Phosphonitrilic Compounds. IX.[1] The Crystal and Molecular Structure of Tris(2,2′-dioxybiphenyl)cyclotriphosphazene[2]

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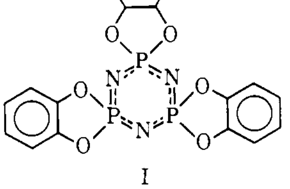
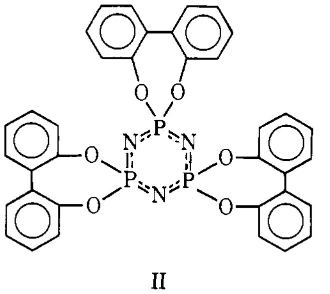
Abstract: The crystal structure of tris(2,2′-dioxybiphenyl)cyclotriphosphazene (II) has been determined by three-dimensional Patterson, Fourier, and difference syntheses, and refinement to an R index of 0.068 was accomplished by difference-Fourier and least-squares techniques. The crystals are monoclinic with the space group $C2/c$, and with a = 15.377 (2), b = 10.810 (1), c = 20.152 (7) Å, β = 108.88 (0.02)°, Z = 4. The cyclotriphosphazene ring has a slight boat conformation. Two of the biphenyldioxyphosphole units are twisted propellor-like at 43° in one direction while the third is twisted at 52° in the opposite direction. The P–N bond distances are 1.568 (7), 1.582 (6), and 1.566 (4) Å; the N–P–N angles are 118.6 (0.3) and 118.3 (0.2)°; the P–N–P angles are 120.8 (0.3) and 121.2 (0.2)°; and the O–P–O angles are 103.0 (0.2) and 102.4 (0.3)°. The asymmetry of twist of the side group units is discussed and reasons are suggested for the failure of this compound to polymerize or form molecular inclusion adducts.

In earlier papers in this series[3,4] attention was directed to the ability of specific cyclotriphosphazenes (phosphonitriles) to form crystalline molecular inclusion adducts with a wide variety of organic molecules. For example, tris(o-phenylenedioxy)cyclotriphosphazene (I) spontaneously forms inclusion adducts with benzene, toluene, heptane, octanes, and many other compounds[3] and tris(2,3-dioxynaphthyl)cyclotriphosphazene, $(NPO_2C_{10}H_6)_3$, behaves similarly.[3,4] This behavior is attributed to the rigid "paddle wheel" shape of the molecules and to the requirements of molecular packing in the crystalline state. The detailed molecular structure of I has been furnished by a single-crystal X-ray study.[5]

By contrast, tris(2,2′-dioxybiphenyl)cyclotriphosphazene (II) forms no inclusion adducts when recrystallized from or brought into contact with organic liquids. Furthermore, this compound is stable at least up to 350°, whereas I polymerizes above 250°.[4] These differences have been attributed to the greater molecular rigidity of I compared to II,[4] and to the stabilizing influence of a seven-membered ring at phosphorus in II. The present crystal structure determination was undertaken to evaluate these theories, and to examine the influence of the bulky substituents on the molecular geometry and crystalline packing.



I



II

Experimental Section

Preparation of Crystals. Tris(2,2′-dioxybiphenyl)cyclotriphosphazene (II) was synthesized from hexachlorocyclotriphosphazene, $(NPCl_2)_3$, and 2,2′-dihydroxybiphenyl in the presence of sodium carbonate by the method reported previously.[4] Crystals suitable for X-ray analysis were grown in sealed tubes from o-xylene (Aldrich) which had been dried over calcium hydride. The tubes were heated to 210° in a thermoregulated oven and then cooled to 25° during 24 hr. The colorless crystals were vacuum dried at 25° (25 mm) for 24 hr. They did not melt below 300°.

Crystal Data. The unit cell is monoclinic[6] with a = 15.377 (2), b = 10.810 (1), c = 20.152 (7) Å, β = 108.88 (0.02)° (measured by least-squares refinement of Cr powder data, λ 2.29092 Å). V = 3171.0 Å^3, D_m = 1.415 g cm^{-3} (by flotation in n-heptane–carbon tetrachloride mixtures), Z = 4, D_c = 1.414 g cm^{-3}, mol wt = 687.2, and $\mu_{Cu\ K\alpha}$ = 21.5 cm^{-1}. The space group is $C2/c$ (C_{2h}^6, no. 15). Lattice parameters were obtained by least-squares refinement of 13 2θ values measured on an automated diffractometer to give values of a = 15.401 (7), b = 10.835 (2), c = 20.161 (9) Å, and β = 108.90 (0.07°), which were considered to be satisfactory parameters for the collection of intensity data. However, since ω_0 had not been found and adjusted to 0°, the lattice parameters determined from Cr-powder pattern data were used in the refinement and for determination of the final atomic parameters.

X-Ray Data Collection and Reduction. A crystal of II with dimensions 0.24 × 0.13 × 0.16 mm, was mounted on a eucentric goniometer head (Electronics and Alloys) with the b axis along the φ axis of a Syntex four-circle, computer-controlled diffractometer. Data were collected at 40 kV and 20 mA using Cu Kα radiation (λ 1.54178 Å), nickel-filtered on the incident beam side. The incident beam collimator was 1 mm in diameter and the receiving collimator 2 mm in diameter. With the 4° takeoff angle used, the focal spot shape was nearly square. The crystal was 13.5 cm from both the X-ray tube and the counter.

The data collection mode was a θ–2θ scan, with a scan rate of 1°/min. The scan range varied linearly from 2.5° at 9.5° (2θ) to 3.0° at 95.0° (2θ). On each side of the scan range, a background count of 15 sec was made. The background was assumed to be linear, and intensities were corrected by the formula $I = [S - (B_1 + B_2)t/30]$, where S is the scan count, B_1 and B_2 are the background counts, t (sec) is the scan time, and 30 sec is the total time spent on the background. After every 26 reflections, a check reflection ($\bar{4}02$) was remeasured. Its intensity fluctuated by only

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(1) Part VIII: H. R. Allcock and R. L. Kugel, *J. Amer. Chem. Soc.*, **91**, 5452 (1969).

(2) A preliminary report of this work was contained in a previous communication: H. R. Allcock, M. T. Stein, and J. A. Stanko, *Chem. Commun.*, 944 (1970).

(3) H. R. Allcock and L. A. Siegel, *J. Amer. Chem. Soc.*, **86**, 5140 (1964).

(4) H. R. Allcock and R. L. Kugel, *Inorg. Chem.*, **5**, 1016 (1966).

(5) L. A. Siegel and J. H. van den Hende, *J. Chem. Soc. A*, 817 (1967).

(6) An earlier analysis of the unit cell parameters by L. A. Siegel suggested a monoclinic cell with a = 7.72, b = 10.92, c = 10.10 Å, β = 108.4°, V = 807.0 Å^3, D_m = 1.417 g cm^{-3}: private communication to H. R. A., May 1967.

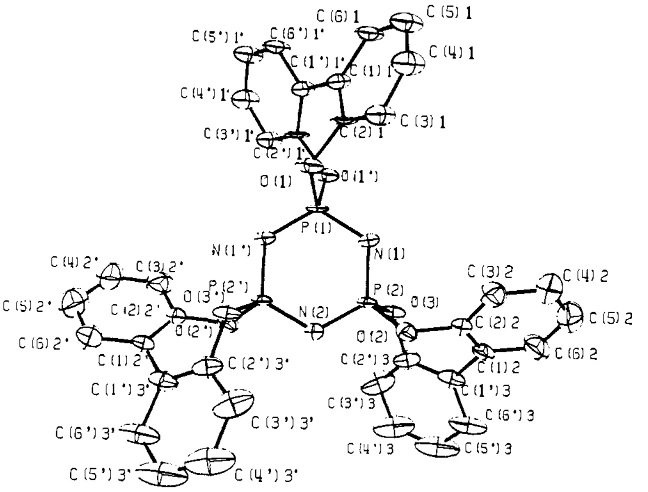

Figure 1. A view of the tris(2,2′-dioxybiphenyl)cyclotriphosphazene molecule showing anisotropic thermal motion and the atomic numbering scheme. Standard biphenyl nomenclature is employed. The right and left halves of the molecule are related by the twofold axis through P(1) and N(2). Phenyl hydrogens are omitted.

±1% throughout data collection. Of the 2400 nonextinct reflections available within the instrument's mechanical limits of $0.032 \leq \sin\theta/\lambda \leq 0.55$, 1600 reflections had $I \geq 3\sigma(I)$, and these were corrected for Lorentz and polarization effects and were used in the refinement of the structure. Twelve intense reflections were found to "saturate" the counter. These were measured at a lower power (34 kV, 5 mA) and scaled up using 25 reflections for which the intensities varied linearly between the two generator settings. A scale factor of 4.59 ± 0.02 was used to adjust the intensities and standard deviations of these reflections.

The standard deviation of the intensity, $\sigma(I)$, was calculated from the relationship $\sigma(I) = [S + (B_1 + B_2)(t/30)^2 + 0.02\,S^2]^{1/2}$, where the symbols are the same as described above, and 0.02 is an empirical factor to account for uncertainties in excess of counting statistics.[7] Since μ, the linear absorption coefficient, was relatively small (21.5 cm^{-1}), and the crystal was nearly equidimensional, rotation of the crystal around the φ axis at $\chi = 90°$ showed little variation in the intensity of the 020 reflection. Accordingly, no absorption corrections were made on the data.

In order to determine whether the thermal parameters were sufficiently large to warrant the collection of data at low temperatures, several crystals were submitted to the Structural Chemistry Laboratory in Groningen, Holland, for low-temperature single crystal examination. The results indicated that no significant advantage would be gained by recourse to low-temperature techniques.

Solution and Refinement of the Structure. The structure was essentially solved through interpretation of a three-dimensional Patterson map followed by analysis of difference Fourier maps. The principal peaks on the Patterson map could be interpreted in terms of intra- and intermolecular P–P vectors from the "heavy atom" phosphorus triangles. The distributions of the intramolecular P–P vectors showed the P–P–P triangle to be perpendicular to the *ac* plane of the cell, with two of the phosphorus atoms having equal *y* coordinates. This observation favored the choice of the space group *C*2/*c* rather than the lower symmetry *Cc*, which was an alternative possibility based on the systematic absences (*hkl* for $h + k = 2n + 1$ and *h*0*l* for $l = 2n + 1$). An analysis of Wilson statistics also confirmed the centrosymmetric structure. The choice of the space group of *C*2/*c* requires one atom of the phosphorus triangle to be placed on a twofold axis at $x = 0$, $z = {}^1/_4$. The *x* and *z* coordinates of the second crystallographically independent phosphorus atom were derived from the intramolecular P–P vectors, and the *y* coordinates of the two phosphorus atoms were derived from the Harker peaks at $(0, 2y, {}^1/_2)$.

Nitrogen atom positions were calculated assuming a P–N bond length of 1.57 Å and P–N–P and N–P–N bond angles of 120°, values which appeared reasonable on the basis of related structures.[8] Thus, one nitrogen atom, N(2), and one phosphorus, P(1) (see Figure 1), were placed in the special position 4e, and the other phosphorus, nitrogen, oxygen, and carbon atoms were placed in the equipoint 8f. Half of a molecule constituted the asymmetric unit.

An initial structure factor calculation including all the phosphorus and nitrogen atoms and one oxygen found from the Patterson map gave an *R* factor of 60%, where *R* is $\Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. Scattering factors for P^0, N^0, C^0, and O^0 were those compiled by Ibers,[9] and these were interpolated using the LaGrange polynomial. A "difference" Fourier revealed the carbon atoms in the biphenyl groups and the oxygen atoms, and the *R* value fell to 45% when these units were included. Five cycles of isotropic least-squares refinement brought *R* down to 16%, but in the next three cycles of refinement *R* was reduced to only 14.1%. In an attempt to improve the model, a difference synthesis was calculated and the residual peaks indicated that the molecule was undergoing anisotropic vibration, with the largest vibrational directions in the *ac* plane. Anisotropic refinement reduced *R* to 7.8% in three additional cycles. A difference Fourier revealed all the hydrogen atoms but one. Their electron density ranged from 0.49 to 0.23 e/Å^3. The largest unidentified peak was 0.39 e/Å^3. This peak could not be correlated with the position of any atom and was assumed to result from noise (background). All the hydrogen positions found agreed well with the positions calculated from HFINDR. Least-squares refinement of the scale factor and the hydrogen isotropic temperature factors gave a final *R* value of 6.8%. The temperature factors for the hydrogen atoms ranged from 11.99 to 7.37. They were greatest for hydrogen atoms on phenyl 3 and smallest for those on phenyl 1. These temperature factors are reasonable for hydrogen electron densities of 0.3 e/Å^3.[10] The convergence of the structure was confirmed by the fact that, in the final refinement cycle, the largest change in both atomic and thermal parameters was 0.01 of the standard deviation. In the final cycles, one of the diagonal elements of the anisotropic temperature factor for C(2) (see Figure 1) became slightly negative (Table III). This was arbitrarily set slightly positive for the ORTEP plots.

Two intense reflections (002 and $\bar{2}02$) appeared to suffer from extinction, and these were omitted from the final calculation of *R*. For several reflections (020, 040, 060, $\bar{1}32$, $\bar{2}41$) the values of F_o were consistently higher than F_c. Two other reflections ($\bar{6}03$

Table II. Final Positional Parameters for Tris(2,2′-dioxybiphenyl)cyclotriphosphazene

Atom	*x*	*y*	*z*
P(1)	0.0000	0.1824 (1)	0.2500
N(1)	0.0620 (4)	0.2564 (5)	0.3151 (3)
P(2)	0.0702 (1)	0.4021 (2)	0.3123 (1)
N(2)	0.0000	0.4732 (7)	0.2500
O(1)	−0.0691 (3)	0.0913 (4)	0.2687 (3)
O(2)	0.0655 (3)	0.4640 (4)	0.3824 (2)
O(3)	0.1727 (3)	0.4295 (4)	0.3157 (2)
C(1), 1	−0.0050 (5)	−0.1142 (6)	0.2853 (4)
C(2), 1	−0.0383 (5)	−0.0125 (5)	0.3121 (4)
C(3), 1	−0.0514 (5)	−0.0104 (6)	0.3771 (4)
C(4), 1	−0.0300 (6)	−0.1200 (7)	0.4181 (5)
C(5), 1	0.0038 (6)	−0.2219 (6)	0.3932 (4)
C(6), 1	0.0169 (5)	−0.2203 (6)	0.3274 (4)
C(1), 2	0.2194 (5)	0.5121 (6)	0.4554 (4)
C(2), 2	0.1390 (6)	0.4490 (6)	0.4445 (5)
C(3), 2	0.1234 (6)	0.3726 (7)	0.4957 (4)
C(4), 2	0.1920 (8)	0.3578 (9)	0.5597 (5)
C(5), 2	0.2751 (8)	0.4225 (9)	0.5727 (5)
C(6), 2	0.2880 (6)	0.4987 (8)	0.5208 (5)
C(1′), 3	0.2331 (5)	0.5895 (6)	0.3992 (4)
C(2′), 3	0.2062 (5)	0.5498 (7)	0.3300 (4)
C(3′), 3	0.2147 (6)	0.6196 (8)	0.2741 (5)
C(4′), 3	0.2540 (8)	0.7391 (9)	0.2899 (7)
C(5′), 3	0.2847 (8)	0.7801 (9)	0.3596 (8)
C(6′), 3	0.2752 (6)	0.7087 (7)	0.4155 (6)

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(7) S. W. Peterson and H. A. Levy, *Acta Crystallogr.*, 10, 70 (1957).

(8) H. R. Allcock, "Heteroatom Ring Systems and Polymers," Academic Press, New York, N. Y., 1967, Appendix II.

(9) J. A. Ibers, Ed., "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, pp 201–207.

(10) G. H. Stout and L. H. Jensen, "X-Ray Structure Determination," Macmillan, New York, N. Y., 1968, pp 381 and 457.

Table III. Final Thermal Parameters, Mean-Square Amplitudes of Vibration (Å), for Tris(2,2′-dioxybiphenyl)cyclotriphosphazene[a]

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P(1)	0.0459 (18)	0.0032 (13)	0.0395 (18)	0.0000 (0)	0.0073 (15)	0.0000 (0)
N(1)	0.0606 (46)	0.0117 (30)	0.0371 (40)	0.0019 (30)	−0.0035 (35)	0.0026 (30)
P(2)	0.0452 (14)	0.0068 (9)	0.0288 (12)	0.0012 (9)	0.0066 (10)	−0.0024 (9)
N(2)	0.0495 (56)	0.0190 (46)	0.0293 (52)	0.0000 (0)	−0.0013 (45)	0.0000 (0)
O(1)	0.0423 (31)	0.0140 (25)	0.0542 (34)	−0.0039 (23)	0.0179 (27)	−0.0031 (25)
O(2)	0.0433 (31)	0.0223 (27)	0.0275 (30)	−0.0024 (23)	0.0097 (26)	−0.0068 (23)
O(3)	0.0462 (32)	0.0152 (26)	0.0483 (33)	0.0037 (24)	0.0224 (27)	−0.0080 (24)
C(1), 1	0.0416 (45)	0.0166 (36)	0.0404 (46)	0.0060 (36)	0.0149 (41)	0.0002 (36)
C(2), 1	0.0415 (45)	−0.0023 (34)	0.0561 (54)	−0.0006 (32)	0.0123 (42)	−0.0013 (37)
C(3), 1	0.0581 (54)	0.0222 (42)	0.0448 (53)	0.0009 (39)	0.0270 (45)	0.0003 (39)
C(4), 1	0.0686 (62)	0.0321 (47)	0.0597 (60)	0.0045 (44)	0.0285 (50)	−0.0032 (46)
C(5), 1	0.0708 (62)	0.0209 (42)	0.0607 (62)	−0.0010 (44)	0.0300 (51)	−0.0061 (45)
C(6), 1	0.0621 (58)	0.0125 (39)	0.0520 (56)	0.0014 (38)	0.0210 (47)	−0.0068 (39)
C(1), 2	0.0410 (48)	0.0197 (39)	0.0374 (49)	0.0012 (37)	0.0079 (41)	−0.0095 (38)
C(2), 2	0.0405 (48)	0.0187 (38)	0.0304 (47)	0.0005 (36)	0.0048 (41)	−0.0019 (36)
C(3), 2	0.0882 (72)	0.0382 (51)	0.0380 (55)	−0.0006 (48)	0.0177 (53)	−0.0013 (44)
C(4), 2	0.0998 (83)	0.0551 (63)	0.0435 (64)	0.0049 (61)	0.0032 (62)	0.0032 (50)
C(5), 2	0.1024 (89)	0.0615 (69)	0.0441 (63)	0.0177 (66)	0.0058 (62)	−0.0047 (57)
C(6), 2	0.0655 (61)	0.0426 (53)	0.0562 (66)	0.0090 (49)	0.0000 (55)	−0.0177 (54)
C(1′), 3	0.0438 (50)	0.0256 (44)	0.0564 (56)	−0.0006 (39)	0.0249 (45)	−0.0085 (45)
C(2′), 3	0.0443 (50)	0.0282 (45)	0.0546 (59)	0.0090 (38)	0.0255 (45)	0.0014 (44)
C(3′), 3	0.0681 (65)	0.0502 (59)	0.0868 (74)	0.0177 (52)	0.0503 (60)	0.0178 (56)
C(4′), 3	0.0964 (86)	0.0417 (64)	0.1326 (107)	0.0062 (58)	0.0773 (85)	0.0147 (69)
C(5′), 3	0.0943 (86)	0.0344 (57)	0.1591 (117)	−0.0124 (55)	0.0869 (90)	−0.0082 (73)
C(6′), 3	0.0720 (66)	0.0256 (46)	0.1101 (82)	−0.0143 (45)	0.0542 (63)	−0.0108 (53)

[a] Standard deviations, shown in parentheses, are in Å × 10^4.

Table IV. Bond Lengths, Å[a]

P(1)–N(1)	1.568 (7)	C(1), 2–C(2), 2	1.366 (10)
N(1)–P(2)	1.582 (6)	C(2), 2–C(3), 2	1.402 (11)
P(2)–N(2)	1.566 (4)	C(3), 2–C(4), 2	1.386 (14)
P(1)–O(1)	1.581 (4)	C(4), 2–C(5), 2	1.405 (16)
P(2)–O(2)	1.586 (5)	C(5), 2–C(6), 2	1.394 (14)
P(2)–O(3)	1.584 (5)	C(6), 2–C(1), 2	1.404 (12)
O(1)–C(2), 1	1.406 (8)	C(1), 3–C(2), 3	1.388 (12)
O(2)–C(2), 2	1.395 (8)	C(2), 3–C(3), 3	1.398 (13)
O(3)–C(2), 3	1.396 (9)	C(3), 3–C(4), 3	1.419 (14)
C(1), 1–C(2), 1	1.393 (10)	C(4), 3–C(5), 3	1.400 (20)
C(2), 1–C(3), 1	1.388 (11)	C(5), 3–C(6), 3	1.410 (17)
C(3), 1–C(4), 1	1.424 (11)	C(6), 3–C(1), 3	1.431 (11)
C(4), 1–C(5), 1	1.389 (11)	C(1), 1–C(1), 1′	1.478 (10)
C(5), 1–C(6), 1	1.405 (12)	C(1), 2–C(1), 3	1.477 (11)
C(6), 1–C(1), 1	1.401 (10)		

[a] The standard deviations shown in parentheses are in Å × 10^3.

and 605) had $I \geq 3\sigma(I)$, but these should have been forbidden by the systematic absence $h0l$: $l = 2n + 1$. Since the crystal was relatively large and had been mounted along b (the symmetry axis), simultaneous reflection may be responsible for these results. Indeed, 020, $\bar{6}03$, and $\bar{2}41$ may have reflected simultaneously with the intense reflections, 310, $\bar{3}10$; $\bar{2}\bar{2}1$, $\bar{4}22$; and $\bar{2}2\bar{1}$, $\bar{4}22$, respectively. None of the other anomalously high intensities was explained. However, the fact that three of these were $0k0$ reflections suggests that perhaps the model should have included more electron density in planes parallel to the *ac* planes.

Another possible explanation of the fact that F_c for $0k0$ reflections was low could be that the model should have included less correlation in the *xz* plane, *i.e.*, the twofold axis should be removed. An attempt was made to refine the structure in the noncentrosymmetric space group *Cc*. The *x* and *z* coordinates of N(2) were held fixed on the twofold axis to define an origin. The refinement gave some large temperature factors and others which were negative. This suggests that the space group is not *Cc*, but it is not absolutely conclusive evidence.[11]

In the refinement, $\Sigma w(|F_o| - |F_c|)^2$ was minimized, with the weights, w, being derived from the relation, $w = 1/\sigma^2(F_o)$, with $\sigma(F_o) = 0.5\sigma(I)[LpI]^{1/2}$.[10] Observed and calculated structure factors are in Table I,[12] and atomic and thermal parameters are given in Tables II and III. Bond distances and angles for the asymmetric unit are shown in Tables IV and V.

Computer Programs. The least-squares program for powder data was written by D. E. Appleman, D. S. Handwerker, and H. T. Evans. Fourier and difference-Fourier calculations were conducted with the use of Program B-149 (Argonne National Laboratory) written by J. Gvildys as a version of ERFR-2 by Shoemaker, Sly, and van den Hende. During the early stages of refinement, the program ANLFLS14E was used for least-squares structure factor calculations. This is J. Gvildys' version of the ORFLS program by Busing, Martin, and Levy.[13a] The final anisotropic refinement was performed with the BULSCOP2 version of the Brown University modification of the Busing–Levy ORFLS program, modified for use with our system. Thermal Ellipsoid plots were obtained using the program by Johnson, "ORTEP: A Fortran Thermal Ellipsoid Plot Program For Crystal Structure Illustration."[13b] The Wilson plot was obtained with the use of Dewar's FAME program.[14] All calculations were carried out on an IBM 360/67 computer.

Results and Discussion

A number of structural features of II are of interest. First, it is important to compare the bond angles, bond lengths, and phosphazene ring conformation of II with those of related cyclotriphosphazenes. The influence, if any, of the bulky dioxybiphenyl unit on bonding within the phosphazene skeleton can then be deduced. Second, it is of interest to examine the conformations assumed by the dioxybiphenyl units and

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(11) O. Ermer and J. D. Dunitz, *Acta Crystallogr., Sect. A*, 26, 163 (1970), have recently noted that least-squares techniques are not always satisfactory for differentiation between centrosymmetric and noncentrosymmetric structures.

(12) The structure factor table (Table I) will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit $3.00 for photocopy or $2.00 for microfiche.

(13) (a) W. R. Busing, K. O. Martin, and H. A. Levy, Report No. ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962; (b) C. K. Johnson, Report No. ORNL-3794, Oak Ridge National Laboratory, Oak Ridge Tenn., revised 1966.

(14) R. B. K. Dewar, Ph.D. Thesis, University of Chicago, March 1968.

Table V. Bond Angles, Deg

N(1′)–P(1)–N(1)	118.6 (0.3)	C(1), 1–C(2), 1–C(3), 1	124.2 (0.7)
N(1)–P(2)–N(2)	118.3 (0.2)	C(2), 1–C(3), 1-C(4), 1	117.3 (0.7)
P(1)–N(1)–P(2)	120.8 (0.3)	C(3), 1–C(4), 1–C(5), 1	119.8 (0.5)
P(2)–N(2)–P(2′)	121.2 (0.2)	C(4), 1–C(5), 1–C(6), 1	121.3 (0.7)
O(1′)–P(1)–O(1)	103.0 (0.2)	C(5), 1–C(6), 1–C(1), 1	120.1 (0.5)
O(2)–P(2)–O(3)	102.4 (0.3)	C(6), 1–C(1), 1–C(2), 1	117.2 (0.7)
N(1)–P(1)–O(1)	113.1 (0.3)	C(1), 2–C(2), 2–C(3), 2	122.5 (0.8)
N(1)–P(2)–O(3)	105.9 (0.3)	C(2), 2–C(3), 2–C(4), 2	119.6 (0.5)
N(2)–P(2)–O(2)	106.8 (0.2)	C(3), 2–C(4), 2–C(5), 2	119.2 (0.6)
P(1)–O(1)–C(2), 1	121.8 (0.4)	C(4), 2–C(5), 2–C(6), 2	119.8 (0.6)
P(2)–O(2)–C(2), 2	119.5 (0.3)	C(5), 2–C(6), 2–C(1), 2	121.3 (0.8)
P(2)–O(3)–C(2′), 3	118.6 (0.4)	C(6), 2–C(1), 2–C(2), 2	117.7 (0.7)
O(1)–C(2), 1–C(1), 1	118.7 (0.4)	C(1′), 3–C(2′), 3–C(3′), 3	124.6 (0.6)
O(2)–C(2), 2–C(1), 2	120.9 (0.6)	C(2′), 3–C(3′), 3–C(4′), 3	117.0 (0.9)
O(3)–C(2′), 3–C(1′), 3	117.8 (0.6)	C(3′), 3–C(4′), 3–C(5′), 3	119.7 (0.6)
O(1)–C(2), 1–C(3), 1	116.8 (0.7)	C(4′), 3–C(5′), 3–C(6′), 3	122.6 (1.2)
O(2)–C(2), 2–C(3), 2	116.5 (0.7)	C(5′), 3–C(6′), 3–C(1′), 3	117.8 (0.8)
O(3)–C(2′), 3–C(3′), 2	117.4 (0.7)	C(6′), 3–C(1′), 3–C(2′), 3	118.3 (0.6)
C(2), 1–C(1), 1–C(1′), 1′	122.6 (0.7)	C(6), 1–C(1), 1–C(1′), 1′	120.2 (0.5)
C(2), 2–C(1), 2–C(1′), 3	120.4 (0.5)	C(6), 2–C(1), 2–C(1′), 3	121.8 (0.7)
C(2′), 3–C(1′), 3–C(1), 2	121.6 (0.7)	C(6′), 3–C(1′), 3–C(1), 2	120.1 (0.5)

to determine the reasons for the existence of particular conformers. Third, it is necessary to explain the differences between chemically equivalent bond angles. Fourth, a structural explanation is needed for the chemical differences between II and tris(*o*-phenylenedioxy)cyclotriphosphazene (I). Each of these aspects will be considered in turn.

General Structural Features. The molecular structure of II is depicted in Figure 1, bond distances and angles for the asymmetric unit are shown in Tables IV and V, and a summary of agreement among chemically equivalent bond lengths and angles is listed in Table VI. In Figure 2 the unit cell of II is drawn in perspective. There are no unexpected abnormalities in the skeletal bond lengths and only two significantly dissimilar sets of bond angles, the N–P–O and C–C–C angles. These differences will be treated later. The observed mean P–N bond length of 1.572 Å, the P–N–P angle of 121.0°, the N–P–N angle of 118.4°, and the O–P–O angle of 102.7° are close to the values reported for hexachlorocyclotriphosphazene, $(NPCl_2)_3$ (P–N = 1.59 Å, P–N–P = 118.3–120.9°, N–P–N = 118.5–120.4°, and Cl–P–Cl = 101.8–102.0°).[15] All the P–N bond lengths in II are equal, a fact which confirms the results of nearly every other X-ray structure determination on symmetrically substituted cyclotriphosphazenes[8] that no separation into alternating σ and σ–π bonds is evident It is perhaps surprising that the presence of a seven-membered exocyclic ring at phosphorus has virtually no effect in widening the O–P–O bond angle, and this result can be attributed to the marked twisting of the seven-membered ring.

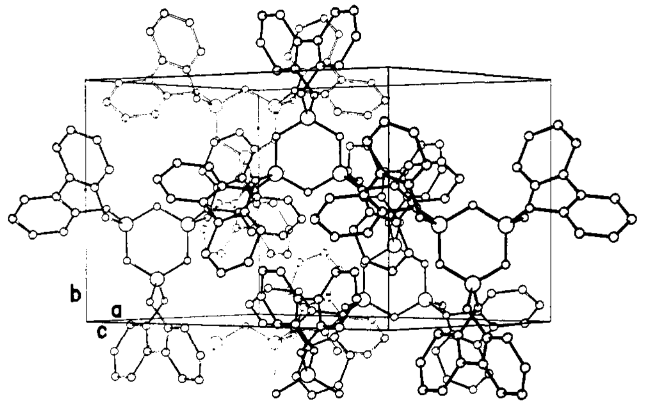

Figure 2. Molecular and cell packing (center) of the unit cell (a clinographic projection). The molecule at the extreme right is outside the unit cell.

The mean aromatic C–C bond length of 1.392 Å is very close to the value of 1.394 Å reported for other aromatic units.[16] Similarly, the phenyl–phenyl C–C bond length (1.478 Å) in II compares well with the value of 1.48 Å reported for biphenyl[17] and for 4,4′-dihydroxybiphenyl,[18] and the C–O bond distance in II of 1.399 Å agrees with the related C–O values of 1.37 Å in 4,4′-dihydroxybiphenyl[18] and 1.39 in I.[5] The P–O bond distance of 1.584 Å in II can be compared with values of 1.570–1.586 Å in $[NP(OCH_3)_2]_3$[19] and 1.576–1.603 Å in I.[5]

Statistical treatment of the deviations from the least-squares ring plane for phenyls 1, 2, and 3 and the cyclotriphosphazene plane indicate that χ^2 has values of 1.87, 1.60, 3.32, and 602.0, respectively. It is apparent that the phenyl rings are planar but that the phosphazene ring is not. Nonplanarity of the cyclotriphosphazene rings in other compounds has also been noted,[15,20–23] but this provides no information about pseudoaromaticity in a d_π–p_π system.[24] In II, the skeletal atoms on the twofold axis (P(1) and N(2)) are in the least-squares ring plane. Atoms P(2) and N(1)

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Table VI. Summary of Agreement between Chemically Equivalent Bonds (Å) and Angles (Deg)

Bond or angle	No. of values	Range, Å or deg	σ_{rms}	Mean	χ^{2} [a]	P [b]
P–N	3	1.566–1.582	0.006	1.572	4.82	0.20–0.10
P–O	3	1.581–1.584	0.005	1.584	0.55	0.95–0.90
O–C	3	1.395–1.406	0.008	1.399	1.07	0.80–0.70
C–C [c]	18	1.37–1.43	0.013	1.392	21.4	0.50–0.30
C–C [d]	2	1.477–1.478	0.010	1.478	0.002	1.00–0.99
NPN	2	118.3–118.6	0.25	118.4	0.7	0.70–0.60
PNP	2	120.8–121.2	0.25	121.0	1.3	0.60–0.50
OPO	3	102.4–103.0	0.25	102.7	2.8	0.30–0.20
NPO	3	105.9–113.1	0.25	108.6	489	<0.01
CCC	18	117.0–124.6	0.72	120.0	170	<0.01

[a] χ^2 is the common statistical quantity, calculated to test the significance of a deviation from the mean. It is the sum of the squares of the deviations from the mean divided by the root-mean-square σ^2. [b] P is the probability that a quantity differs from its mean by a certain per cent of σ. A normal distribution is assumed. Statisticians usually consider $P > 0.05$ (or 0.67σ) as being an insignificant deviation, $0.05 > P > 0.01$ (or 0.67σ–1.65σ) as possibly significant, and $P < 0.01$ (or 1.65σ) as a definitely significant difference. [c] Aromatic C–C bonds within phenyl groups. [d] Biphenyl C–C bonds.

are +0.076 and −0.076 Å above and below this plane, respectively, and, because of the twofold symmetry, P(2′) and N(1′) are −0.076 and +0.076 Å, respectively, from the plane. Thus, the phosphazene ring occupies a distorted boat arrangement.

Conformation of the Side Groups. The average angle of twist between phenyl groups in each biphenyl unit is 41°. This can be compared with the 75° twist reported for 2,2′-disubstituted biphenyls and the 45 ± 10° value found in free biphenyl or para-substituted biphenyls.[17] Thus, the seven-membered aryldioxyphosphole ring in II serves to minimize the angle of twist within the biphenyl grouping to that required to avoid 6,6′, hydrogen–hydrogen contacts.

One of the most interesting structural features of II is connected with the overall side-group conformations. Consider the two independent biphenyl units, phenyl groups 2 and 3, and phenyl groups 1 and 1′. Unit 2–3 is twisted −43° from the mean phosphazene ring plane, whereas unit 1–1′ is twisted +52°. In this convention, a positive angle represents a clockwise twist of the biphenyl axis from the ring plane when viewed from the phosphorus atom toward the biphenyl unit. Thus, as illustrated in Figure 1, only two side units per molecule are arranged in the form of a propellor, the third being twisted in the opposite direction. Biphenyl unit 1–1′ is not only of opposite twist to units 2–3 and 2′–3′, but its angle of twist is larger.

The reason for this distortion becomes clear when the intercellar contact distances are examined. Each molecule is approximately 10.8 Å long in the *b*-axis direction, whereas the *b* axis itself is only 10.81 Å. Very short contacts would be created along *b* between side groups in adjoining unit cells if all three side groups assumed the same direction of twist to give a propellor-like conformation. This is particularly serious for interactions between phenyl groups 1 and 1′ and phenyl groups 3 and 3′. Figure 2 shows this clearly for several molecules. Thus, for the propellor conformation, the contacts C(5),1 · · · C(4),3; C(5),1 · · · H(4),3; H(5),1 · · · C(4),3; and H(5),1 · · · H(4),3 would be 1.15, 1.72, 0.88, and 1.86 Å, respectively. The normal van der Waals contacts are 3.54 Å (aromatic C · · · C), 2.77 Å (aromatic C · · · H), and 2.00 Å (H · · · H). There are two ways in which these repulsions could be avoided: first, by lengthening of the *b*-axis cell dimension, or second, by reversal of the twist direction of one diphenylenenedioxy unit on each molecule. The second alternative is favored. Advantageous van der Waals dispersion-type forces presumably result from this conformation.

Within each biphenyl unit there are also small differences in the angle of twist of the two phenyl groups. Thus, the torsional angle between phenyl groups 3 and 2 is −43° and between groups 1 and 1′ it is 39°, the sign differences representing the different gross twists of the biphenyl axis. The dihedral angle between the phosphazene ring and the O–P–O planes is 84° for O(2)–P(2)–O(3) and −80° for O(1)–P(1)–O(1′), and this again reflects the different degrees of twist of the biphenyl axes. The latter angle is further from 90° as a result of the larger biphenyl twist for phenyls 1 and 1′. Finally, since P(2) and P(2′) are not in the ring plane, the biphenyl units are not bisected by the ring plane. The unit at P(2) is tilted upward at about 8° from the mean phosphazene ring plane, and, from the twofold symmetry, the unit at P(2′) is tilted downward by the same amount.

It seems clear that the conformation found for this molecule results mainly from crystal packing forces. In solution or in the molten state, an averaging undoubtedly occurs over many conformational possibilities.

Abnormalities in Chemically Equivalent Bond Lengths and Angles. Table VI summarizes the statistical treatment of chemically equivalent bond lengths and angles. The differences between these values are not significant except for the 3 N–P–O angles and the 18 C–C–C angles. The N–P–O angles are significantly different because of the different angles of twist of the side units and the different twist directions. Thus, the fact that the N(1)–P(1)–O(1) angle of 113.1° is larger than the N(2)–P(2)–O(2) angle of 106.8° and the N(1)–P(2)–O(3) angle of 105.9° is understandable in these terms.

The differences between the C–C–C angles can be explained in terms of ring distortion. The average C(1)–C(2)–C(3) angle is 123.8°, O–C(2)–C(3) is 116.9°, and O–C(2)–C(1) is 119.2°. Thus, the distortion from the expected sp^2 angle of 120° at carbon is significant. It is also noteworthy that abnormally short contact distances are found between oxygen atoms in the same side-group unit (2.47 Å). The normal van der Waals contact distance for two oxygen atoms is 3.00 Å.[25] In addition, there is some evidence for slight distortion of the biphenyl axes from linearity. All these data support the view that the biphenyl groups are strained by incorporation into the seven-membered diphenylenedioxyphosphole units and possibly by the requirements of lattice packing. In order to relieve the strain, the C(1)–C(2)–C(3) angle widens slightly, despite the fact that short oxygen–oxygen contact distances are created in the process.

Comparisons between I and II. Structural data for compounds I and II are shown in Table VII. The skeletal parameters are very similar in the two cases, but the O–P–O bond angles and the side group configurations are different. In II, the exocyclic angles at phosphorus are in the range of 102.4–103°. Since these angles are comparable to those found in most cyclotriphosphazenes which have two independent ligands at each phosphorus (except fluorophosphazenes), it must be assumed that this corresponds to an unstrained angle. By contrast, the five-membered exocyclic ring in I constrains the O–P–O angle to 97°, and the resultant strain becomes strikingly manifest in the chemistry of this compound. Thus, I hydrolyzes almost instantly in dilute base whereas II does not.[26] Compound I degrades to phosphoranes in the presence of *o*-aminophenol[1] or with catechol and base,[27] but II is unreactive. Phosphazene I polymerizes at moderate temperatures, but II is one of the most thermally stable phosphazenes known.

Table VII. Comparison of Average Bond Lengths (Å) and Angles (Deg) for I[a] and II

	I	II		I	II
P–N	1.576 (1.573)	1.572	N–P–N	119 (116)	118.4
P–O	1.598 (1.589)	1.584	P–N–P	122 (123)	121.0
O–C	1.40 (1.40)	1.399	N–P–O	107 (107)	105.6
C–C	1.42 (1.41)	1.392	C–C–C	117 (117)	120.0
Side-group twist,[b] deg	89	48	O–P–O	97 (97)	102.7

[a] Values for the benzene adduct of I are listed first and those for the bromobenzene adduct are in parentheses: L. A. Siegel and J. H. van den Hende, *J. Chem. Soc. A*, 817 (1967). [b] The twist refers to the twist of the phenyl with respect to the phosphazene ring in I and to the twist of the long biphenyl axis (C(4)–C(1)–C(1′)–C(4′)) to the central ring in II.

The second significant structural difference between I and II is connected with the side-group conformations. In I, the *o*-phenylenedioxy side groups are almost perpendicular to the phosphazene ring, whereas in II the principal axis of each biphenyl group is twisted an average of 47.5° to the phosphazene ring plane. Furthermore, the average 41° twist between phenyl units within each biphenyl group further increases the molecular volume occupied by the ligands.

These differences are apparently responsible for the fact that I readily forms channel inclusion clathrates whereas II does not. The rigid "paddle-wheel" structure of I is particularly favorable for the compound to crystallize in a hexagonal form, with channels existing between the side groups. Clathrated molecules occupy these channels.[3,5] However, the side-group structure of II precludes such a symmetrical crystalline packing arrangement. In fact, for II, the 2,2′-dioxybiphenyl ligands effectively fill the only potential cavity sites in the lattice (Figure 2) and the irregularity of the ligand twist direction further reduces the possibility of clathration in this crystallographic form.

The pronounced angle of twist of the side-group units in II also suggests a reason for the resistance of this compound to thermal polymerization. In a linear polymer derived from II, most of the possible conformations are precluded by serious intramolecular steric repulsions. Conformations with reasonable intramolecular contacts can be visualized only if the side groups are twisted at 52° or more from the skeletal plane and if side group thermal motions are minimal. By contrast, the perpendicularly oriented ligands in I would encounter no serious repulsions during conversion of I to a macrocyclic or linear polymer.

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