

## Crystal and Molecular Structure of Triphenyl 4,4,6-Trimethyl-1-oxa-3-azacyclohex-2-enylcarbenyl Phosphonium Chloride

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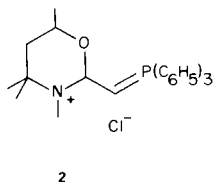
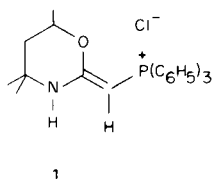
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The structure of the title compound has been determined by a single crystal, x-ray diffraction study. The compound crystallizes in a monoclinic unit cell of  $P2_1/c$  symmetry and dimensions,  $a = 9.832 \pm .001 \text{ \AA}$ ,  $b = 15.398 \pm .001 \text{ \AA}$ ,  $c = 19.762 \pm .002 \text{ \AA}$ , and  $\beta = 123.06 \pm .01^\circ$  with four molecules per unit cell. The 1633 statistically significant reflections (from a total of 2743 out to  $2\theta = 100^\circ$ ) refined to a final value of  $R = 0.05_3$ . The molecule itself consists of a chloride ionically bonded to a cation containing a tetrahedral phosphorus bound to three phenyl rings and a fourth oxazine ring. It is the latter ring which displays extensive delocalization as discussed in the paper.

### Introduction.

An oxazinyl phosphonium chloride prepared by Professor A. I. Meyers (1) has spectral data consistent with structure 1, namely; a relatively low uv maximum at



267m (in ethanol); an ir maximum at  $1603 \text{ cm}^{-1}$  (potassium bromide); and an nmr spectrum with non-equivalent protons in the *gem*-methyl groups, a broad singlet at  $9.3 \delta$  (proton on nitrogen) and a signal at  $4.22 \delta$  (d, 1, J = 7 Hz) consistent with that expected for a vinyl proton. Both the N-proton and the vinyl proton exchange with deuterium oxide implying, at the least, an equilibrium with the tautomeric form, structure 2.

Treatment of a suspension containing this compound with a base in an ether solvent leads to a yellow solution assumed to contain the neutral phosphorane. Further reactions indicate that this compound is a potential source of  $\alpha,\beta$ -unsaturated aldehydes, ketones, acids, and esters. The application of this compound in syntheses leading to functionally substituted aldehydes is now under active investigation (2).

To understand the mechanism of these reactions, it is necessary to know fully the bonding, delocalization and whatever other unusual features that are present in this compound. Consequently, a single crystal x-ray structure determination of this compound was undertaken. We are

indebted to Professor A. I. Meyers for supplying us with a crystalline sample of the compound.

### EXPERIMENTAL

Crystals of the title compound were grown from acetonitrile. A single crystal measuring  $.20 \times .20 \times .15 \text{ mm}$  was mounted with the b-axis coincident with the Phi-axis of the G.E. XRD-5 diffractometer. Extinctions of the  $(h0l)$  reflections with odd, and  $(Ok0)$  with k odd uniquely characterized the space group as  $P2_1/c$ . Least-squares lattice constants were determined from 20 measurements of the copper  $K\alpha_1 - K\alpha_2$  doublet at values of  $2\theta$  greater than  $70^\circ$  under fine conditions ( $1^\circ$  take-off angle and  $0.05^\circ$  slit). The resultant lattice constants are:

$$\begin{aligned} a &= 9.832(1) \text{ \AA} \\ b &= 15.398(1) \text{ \AA} \\ c &= 19.762(2) \text{ \AA} \\ \beta &= 123.06(1)^\circ \end{aligned}$$

The experimental density of  $1.18 \pm .02 \text{ g/cc}$  (measured by a flotation technique) agrees with a density of  $1.20 \text{ g/cc}$  calculated by assuming four molecules per unit cell.

Three-dimensional intensity data were collected on a G.E. XRD-490 automated diffractometer system using the stationary counter, stationary crystal method; balanced Ni and Co Ross filters; and Cu- $K\alpha$  radiation. A total of 2743 reflections were measured to a two-theta limit of  $100^\circ$ . Of these, 1633 reflections were considered statistically significant by the criterion.

$$(I_{Ni} - 2\sigma(I_{Ni})) - (I_{Co} + 2\sigma(I_{Co})) > 100$$

$\sigma$  based on counting statistics (10 second counting time)

The intensities were corrected for  $\alpha_1 - \alpha_2$  splitting as a function of two-theta and absorption as a function of  $\phi$  (maximum difference in  $\phi$ -scan at  $\chi = 90^\circ$  was 5% and  $\mu = 2.1 \text{ cm}^{-1}$ ). The usual Lorentz-polarization corrections were made and the intensities were reduced to structure amplitudes.

### Structure Determination.

The coordinates of the phosphorus and chlorine atoms were determined from a three-dimensional Patterson

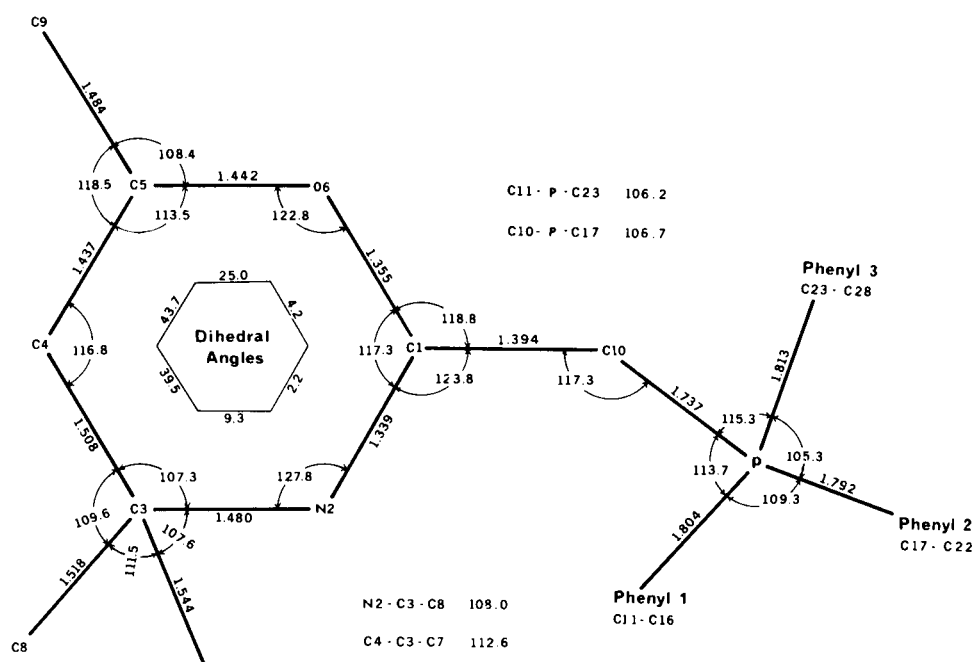


Figure 1. Schematic Drawing of the Oxazinyli Moiety With Bond Distances, Bond Angles and Dihedral Angles Indicated.

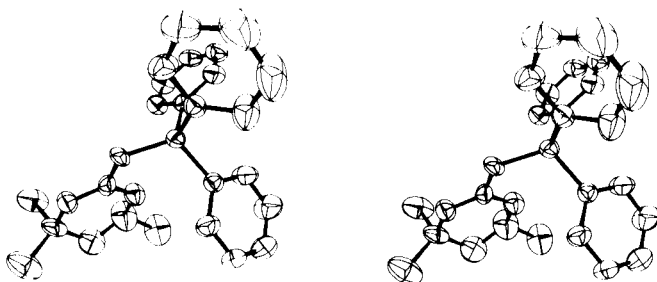


Figure 2. ORTEP Stereodrawing of the Entire Organic Moiety.

function and refined isotropically to  $R = 0.47$ . A subsequent electron density map phased by these two atoms was used to locate 23 other atoms within the structure. These 25 atoms were refined isotropically by a block-diagonal least-squares program, using  $\sigma^2$  weights, to  $R = 0.24$ . A second electron density map was calculated at this stage and clearly indicated the anticipated 30 atoms plus an additional isolated peak subsequently assumed to belong to a water molecule.

Similar least-squares refinements, first isotropically and then anisotropically reduced the value of the residual factor to  $R = 0.08$ . A difference map, phased by all of these atoms was calculated in an attempt to locate the hydrogen atoms. All of the anticipated hydrogen atoms (with the exception of that to be found on C10) showed

up clearly at essentially the expected locations. After calculating a position for the hydrogen on C10, least-squares refinement was again initiated with the coordinates of *all* atoms being allowed to vary, non-hydrogens having variable anisotropic temperature factors and the hydrogen atoms having fixed isotropic factors with a value of  $4.0 \text{ \AA}^2$ .

Convergence was assumed and refinement was terminated when the shifts of all parameters were less than one-tenth of their respective estimated standard deviations. The final value of the reliability index was  $R = 0.05_3$ .

#### Results and Discussion.

The final coordinates and temperature factors are tabulated in Table I with estimated standard deviations given in parentheses. Figure 1 is a schematic drawing of the molecule showing bond distances, bond angles and dihedral angles within the oxazine moiety. Figure 2 is an ORTEP stereoview of the molecule. The estimated standard deviations for C-C bonds are less than  $0.015 \text{ \AA}$  and for C-C-C angles they are less than  $0.7^\circ$ .

The reliability of the structure determination can be gauged from the triphenyl phosphine moiety. The C-C distances, averaged over the three phenyl rings, is  $1.38_2 \pm 0.007 \text{ \AA}$  and the C-C-C angles average to  $120.0 \pm 1.0^\circ$  as compared to the literature (3) values of  $1.396 \text{ \AA}$  and  $120.0^\circ$ , respectively. The presumed planarity of each phenyl ring can also be compared to the ESD values obtained by a best least-squares plane fit. The first ring (C11-C16) has an ESD value of  $0.008 \text{ \AA}$  whereas the

TABLE I

Fractional Coordinates and Thermal Parameters  
(Anisotropic Thermal Parameters  $\times 10^4$ , Estimated Standard Deviations in Parentheses Refer to Last Decimal Place)

Atom	X	Y	Z	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Cl	0.7437( 3)	0.6030( 2)	0.4377( 1)	337( 6)	70( 2)	59( 1)	-4( 3)	89( 3)	0( 1)
P	0.9736( 2)	0.4770( 1)	0.2235( 1)	97( 3)	29( 1)	26( 1)	4( 2)	27( 1)	0( 1)
O6	1.2897( 5)	0.4001( 3)	0.3012( 3)	115( 9)	55( 3)	36( 2)	16( 5)	31( 4)	4( 2)
N2	1.3309( 6)	0.3700( 3)	0.4251( 3)	145(12)	42( 4)	29( 3)	4( 5)	28( 5)	5( 3)
C1	1.2351( 8)	0.4034( 4)	0.3510( 4)	157(15)	31( 4)	22( 3)	-19( 7)	31( 6)	-2( 3)
C3	1.4944( 8)	0.3318( 4)	0.4613( 4)	116(15)	34( 4)	45( 4)	25( 7)	13( 7)	11( 4)
C4	1.5137( 9)	0.3081( 5)	0.3930( 5)	153(18)	79( 6)	61( 5)	40( 9)	41( 8)	6( 5)
C5	1.4484( 9)	0.3679( 6)	0.3266( 5)	169(18)	119( 8)	63( 5)	73(10)	55( 8)	14( 5)
C7	1.6193( 8)	0.4002( 5)	0.5187( 5)	133(16)	56( 6)	63( 5)	-1( 8)	-9( 8)	1( 4)
C8	1.5027(10)	0.2503( 5)	0.5067( 5)	186(18)	64( 6)	74( 5)	14( 9)	22( 8)	28( 5)
C9	1.4465( 9)	0.3422( 6)	0.2538( 5)	208(21)	133( 8)	76( 5)	65(11)	99( 9)	10( 6)
C10	1.0841( 7)	0.4406( 4)	0.3227( 4)	76(13)	31( 4)	25( 3)	17( 6)	8( 5)	5( 3)
C11	0.9679( 7)	0.4008( 4)	0.1527( 4)	107(13)	32( 4)	29( 3)	1( 6)	27( 6)	1( 3)
C12	0.9644( 9)	0.4280( 5)	0.0845( 4)	299(21)	35( 5)	49( 4)	13( 8)	84( 8)	2( 4)
C13	0.9697(10)	0.3671( 5)	0.0345( 4)	393(25)	62( 6)	51( 5)	10(10)	111( 9)	-3( 4)
C14	0.9796( 9)	0.2797( 5)	0.0507( 4)	279(21)	52( 5)	49( 5)	8( 9)	65( 9)	-14( 4)
C15	0.9806( 9)	0.2539( 4)	0.1174( 4)	215(19)	29( 4)	46( 4)	-1( 7)	37( 8)	-7( 4)
C16	0.9731( 8)	0.3127( 4)	0.1673( 4)	182(17)	32( 4)	39( 4)	-11( 7)	46( 7)	-4( 3)
C17	0.7709( 7)	0.4966( 4)	0.1978( 4)	113(14)	31( 4)	28( 3)	-1( 6)	25( 6)	1( 3)
C18	0.6373( 8)	0.4721( 5)	0.1229( 4)	125(15)	93( 6)	36( 4)	5( 8)	34( 7)	-8( 4)
C19	0.4819( 8)	0.4943( 6)	0.1006( 4)	103(16)	139( 8)	46( 4)	-1(10)	18( 7)	-12( 5)
C20	0.4576( 9)	0.5414( 6)	0.1520( 5)	156(17)	102( 8)	62( 5)	31( 9)	56( 8)	8( 5)
C21	0.5880( 9)	0.5646( 5)	0.2266( 5)	184(18)	74( 6)	63( 5)	29( 9)	69( 8)	-2( 5)
C22	0.7440( 8)	0.5428( 4)	0.2492( 4)	140(15)	51( 5)	45( 4)	10( 7)	46( 7)	-7( 4)
C23	1.0406( 7)	0.4794( 4)	0.2060( 4)	106(13)	30( 4)	27( 3)	1( 6)	30( 6)	-1( 3)
C24	1.2000( 8)	0.6036( 4)	0.2552( 4)	135(15)	35( 4)	41( 4)	-7( 7)	32( 6)	3( 4)
C25	1.2498( 8)	0.6818( 5)	0.2404( 4)	165(17)	47( 5)	60( 5)	-19( 8)	56( 8)	1( 4)
C26	1.1437( 9)	0.7381( 4)	0.1791( 4)	215(19)	34( 5)	59( 5)	11( 7)	77( 8)	8( 4)
C27	0.9822( 8)	0.7128( 4)	0.1308( 4)	212(18)	39( 5)	44( 4)	26( 7)	63( 8)	13( 4)
C28	0.9311( 8)	0.6341( 4)	0.1446( 4)	153(16)	36( 4)	43( 4)	5( 7)	43( 7)	2( 4)
W	0.8824( 6)	0.4169( 3)	0.4257( 3)	311(14)	62( 4)	69( 3)	-32( 6)	84( 6)	-22( 3)
H2	1.2823(56)	0.3757(32)	0.4535(28)	4.0( 0)					
H4	1.3987(58)	0.2616(32)	0.3481(29)	4.0( 0)					
H4'	1.6332(57)	0.2988(33)	0.4089(28)	4.0( 0)					
H5	1.5515(56)	0.4195(32)	0.3694(28)	4.0( 0)					
H7	1.6148(56)	0.4586(32)	0.4805(28)	4.0( 0)					
H7'	1.5868(56)	0.4031(32)	0.5667(28)	4.0( 0)					
H7''	1.7254(57)	0.3785(32)	0.5409(28)	4.0( 0)					
H8	1.4727(58)	0.2656(32)	0.5500(29)	4.0( 0)					
H8'	1.6250(57)	0.2224(33)	0.5319(28)	4.0( 0)					
H8''	1.4166(56)	0.2162(32)	0.4591(28)	4.0( 0)					

H9	1.5674(56)	0.3229(32)	0.2662(28)	4.0( 0)
H9'	1.3910(55)	0.3837(33)	0.2096(28)	4.0( 0)
H9''	1.3410(58)	0.3046(32)	0.2337(28)	4.0( 0)
H12	0.9674(57)	0.4885(32)	0.0756(28)	4.0( 0)
H13	0.9591(57)	0.3836(32)	-0.0128(29)	4.0( 0)
H14	0.9678(59)	0.2287(33)	0.0039(30)	4.0( 0)
H15	0.9867(58)	0.1926(32)	0.1268(28)	4.0( 0)
H16	0.9632(58)	0.3021(32)	0.2148(28)	4.0( 0)
H18	0.6570(57)	0.4332(32)	0.0855(28)	4.0( 0)
H19	0.3841(57)	0.4696(33)	0.0495(28)	4.0( 0)
H20	0.3211(57)	0.5596(32)	0.1346(28)	4.0( 0)
H21	0.5758(55)	0.5947(33)	0.2667(28)	4.0( 0)
H22	0.8454(57)	0.5539(32)	0.3088(28)	4.0( 0)
H24	1.2704(57)	0.5611(32)	0.2953(28)	4.0( 0)
H25	1.3527(58)	0.7066(32)	0.2762(29)	4.0( 0)
H26	1.1625(57)	0.8126(32)	0.1566(28)	4.0( 0)
H27	0.9147(58)	0.7555(32)	0.0844(29)	4.0( 0)
H28	0.8183(56)	0.6173(32)	0.1124(28)	4.0( 0)

(a) Anisotropic temperature factors of the form:  $\exp[-\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl]$ . Hydrogen atoms have fixed isotropic temperature factors of  $4.0 \text{ \AA}^2$ .

second (C17-C22) and the third (C23-C28) phenyl rings each have ESD values of  $0.006 \text{ \AA}$ .

The three P-C distances of 1.804, 1.792 and 1.813  $\text{\AA}$  average to  $1.813 \pm 0.007 \text{ \AA}$  in agreement with values for the corresponding distance in other phosphonium derivatives (4,5,6). The C-P-C angles average to  $109.4 \pm 0.4^\circ$ , characteristic of tetrahedrally hybridized phosphorus. The significant shortening of the fourth P-C distance (1.737  $\text{\AA}$  for C10-P), which is only slightly longer than the 1.661  $\text{\AA}$  value for C=P previously quoted (7), together with the opened angles at the phosphorus (C10-P-C11 =  $113.7^\circ$ ) and (C10-P-C23 =  $115.3^\circ$ ) suggests partial hybridization of the phosphorus to accommodate a C10-P bond order greater than one. The delocalization involves a number of additional bonds. Thus, the C1-N2 bond of 1.339  $\text{\AA}$ , typical of CN bond distances found in amide systems (8,9), is considerably shorter than the N2-C3 of 1.480  $\text{\AA}$  which closely approximates a paraffinic CN single bond. Again, the C1-O6 distance of 1.355  $\text{\AA}$  is intermediate between the carbonyl double bond distance of 1.23  $\text{\AA}$  and the aliphatic single bond CO distance of 1.43  $\text{\AA}$ . This C-O distance most closely resembles the 1.36  $\text{\AA}$  found in carboxylic acids. Finally, the C1-C10 distance of 1.394  $\text{\AA}$  is essentially the same as the corresponding distance in benzene.

The bond angles and dihedral angles at each of these sites further supports this reasoning. (See Figure 1 for both). The bond angles at C1, N2 and C10 are  $117.3^\circ$ ,

$127.8^\circ$ ,  $122.8^\circ$ , respectively, while the small dihedral angles (10) about each of these bonds (4.2, 2.2,  $9.3^\circ$ ) compared to the larger dihedral angles in the C3, C4, C5 region of the ring ( $39.5$ ,  $43.7$ ,  $25.0^\circ$ , respectively) suggest a geometry for the oxazine ring where the ring atoms except for C4 and C5 are in the same plane. A series of least-squares best planes calculations verify this. In addition C1, N2, C3, O6, C10 are planar within an ESD of 0.01  $\text{\AA}$ . The phosphorus atom lies only slightly out of this plane since the dihedral angle between the plane above and the plane formed by C1, C10, P is only  $2^\circ$ .

There are three contact distances between non-hydrogen atoms which are less than 3.25  $\text{\AA}$ . Two of these are with waters of hydration: C1-W(x,y,z) 3.24  $\text{\AA}$  and C1-S(2.0-x, 1.0-y, 1.0-z) 3.18  $\text{\AA}$ ; the third contact distance is between the chlorine and nitrogen (2.0-x, 1.0-y, 1.0-z) 3.20  $\text{\AA}$  and lends itself to the argument of a quaternary nitrogen.

One can conclude then, that the double bond appears to be delocalized through a major part of the oxazinyl system with the primary region of delocalization being in the C1-N2-C10 region. The C1-N2, C1-C10 bond lengths; the bond angles and dihedral angles within the heterocyclic ring and the close C-N contact distance all support these arguments.

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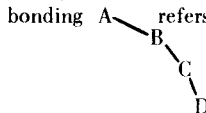
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"BCD") which have atoms B and C in common.