | 1·370 (5) | C(25)–C(20) | 1·381 (5) |

| | | | |
|---|---|---|---|
| N(1)—P(2)—N(3) | 116·6 (2) | P(6)—C(20)–C(21) | 120·6 (3) |
| N(3)—P(4)—N(5) | 117·6 (2) | P(6)—C(20)–C(25) | 119·9 (3) |
| N(5)—P(6)—N(1) | 117·7 (2) | C(7)—C(2)—C(3) | 119·1 (3) |
| P(2)—N(1)—P(6) | 120·5 (2) | C(2)—C(3)—C(4) | 120·1 (4) |
| P(2)—N(3)—P(4) | 120·9 (2) | C(3)—C(4)—C(5) | 120·1 (4) |
| P(4)—N(5)—P(6) | 121·7 (2) | C(4)—C(5)—C(6) | 119·7 (4) |
| N(1)—P(2)—P(2′) | 109·4 (2) | C(5)—C(6)—C(7) | 120·7 (4) |
| N(3)—P(2)—P(2′) | 107·9 (2) | C(6)—C(7)—C(2) | 120·2 (4) |
| C(1)—P(2)—P(2′) | 104·2 (2) | C(13)–C(8)—C(9) | 118·7 (3) |
| C(1)—P(2)—N(1) | 108·8 (2) | C(8)—C(9)—C(10) | 120·4 (4) |
| C(1)—P(2)—N(3) | 109·2 (2) | C(9)—C(10)–C(11) | 120·0 (4) |
| C(2)—P(4)—N(3) | 107·0 (2) | C(10)–C(11)–C(12) | 120·1 (4) |
| C(2)—P(4)—N(5) | 108·5 (2) | C(11)–C(12)–C(13) | 120·5 (4) |
| C(8)—P(4)—N(3) | 109·3 (2) | C(12)–C(13)–C(8) | 120·3 (4) |
| C(8)—P(4)—N(5) | 107·0 (2) | C(19)–C(14)–C(15) | 119·2 (3) |
| C(14)–P(6)—N(5) | 108·7 (2) | C(14)–C(15)–C(16) | 120·2 (4) |
| C(14)–P(6)—N(1) | 108·6 (2) | C(15)–C(16)–C(17) | 120·0 (4) |
| C(20)–P(6)—N(5) | 108·2 (2) | C(16)–C(17)–C(18) | 120·3 (5) |
| C(20)–P(6)—N(1) | 108·7 (2) | C(17)–C(18)–C(19) | 120·4 (4) |
| C(2)—P(4)—C(8) | 107·2 (2) | C(18)–C(19)–C(14) | 119·9 (4) |
| C(14)–P(6)—C(20) | 104·0 (2) | C(25)–C(20)–C(21) | 119·5 (3) |
| P(4)—C(2)—C(3) | 116·7 (3) | C(20)–C(21)–C(22) | 119·2 (4) |
| P(4)—C(2)—C(7) | 124·1 (3) | C(21)–C(22)–C(23) | 121·1 (4) |
| P(4)—C(8)—C(9) | 120·9 (3) | C(22)–C(23)–C(24) | 120·0 (5) |
| P(4)—C(8)—C(13) | 120·3 (3) | C(23)–C(24)–C(25) | 120·0 (5) |
| P(6)—C(14)–C(15) | 120·1 (3) | C(24)–C(25)–C(20) | 120·3 (4) |
| P(6)—C(14)–C(19) | 120·7 (3) | | |

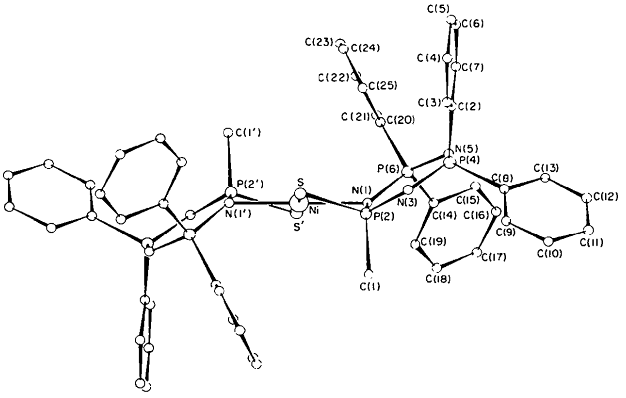


Fig. 2. The molecular structure of $C_{50}H_{46}N_6P_6S_2Ni$.

Table 6. *Bond lengths* (Å) *and valency angles* (°) *of compound* (III)

The standard deviations have been increased by 50% to allow for the parameters' covariance.

| | | | |
|---|---|---|---|
| Ni—S | 2·229 (2) | C(7)—C(2) | 1·372 (7) |
| Ni—N(1) | 1·944 (4) | C(8)—C(9) | 1·377 (7) |
| S—P(2) | 2·005 (2) | C(9)—C(10) | 1·381 (9) |
| N(1)–P(2) | 1·649 (4) | C(10)–C(11) | 1·359 (9) |
| P(2)–N(3) | 1·581 (4) | C(11)–C(12) | 1·370 (9) |
| N(3)–P(4) | 1·590 (5) | C(12)–C(13) | 1·375 (8) |
| P(4)–N(5) | 1·591 (4) | C(13)–C(8) | 1·393 (7) |
| N(5)–P(6) | 1·588 (4) | C(14)–C(15) | 1·386 (7) |
| P(6)–N(1) | 1·635 (4) | C(15)–C(16) | 1·382 (8) |
| P(2)–C(1) | 1·787 (7) | C(16)–C(17) | 1·367 (9) |
| P(4)–C(2) | 1·799 (5) | C(17)–C(18) | 1·357 (9) |
| P(4)–C(8) | 1·799 (5) | C(18)–C(19) | 1·384 (9) |
| P(6)–C(14) | 1·798 (5) | C(19)–C(14) | 1·374 (7) |
| P(6)–C(20) | 1·800 (5) | C(20)–C(21) | 1·380 (8) |
| C(2)–C(3) | 1·391 (8) | C(21)–C(22) | 1·386 (10) |
| C(3)–C(4) | 1·393 (10) | C(22)–C(23) | 1·354 (12) |
| C(4)–C(5) | 1·358 (10) | C(23)–C(24) | 1·362 (14) |
| C(5)–C(6) | 1·358 (10) | C(24)–C(25) | 1·380 (11) |
| C(6)–C(7) | 1·377 (9) | C(25)–C(20) | 1·377 (9) |

| | | | |
|---|---|---|---|
| N(1)—P(2)–N(3) | 116·4 (2) | P(6)—C(14)–C(15) | 119·1 (4) |
| N(3)—P(4)–N(5) | 117·3 (2) | P(6)—C(14)–C(19) | 121·7 (4) |
| N(5)—P(6)–N(1) | 114·2 (2) | P(6)—C(20)–C(21) | 123·2 (4) |
| P(2)—N(1)–P(6) | 123·0 (3) | P(6)—C(20)–C(25) | 118·2 (4) |
| P(2)—N(3)–P(4) | 123·3 (3) | C(7)—C(2)—C(3) | 118·2 (5) |
| P(4)—N(5)–P(6) | 125·4 (3) | C(2)—C(3)—C(4) | 119·6 (6) |
| Ni—N(1)–P(6) | 130·2 (2) | C(3)—C(4)—C(5) | 120·6 (7) |
| Ni—N(1)–P(2) | 95·4 (2) | C(4)—C(5)—C(6) | 120·1 (7) |
| N(1)—P(2)–S | 98·3 (2) | C(5)—C(6)—C(7) | 120·0 (6) |
| P(2)—S—Ni | 77·8 (1) | C(6)—C(7)—C(2) | 121·5 (6) |
| S—Ni—N(1) | 83·0 (1) | C(13)–C(8)—C(9) | 118·4 (5) |
| S—P(2)–C(1) | 107·8 (3) | C(8)—C(9)—C(10) | 120·7 (5) |
| S—P(2)–N(3) | 117·6 (2) | C(9)—C(10)–C(11) | 120·3 (6) |
| C(1)—P(2)–N(1) | 107·9 (3) | C(10)–C(11)–C(12) | 119·8 (6) |
| C(1)—P(2)–N(3) | 108·0 (3) | C(11)–C(12)–C(13) | 120·5 (6) |
| C(2)—P(4)–N(3) | 109·1 (2) | C(12)–C(13)–C(8) | 120·2 (5) |
| C(2)—P(4)–N(5) | 108·2 (2) | C(19)–C(14)–C(15) | 119·2 (5) |
| C(8)—P(4)–N(3) | 107·9 (2) | C(14)–C(15)–C(16) | 119·6 (5) |
| C(8)—P(4)–N(5) | 108·5 (2) | C(15)–C(16)–C(17) | 120·7 (6) |
| C(14)–P(6)–N(5) | 108·7 (2) | C(16)–C(17)–C(18) | 119·7 (6) |
| C(14)–P(6)–N(1) | 109·3 (2) | C(17)–C(18)–C(19) | 120·6 (6) |
| C(20)–P(6)–N(5) | 108·3 (2) | C(18)–C(19)–C(14) | 120·1 (5) |
| C(20)–P(6)–N(1) | 109·7 (2) | C(25)–C(20)–C(21) | 118·6 (5) |
| C(2)—P(4)–C(8) | 105·3 (2) | C(20)–C(21)–C(22) | 120·6 (6) |
| C(14)–P(6)–C(20) | 106·3 (2) | C(21)–C(22)–C(23) | 120·1 (7) |
| P(4)—C(2)–C(3) | 120·1 (4) | C(22)–C(23)–C(24) | 119·7 (8) |
| P(4)—C(2)–C(7) | 121·7 (4) | C(23)–C(24)–C(25) | 121·0 (8) |
| P(4)—C(8)–C(9) | 121·6 (4) | C(24)–C(25)–C(20) | 119·9 (7) |
| P(4)—C(8)–C(13) | 120·0 (4) | | |

## *Molecular conformation*

Each molecule of the three compounds has an inversion centre coincident with a crystallographic centre of symmetry. Hence, in each case, the substituents on P(2) and P(2′) [or P(1) and P(1′) of (I) according to Zoer & Wagner's numbering] are in the *trans* configuration relative to the central P–P′ bond of (I) and (II) or relative to the pair of four-membered rings of (III).

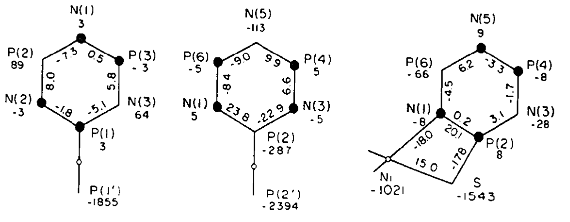
In all three compounds the phosphazene rings are non-planar and adopt a slight boat conformation, as described in Fig. 3 by the torsion angles and the deviations of the atoms from selected mean planes. These show clearly that the phosphazene ring of (II) has the highest deviation from planarity, while that of (III) is the closest to being planar.

Some angles between selected planes of the three compounds are summarized in Table 8. The mean plane of the phosphazene ring makes angles of more than 85° with the planes of its ligands, except in (III) where the angle with the C(1)P(2)S plane is only 82·8°. The decrease in the latter dihedral angle represents an attraction of the S atom towards the Ni atom to which it is bonded. Also, in both (II) and (III), one of the four phenyl substituents is nearly perpendicular to the phosphazene ring. The corresponding dihedral angles are: $N_3P_3$ to phenyl I = 87·3° in (II), and $N_3P_3$ to phenyl IV = 83·5° in (III), while the corresponding dihedral angles in other phenylphosphazene derivatives are always less than 60°. The two views of (II) (Fig. 1) do not suggest that the abnormal orientation of phenyl I [which contains C(2) to C(7)] is adopted because of intramolecular interactions. It is plausible, therefore, that the abnormal orientation is preferable for efficient packing of the molecules in the unit cell. With this change in orientation, the corresponding C–P–C angle increases to 107·2° in (II) and 106·3° in (III) from the regular value of 104·2°.

The Ni atom in (III) has an exact planar configuration since it occupies a crystallographic centre of symmetry. The four-membered chelate ring is non-planar, and its two planes Ni–S–N(1) and N(1)–S–P(2) have an angle of 25·4° between them.

### *Residual electron density*

The residual peaks and troughs in the final difference maps of (II) and (III) are presented in Fig. 4. In both cases the peaks occur on the bonds and represent the bonding electrons. In (II) the highest peak (0·32 e Å$^{-3}$) occurs on the central P(2)–P(2′) bond. However, in (III) the highest peak (0·35 e Å$^{-3}$) is found on the N(1)–P(2) bond, which is the longest bond in the phosphazene ring. In (III) both the Ni and S sites have significant residual troughs of −0·60 and −0·35 e Å$^{-3}$, respectively, and there are no significant residual peaks on either the Ni–N(1) or Ni–S bond.



(I) (II) (III)

Fig. 3. Conformation angles (°) of the phosphazene and chelate rings in (I), (II), and (III); and the displacements (× 10³ Å) of the atoms from the mean planes through those atoms identified by circles.

Table 7. *Comparison of the main bond lengths* (Å) *and valency angles* (°) *in the three bicyclophosphazene compounds*

The electronegativities of the substituents are based on Pauling's (1960) list.

| | | (I) | (II) | (III) |
|---|---|---|---|---|
| ⟨Electronegativity⟩ | | 2·78 | 2·43 | 2·40* |
| P–P′ | | 2·208 (2) | 2·210 (2) | – |
| P–N | Range | 1·565–1·606 (4) | 1·595–1·607 (3) | 1·581–1·649 (4) |
| | Mean | 1·583 | 1·600 | 1·606 |
| | Expected | 1·582 | 1·602 | 1·604 |
| $P–C_6H_5$ | Range | 1·791 (4) | 1·806–1·814 (4) | 1·798–1·800 (5) |
| | Mean | 1·791 | 1·810 | 1·799 |
| | Expected | 1·789 | 1·811 | 1·814 |
| $P–CH_3$ | | – | 1·787 (3) | 1·787 (7) |
| N–P–N | Range | 117·3–119·9 (2) | 116·6–117·7 (2) | 114·2–117·3 (2) |
| | Mean | 118·8 | 117·3 | 116·0 |
| | Expected | 118·2 | 117·6 | 117·5 |
| P–N–P | Range | 120·4–121·4 (3) | 120·5–121·7 (2) | 123·0–125·4 (3) |
| | Mean | 121·0 | 121·0 | 123·9 |
| | Expected | 121·6 | 122·2 | 122·4 |
| C–P–P′ | | 104·6 (2) | 104·2 (2) | – |
| C–P–S | | – | – | 107·8 (3) |
| C–P–C | Observed | – | 104·2, 107·2 (2) | 105·3, 106·3 (2) |
| | Expected | – | 104·2 | 104·2 |

* The ⟨electronegativity⟩ of (III) is calculated as $(5e_C + e_S + e_{Ni})/7 = (5 \times 2·5 + 2·5 + 1·8)/7 = 2·40$.

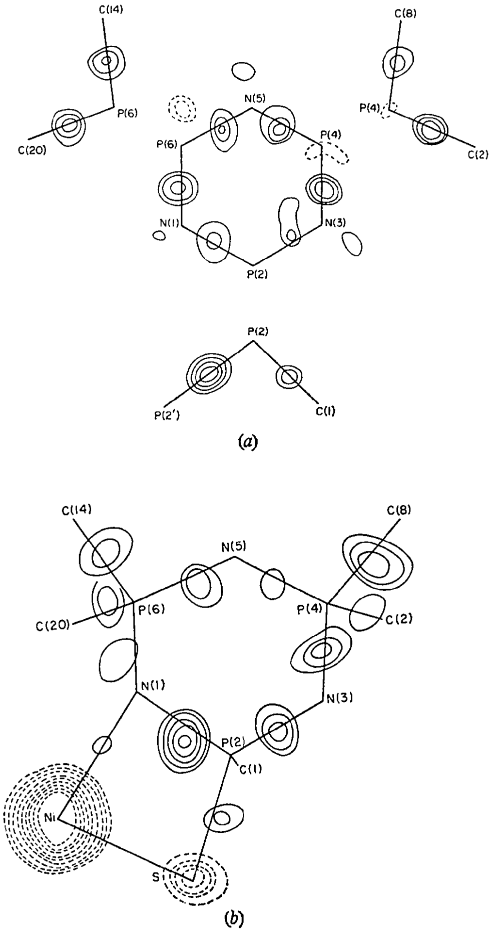


Fig. 4. Residual electron density distribution (*a*) in (II), and (*b*) in (III). The contour lines start at ±0·15, then are at intervals of ±0·05 e Å$^{-3}$. The peaks are shown as solid lines and the troughs as broken lines.

The author is grateful to Professor A. Schmidpeter of Münich University for proposing the investigations and supplying the crystals, and to Mrs M. E. Pippy for assistance with the computations. All calculations were carried out with the computer programs by Ahmed, Hall, Pippy & Huber (1973).

Table 8. *Dihedral angles* (°) *of the three compounds*

| | | | |
|---|---|---|---|
| (I) | $C_{12}H_{10}N_6P_6Cl_8$ | | |
| | Phosphazene | –C(1)P(1)P(1′)C(1′) | 88·1 |
| | | –Cl(1)P(2)Cl(2) | 89·4 |
| | | –Cl(3)P(3)Cl(4) | 89·5 |
| | | –phenyl | 47·5 |
| (II) | $C_{50}H_{46}N_6P_6$ | | |
| | Phosphazene | –C(1)P(2)P(2′)C(1′) | 89·4 |
| | | –C(2)P(4)C(8) | 87·2 |
| | | –C(14)P(6)C(20) | 85·5 |
| | | –phenyl I* | 87·3 |
| | | –phenyl II | 54·3 |
| | | –phenyl III | 50·7 |
| | | –phenyl IV | 58·4 |
| (III) | $C_{50}H_{46}N_6P_6S_2Ni$ | | |
| | Phosphazene | –C(1)P(2)S | 82·8 |
| | | –C(2)P(4)C(8) | 88·2 |
| | | –C(14)P(6)C(20) | 89·2 |
| | | –phenyl I | 56·0 |
| | | –phenyl II | 53·5 |
| | | –phenyl III | 51·8 |
| | | –phenyl IV | 83·5 |
| | NiN(1)S | –SN(1)P(2) | 25·4 |
| | SN(1)P(2) | –phosphazene | 51·6 |

* The phenyl rings are numbered I, II, III and IV for atoms C(2) to C(7), C(8) to C(13), C(14) to C(19) and C(20) to C(25) respectively.

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