The large amplitudes of thermal motion and the size of the molecule with the attendant complexity of possible vibrations, librations, and other motions would make any detailed discussion of the thermal motion somewhat pretentious. Since the accuracy of these parameters is quite low, we have not quoted the individual values but have given only the root-mean-square displacements in Table II. There are significant anisotropies, and the amplitudes of motion are in general larger as the distance from the P atom increases.

The intermolecular packing is apparently determined entirely by interactions between carbon atoms or the hydrogens attached to them. There are six independent distances less than 4.0 A between carbon atoms of phenanthrene groups in adjacent molecules: 3.55, 3.73, 3.77, 3.78, 3.79, 3.87. There are two such distances between carbon atoms of isopropyl groups: 3.86, 3.90. The remaining eleven distances are between phenanthrene carbon and isopropyl carbon: 3.50, 3.72, 3.72, 3.75, 3.75, 3.76, 3.89, 3.89, 3.94, 3.95, 3.97. There is nothing singular to be noted about these distances. Any detailed discussion of the intermolecular forces would require knowledge of the hydrogen-atom positions—which were not determined.

The intramolecular nonbonded distances are normal except for the four short distances between oxygen atoms and the central carbon atom of neighboring isopropyl groups. These are (in A) O_2–C_{31}, 2.804; O_1–C_{41}, 2.695; O_4–C_{31}, 2.960; O_3–C_{51}, 2.700. This represents what must be an extreme overcrowding of the molecule, a factor which perhaps explains the relative instability of these kinds of molecules and perhaps the advantage derived from having a five-membered ring involving two of the oxygen atoms which may minimize such interactions. Intramolecular overcrowding might be, at least partially, responsible for the differences in molecular structure observed among adducts of phenanthrenequinone with tris(dialkylamino)phosphines, for example, V and VI.

Crystal and Molecular Structures of Pentacoordinated Group V Compounds. II. 2,2,2-Triisopropoxy-4,5-(2′,2″-biphenyleno)-1,3,2-dioxaphospholene. Monoclinic[1a]

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Abstract: The crystal and molecular structures of the monoclinic allotrope of the phenanthrenequinone–triisopropyl phosphite 1:1 adduct have been determined by single crystal X-ray diffraction techniques. The space group is $P2_1/c$ with four molecules in a unit cell of dimensions $a = 25.997 \pm 0.001$ A, $b = 8.894 \pm 0.001$ A, $c = 9.880 \pm 0.001$ A, and $\beta = 94.25 \pm 0.01°$. The final R factor for 2183 independent reflections is 0.109. The molecular structure is a trigonal bipyramid of oxygen atoms around the phosphorus with two isopropoxy groups in equatorial positions and one in an apical position. The phenanthrenequinone moiety bridges one apical and one equatorial position, thereby forming a C_2O_2P five-membered ring. The apical P–O bonds show the lengthening (relative to the equatorial bonds) commonly observed in PX_5 structures. In addition, P–O bonds in the five-membered ring are further lengthened, an effect that can be attributed to molecular π bonding.

A preliminary account of the molecular and crystal structures of the phenanthrenequinone–triisopropyl phosphite 1:1 adduct (PQTP), orthorhombic form, has been given.[2] A fuller account of this work including details of the preparative chemistry is in paper I of this series.[3] This paper reports the results of a single crystal X-ray investigation of a second crystal modification of this species. Although the work reported in paper I established the molecular geometry in the compound beyond any doubt, the present study has resulted in bond lengths of much greater accuracy. The crystal data show a monoclinic form of probable space group $P2_1/c$; $a = 25.997 \pm 0.001$ A, $b = 8.894 \pm 0.001$ A, $c = 9.880 \pm 0.001$ A, $\beta = 94.25 \pm 0.01°$, $\rho_{\text{X-ray}} = 1.213$ g cm^{-3}.

Experimental Section

A suitable crystal prepared as described in I was ground into a sphere of diameter 0.432 mm and mounted in a Lindemann glass capillary; the intensities of 2817 reflections were measured on the automatic single crystal X-ray diffractometer PAILRED[4] using monochromatized copper Kα radiation. The following reciprocal lattice layers were investigated: $hk0$, $hk\bar{1}$, $hk\bar{2}$, $hk\bar{3}$, $hk\bar{4}$, $hk\bar{5}$, $hk\bar{6}$, $hk\bar{7}$, $0kl$, $2kl$, $3kl$, $4kl$, and $5kl$. Structure factors were derived in the usual way by application of Lorentz and polarization factors and an absorption correction. The absorption correction was calculated by the expression

$$A = K_0 + K_1\theta + K_2\theta^2 + K_3\theta^3$$

where the expansion coefficients K_i were obtained from a least-squares fit to values tabulated for a spherical specimen.[5] The observed intensities were placed on approximate absolute scales by Wilson's method[6] and the resulting 14 scale factors reduced to a

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[1] (a) This work supported in part by the U. S. Atomic Energy Commission; (b) Brookhaven National Laboratory; (c) Philips Laboratories.

[2] W. C. Hamilton, S. J. LaPlaca, and C. P. Smith, *J. Am. Chem. Soc.*, 87, 127 (1965).

[3] Paper I: W. C. Hamilton, S. J. LaPlaca, F. Ramirez, and C. P. Smith, *ibid.*, 89, 2268 (1967).

[4] See, for example, J. Ladell, *Trans. Am. Cryst. Assoc.*, 1, 86 (1965).

[5] "International Tables for X-Ray Crystallography," Vol. II, The Kynoch Press, Birmingham, 1959.

[6] A. J. C. Wilson, *Nature*, 150, 152 (1942).

Table I. Observed (FO) and Calculated (FC) Structure Amplitudes (×10) for Monoclinic Phenanthrenequinone–Triisopropyl Phosphite 1:1 Adduct

H	K	L	FO	FC
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

single scale factor by a least-squares method.[7] At this point all duplicate and symmetrically equivalent reflections were averaged, resulting in 2183 independent observations.

The structure was solved by location of the phosphorus atom from a three-dimensional Patterson function and by a series of difference electron density syntheses. In addition, the symbolic addition method was used for an independent determination of a trial structure (see Appendix). Both methods gave the same model.

Anisotropic temperature factors for each atom and a single scale factor were used in a series of least-squares refinements. The data were first weighted by the function

$$w = (\sigma^2 + 0.0009F^2)^{-1}$$

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[7] W. C. Hamilton, J. Rollett, and R. Sparks, *Acta Cryst.*, **18**, 129 (1965).

Table II. Positional and Thermal Parameters[a] in Monoclinic PQTIP

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
P	0.35646 (7)	0.17295 (18)	0.27456 (18)	0.00119 (3)	0.0092 (2)	0.0063 (2)	0.0005 (1)	0.0006 (1)	0.0004 (2)
O_1	0.40686 (19)	0.0783 (5)	0.2040 (5)	0.0014 (1)	0.0105 (6)	0.0063 (5)	0.0006 (2)	0.0006 (2)	0.0017 (5)
O_2	0.37326 (19)	0.0948 (5)	0.4202 (5)	0.0017 (1)	0.0111 (6)	0.0070 (6)	0.0016 (2)	0.0009 (2)	0.0008 (5)
O_3	0.31302 (18)	0.2690 (5)	0.3486 (5)	0.0013 (1)	0.0113 (6)	0.0111 (6)	0.0006 (2)	0.0015 (2)	−0.0002 (5)
O_4	0.31346 (18)	0.0904 (6)	0.1800 (5)	0.0011 (1)	0.0146 (7)	0.0092 (6)	0.0003 (2)	0.0000 (2)	−0.0021 (5)
O_5	0.38136 (18)	0.3181 (5)	0.2165 (5)	0.0016 (1)	0.0084 (6)	0.0116 (7)	0.0004 (2)	0.0008 (2)	0.0018 (5)
C_1	0.4306 (3)	−0.0185 (7)	0.2923 (7)	0.0013 (1)	0.0094 (8)	0.0069 (8)	0.0003 (3)	0.0008 (3)	0.0005 (6)
C_2	0.4138 (3)	−0.0128 (7)	0.4161 (7)	0.0013 (1)	0.0100 (9)	0.0073 (8)	−0.0002 (3)	0.0010 (3)	−0.0009 (7)
C_3	0.4313 (3)	−0.1002 (7)	0.5278 (7)	0.0013 (1)	0.0106 (8)	0.0062 (8)	−0.0010 (3)	0.0003 (3)	−0.0013 (7)
C_4	0.4109 (3)	−0.910 (9)	0.6574 (8)	0.0019 (1)	0.0143 (11)	0.0069 (8)	−0.0011 (3)	0.0003 (3)	0.0018 (8)
C_5	0.4301 (4)	−0.1830 (9)	0.7603 (8)	0.0022 (2)	0.0162 (12)	0.0084 (9)	−0.0005 (4)	0.0005 (3)	−0.0000 (9)
C_6	0.4707 (4)	−0.2810 (10)	0.7376 (9)	0.0022 (2)	0.0179 (14)	0.0122 (12)	−0.0011 (4)	−0.0007 (4)	0.0045 (10)
C_7	0.4916 (3)	−0.2916 (9)	0.6148 (8)	0.0020 (1)	0.0145 (11)	0.0092 10)	−0.0002 (3)	0.0001 (3)	0.0020 (8)
C_8	0.4729 (3)	−0.2015 (7)	0.5054 (7)	0.0016 (1)	0.0100 (9)	0.0078 (8)	−0.0003 (3)	−0.0000 (3)	0.0008 (7)
C_9	0.4935 (3)	−0.2084 (7)	0.3717 (7)	0.0014 (1)	0.0089 (8)	0.0083 (8)	−0.0001 (3)	0.0009 (3)	−0.0014 (7)
C_{10}	0.5351 (3)	−0.3009 (8)	0.3436 (9)	0.0019 (1)	0.0111 (10)	0.0141 (12)	0.0007 (3)	0.0007 (4)	0.0015 (9)
C_{11}	0.5519 (3)	−0.3105 (9)	0.2151 (10)	0.0022 (2)	0.0150 (13)	0.0146 (12)	0.0016 (4)	0.0033 (4)	0.0008 (10
C_{12}	0.5300 (3)	−0.2262 (9)	0.1085 (9)	0.0020 (2)	0.0139 (11)	0.0128 (11)	0.0001 (4)	0.0010 (4)	−0.0003 (10)
C_{13}	0.4879 (3)	−0.1300 (8)	0.1315 (8)	0.0015 (1)	0.0110 (9)	0.0101 (9)	−0.0001 (3)	0.0016 (3)	−0.0006 (7)
C_{14}	0.4714 (3)	−0.1202 (7)	0.2618 (7)	0.0010 (1)	0.0098 (8)	0.0069 (8)	−0.0007 (2)	0.0006 (3)	−0.0001 (6)
C_{31}	0.2741 (3)	0.1953 (9)	0.4245 (8)	0.0017 (1)	0.0166 (13)	0.0103 (10)	0.0010 (3)	0.0018 (3)	0.0026 (9)
C_{32}	0.2820 (5)	0.2418 (14)	0.5717 (10)	0.0033 (2)	0.0272 (20)	0.0113 (12)	0.0028 (6)	0.0026 (5)	0.0013 (13)
C_{33}	0.2221 (4)	0.2414 (17)	0.3596 (14)	0.0015 (2)	0.0388 (26)	0.0277 (22)	0.0030 (6)	0.0027 (5)	0.0113 (22)
C_{41}	0.3185 (3)	−0.0212 (8)	0.0737 (8)	0.0019 (2)	0.0124 (10)	0.0103 (10)	−0.0005 (3)	0.0004 (3)	−0.0043 (8)
C_{42}	0.2678 (5)	−0.1067 (15)	0.0640 (12)	0.0024 (2)	0.0319 (23)	0.0199 (17)	−0.0047 (6)	0.0011 (5)	−0.0094 (17)
C_{43}	0.3300 (4)	0.0588 (12)	−0.0580 (9)	0.0028 (2)	0.0262 (19)	0.0095 (11)	−0.0000 (5)	0.0022 (4)	−0.0019 (12)
C_{51}	0.3592 (3)	0.4709 (8)	0.2069 (9)	0.0021 (2)	0.0088 (9)	0.0144 (12)	0.0006 (3)	0.0017 (4)	0.0015 (8)
C_{52}	0.3757 (5)	0.5586 (11)	0.3333 (13)	0.0032 (3)	0.0138 (13)	0.0248 (20)	0.0000 (5)	−0.0003 (6)	−0.0069 (14)
C_{53}	0.3813 (5)	0.5355 (10)	0.0774 (13)	0.0036 (3)	0.0140 (13)	0.0259 (20)	0.0019 (5)	0.0043 (6)	0.0077 (13)

[a] Thermal parameters are those in the expression $\exp\{-\Sigma_{i,j}\beta_{ij}h_ih_j\}$. Estimated standard deviations in parentheses.

where σ is the estimated variance of F^2 based on the Poisson counting statistics. An analysis of variance with the reflections sorted into intensity classes indicated that this weighting scheme still assigned too much weight to the more intense reflections. The final weighting scheme was chosen so that the mean value of $w\Delta(F^2)$ was independent of the intensity class. This weighting scheme resulted in substantially improved estimated standard deviations on the parameters and to a final value of

$$R = \frac{\Sigma||F_o| - |F_c||}{\Sigma|F_o|} = 0.109$$

Since the least-squares program used did not permit simultaneous refinement of the 262 parameters, the final refinement consisted of alternating cycles of refinement of partial parameter sets as shown in tabular form below.

Cycle	Parameters refined
N-3	14 atoms in phenanthrene ring (all parameters) + scale
N-2	15 other atoms (all parameters) + scale
N-1	6 × 29 thermal parameters
N	3 × 29 position parameters + scale

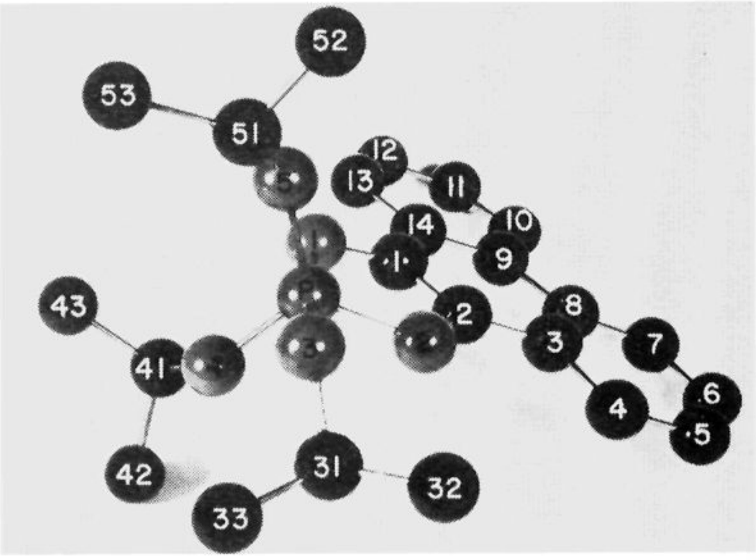

Figure 1. Molecular structure of phenanthrenequinone–triisopropyl phosphite 1:1 adduct. The numbering of the atoms corresponds to that in the tables and is not an official numbering.

The standard deviations on the parameters given in the next section are those estimated by the usual methods[8] from the least-squares refinements on cycles N and N-1. These will be underestimates of the marginal standard deviations if there is any correlation between the two parameter sets refined as blocks. Various considerations suggested that conservative estimates of the marginal standard deviations in the derived bond lengths and angles could be taken as 1.5 times those estimated from the least-squares refinement, and the errors for the *derived* functions in the following sections include this factor of 1.5. The error estimates obtained in this way for the C–C bond lengths in the isopropoxy groups are in agreement with those obtained by considering the agreement between the six such distances which should be equal.

A final difference Fourier synthesis ($\rho_o - \rho_c$) was calculated. The maximum electron density in this synthesis was less than 0.5 A^{-3}, showing that only hydrogen atoms remained to be located. No serious attempt was made to determine the hydrogen positions.

The observed and calculated structure factors are given in Table I.

Description of the Structure

The final positional and thermal parameters are given in Table II with the least-squares estimates of their standard deviations. A model of the molecule is shown in Figure 1.[9] Tables III–VI present the bond distances and angles for the monoclinic crystal. The precision and general quality of the data are better for the monoclinic form, and these should be taken in preference to those for the orthorhombic crystal as the standard values for this compound. It should be noted, however, that there are no differences between the two which the authors consider to be significant.

(8) W. C. Hamilton, "Statistics in Physical Science," The Ronald Press Co., New York, N. Y., 1964.

(9) A standard numbering system is not used. The IUC name of the compound is 2,2,2-triisopropoxy-4,5-(2′,2′′-biphenylene)-1,3,2-dioxaphospholene.

Trigonal Bipyramid. Distances and angles in the trigonal bipyramid are given in Table III. The phosphorus atom lies almost exactly at the center of the equatorial plane of the trigonal bipyramid composed of the five oxygen atoms covalently bound to the phosphorus. As the bond angles indicate, the distortions from ideal O–P–O angles of 90 and 120° are slight. Two of the isopropoxy groups are bound to phosphorus equatorial positions, and one is in an apical position. The P–O bond lengths show large differences which are well outside the limits of experimental error and which depend in a systematic way on the position of the bond in the trigonal bipyramid. Of the three bonds in the equatorial plane, that which is also in the five-membered ring is 0.057 A longer than the average of the other two bond lengths. Similarly, the apical bond in the five-membered ring is longer than the other apical bond, which is in turn longer than the average length of the two equatorial bonds to isopropoxy oxygens. In short, the variation in bond lengths may be regarded as a superposition of two effects: the first, the tendency of apical bonds to be longer than equatorial bonds in pentacoordinated phosphorus compounds; and second, a lengthening of the bonds joining the phosphorus to the phenanthrene ring system. Possible explanations will be discussed in a following section.

Table III. Bond Lengths and Angles in PO_5 Trigonal Bipyramid

	Bond length, A	Bond length corrected for thermal motion, A	Bond angle, deg	
$P–O_1$	1.751 (7)	1.753 (7)	$O_1–P–O_2$	89.3 (3)
$P–O_2$	1.633 (7)	1.641 (7)	$O_3–P–O_2$	88.6 (4)
$P–O_3$	1.638 (6)	1.649 (7)	$O_3–P–O_4$	91.3 (4)
$P–O_4$	1.588 (8)	1.601 (8)	$O_3–P–O_5$	93.1 (5)
$P–O_5$	1.574 (7)	1.586 (7)	$O_2–P–O_4$	117.2 (4)
			$O_4–P–O_5$	117.2 (4)
			$O_5–P–O_2$	125.5 (4)

Five-Membered Ring. The phenanthrenequinone moiety bridges an apical and an equatorial position, thus forming a PO_2C_2 five-membered ring. The bond lengths and angles are summarized in Table IV. The P–O bonds have been discussed. The C–C distance is short (1.33 A), and, although a correction for thermal motion might slightly increase this apparent bond length, it seems unlikely that it is much longer than the normal C=C double-bond length of 1.33 A. It is significantly shorter than the corresponding distance in phenanthrene itself, 1.37 A,[10] and in agreement with the observed rather high infrared frequency of 1650 cm^{-1} (I). This distance was also very short in the orthorhombic crystal.

Table IV. Bond Lengths and Angles in C_2PO_2 Five-Membered Ring

	Bond length, A		Bond angle, deg
$P–O_1$	1.751 (7)	$O_2–P–O_1$	89.3 (3)
$P–O_2$	1.633 (7)	$P–O_1–C_1$	111.9 (6)
$O_1–C_1$	1.347 (11)	$O_1–C_1–C_2$	113.9 (9)
$O_2–C_2$	1.433 (12)	$C_1–C_2–O_2$	110.3 (9)
$C_1–C_2$	1.333 (14)	$C_2–O_2–P$	114.2 (6)

Phenanthrene Ring. Distances and angles in the phenanthrene ring are given in Table V. The variation in bond distances shows a qualitative agreement with Trotter's results; however, the large standard deviations on the bond lengths in both studies make it difficult to attach much meaning to the differences. The phenanthrene ring, the phosphorus atom, and three oxygen atoms lie nearly in a single plane. The best least-squares plane through these atoms is given by

$$16.677x + 6.4125y + 2.1108z = 7.6559$$

where x, y, and z are the fractional coordinates of the atoms. The maximum distance from this plane is 0.07 A.

Table V. Bond Lengths and Angles in Phenanthrene Ring

	Bond length, A		Bond angle, deg
$C_1–C_2$	1.333 (14)	$C_1–C_2–C_3$	126.5 (9)
$C_2–C_3$	1.402 (15)	$C_2–C_3–C_8$	115.5 (9)
$C_3–C_4$	1.429 (16)	$C_8–C_3–C_4$	120.7 (10)
$C_4–C_5$	1.373 (16)	$C_3–C_4–C_5$	119.5 (12)
$C_5–C_6$	1.403 (19)	$C_4–C_5–C_6$	119.4 (12)
$C_6–C_7$	1.373 (18)	$C_5–C_6–C_7$	122.6 (12)
$C_7–C_8$	1.406 (15)	$C_6–C_7–C_8$	120.5 (12)
$C_8–C_3$	1.441 (15)	$C_7–C_8–C_3$	117.4 (10)
$C_8–C_9$	1.467 (15)	$C_3–C_8–C_9$	119.7 (9)
$C_9–C_{14}$	1.428 (14)	$C_8–C_9–C_{14}$	120.8 (9)
$C_9–C_{10}$	1.409 (15)	$C_9–C_{14}–C_1$	116.5 (9)
$C_{10}–C_{11}$	1.379 (15)	$C_{14}–C_1–C_2$	120.9 (9)
$C_{11}–C_{12}$	1.384 (19)	$C_{14}–C_9–C_{10}$	116.3 (9)
$C_{12}–C_{13}$	1.425 (19)	$C_9–C_{10}–C_{11}$	121.4 (11)
$C_{13}–C_{14}$	1.395 (17)	$C_{10}–C_{11}–C_{12}$	122.0 (11)
$C_{14}–C_1$	1.448 (15)	$C_{11}–C_{12}–C_{13}$	118.9 (11)
		$C_{12}–C_{13}–C_{14}$	118.7 (11)
		$C_{13}–C_{14}–C_9$	122.5 (10)

Isopropoxy Groups. Distances and angles in the isopropoxy groups are presented in Table VI and are normal.

Table VI. Bond Lengths and Angles in Isopropoxy Groups

	Bond length, A		Bond angle, deg
$C_{31}–O_3$	1.463 (13)	$C_{31}–O_3–P$	121.8 (6)
$C_{32}–C_{31}$	1.515 (21)	$C_{32}–C_{31}–O_3$	108.8 (11)
$C_{33}–C_{31}$	1.515 (19)	$C_{33}–C_{31}–O_3$	107.2 (10)
		$C_{32}–C_{31}–C_{33}$	112.8 (13)
$C_{41}–O_4$	1.461 (13)	$C_{41}–O_4–P$	129.9 (7)
		$C_{42}–C_{41}–O_4$	105.1 (11)
$C_{42}–C_{41}$	1.537 (19)	$C_{43}–C_{41}–O_4$	109.3 (9)
$C_{43}–C_{41}$	1.525 (18)	$C_{42}–C_{41}–C_{43}$	113.6 (12)
$C_{51}–O_5$	1.478 (12)	$C_{51}–O_5–P$	127.5 (7)
$C_{52}–C_{51}$	1.511 (20)	$C_{52}–C_{51}–O_5$	109.6 (10)
$C_{53}–C_{51}$	1.556 (19)	$C_{53}–C_{51}–O_5$	103.0 (9)
		$C_{52}–C_{51}–C_{53}$	113.1 (13)

Thermal Motion. Root-mean-square components of the thermal motion along principal axes of the vibrational ellipsoids are presented in Table VII. The errors quoted are those estimated from the least-squares refinement. A stereo view of the molecule is shown in Figure 2 in which these ellipsoids of thermal motion

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[10] J. Trotter, *Acta Cryst.*, **16**, 605 (1963).

Figure 2. The molecular structure of phenanthrenequinone–triisopropyl phosphite 1:1 adduct found in the monoclinic crystal. The equiprobability ellipsoids illustrate the thermal motion of the atoms. This is a stereo pair and may be viewed by a hand-held stereoscope. Note especially the large amplitudes of vibration for the end carbons of the isopropyl groups.

can be observed. In this view, the ellipsoid boundaries are drawn at 50% probability. The increased thermal motion at the extremities of the molecule is quite obvious. The motions are undoubtedly complex, and, although the accuracy here is high, no attempt will be made to give a detailed analysis of these motions.

Molecular Packing. A comparison of the packing in the two crystalline modifications of PQTP is shown in the stereo views of Figure 3 (monoclinic) and Figure 4 (orthorhombic). Both modifications exhibit alternating layers of phenanthrene rings and isopropyl groups. In the orthorhombic crystal the phenanthrene rings occur in perpendicular pairs, while in the monoclinic case the pairs are parallel with a separation between planes of about 3.5 A (agreeing well with Pauling's estimate of the half-thickness of an aromatic molecule of 1.85 A[11]). There are four intramolecular nonbonded oxygen–carbon distances less than 3 A (2.63, 2.70, 2.74, 2.86 A) which must represent a severe internal overcrowding of the molecule, as in the orthorhombic form.

Table VII. Rms Displacements (in A) along Principal Axes

Atom	Rmsd 1	Rmsd 2	Rmsd 3
P	0.166(3)	0.182(2)	0.216(2)
O_1	0.164(8)	0.198(6)	0.239(6)
O_2	0.170(8)	0.185(7)	0.272(7)
O_3	0.171(7)	0.218(6)	0.257(7)
O_4	0.196(7)	0.202(7)	0.254(6)
O_5	0.175(7)	0.221(7)	0.256(7)
C_1	0.172(13)	0.191(9)	0.228(9)
C_2	0.167(13)	0.197(9)	0.229(9)
C_3	0.166(11)	0.185(10)	0.241(9)
C_4	0.175(12)	0.226(10)	0.279(10)
C_5	0.203(12)	0.250(10)	0.281(10)
C_6	0.212(11)	0.247(11)	0.322(12)
C_7	0.203(11)	0.247(10)	0.267(10)
C_8	0.189(10)	0.203(10)	0.243(9)
C_9	0.175(10)	0.197(10)	0.236(10)
C_{10}	0.201(10)	0.253(12)	0.275(11)
C_{11}	0.175(13)	0.244(11)	0.339(12)
C_{12}	0.232(11)	0.241(11)	0.274(11)
C_{13}	0.180(12)	0.209(9)	0.264(10)
C_{14}	0.164(11)	0.188(10)	0.218(9)
C_{31}	0.181(12)	0.232(10)	0.295(11)
C_{32}	0.203(11)	0.290(13)	0.387(14)
C_{33}	0.195(12)	0.308(14)	0.456(16)
C_{41}	0.176(11)	0.252(11)	0.272(11)
C_{42}	0.203(14)	0.292(14)	0.426(16)
C_{43}	0.185(15)	0.318(12)	0.330(13)
C_{51}	0.183(10)	0.233(11)	0.302(11)
C_{52}	0.208(12)	0.328(13)	0.376(14)
C_{53}	0.205(12)	0.277(13)	0.428(14)

Discussion of the Bonding

It has become well known, as observed in the present molecule, that apical bonds in pentacoordinated phosphorus compounds are longer and weaker than equatorial bonds.[12–15] Qualitative molecular orbital descriptions of the bonding in these molecules have been given by several authors,[13,15,16] and recent calculations on bonding in phosphorus chlorfluorides[17] have shown these descriptions to be reasonable. The essence of the approach is to consider the X–P–X apical bonds to be formed from three p orbitals forming the type of three-center, four-electron bond that so successfully describes the bonding in interhalogen ions and rare gas halides.[15] It is not necessary to invoke the use of higher energy phosphorus d orbitals. This method accounts well for the σ bonding in PQTP and will not be discussed further.

π Bonding

Cruickshank[18] has used the concept of pd–π bonding to explain observed bond lengths in tetrahedral XO_4^{-n} ions (X = Si, P, S, Cl). He found that X–O bond lengths were consistently shorter than those predicted for single bonds by the Schomaker–Stevenson rule.[19] In the case of phosphorus compounds, he defines the following bond lengths as representative: P–O single bond (predicted), 1.76 A; P–O(R), 1.62–1.63 A; P–O (free PO_4^{-3}), 1.4 A. An examination of the P–O bond lengths in PQTP suggests that, if Cruickshank's approach is justified, a considerable amount of double-bond character is present in the PO_5 group.

The ten oxygen 2p orbitals available for π bonding yield, on group-theoretical analysis assuming D_{3h} symmetry, orbitals which may be designated $a_1' + a_2'' + 2e' + 2e''$. Phosphorus 3d orbitals of suitable symmetry for interaction with these oxygen symmetry orbitals are $(d_{x^2-y^2}, d_{xy})e''$ and $(d_{xz}, d_{yz})e'$. Although these 3d orbitals are quite diffuse in the free ion,[20] it is conceivable that the highly electronegative oxygen

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[11] L. Pauling, "Nature of the Chemical Bond," 2nd ed, Cornell University Press, Ithaca, N. Y., 1948, p 189.

[12] K. W. Hansen and L. S. Bartell, *Inorg. Chem.*, **4**, 1775 (1965).

[13] L. S. Bartell and K. W. Hansen, *ibid.*, **4**, 1777 (1965).

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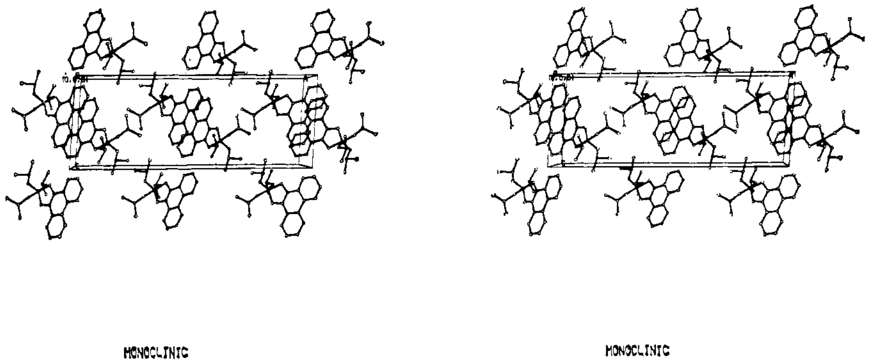

Figure 3. Stereo drawing of the packing in the monoclinic crystals. Note the planar packing of pairs of phenanthrene rings.

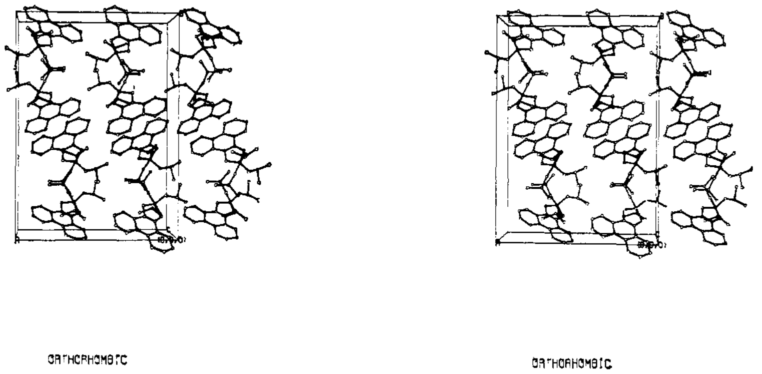

Figure 4. Stereo drawing of the packing of the orthorhombic crystals. Note that here the phenanthrene rings are nearly perpendicular at their point of closest approach. It is also interesting to observe the pronounced separation of the crystal into alternating horizontal layers of aromatic rings and isopropyl groups. The same effect exists in the monoclinic crystal, where the layers are vertical in the drawing in Figure 3.

ligands attract charge away from the phosphorus atom, causing contraction of the 3d orbitals.

The fact that the bonds to the phenanthrenequinone ring are longer than those to the isopropoxy groups in equivalent geometric positions (Δr = 0.05 A for the equatorial bond and Δr = 0.11 A for the apical bond) may be taken as firm evidence of P–O pd–π bonding in these and similar compounds. In PQTP, there is the possibility of interaction of any PO_5 π system with that of the phenanthrene ring. The phenanthrene ring is a competitor for the π-bonding electrons of the oxygen atoms. These electrons are thus not as available for bonding to phosphorus, and the bonds to the ring thus do not show the π-bond-caused shortening, relative to the expected single bond distances, which is apparent for the isopropoxy groups. The apical bond to the ring has just the length of 1.76 A suggested by Cruickshank for a P–O single bond. An apical single bond in a trigonal bipyramid would be expected to be somewhat longer; thus the π-bond character of this bond, although small, is not altogether zero.

Conclusions

The accurate molecular geometry of a pentacoordinated phosphorus-oxygen compound has been given. It is found that the PO_5 unit exhibits the lengthening of the apical bonds that is observed in other PX_5 species; this lengthening is due to the different character of the σ bonding. In addition, the bonds to the isopropoxy group are shortened considerably by pd–π bonding between O and P. This shortening is considerably less for the bonds to the phenanthrenequinone system, which acts as a competitor for the bonding power of the oxygen 2pπ electrons.

Acknowledgments. We have profited from many valuable discussions with Professor F. Ramirez whose chemical work stimulated this investigation. The assistance of Dr. Paul Goldstein in the collection of the data is greatfully acknowledged. We thank Dr. D. F. Koenig for solving the structure by the symbolic addition method.

Appendix

Phase Determination by the Symbolic Addition Method.[21] The symbolic addition method[22] was used to determine signs of 362 structure factors. The distribution of magnitudes of quasi-normalized structure factors agreed well with the theoretical distribution for centrosymmetric structures. The signs of six reflections having *E*'s greater than 2.5 were designated by letters. (To permit later correlation with early stages of a parallel attempt to determine the structure by Patterson methods, the origin was not specified.) Symbolic phase determination was first restricted to the 92 reflections having *E*'s not less than 2.35 until 60 of the signs were determined in three cycles of an IBM 7094 program. The lower limit of *E* was then reduced to 2.00, and the symbolic signs of 139 of the 169 reflections were determined at the fourth cycle. Within two further cycles, signs of 362 of the 369 reflections having *E*'s not less than 1.60 were determined. After the fourth

[21] Prepared by D. F. Koenig, Biology Department, Brookhaven National Laboratory, Upton, N. Y. 11973.

[22] I. Karle and J. Karle, *Acta Cryst.*, **16**, 969 (1963).

cycle, it was clear that $c = 0°$ and $b = 180°$. After the fifth and final cycle, it was certain that $a = d + e$. Thus only symbols d, e, and f remained and could be chosen at will to fix the origin; they were all chosen equal to 0°. The first Fourier synthesis (E map), using 367 reflections with all E's taken as 2.0, clearly showed 23 of the 29 nonhydrogen atoms and several more probable atoms. The subsequent difference Fourier synthesis (electron density difference map) computed from these 23 atoms revealed the remaining 6 carbon atoms as well as indicating moderate shifts in the positions of the 23 input atoms.

Identification of Two Reduction Products of Glyoxal Bis(2-mercaptoanil)nickel. Characterization of the One-Electron Reduction Product and the Partially Hydrogenated Anion

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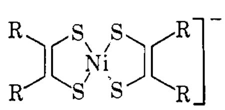
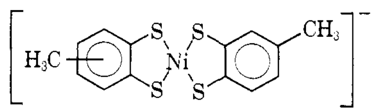
Contribution from the Department of Chemistry, University of California, Riverside, California. *Received January 12, 1967*

Abstract: Two different paramagnetic monoanions have been previously identified as the one-electron reduction product of glyoxal bis(2-mercaptoanil)nickel, Ni(gma). These anions result from (a) the initial borohydride reduction of Ni(gma), and (b) the sodium amalgam reduction of Ni(gma). These ions differ in their physical properties. The ion resulting from (a) has a green color, with $\langle g \rangle = 2.051$, $g_1 = 2.009$, $g_2 = 2.027$, and $g_3 = 2.119$, while the ion resulting from (b) is red-brown, with $\langle g \rangle = 2.0042$, $g_1 = 1.979$, $g_2 = 2.006$, and $g_3 = 2.028$ in 2-methyltetrahydrofuran. In this communication, we demonstrate that the product from (b) is identical in its properties with the one-electron electroreduction product of Ni(gma) in dimethylformamide and, since the reduction wave is reversible, is identified as the monoanion of Ni(gma). The green anion from (a) is shown to result from hydrogen addition across the conjugated bridge and is identified as $\mathrm{Ni(H_2gma)^-}$.

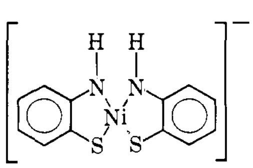
The characterization of stable, square-planar nickel complexes in unusual formal oxidation states has opened an area of discussion concerning their electronic formulation.[2–5] Four types of complexes have played a key role in the discussion and are shown below (I–IV).



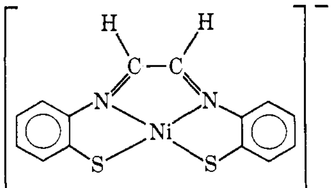
I, R = CN, CF_3, Ph
R = CN, $\mathrm{Ni(mnt)_2^-}$



II, $\mathrm{Ni(tdt)_2^-}$



III, $\mathrm{Ni(abt)_2^-}$



IV, $\mathrm{Ni(gma)^-}$

As an example of the problem, the paramagnetic ($S = ^1/_2$) $\mathrm{Ni(mnt)_2^-}$ complex has been described in two different ways: as an effectively d^7 Ni(III) complex, $[\mathrm{Ni^{III}(mnt)_2{}^{4-}}]^-$ [2–5] and as an effectively d^8 Ni(II)-stabilized radical ligand [Ni(II) srl] system, $[\mathrm{Ni^{II}(mnt)_2{}^{3-}}]^-$.[3,4]

In many cases the same polarographic and esr results have been interpreted as supporting the Ni(III) or the Ni(II) srl picture, depending on the relative emphasis placed on various details of these experiments. A particularly unfortunate controversy has arisen concerning the interpretation of polarographic and esr experiments on various reduction products of Ni(gma).[4,5] Specifically, the borohydride[4] and sodium amalgam[5] reduction products are clearly different, and this has led to considerable confusion about the identity of the authentic $\mathrm{Ni(gma)^-}$ complex. We have now thoroughly characterized the monoanionic borohydride reduction product of Ni(gma) as a partially hydrogenated species designated $\mathrm{Ni(H_2gma)^-}$ (V).

On the other hand, the sodium amalgam reduction product of Ni(gma)[5] has been shown to be the actual anion, $\mathrm{Ni(gma)^-}$. These results should give added impetus to the total resolution of the outstanding problems.

It is also our view that in a number of situations the Ni(III) and Ni(II) srl descriptions approach each other. On careful examination of the allegedly opposed formulations,[4,5] it is apparent that there is no significant basis for controversy. Therefore, it is the purpose of this paper to present the characterization of the $\mathrm{Ni(H_2gma)^-}$

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[2] A. H. Maki, N. Edelstein, A. Davison, and R. H. Holm, *J. Am. Chem. Soc.*, **86**, 4580 (1964).

[3] S. I. Shupack, E. Billig, R. J. H. Clark, R. Williams, and H. B. Gray, *ibid.*, **86**, 4594 (1964).

[4] E. I. Stiefel, J. H. Waters, E. Billig, and H. B. Gray, *ibid.*, **87**, 3016 (1965). The complex referred to as $\mathrm{Ni(gma)^-}$ in the esr work in this communication is probably $\mathrm{Ni(H_2gma)^-}$.

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