The Crystals and Molecular Structure of 1,1,4,4-Tetraphenyl-2,5-di-(t-butyl)-1,4-diphosphoniacyclohexadiene-2,5-dichloride

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The crystal and molecular structure of the title compound has been determined by single crystal, x-ray diffraction techniques. The compound crystallizes in a monoclinic space group of C2/c symmetry with four molecules in a unit cell of dimensions a = 24.578(1), b = 10.503(1), c = 17.579(1) Å and β = 130.93 ± .01°. The unit cell also contains two waters of crystallization which are involved in hydrogen bonds to the chloride ions. The central ring has been shown to be a diene which resides in a boat conformation defined by dihedral angles of 157°. The structure has been refined to a value of R = 0.08 using the 1535 statistically significant reflections measured out ot a 2θ value of 140°.

Introduction.

The series of compounds (Ia-Id) containing the title compound (Ia) were prepared and characterized chemically in 1969 (1). A series of diphosphoniacyclohexadiene compounds (Ib-Id) have been investigated in this laboratory

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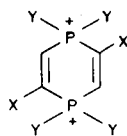
(a) X = C₄H₉, Y = C₆H₅
(b) X = CH₃, Y = C₂H₅
(c) X = H, Y = C₆H₅
(d) X = , Y = C₆H₅

(2,3,4) to resolve the controversy over the existence of π-electron delocalization (5,6). Although that question has been resolved, the structure of this compound (Ia) forms an ideal intermediate in the above series in investigating the effects of steric crowding on the conformation of the diphosphoniacyclohexadiene ring. The structures of the compounds at the two extremes are already known (2,4), namely; the crowded case where all six substituents are phenyls (Id) and the central ring is in the boat conformation; versus the uncrowded situation where only ethyl and methyl groups are involved (Ib) and the central ring is planar. This compound where t-butyl groups replace two of the six phenyl groups was thus studied to investigate the point at which steric overcrowding begins to alter the geometry of the system.
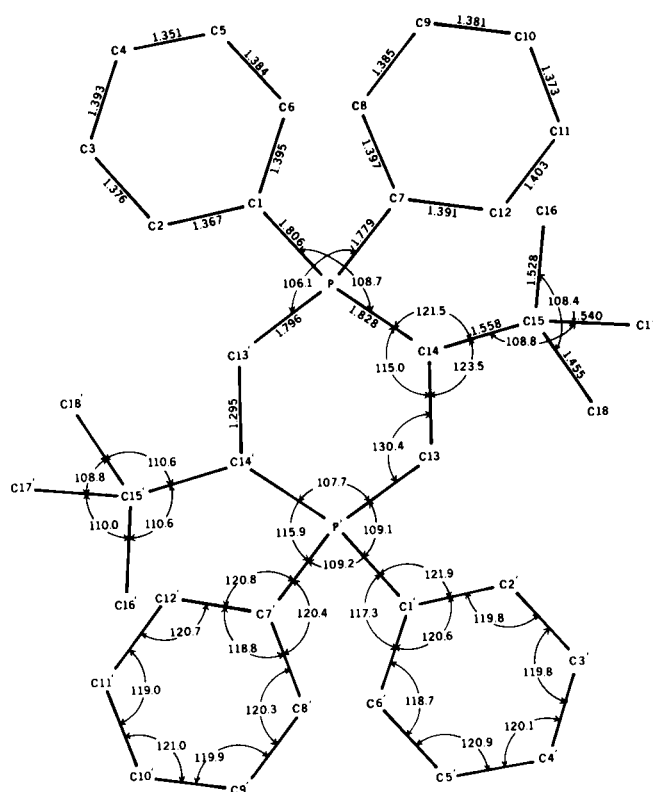

Figure 1

Schematic drawing of the molecule showing bond distances and bond angles.

EXPERIMENTAL

A sample of the title compound was kindly furnished to us by Professor Adam Aguiar. A suitable crystal of dimensions .14 x .21

TABLE I

Fractional Coordinates and Anisotropic Thermal Parameters (a)

(Anisotropic Thermal Parameters x 10^4. Estimated Standard Deviations in Parentheses Refer to Last Decimal Place)

Atom	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
CL-	-0.0382(2)	0.1715(4)	0.0475(3)	42(2)	170(6)	82(3)	26(3)	38(2)	10(4)
P	0.4225(2)	0.0819(3)	0.2216(2)	9(1)	68(3)	25(2)	0(2)	10(1)	2(2)
C1	0.4079(5)	0.2514(10)	0.2158(7)	9(3)	77(13)	25(6)	8(6)	10(4)	5(8)
C2	0.4089(5)	0.3292(11)	0.1545(7)	17(4)	65(13)	31(7)	7(6)	13(4)	6(9)
C3	0.3996(6)	0.4583(10)	0.1545(8)	26(5)	56(14)	49(8)	-6(6)	21(5)	1(9)
C4	0.3932(6)	0.5098(11)	0.2216(9)	28(5)	80(16)	86(11)	-1(7)	39(7)	-17(11)
C5	0.3955(6)	0.4330(11)	0.2853(8)	18(4)	97(17)	59(9)	-11(7)	21(5)	-23(10)
C6	0.4022(5)	0.3025(11)	0.2837(8)	17(4)	101(17)	40(8)	-3(7)	17(5)	0(9)
C7	0.3552(5)	0.0007(11)	0.2133(8)	11(4)	89(15)	39(7)	3(6)	15(5)	6(9)
C8	0.3685(5)	-0.1210(11)	0.2543(7)	18(4)	84(15)	40(8)	1(6)	18(5)	-9(9)
C9	0.3149(6)	-0.1868(11)	0.2433(8)	34(5)	91(17)	49(8)	-20(8)	32(6)	-16(10)
C10	0.2472(6)	-0.1340(13)	0.1886(9)	24(5)	153(20)	71(10)	-17(8)	36(6)	-17(12)
C11	0.2333(6)	-0.0125(12)	0.1510(8)	16(4)	156(19)	46(8)	-7(8)	21(5)	-5(11)
C12	0.2879(6)	0.0553(12)	0.1636(8)	17(4)	101(18)	40(8)	13(7)	8(5)	11(10)
C13	0.4930(5)	0.0425(10)	0.1573(7)	15(4)	70(14)	27(7)	1(6)	14(4)	6(8)
C14	0.4286(5)	0.0395(10)	0.1266(7)	12(3)	49(12)	28(6)	0(5)	12(4)	2(7)
C15	0.3603(5)	0.0066(11)	0.0164(7)	15(4)	79(14)	30(7)	-5(6)	11(5)	-8(9)
C16	0.3054(6)	0.1146(12)	-0.0294(8)	18(4)	118(20)	37(8)	5(7)	-6(5)	7(10)
C17	0.3271(6)	-0.1172(12)	0.0172(8)	30(5)	108(18)	48(9)	-15(8)	20(6)	-11(11)
C18	0.3795(6)	-0.0127(13)	-0.0455(7)	25(5)	174(22)	18(7)	-14(9)	11(5)	-5(11)
OX1	0.0700(4)	0.1443(9)	0.0180(5)	10(3)	250(17)	23(5)	-23(6)	-1(3)	35(8)
OX2	0.0000(0)	0.2684(11)	0.2500(0)	29(5)	87(16)	113(12)	0(0)	42(7)	0(0)

(a) Anisotropic temperature factors of the form: $\exp[-\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}\ell^2 + 2\beta_{12}hk + 2\beta_{13}h\ell + 2\beta_{23}k\ell]$.
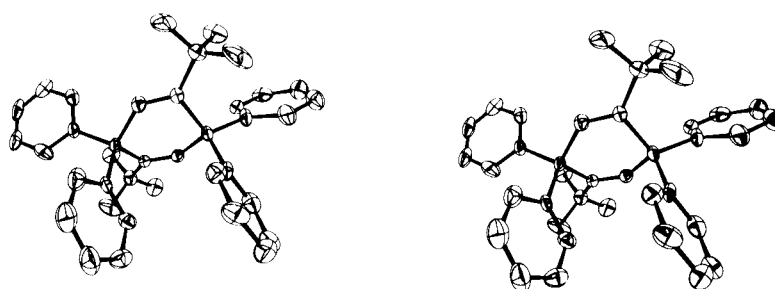

Figure 2. ORTEP stereo drawing of the molecule.

x .15 mm was recrystallized from acetonitrile. The symmetry and cell dimensions were determined on an XRD-5 diffractometer using Cu-Kα radiation. Extinctions of h + k = 2n for general reflections, ℓ = 2n for the (h0ℓ) reflections and k = 2n for the (0k0) reflections narrowed the possible space group choices to C2/c or Cc. Statistical tests supported the centrosymmetric space group (C2/c) and the ultimate solution of the structure confirmed this choice. Lattice constants were determined by a least-squares fit of 20 carefully measured two theta values of the Cu Kα_1-Kα_2 doublet for $2\theta > 70°$ under fine conditions (1° take-off angle and

TABLE II

Hydrogen Fractional Coordinates
(Isotropic Thermal Parameter Fixed at 4.0 Å^2)

Atom (a)	X	Y	Z
H2	0.417	0.291	0.107
H3	0.398	0.518	0.106
H4	0.387	0.608	0.221
H5	0.392	0.471	0.333
H6	0.405	0.246	0.331
H8	0.420	-0.164	0.294
H9	0.327	-0.277	0.278
H10	0.211	-0.191	0.181
H11	0.184	0.026	0.120
H12	0.277	0.145	0.132
H13	0.500	0.040	0.100
H16	0.267	0.096	-0.025
H16'	0.280	0.129	-0.102
H16"	0.330	0.196	0.008
H17	0.364	-0.183	0.069
H17'	0.291	-0.107	0.027
H17"	0.305	-0.140	-0.051
H18	0.388	0.055	-0.077
H18'	0.340	-0.067	-0.106
H18"	0.425	-0.065	-0.004

(a) Numbers following H refer to bonding atom.

0.05° slit). The resultant lattice constants and their estimated standard deviations are:

$$a = 24.578 \pm 0.001 \text{ Å}$$
$$b = 10.503 \pm 0.001 \text{ Å}$$
$$c = 17.579 \pm 0.001 \text{ Å}$$
$$\beta = 130.93° \pm 0.01°$$

The calculated density of 1.17 gm/cc for 4 molecules per unit cell differs significantly from the experimentally measured (by flotation methods) value of 1.26 ± .02 gm/cc. The ultimate solution of the structure included two waters of crystallization, one in a general position, the other in a four-fold position. The calculated density becomes 1.27 gm/cc when these waters of recrystallization are included.

Intensity data were collected on a General Electric XRD-490 automated diffractometer using stationary crystal-stationary counter methods, balanced Ni and Co filters and Cu-Kα radiation. A total of 3272 reflections were measured, of which 1535 were considered as statistically significant by the criterion:

$(I_{Ni} -2\sigma(I_{Ni})) - (I_{Co} + 2\sigma(I_{Co})) > 200$ counts where σ is based on counting statistics and a counting time of 10 seconds was used.

The intensities were converted into structure factors after correction for Lorentz-polarization effects, Kα_1 -Kα_2 splitting and absorption. Absorption was corrected as a function of phi only (linear absorption coefficient = 28.9 and absorption corrections

ranged from 1.0 - 1.13).

Structure Determination.

A three dimensional Patterson map was calculated and contained peaks for the phosphorus and chlorine atoms which were consistent with either space group C2/c or Cc. Assuming that the molecule contained a center of symmetry and using the space group C2/c, a Fourier map phased by these heavy atoms was calculated to locate the other non-hydrogen atoms. Nineteen additional peaks were found on the map corresponding to the seventeen necessary to complete half of the centrosymmetric molecule and two prominent peaks away from the molecule (one in a general position, the other in a four-fold position). The structure (excluding the two peaks in space) was refined using block-diagonal least-squares (7) with isotropic temperature factors and $\frac{1}{\sigma^2}$ weights. Refinements were carried out in both space groups. In the non-centrosymmetric space group (Cc) the refinements led to a value of R = 0.18 with the refined structure having very poor chemical consistency. In the centrosymmetric space group (C2/c) the refinements led to a value of R = 0.13 with a chemically reasonable molecule resulting from the refinement. All further refinements were thus carried out in C2/c. Another Fourier map at this stage revealed the same two peaks previously observed, isolated in space, and at the expected heights for oxygen atoms, hence they were presumed to be waters of crystallization and were included in subsequent refinements.

After a number of additional isotropic cycles of least-squares, the temperature factors were made anisotropic and further refinement led to a value of R = 0.10. At this stage a difference electron density map was computed and positive regions (0.3 - 0.5 $\bar{e}/\text{Å}^3$) were found which corresponded to locations calculated for hydrogen atom except that those hydrogens attached to the water molecules were not found. A final series of least-squares refinements were run in which all of the non-hydrogen atoms were allowed to vary anisotropically while those hydrogen atoms found were assigned fixed isotropic temperature factors of 4.0 Å^2 and only their coordinates were allowed to vary. When all shifts become less than one tenth the estimated standard deviation in the value of their respective parameter, refinement was considered complete. The final value of the reliability index was R = 0.082.

Discussion and Results.

Table I lists the final coordinates and anisotropic temperature factors for the non-hydrogen atoms. Table II lists the refined hydrogen coordinates. Figure I is a schematic drawing of the molecule with the distances and angles indicated on the drawing. Figure II is an ORTEP stereodrawing of the molecule. The ESD are less than 0.01 Å in the P-C and less than 0.02 Å in C-C distances. All of the angles have ESD values less than 1°.

The phenyl rings individually have average bond distances of 1.38, 1.39 Å and bond angles of 120, 120°, respectively. Both values are well within one ESD value of the normally cited values of 1.39$_8$ Å and 120.0° (8). The t-butyl distances average to 1.52 Å overall or 1.54 Å if the C15 - C18 distance of 1.46 Å is not included. There is no obvious crystallographic or chemical reason why this one value should vary by four ESD values from the other distances and so it is presumed to be an artifact of the data. The angles about the t-butyl carbon (C15) average to the tetrahedral angle of 109.6° as anticipated.

The central diphosphoniacyclohexadiene ring is, of course, the focus of interest. That it is a diene is obvious from the C13-C14 distance of 1.30 Å which is shorter (but not of statistical significance) than the analogous distance found in earlier studies (2,4,9) of 1.33 Å, 1.34 Å and 1.41 Å, respecitvely. The angles about the

double bond range from 115° to 130° confirming the sp² hybridization, in general. The P-C average distance of 1.80 Å fits nicely within the range of 1.79-1.82 Å found in previous studies (2,3,4,9) for this bond.

The geometry of the ring system is again that of the boat conformation. Calculations of the best planes fit using the four diene carbon atoms as the central plane (ESD = .016 Å) and each phosphorus and its adjacent carbons as secondary planes readily confirm this, resulting in dihedral angles of 157° in each case. This is somewhat more flattened than the hexaphenyl substituted compound (also in the boat conformation) which has dihedral angles of 151° (4). However, it is still appreciably non-planar and it suggests a next compound that ought to be investigated in this series is one which has phenyls on the phosphorus atoms and methyl groups on the centrosymmetrically related diene carbons.

The present compound contains no close contacts between the ions but does have relatively short oxygen-chlorine contact distances of 3.04 Å (01 - Cl) and 3.20 Å (02 - Cl). This suggests that the waters of crystallization are held by hydrogen bonds to the chloride ions.

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