

The Crystal and Molecular Structure of 3,5-Di-(*t*-Butyl)-1-phenylphosphoryl-4-aza-2,5-cyclohexadiene

Lynn Hungerford and L. M. Trefonas

Department of Chemistry, Louisiana State University in New Orleans, New Orleans, Louisiana 70122

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The crystal and molecular structure of the title compound ($C_{18}H_{26}NOP$) has been determined by a single crystal, x-ray diffraction study using $Cu-K\alpha$ radiation. The compound was found to crystallize in the orthorhombic space group $Pnma$ with unit cell constants $a = 12.686 \pm .001 \text{ \AA}$, $b = 14.776 \pm .001 \text{ \AA}$, and $c = 9.540 \pm .001 \text{ \AA}$. The structure was solved by the heavy atom method and refined by block-diagonal least-squares to a final $R = 0.09$, for the 696 statistically significant reflections. The compound exhibits orientational disorder in the crystalline state. Nevertheless, the planarity of this ring; the lengthening of the diene carbon-carbon bond to 1.41 \AA ; the resultant shortening of both the carbon-nitrogen bond (1.43 \AA) and the carbon-phosphorus bond (1.74 \AA), and the CNC bond angle of 121° all strongly support the assumption of delocalization of the diene π -electrons within the heterocyclic ring system.

Introduction.

The existence, nature and extent of π -electron delocalization in phosphonitrilic systems has been a matter of some controversy (1,2,3). Early attempts designed to explore this possibility proved rather unsuccessful (4,5). Anomalous ^{31}P nmr shifts on phosphoniacyclohexadiene systems (3) led to the conjecture that one or more of these systems did indeed have extensive delocalization. Subsequent structure determinations of two compounds within these systems (6,7) showed instead a completely localized diene system. With the availability of an analogous heterocyclic system in which the hetero atoms were phosphorus and nitrogen rather than two phosphorus atoms, the question of delocalization again assumed significance. Consequently, the structure of the title compound (I) was undertaken.

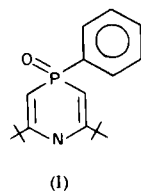


Figure 1

EXPERIMENTAL

A sample of the title compound, kindly furnished by Professor Adam Aguiar, Tulane University (8), was recrystallized from methanol. A crystal with dimensions .09 x .11 x .16 mm was

mounted on a General Electric XRD-5 diffractometer. Extinctions of $k + l = 2n + 1$ for the $(Ok\bar{l})$ reflections, and $h = 2n + 1$ for the $(hk0)$ reflections were consistent with either space groups $Pnma$ or $Pna2_1$. Statistical tests supported the higher space group ($Pnma$) and the ultimate solution of the structure confirmed this choice. Lattice constants were determined by a least-squares fit of 29 carefully measured two-theta values of the $Cu K\alpha_1 - K\alpha_2$ doublet for $2\theta > 70^\circ$ (1° take-off angle and 0.05° slit). The resultant lattice constants and their estimated standard deviations are:

$$\begin{aligned} a &= 12.686 \pm 0.001 \text{ \AA} \\ b &= 14.776 \pm 0.001 \text{ \AA} \\ c &= 9.540 \pm 0.001 \text{ \AA} \end{aligned}$$

The calculated density of 1.02 gm/cc for 4 molecules per unit cell is in agreement with the experimentally determined density of 1.08 gm/cc using flotation techniques.

Intensity data were collected on a General Electric XRD-490 automated diffractometer using the stationary crystal, stationary counter method, balanced Ni and Co filters, and copper $K\alpha$ radiation. A total of 696 reflections were considered observed by the criterion:

$(I_{Ni} - 2\sigma(I_{Ni})) - (I_{Co} + 2\sigma(I_{Co})) > 200$ counts, where σ 's are based entirely on counting statistics. The intensities were converted into structure amplitudes after being corrected for absorption as a function of ϕ , for $K\alpha_1 - K\alpha_2$ splitting, and for Lorentz-polarization effects.

Structure Determination.

The coordinates of the phosphorus atom were located from a three-dimensional Patterson function. Alternating least-squares and Fourier maps, initially in space group $Pnma$, were used to locate all non-hydrogen atoms. Block diagonal isotropic refinement using $1/\sigma^2$ weights terminated at a value of $R = 0.11$, (9). The structure at this stage appeared chemically reasonable although possessing a benzene ring (in the mirror plane) whose

distances and angles varied significantly from those normally assumed.

The lower space group ($Pna2_1$) was then tried, using the final parameters and their generated equivalents, as a trial structure. Ten cycles of block-diagonal least-squares led to a value of $R = 0.14_6$ and to a structure whose features throughout were chemically non-reasonable. The remaining alternative was to go back to the higher space group ($Pnma$) and test a variety of disordered structures which differed primarily in the assumption of the amount of disordering to be expected in the benzene ring. The structure which behaved most reasonably crystallographically also was the structure which conformed most closely to the prejudices of a chemist. In this structure, the carbon attached to the phosphorus atom (C1) and the carbon para to this (C4) were assumed to lie in the mirror plane, with the benzene ring then rotated about 20° out of the mirror plane about the axis formed by a line connecting C1-C4.

After conversion to anisotropic temperature factors and further least-squares refinement, a difference Fourier map was calculated. Positive regions with electron densities up to $0.5 e/\text{\AA}^3$ were found which corresponded well with the anticipated positions of hydrogen atoms which were previously calculated by assuming the usual chemical bonding at each location. A final series of refinements were carried out in which the non-hydrogen atoms were allowed to refine anisotropically while only the coordinates of the isotropic hydrogen atoms were refined. Refinements culminated in a value of $R = 0.09_9$ and were considered complete when the maximum shifts in both coordinates and temperature factors were less than one-tenth the estimated standard deviation of the respective variable.

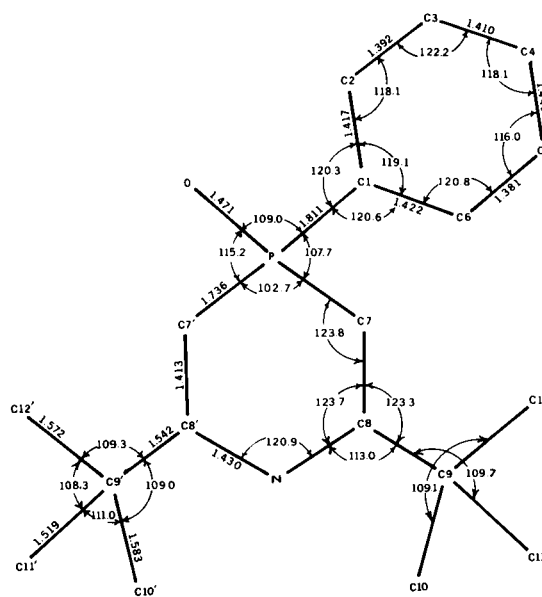


Figure 2. Schematic drawing of the molecule with bond distances and angles indicated.

TABLE I

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

Atom									
P	0.3420(4)	0.2500(0)	0.4625(6)	42(3)	27(2)	85(7)	0(0)	1(6)	0(0)
Ox	0.4510(9)	0.2500(0)	0.4093(13)	50(10)	91(10)	121(22)	0(0)	0(13)	0(0)
N	0.1338(10)	0.2500(0)	0.2757(14)	72(13)	17(6)	97(23)	0(0)	40(15)	0(0)
Cl	0.3466(14)	0.2500(0)	0.6514(18)	76(16)	30(10)	96(28)	0(0)	6(21)	0(0)
C2	0.4462(15)	0.2417(12)	0.7218(22)	60(16)	43(37)	101(34)	-26(47)	-18(21)	34(68)
C3	0.4453(15)	0.2659(47)	0.8717(22)	63(16)	12(41)	131(36)	7(17)	-8(21)	2(24)
C4	0.3498(15)	0.2500(0)	0.9466(21)	131(21)	52(12)	101(30)	0(0)	-12(27)	0(0)
C5	0.2500(16)	0.2367(07)	0.8735(21)	72(17)	18(68)	107(33)	9(26)	-10(20)	-8(34)
C6	0.2501(15)	0.2593(88)	0.7297(22)	38(15)	75(84)	94(32)	-26(58)	-4(20)	26(71)
C7	0.2657(8)	0.3419(8)	0.4109(12)	53(10)	54(8)	70(19)	-6(8)	-8(12)	5(11)
C8	0.1763(8)	0.3343(8)	0.3233(12)	70(11)	40(7)	98(20)	-3(8)	34(13)	0(11)
C9	0.1158(9)	0.4169(7)	0.2652(14)	70(11)	15(6)	159(22)	9(7)	5(14)	8(12)
C10	-0.0014(9)	0.4133(9)	0.3205(13)	43(9)	72(10)	153(25)	16(9)	28(14)	7(14)
C11	0.1195(9)	0.4162(9)	0.1041(13)	79(12)	73(10)	75(19)	11(10)	2(13)	25(12)
C12	0.1692(10)	0.5060(8)	0.3204(15)	101(13)	32(7)	236(30)	-5(9)	-44(18)	-8(14)

(a) Anisotropic temperature factors of the form:

$$\exp[-\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl]$$

TABLE II
Refined Hydrogen Coordinates
(Isotropic Temperature Factors Fixed at 4.0 Å²)

Atom (a)	X	Y	Z
H2	0.514	0.245	0.668
H3	0.511	0.218	0.923
H4	0.351	0.269	1.047
H5	0.186	0.213	0.921
H6	0.186	0.288	0.684
H7	0.286	0.403	0.445

(a) Numbers refer to bonding atom.

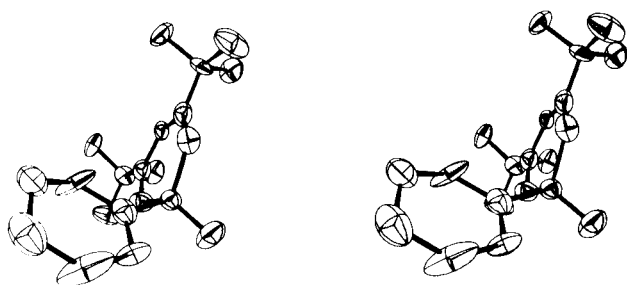


Figure 3. ORTEP drawing of the molecule.

Results and Discussion.

Table I lists the final coordinates and anisotropic temperature factors for the non-hydrogen atoms. Table II lists the refined hydrogen coordinates. Figure II is a schematic drawing of the molecule with the bond angles and bond distances indicated on the drawing. Primarily as a result of the disordering, the estimated standard deviations (ESD) are somewhat larger than would have been anticipated. Thus, distances and angles involving the phosphorus have ESD values of 0.01 Å and 1.5°, respectively. All other bond distances and bond angles have ESD values less than 0.02 Å and 2°, respectively.

The phenyl ring, which is the site of the orientational disordering, can serve to define the lower limits of the accuracy of the structure since its molecular parameters in an ordered structure are known quite well. The C-C distances in the phenyl ring average 1.41 Å and the internal angles average to 119°. Both values closely approximate the literature values (10) of 1.397 Å, 120°, respectively, within one ESD although the values for the angles have a range of ± 2 ESD. The refined phenyl

hydrogens result in a CH average distance of 1.04 Å (somewhat longer than would be anticipated) and HCC average angles of 120°.

The remaining predictable features: the *t*-butyl group and the P = O; display both distances and angles in accord with those found in analogous structures.

The unique feature of this structure and the focus of interest in this study is the 1-aza, 4-phospha ring. The diene character of this ring system has been dramatically altered. The P-C distance of 1.74 Å is significantly shorter than the range of values (1.78-1.82 Å) found in previous studies (6,7) or even by comparison to the P-C distance of 1.81 Å external to this ring system found in this study. Similarly, the C-N distance of 1.43 Å is shorter than the usual C-N single bond distance of 1.48 Å (10). The C-C double bond on the other hand has been lengthened from the expected value of 1.33 Å to a value of 1.41 Å. All of these distances support the concept of extensive delocalization within the ring. The internal angles in the ring (CNC = 121°; NCC and CCP = 124°; CPC = 103°) lend further credence to this concept with the exception of the CPC angle. The phosphorus atom lies slightly out of the best least-squares plane for this ring and, in large part, accounts for this best plane having an ESD value of 0.03 Å. An ORTEP drawing (Figure 3) of the molecule more clearly indicates the conformation. An intermolecular scan of the contents of the unit cell shows only one close contact. This distance of 2.91 Å between the nitrogen of one molecule and the oxygen of another molecule (related by $x - \frac{1}{2}, y, \frac{1}{2} - z$) is strongly suggestive of hydrogen bonding. However, it seems unlikely in view of the overall pattern (distances and angles) that the previous conclusions regarding partial delocalization are compromised by this one close contact.

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