Internal Molecular Motion of Triphenylphosphine Oxide: Analysis of Atomic Displacement Parameters for Orthorhombic and Monoclinic Crystal Modifications at 100 and 150 K

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Abstract: The structures of the orthorhombic and monoclinic crystal modifications of triphenylphosphine oxide have been redetermined from new X-ray diffraction data collected at 100 and 150 K. From the atomic displacement parameters it is clear that the molecules do not behave as rigid bodies in the crystal but carry out appreciable internal rotations of the phenyl groups about their respective P–C bonds. The mean-square amplitudes of these rotations for the individual phenyl groups have been estimated from the observed atomic displacement parameters. In both structures, one of the phenyl groups (the one with its plane most nearly perpendicular to the P=O bond direction) shows a much larger libration amplitude than the other two. This dependence on the phenyl group orientation can be expected from features of the molecular potential energy surface derived previously from the distribution of triphenylphosphine oxide conformations in 62 crystal structures (Bye, E.; Schweizer, W. B.; Dunitz, J. D. *J. Am. Chem. Soc.* **1982**, *104*, 5893–5898). Semiempirical potential energy calculations for the free molecule reproduce the main features of this surface reasonably well, but similar calculations for the two crystal modifications do not lead to entirely satisfactory results. Some possible reasons for this are discussed.

In a previous study[2] (referred to hereinafter as BSD) the structure correlation method[3] was used to map low-energy paths for the stereoisomerization of triphenylphosphine oxide (and related molecules); in addition the approximate structure of the transition state for this isomerization process could be deduced. Each of the circa 60 Ph_3PO fragments observed in crystal structures and retrieved from the Cambridge Crystallographic Database[4] was regarded as a sample point $\mathbf{p}(\phi_1,\phi_2,\phi_3)$ where ϕ_1, ϕ_2, and ϕ_3 are values of the torsion angles about the three Ph–P bonds (Figure 1). The basic assumption behind the structure correlation method is that such sample points tend to concentrate in low-energy regions of the corresponding three-dimensional vector space. The distribution of the sample points thus delineates the shapes of the energy valleys.

In the present paper we take the argument a stage further. Any displacement of the representative point corresponds to an internal molecular motion involving a particular coupling of torsional motions about the three Ph–P bonds. By definition, the energy change for an infinitesimal displacement of a representative point along a valley must be less than the energy changes for perpendicular displacements. Hence, insofar as the derived path actually follows an energy valley its direction should correspond to a "soft" vibrational mode of the molecule.[5] Of couse, the conformation in question will not in general coincide with the equilibrium conformation of the isolated molecule. On the other hand, any conformation corresponding to an *observed* sample point must correspond to an energy minimum under the perturbation produced by the packing forces in the crystal where the corresponding molecular fragment was found. Also, the direction of the energy valley at that point will not be appreciably affected by the packing forces provided the sides of the valley are sufficiently steep.

The above argument suggests that inferences about large-amplitude internal motions in a given molecule in a crystalline environment can be made from knowledge of the equilibrium crystal structure together with information about crystal structures of related molecules: dynamic information from static.

For definiteness we consider the distribution of Ph_3PO sample points shown in Figure 3 of BSD[2] and reproduced for convenience as Figure 2 of the present paper. The clusters of sample points around the threefold axes[6] centered at 0, 0, 40° and 120, 60, 20° (hexagonal coordinates, images respectively of molecules with torsion angles 40, 40, 40° and those of enantiomeric molecules with torsion angles 140, −40, −40°) are connected by a path running in the general direction $x_H = 2y_H$. Other pairs of clusters are connected by symmetry-equivalent paths. Rewriting the condition $x_H = 2y_H$ in terms of individual torsion angles gives $\Delta\phi_A = -2\Delta\phi_B = -2\Delta\phi_C$. Starting with a molecule with torsion angles 40, 40, 40° the stereoisomerization path begins with a rotation of one ring, say A (Figure 1) toward 90° (perpendicular to its C–P–O plane) coupled with a rotation of the other two rings in the opposite sense (toward 0°) and by half the amount. This is essentially the same kind of process as was derived by Mislow and his co-workers from dynamic NMR studies of variously substituted triarylboranes, triarylmethanes, and related molecules and termed by them the "two-ring flip" mechanism.[9]

Assume now that for a given Ph_3PO molecule in a crystal, the torsional vibrations of the three rings are coupled in such a way as to correspond to displacement of the sample point $\mathbf{p}(\phi_1,\phi_2,\phi_3)$ along the stereoisomerization path. The way in which the ring rotations are coupled along this path leads us to expect that for a molecule which deviates sufficiently from C_3 symmetry, ring A (defined as the one with the value of $\phi = \phi_1$ closest to 90°) would have a mean libration amplitude about double that of the

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(2) Bye, E.; Schweizer, W. B.; Dunitz, J. D. *J. Am. Chem. Soc.* **1982**, *104*, 5893–5898.

(3) For a recent review with references to earlier literature see: Bürgi, H. B.; Dunitz, J. D. *Acc. Chem. Res.* **1983**, *16*, 153–161.

(4) Cambridge Crystallographic Data Centre, University Chemical Laboratories, Cambridge, England. For a recent review of applications to problems in structural organic chemistry see: Allen, F. H.; Kennard, O.; Taylor, R. *Acc. Chem. Res.* **1983**, *16*, 146–153.

(5) The question whether and under what circumstances sample-point distributions may be interpreted as minimum-energy paths or as response paths is discussed (but not completely answered) in ref 3.

(6) Since torsion angles are cyclic coordinates, the distribution in question is periodic.[7,8] Its space group is R32 and it is conveniently referred to hexagonal axes where the coordinates are linear combinations of the torsion angles ϕ_1, ϕ_2, ϕ_3: $x_H = (2\phi_1 - \phi_2 - \phi_3)/3$, $y_H = (\phi_1 + \phi_2 - 2\phi_3)/3$, $z_H = (\phi_1 + \phi_2 + \phi_3)/3$. The inverse transformation is the following: $\phi_1 = x_H + z_H$, $\phi_2 = -x_H + y_H + z_H$, $\phi_3 = -y_H + z_H$.

(7) Murray-Rust, P.; Bürgi, H. B.; Dunitz, J. D. *Acta Crystallogr., Sect. A* **1979**, *35*, 703–713.

(8) Dunitz, J. D. "X-Ray Analysis and the Structure of Organic Molecules"; Cornell University Press: Ithaca, NY, 1979; Chapter 10.

(9) For a review see: Mislow, K. *Acc. Chem. Res.* **1976**, *9*, 26–33.

Table I. Lattice Dimensions of the Two Crystalline Modifications of Triphenylphosphine Oxide, Each at Three Temperatures

	orthorhombic, *Pbca*			monoclinic, *P2₁/c*		
temp, K	100 (2)[a]	153 (2)	295 (2)	100 (2)	152 (2)	293 (2)
a, Å	28.838 (3)	28.898 (3)	29.104 (2)	10.915 (2)	10.952 (2)	11.061 (1)
b, Å	9.075 (2)	9.094 (2)	9.152 (2)	8.672 (6)	8.687 (2)	8.721 (1)
c, Å	11.097 (4)	11.138 (2)	11.276 (2)	16.205 (8)	16.221 (6)	16.259 (2)
β, deg				109.02 (3)	108.78 (2)	107.91 (1)
Z		8			4	
V/Z, Å³·mol⁻¹	363.0	365.9	375.4	362.5	365.3	373.1

[a] Estimated standard deviations in the least significant figure are given in parentheses in this and all subsequent tables.
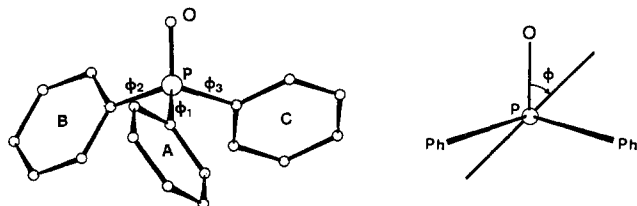
Figure 1. Definition of torsion angles ϕ_1, ϕ_2, and ϕ_3. The phenyl groups are labeled A, B, and C in a clockwise sequence when viewed down the O–P direction.
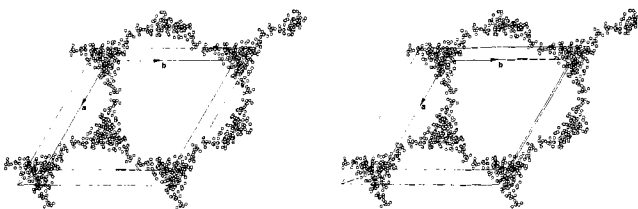
Figure 2. Stereoscopic view of distribution of Ph₃PO sample points in a section of the hexagonal cell with $0 \leq z_H \leq 60°$ (from ref 2). The unit translations of the hexagonal cell are 180°.

other two rings. Its mean-square amplitude $\langle \Omega^2 \rangle$ would then be around four times that of the other two rings, a ratio that should be easily detectable by analyzing the atomic vibration tensors derived from a reasonably accurate X-ray study.

We decided to investigate this problem experimentally by carrying out new X-ray diffraction measurements at 100 and 150 K of the two known crystal modifications of triphenylphosphine oxide itself.[10,11] The availability of the two polymorphs having different packing arrangements and molecular conformations is useful for checking some of our conclusions. In addition, we have also made force-field calculations for the free molecule and for the two crystal forms.

The calculations can be regarded as a kind of sequel to an earlier investigation[12] on the conformations of the triphenylphosphine molecule in the free and solid states. These calculations showed that energy minima associated with C_3 symmetric (enantiomeric) molecules in the free state are connected in the potential energy surface by a single, flat valley (along which the calculated energy variation was less than 2 kcal mol⁻¹). The conformation observed in crystalline triphenylphosphine[13] corresponds to an intermediate position along the valley. It is of interest to see to what extent the introduction of the oxygen atom on the molecular symmetry axis will affect these results. The molecular conformation found in crystalline triphenylphosphine[13] is similar to that observed in the orthorhombic modification of triphenylphosphine oxide.[11]

Experimental Section

Crystals of the orthorhombic and monoclinic modifications of triphenylphosphine oxide often grow together in the same evaporating dish

Table II. Some Experimental Data and Agreement Factors

	orthorhombic		monoclinic	
temp, K	100	153	100	152
unique reflections	5025	5062	5009	5040
reflections with $I > 3\sigma(I)$	3253	2886	2383	1883
final no. of variables	242	242	242	242
R, R_w on $F[I > 3\sigma(I)]$	0.035, 0.038	0.036, 0.039	0.036, 0.039	0.040, 0.045

and are difficult to tell apart. The monoclinic crystals were easier to obtain, at least in our experience. They grow in a variety of habits, are often elongated along **b**, and usually exhibit {10$\bar{2}$}, {001}, {100}, and {110} faces. The orthorhombic crystals are lathes, thin along **a**, elongated along **c**, and bounded by {100}, {2̄10}, {111}, and sometimes {001} faces. Both monoclinic and orthorhombic crystals are formed when hexane solutions are evaporated slowly. Orthorhombic crystals can be used to seed toluene solutions, although evaporation of unseeded toluene solutions yields only monoclinic crystals.

Crystals for data collection were cut from larger specimens (orthorhombic, 0.2 × 0.4 × 0.4 mm; monoclinic, circa 0.3 mm on edge). All X-ray measurements were made with an Enraf-Nonius CAD-4 diffractometer equipped with graphite monochromator (Mo Kα radiation) and cooling device. Data were measured for both crystal forms at 100 and 150 K to 32 deg θ with maximum scan times per reflection of 220 (orthorhombic form) and 240 s (monoclinic form). The structures were refined, starting from the published coordinates,[10b,11] by full-matrix least-squares analysis with use of the XRAY system.[14] The final refinement included an isotropic extinction correction and utilized an exponentially modified weighting system ($r = 6.0$ Å²).[15] Lattice dimensions[16,17] are given in Table I, details of the refinements in Table II, and positional and vibrational parameters (for the 100 K structures[19]) in Table III.

Molecular Geometry

Although we did not set out to determine the molecular geometry with particular accuracy, and although our analysis falls far short of the highest standards attainable today, nevertheless our results represent a considerable improvement over the earlier ones.[10,11] This gain is mainly due to our use of low-temperature measurements.[20] Apart from the slight improvement in precision and accuracy on going from 150 to 100 K, there are no significant differences in the molecular dimensions obtained at the two temperatures for each crystal modification. We shall therefore restrict the discussion to the results obtained at the lower temperature.

(10) Monoclinic: (a) Guser, A. I.; Bokij, N. G.; Afanina, N. N.; Timofeeva, T. V.; Kalinin, A. E.; Struchkov, J. T. *Z. Strukt. Khim.* **1973**, *14*, 115–125; *J. Struct. Chem.* **1973**, *14*, 101–108. (b) Ruban, G.; Zabel, V. *Cryst. Struct. Commun.* **1976**, *5*, 671–677.

(11) Orthorhombic: Bandoli, G.; Bortolozzo, G.; Clemente, D. A.; Croatto, U.; Panattoni, C. *J. Chem. Soc., Sect. A*, **1970**, 2778–2780.

(12) Brock, C. P.; Ibers, J. A. *Acta Crystallogr., Sect. B* **1973**, *29*, 2426–2433.

(13) Daly, J. J. *J. Chem. Soc.* **1964**, 3799–3810.

(14) Stewart, J. M.; Kruger, G. J.; Amman, H. L.; Dickinson, C.; Hall, S. R. "The XRAY system: Version of June 1972", Technical Report TR192; Computer Science Center, University of Maryland: College Park, MD.

(15) Dunitz, J. D.; Seiler, P. *Acta Crystallogr., Sect. B* **1973**, *29*, 589–595.

(16) Lattice dimensions (Table I) were obtained at each temperature from diffractometer settings for 22 (orthorhombic) or 10 (monoclinic) reflections in the range between 8 and 15 deg. Our room-temperature values differ somewhat from those reported in the earlier studies.[10,11]

(17) The axial orientation chosen for the monoclinic crystal form (Table I) corresponds to the standard [18]*b* axis unique setting. In the earlier studies other orientations were used: $P2_1/b$ in ref 9a, and $P2_1/a$ in ref 9b.

(18) "International Tables for X-Ray Crystallography", 3rd ed.; Kynoch Press: Birmingham, England, 1969; Vol. I (Symmetry Groups).

(19) Positional and displacement parameters for the two structures at 150 K are given in supplementary Table S1.

(20) The reduction in the thermal motion not only allows better precision in estimating the mean atomic positions (centroids of atomic distributions that are undergoing vibrations) but also lowers the systematic errors involved in estimating interatomic distances as separations between these positions.[21]

(21) Busing, W. R.; Levy, H. A. *Acta Crystallogr.* **1964**, *17*, 142–146.

Table III. Positional and Atomic Displacement Parameters (Å^2) for the Two Crystalline Modifications at 100 K (Corresponding Parameters at 150 K Are Given in Supplementary Table S1 a,b)

| atom	x	y	z	U_{11} (or U)	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
\(\)			(a) Orthorhombic Modification, 100 K						
O(1)	0.11470 (4)	0.0855 (1)	0.34152 (8)	0.0242 (4)	0.0193 (4)	0.0141 (4)	−0.0011 (4)	−0.0005 (3)	0.0022 (3)
P(1)	0.11779 (1)	0.14029 (3)	0.21502 (3)	0.0142 (1)	0.0123 (1)	0.0110 (1)	−0.0001 (1)	−0.0008 (1)	−0.0001 (1)
C(1)	0.06716 (4)	0.2396 (1)	0.1664 (1)	0.0140 (4)	0.0176 (5)	0.0158 (5)	0.0014 (4)	0.0015 (4)	0.0006 (4)
C(2)	0.05449 (5)	0.3661 (2)	0.2297 (1)	0.0255 (6)	0.0299 (7)	0.0279 (7)	0.0101 (6)	−0.0023 (5)	−0.0083 (6)
C(3)	0.01369 (6)	0.4398 (2)	0.2016 (2)	0.0289 (7)	0.0375 (9)	0.0340 (8)	0.0174 (6)	0.0024 (6)	−0.0045 (7)
C(4)	−0.01493 (5)	0.3876 (2)	0.1104 (2)	0.0181 (5)	0.0377 (9)	0.0332 (7)	0.0102 (5)	0.0036 (5)	0.0083 (6)
C(5)	−0.00238 (5)	0.2636 (2)	0.0459 (2)	0.0219 (6)	0.0342 (8)	0.0337 (7)	0.0050 (6)	−0.0093 (5)	0.0020 (6)
C(6)	0.03861 (5)	0.1894 (2)	0.0734 (1)	0.0211 (5)	0.0238 (6)	0.0256 (6)	0.0040 (5)	−0.0071 (5)	−0.0014 (5)
C(7)	0.16651 (4)	0.2621 (1)	0.1938 (1)	0.0147 (4)	0.0140 (4)	0.0150 (5)	0.0005 (5)	−0.0009 (3)	−0.0033 (4)
C(8)	0.20367 (4)	0.2487 (2)	0.2741 (1)	0.0173 (4)	0.0220 (5)	0.0203 (6)	0.0030 (4)	−0.0053 (4)	−0.0051 (4)
C(9)	0.24363 (5)	0.3320 (2)	0.2574 (2)	0.0168 (6)	0.0320 (7)	0.0341 (7)	−0.0012 (5)	−0.0057 (5)	−0.0110 (6)
C(10)	0.24668 (5)	0.4284 (2)	0.1604 (2)	0.0211 (6)	0.0287 (7)	0.0367 (8)	−0.0093 (5)	0.0056 (6)	−0.0122 (6)
C(11)	0.20947 (6)	0.4441 (2)	0.0817 (1)	0.0281 (6)	0.0219 (6)	0.0268 (6)	−0.0079 (5)	0.0061 (5)	−0.0022 (5)
C(12)	0.16932 (4)	0.3610 (2)	0.0977 (1)	0.0205 (5)	0.0164 (5)	0.0185 (5)	−0.0021 (4)	0.0003 (4)	−0.0007 (5)
C(13)	0.12558 (4)	−0.0093 (1)	0.1093 (1)	0.0147 (4)	0.0141 (4)	0.0151 (4)	0.0003 (4)	−0.0020 (4)	−0.0020 (4)
C(14)	0.11265 (4)	−0.1503 (1)	0.1468 (1)	0.0208 (5)	0.0148 (4)	0.0213 (5)	−0.0001 (4)	−0.0022 (4)	0.0002 (4)
C(15)	0.11928 (6)	−0.2704 (1)	0.0706 (1)	0.0271 (6)	0.0147 (5)	0.0297 (6)	0.0012 (5)	−0.0064 (5)	−0.0034 (4)
C(16)	0.13858 (6)	−0.2505 (2)	−0.0428 (1)	0.0267 (6)	0.0196 (5)	0.0268 (6)	0.0032 (5)	−0.0060 (5)	−0.0090 (5)
C(17)	0.15075 (5)	−0.1100 (2)	−0.0813 (1)	0.0289 (6)	0.0240 (7)	0.0198 (5)	0.0015 (5)	0.0000 (5)	−0.0070 (5)
C(18)	0.14445 (5)	0.0107 (2)	−0.0059 (1)	0.0251 (6)	0.0186 (5)	0.0167 (5)	−0.0017 (5)	0.0013 (4)	−0.0032 (4)
H(2)	0.074 (1)	0.402 (3)	0.297 (3)	0.046 (8)					
H(3)	0.007 (1)	0.530 (3)	0.241 (3)	0.055 (8)					
H(4)	−0.0421 (9)	0.439 (3)	0.092 (2)	0.034 (6)					
H(5)	−0.0210 (9)	0.232 (3)	−0.019 (2)	0.037 (6)					
H(6)	0.0467 (9)	0.099 (3)	0.029 (2)	0.033 (6)					
H(8)	0.2015 (9)	0.180 (3)	0.342 (2)	0.032 (6)					
H(9)	0.270 (1)	0.319 (3)	0.310 (2)	0.044 (7)					
H(10)	0.2759 (9)	0.486 (3)	0.146 (2)	0.037 (6)					
H(11)	0.2122 (9)	0.513 (3)	0.013 (2)	0.038 (7)					
H(12)	0.1438 (8)	0.373 (2)	0.040 (2)	0.022 (5)					
H(14)	0.0984 (8)	−0.164 (3)	0.225 (2)	0.027 (5)					
H(15)	0.1103 (8)	−0.372 (3)	0.097 (2)	0.028 (5)					
H(16)	0.1426 (9)	−0.336 (3)	−0.091 (2)	0.031 (6)					
H(17)	0.1636 (9)	−0.096 (3)	−0.162 (2)	0.034 (6)					
H(18)	0.1536 (8)	0.106 (3)	−0.033 (2)	0.028 (6)					
			(b) Monoclinic Modification, 100 K						
O(1)	0.2153 (2)	0.1360 (2)	−0.00708 (9)	0.0235 (7)	0.0142 (6)	0.0108 (6)	−0.0015 (5)	0.0055 (5)	−0.0023 (5)
P(1)	0.26796 (5)	0.22422 (6)	0.07633 (3)	0.0151 (2)	0.0086 (2)	0.0092 (2)	−0.0002 (2)	0.0050 (2)	−0.0003 (2)
C(1)	0.2486 (2)	0.4294 (2)	0.0615 (1)	0.0158 (9)	0.0108 (7)	0.0116 (7)	−0.0007 (6)	0.0043 (6)	0.0009 (5)
C(2)	0.3293 (2)	0.5067 (2)	0.0239 (1)	0.023 (1)	0.0159 (8)	0.0266 (9)	0.0021 (8)	0.0140 (8)	0.0059 (8)
C(3)	0.3105 (2)	0.6625 (3)	0.0038 (1)	0.028 (1)	0.0154 (8)	0.029 (1)	−0.0005 (8)	0.0116 (9)	0.0077 (8)
C(4)	0.2111 (2)	0.7430 (2)	0.0210 (1)	0.025 (1)	0.0111 (9)	0.0244 (9)	0.0004 (7)	0.0033 (8)	0.0025 (6)
C(5)	0.1300 (2)	0.6663 (3)	0.0579 (2)	0.025 (1)	0.0129 (8)	0.030 (1)	0.0056 (8)	0.0099 (9)	0.0004 (8)
C(6)	0.1490 (2)	0.5098 (2)	0.0784 (1)	0.0201 (9)	0.0140 (8)	0.0235 (9)	0.0016 (7)	0.0118 (8)	0.0005 (7)
C(7)	0.1925 (2)	0.1649 (2)	0.1550 (1)	0.0162 (8)	0.0106 (7)	0.0128 (7)	0.0003 (6)	0.0051 (6)	−0.0008 (6)
C(8)	0.2405 (2)	0.2097 (3)	0.2422 (1)	0.0256 (9)	0.0165 (8)	0.0141 (7)	−0.0051 (8)	0.0090 (7)	−0.0032 (7)
C(9)	0.1830 (2)	0.1544 (3)	0.3016 (1)	0.031 (1)	0.025 (1)	0.0155 (9)	0.0002 (9)	0.0128 (8)	0.0000 (7)
C(10)	0.0795 (2)	0.0529 (3)	0.2737 (2)	0.026 (1)	0.026 (1)	0.025 (1)	0.0011 (9)	0.0180 (9)	0.0038 (8)
C(11)	0.0300 (2)	0.0085 (3)	0.1869 (2)	0.0197 (9)	0.0220 (9)	0.030 (1)	−0.0043 (8)	0.0128 (8)	0.0004 (8)
C(12)	0.0867 (2)	0.0659 (2)	0.1276 (1)	0.0166 (9)	0.0182 (8)	0.0166 (8)	−0.0002 (7)	0.0056 (7)	−0.0013 (7)
C(13)	0.4402 (2)	0.1978 (2)	0.1277 (1)	0.0178 (8)	0.0138 (9)	0.0136 (7)	0.0016 (6)	0.0075 (6)	0.0014 (6)
C(14)	0.4988 (2)	0.0707 (2)	0.1031 (1)	0.0231 (9)	0.0141 (8)	0.0170 (8)	0.0030 (7)	0.0104 (7)	0.0025 (6)
C(15)	0.6325 (2)	0.0488 (3)	0.1389 (1)	0.026 (1)	0.024 (1)	0.0210 (9)	0.0115 (8)	0.0127 (8)	0.0086 (8)
C(16)	0.7067 (2)	0.1504 (3)	0.2012 (2)	0.020 (1)	0.033 (1)	0.024 (1)	0.0082 (9)	0.0075 (8)	0.0077 (9)
C(17)	0.6493 (2)	0.2764 (3)	0.2273 (1)	0.0184 (9)	0.0300 (9)	0.0218 (9)	0.002 (1)	0.0037 (7)	−0.002 (1)
C(18)	0.5167 (2)	0.3011 (2)	0.1901 (1)	0.0161 (8)	0.017 (1)	0.0187 (8)	0.0007 (6)	0.0041 (7)	−0.0023 (6)
H(2)	0.400 (3)	0.455 (4)	0.015 (2)	0.029 (8)					
H(3)	0.369 (4)	0.714 (4)	−0.021 (2)	0.039 (9)					
H(4)	0.201 (3)	0.852 (4)	0.013 (2)	0.026 (8)					
H(5)	0.059 (3)	0.721 (4)	0.069 (2)	0.032 (8)					
H(6)	0.091 (3)	0.460 (4)	0.104 (2)	0.032 (9)					
H(8)	0.313 (3)	0.279 (4)	0.264 (2)	0.023 (7)					
H(9)	0.213 (4)	0.192 (4)	0.359 (2)	0.036 (9)					
H(10)	0.046 (3)	0.006 (4)	0.316 (2)	0.031 (8)					
H(11)	−0.038 (4)	−0.056 (4)	0.171 (2)	0.038 (9)					
H(12)	0.054 (3)	0.034 (4)	0.069 (2)	0.032 (9)					
H(14)	0.444 (3)	0.002 (4)	0.061 (2)	0.022 (7)					
H(15)	0.673 (3)	−0.036 (4)	0.118 (2)	0.021 (7)					
H(16)	0.797 (4)	0.137 (4)	0.225 (2)	0.04 (1)					
H(17)	0.698 (3)	0.347 (4)	0.270 (2)	0.026 (8)					
H(18)	0.478 (3)	0.390 (3)	0.208 (2)	0.017 (7)					

Table IV gives selected bond distances, bond angles, and torsion angles for the orthorhombic and monoclinic crystal modifications at 100 K. The molecular conformations are quite similar (Figure 3); in both structures the normal to one phenyl ring (A) is roughly

Table IV. Bond Distances (Å), Bond Angles (deg), and Torsion Angles (deg) for the 100 K Structures[a]

P–O	1.491	1.494						
P–C(1)	1.798	1.797	P–C(7)	1.803	1.802	P–C(13)	1.808	1.802
C(1)–C(2)	1.394	1.394	C(7)–C(8)	1.399	1.395	C(13)–C(14)	1.396	1.388
C(2)–C(3)	1.388	1.388	C(8)–C(9)	1.390	1.394	C(14)–C(15)	1.392	1.392
C(3)–C(4)	1.389	1.391	C(9)–C(10)	1.389	1.384	C(15)–C(16)	1.387	1.386
C(4)–C(5)	1.381	1.387	C(10)–C(11)	1.390	1.391	C(16)–C(17)	1.389	1.384
C(5)–C(6)	1.394	1.395	C(11)–C(12)	1.393	1.388	C(17)–C(18)	1.390	1.393
C(6)–C(1)	1.396	1.390	C(12)–C(7)	1.396	1.403	C(18)–C(13)	1.401	1.392
C(1)–P–O	113.6	113.0	C(7)–P–O	111.9	112.8	C(13)–P–O	111.6	111.4
P–C(1)–C(2)	118.3	118.1	P–C(7)–C(8)	117.4	118.2	P–C(13)–C(14)	117.5	118.2
P–C(1)–C(6)	122.5	122.3	P–C(7)–C(12)	122.6	122.4	P–C(13)–C(18)	122.9	122.1
C(6)–C(1)–C(2)	119.1	119.3	C(12)–C(7)–C(8)	119.9	119.3	C(18)–C(13)–C(14)	119.6	119.6
C(1)–C(2)–C(3)	120.4	120.3	C(7)–C(8)–C(9)	120.2	120.2	C(13)–C(14)–C(15)	120.0	120.6
C(2)–C(3)–C(4)	120.2	120.4	C(8)–C(9)–C(10)	119.9	120.0	C(14)–C(15)–C(16)	120.3	119.2
C(3)–C(4)–C(5)	120.0	119.5	C(9)–C(10)–C(11)	120.1	120.5	C(15)–C(16)–C(17)	120.0	120.9
C(4)–C(5)–C(6)	120.1	120.1	C(10)–C(11)–C(12)	120.4	119.8	C(16)–C(17)–C(18)	120.3	119.7
C(5)–C(6)–C(1)	120.3	120.3	C(11)–C(12)–C(7)	119.6	120.2	C(17)–C(18)–C(13)	119.9	120.0
O–P–C(1)–C(2)	59.8	74.1	O–P–C(6)–C(7)	23.6	18.8	O–P–C(13)–C(14)	20.8	8.7
O–P–C(1)–C(6)	–115.8	–99.7	O–P–C(6)–C(12)	–160.2	–160.3	O–P–C(13)–C(18)	–158.2	–168.4

[a] Of the two values listed for each parameter, the first refers to the orthorhombic crystal form and the second to the monoclinic. Estimated standard deviations in C–C distances are about 0.002 Å (C–C–C angles 0.1–0.2°) for the orthorhombic crystal and about double for the monoclinic, with somewhat lower values for parameters involving the P atom.
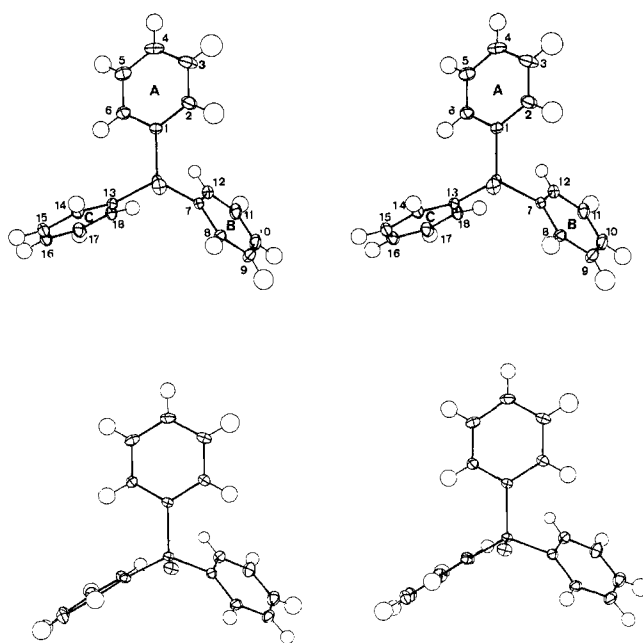
Figure 3. Stereoscopic views of the triphenylphosphine oxide molecule as observed at 100 K in the orthorhombic modification (top) and the monoclinic modification (bottom). The ellipsoids are drawn at the 50% probability level. In each drawing the plane of the three α-C atoms [C(1), C(7), and C(13)] is rotated 6° about a horizontal axis from the plane of the paper. The ring with the torsion angle closest to 90° is ring A, followed in the clockwise direction by rings B and C. The ortho C atoms C(2), C(8), and C(14) are on the same side of the plane of the three α-C atoms as the O atom.

(within 30°) parallel to the P=O bond while the other two ring normals (B and C) are roughly perpendicular to this bond. However, there are obvious differences in detail between the phenyl orientations in the two structures, as expressed by the numerical values of the torsion angles. Apart from these, there do not appear to be any important differences between the molecular dimensions in the two crystals, as already noted by Ruban and Zabel[10b] in their comparison of the room-temperature results. Indeed, even some quite small structural trends are shared by the two molecules: (i) Of the three P–C distances, 1.798, 1.803, 1.808 Å in the orthorhombic and 1.797, 1.802, 1.802 Å in the monoclinic structure, the smallest is to ring A, the one whose plane is most nearly perpendicular to the P–O bond (indication of delocalization

Table V. Some Measures Describing the Precision of the Displacement Parameters and Their Fit to the Rigid-Body Vibration Model

	orthorhombic		monoclinic	
temp, K	100	153	100	152
$\langle \sigma^2(U_0{}^{ii}) \rangle^{1/2}$, Å^2	0.0005	0.0008	0.0008	0.0012
$\langle (z_{A,B}{}^2 - z_{B,A}{}^2) \rangle^{1/2}$				
within phenyl rings	0.0009	0.0013	0.0012	0.0023
between phenyl rings	0.0037	0.0057	0.0032	0.0063
$\{\sum [w(U_0{}^{ij} - U_c{}^{ij})]^2 / \sum w^2\}^{1/2}$	0.0013	0.0018	0.0014	0.0022
$(w = \sigma^{-2}(U_0{}^{ij}))$				

of the aromatic π system into the P–O π* orbital?). (ii) The P–C–C angles on the lower side of the molecule (opposite the P–O bond) are 4–5° larger than those on the upper side (steric repulsion?). (iii) The C–C–C angles at the ipso C atoms are all slightly (0.1–0.9°) smaller than 120° (inductive effect of P=O substituent[22] with a possible dependence on the ring torsion angle, cf. (i)?). (iv) The mean C–C distances are practically equal, 1.392 Å in the orthorhombic and 1.391 Å in the monoclinic structure, but they show a systematic variation, an apparent shortening (by about 0.01 Å) from the inner to the outer bonds of the phenyl groups. Although one might suspect that this could be an artificial effect caused by molecular libration, it may nevertheless be genuine for it is not eliminated by corrections based on reasonable libration models (vide infra) for either structure. Indeed, the main effect of the libration corrections for the 100 K structures is to increase all interatomic distances within the molecules by approximately the same amount, 0.003 ± 1 Å. The mean C–C distances corrected for librational motion are both 1.394 Å, practically the same as in benzene (1.396 Å).[23]

Thermal Motion Analysis

The first conclusion that may be reached by analysis of the atomic displacement parameters (listed in Table III for the 100 K and in Tables S1 and S2 for the 150 K structures) is that the molecules do not behave as rigid bodies in the crystals but show appreciable internal motion at both temperatures. As a criterion of molecular rigidity, and also to assess the quality of the atomic displacement parameters, we use Hirshfeld's "rigid bond" test[24] and its generalization.[25] The rigid bond test is based on the

(22) Domenicano, A.; Murray-Rust, P. *Tetrahedron Lett.* **1979**, 2283–2286.
(23) Tomagawa, K.; Iijima, T.; Kimura, M. *J. Mol. Struct.* **1976**, *30*, 243–253.
(24) Hirshfeld, F. L. *Acta Crystallogr., Sect. A* **1976**, *32*, 239–244.

Table VI. Description of the Vibrational Model Fitted to the Atomic Displacement Parameters

	orthorhombic						monoclinic					
T, K	100			153			100			152		
T_c, ×10^{-4} Å²	132 (4)	2 (4)	1 (4)	192 (6)	5 (5)	-4 (5)	142 (5)	1 (4)	16 (4)	221 (8)	4 (6)	20 (5)
		130 (4)	-1 (4)		189 (6)	3 (5)		97 (4)	-8 (4)		148 (7)	-13 (6)
			112 (4)			166 (5)			96 (5)			159 (7)
T_i	134	128	112	196	186	164	148	102	85	227	165	136
L_c, deg²	3.6 (4)	0.0 (3)	0.1 (3)	5.5 (5)	0.0 (5)	0.1 (4)	2.8 (4)	-0.7 (3)	0.1 (2)	4.8 (6)	-1.5 (5)	0.1 (4)
		4.4 (4)	0.7 (2)		6.8 (6)	1.1 (3)		3.4 (3)	-1.2 (3)		5.3 (6)	-2.0 (5)
			3.7 (3)			5.3 (4)			3.2 (3)			4.6 (5)
L_i	4.8	3.6	3.2	7.3	5.5	4.7	4.7	2.8	1.9	7.5	4.6	2.6
S_c, ×10^{-2} Å·deg	2 (1)	1 (1)	0 (1)	4 (1)	3 (1)	1 (2)	3 (1)	2 (1)	-2 (1)	5 (1)	2 (2)	-4 (2)
	1 (1)	4 (1)	-1 (1)	3 (1)	7 (1)	-3 (2)	0 (1)	1 (1)	0 (1)	1 (2)	2 (1)	2 (2)
	-1 (1)	-1 (1)	-7 (1)	-2 (1)	-1 (1)	-10 (1)	0 (1)	-2 (1)	-4 (1)	1 (1)	-2 (1)	-7 (1)
ϕ_A, $\langle\Omega_A^2\rangle$, ν_A	62[a]	42 (5)[b]	52 (3)[c]	62[a]	62 (7)[b]	52 (3)[c]	77[a]	22 (4)[b]	73 (7)[c]	77[a]	34 (7)[b]	75 (7)[c]
ϕ_B, $\langle\Omega_B^2\rangle$, ν_B	22	5 (4)	177 (56)	22	5 (6)	219 (88)	19	8 (4)	128 (35)	19	11 (7)	136 (31)
ϕ_C, $\langle\Omega_C^2\rangle$, ν_C	21	7 (4)	148 (36)	22	10 (6)	138 (31)	10	7 (4)	141 (28)	11	19 (7)	104 (16)

[a] Degrees. [b] Degrees squared. [c] Reciprocal centimeters.

postulate that if $z_{A,B}^2$ is the mean-square displacement amplitude (MSDA) of atom A in the direction of atom B, then

$$\Delta_{A,B} = z_{A,B}^2 - z_{A,B}^2 \sim 0$$

for any pair of bonded atoms of roughly similar mass.[24] In a rigid molecule, by definition, $\Delta_{AB} = 0$ for every pair of atoms so the value of $\langle\Delta_{A,B}^2\rangle$ should be approximately the same when averaged over nonbonded as over bonded pairs of atoms. Table V shows that values of $\langle\Delta_{A,B}^2\rangle^{1/2}$ calculated from the experimental U^{ij} values for all atom pairs *within* the benzene rings are approximately $\sqrt{2}$ times larger than the overall esd of the atomic U^{ii}'s, as expected for rigid units. However, values of $\langle\Delta_{A,B}^2\rangle^{1/2}$ for atom pairs in different benzene rings are several times larger still, indicating that the phenyl groups are carrying out motions relative to each other in the crystal.

More detailed analyses of the vibrational motion were performed with the computer program THMB[26] which gives a least-squares fit to the experimental atomic displacement tensor components U^{ij} (Tables III, S1, and S2) of various parameters designed to describe the molecular motion: components of the **T**, **L**, and **S** tensors that describe the rigid-body vibrations[27] together with mean-square libration amplitudes $\langle\Omega^2\rangle$ about defined axes[28] to describe the internal motion. Trueblood has shown[26] that this simple one-parameter model for torsional libration gives results not significantly different from those of more elaborate models, even for root-mean-square amplitudes as high as 0.4 rad.

Table VI gives results obtained for both crystal modifications at the two temperatures, allowing for torsional vibrations of the phenyl groups about the P–C axes.[29] Clearly, for all four analyses the value of $\langle\Omega^2\rangle$ is much the largest for ring A, so the arguments presented in the introduction would appear to be vindicated, at least qualitatively, which is about as much as could be expected.

We performed several other analyses based on different models for the internal molecular motion. For example, for the ortho-

(25) Rosenfield, R. E.; Trueblood, K. N.; Dunitz, J. D. *Acta Crystallogr., Sect. A* **1978**, *34*, 828–829.

(26) Trueblood, K. N. *Acta Crystallogr., Sect. A* **1978**, *34*, 950–954.

(27) Schomaker, V.; Trueblood, K. N. *Acta Crystallogr., Sect. B* **1968**, *24*, 63–76.

(28) Dunitz, J. D.; White, D. N. J. *Acta Crystallogr., Sect. A* **1973**, *29*, 93–94.

(29) In calculations with program THMB, correlations between the internal rotations and the overall rigid-body motions are neglected. Schomaker and Trueblood[30] have recently drawn attention to the possible importance of such correlations, which are now incorporated in their new program THMV. Calculations with this program with inclusion of correlation parameters for the 150 K data yield only small changes in the $\langle\Omega^2\rangle$ values, and the main conclusions of the present work are unaffected.

(30) Schomaker, V.; Trueblood, K. N. *Acta Crystallogr., Sect. A* **1984**, *40* (Supplement) C-339.

Table VII. Comparison of Calculated Cell Constants and Phenyl-Ring Rotations for the Two Crystal Modifications with the Values Observed at 150 K

	orthorhombic form Δ(calcd − obsd$_{150\ K}$)^a	monoclinic form Δ(calcd − obsd$_{150\ K}$)
a, Å	0.328 (1.1%)	0.033 (0.3%)
b, Å	0.114 (1.3%)	0.076 (0.9%)
c, Å	-0.149 (-1.3%)	0.198 (1.2%)
β, deg		2.23
V/Z, Å³·molecule^{-1}	3.8 (1.0%)	3.6 (1.0%)
ϕ_A, deg	-0.7	0.0
ϕ_B, deg	6.4	0.5
ϕ_C, deg	2.1	3.2

^{a}Structure does not correspond to a true minimum of the energy surface (see text).

rhombic form, **T**, **L**, and **S** tensors were determined for the motion of the individual benzene rings separately (including the P atom in each case to prevent the well known singularity[27,31] in the normal equations). For ring A at 100 K the eigenvalues (and corresponding eigenvectors) of **L** were 43.0 deg² (nearly along the P–C direction), 4.6 deg² (nearly normal to the ring plane), and 1.7 deg². The same pattern was found at 150 K for ring A and roughly the same, with allowance for the smaller libration amplitudes, for rings B and C at both temperatures. Thus, of the three types of motion of phenyl groups, recently described[32] picturesquely as yawing, pitching, and rolling, the third is by far the most important and the second the least important. Calculations were also made for a model that included six degrees of internal motion instead of only three (yawing as well as rolling of the phenyl groups). The main effect is to reduce the rigid-body **L** tensor by 20–25%;, the new internal motions (expressed as librations about axes perpendicular to the phenyl planes) are 5.5 (13), 6.6 (14), and 1.7 (13) deg² for rings A, B, and C, respectively, for the orthorhombic crystal at 100 K (roughly 50% larger at 150 K) while the $\langle\Omega^2\rangle$ values for the main librational ring motions increase slightly (by circa 2 deg² at 100 K). All the calculations agree about the main point: that the mean libration amplitude of ring A is several times larger than those of rings B and C.

Program THMB can provide libration corrections either for rigid-body molecular motion or for specifiec types of internal motion, but not for both since this would involve unverifiable assumptions about the relative phases of the two kinds of motion. The corrections obtained for the two kinds of motion do not differ

(31) First noted by: Cruickshank, D. W. J. *Acta Crystallogr.* **1956**, *9*, 754–756.

(32) Domenicano, A.; Murray-Rust, P.; Vaciago, A. *Acta Crystallogr., Sect. B* **1983**, *39*, 457–468.

greatly for the same molecule at the same temperature. They are anyway small: 0.002–0.003 Å for the orthorhombic modification and 0.003–0.005 Å for the monoclinic (both at 100 K). The patterns of observed bond distances (Table IV) are not thereby affected.

Semiempirical Energy Calculations: Isolated Molecule

Maps of the variation in molecular energy with rotation of the phenyl rings were calculated with Busing's program WMIN,[33] an idealized molecular geometry,[34] and a very simple force field;[35] these maps are in good qualitative agreement with conclusions drawn from the distribution of Ph_3PO sample points (Figure 2). The exact position of the global minimum varies a few degrees along the $(0, 0, z_H)$ axis depending on the potential functions used. The precise location of the transition state and the details of the minimum energy path for inversion are also somewhat sensitive to the chosen energy parameters. Overall, however, the energy calculations confirm the results obtained from the structure correlation method. The calculated energy variation along the path is only a few kcal/mol, which confirms BSD's estimate.[2] The calculated maps are also very similar to those obtained by Brock and Ibers[12] for triphenylphosphine, except that the presence of the oxygen atom causes the global minimum they found around $(x_H, y_H, z_H) = (40°, 30°, 35°)$ to become much shallower, or even to disappear.

Semiempirical Energy Calculations: Crystal Forms

Calculations for the two crystalline phases with WMIN[33] were less satisfactory and raised as many questions as they answered. In both cases, minimization started from the structure as observed at 150 K, but with the C–H bonds lengthened to 1.04 Å as is appropriate for William's potentials.[36] The charges used were ±0.13 e⁻ for the C and H atoms and ±0.61 e⁻ for the O and P atoms;[39] however, neither the exact molecular geometry nor the specific charges chosen affect the conclusions that can be drawn from these calculations. General procedures for the minimizations were similar to those described previously;[40] the Ewald–Bertaut–Williams method[41] for accelerated convergence was employed, and summations were carried to a precision of about 0.4 kcal/mol. At convergence, the energies of the two crystalline forms differed by less than 0.03 kcal/mol.

Energy minimization of the monoclinic crystal reproduces the observed structure (Figure 4b) nicely (see Table VII). In the final cycle there were 13 variables: 4 for the unit-cell parameters, 6 to describe the translation and rotation of the whole molecule, and 3 for the torsion angles of the phenyl groups. Convergence was followed by a normal-mode calculation, which showed that the 3 internal modes mix extensively with the 6 lattice modes. The eigenvectors are not simple, and it is not possible to single out one with an especially large contribution from ϕ_A. A calculation[42]

(33) Busing, W. R. "WMIN, A Computer Program to Model Molecules and Crystals in Terms of Potential-Energy Functions"; Oak Ridge National Laboratory: Oak Ridge, TN, 1981; ORNL-5747.

(34) The framework of the molecule was taken to have C_{3v} symmetry with bond lengths C–C = 1.40 Å, C–H = 1.04 Å, C–P = 1.80 Å, and P–O = 1.49 Å and bond angles C–P–C = 106°. The only degrees of freedom allowed were the three rotations of the phenyl rings about their respective C–P bonds.

(35) The C and H atom potentials and the O atom potential were taken from standard sources (ref 36 and 37); the P atom potential was as used in ref 12. Several sets of partial charges were used (including zero charges); one set had partial charges of ±0.15 e⁻ on the C and H atoms and ±0.25 e⁻ on the P and O atoms. These values for the C and H atoms are the same as used by Williams in his study of benzene clusters (ref 38).

(36) Williams, D. E.; Starr, T. L. *Comput. Chem.* **1977**, *1*, 173–177.

(37) Cox, S. R.; Hsu, L.-Y.; Williams, D. E. *Acta Crystallogr., Sect. A* **1981**, *37*, 293–301.

(38) Williams, D. E. *Acta Crystallogr., Sect. A* **1980**, *36*, 715–723.

(39) These partial charges were determined by adjustment (ref 33) to give the best possible fit to the two crystal structures as observed at 150 K (2 adjustable parameters, 25 observations including unit cell dimensions, molecular translations and rotations, and internal rotations ϕ_i for the two phases).

(40) (a) Brock, C. P. *Acta Crystallogr., Sect. A* **1977**, *33*, 193–197. (b) Brock, C. P. *Ibid.* **1977**, *33*, 898–902.

(41) Williams, D. E. *Acta Crystallogr., Sect. A* **1971**, *27*, 452–455.
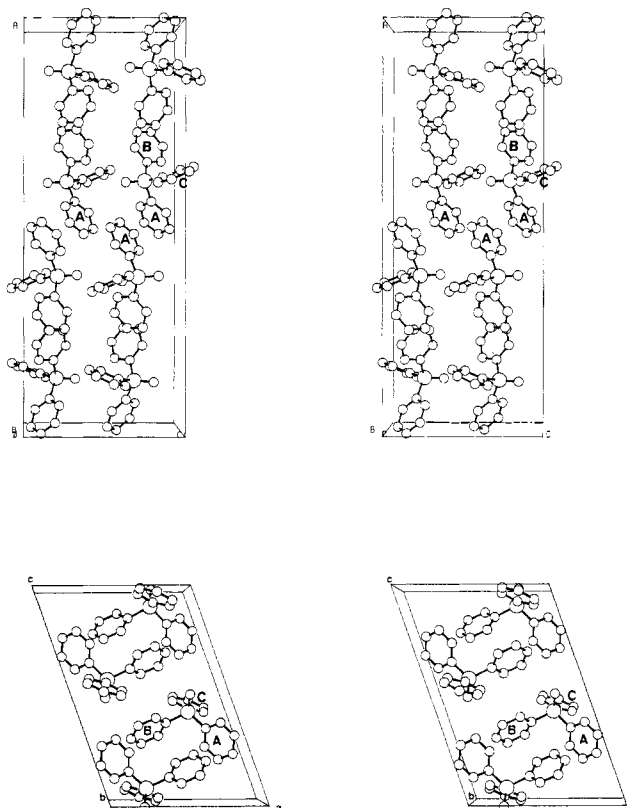

Figure 4. Stereoscopic views of the orthorhombic (top) and monoclinic (bottom) crystal structures of triphenylphosphine oxide.

to give $\langle \Omega_i^2 \rangle^{1/2}$ averaged over all 9 modes at 150 K indicates that the root-mean-square torsional amplitudes of the rings should be about equal, contrary to the results from the thermal motion analysis (Table VI). An examination of the energy changes as one phenyl ring at a time is rotated leads to a similar discrepancy.

Energy minimization of the orthorhombic modification (12 variables) seems to reproduce the experimental results satisfactorily (see Table VII). There is a fundamental flaw, however; the calculation always gives one very negative eigenvalue corresponding to an imaginary frequency. Major contributors to the associated eigenvector are the unit-cell dimension a, the torsion angle ϕ_A, and to a lesser extent c and ϕ_B. The negative eigenvalue is not eliminated by changing the charges on the P or O atoms nor by choosing a different C–H bond length. If the cell constants are fixed at the 150 K values, the minimization diverges.

Examination of the crystal packing for the orthorhombic modification (Figure 4) shows that the A rings are all located near planes at $x = 0$ and $^1/_2$ where they are related by inversion centers and 2_1 axes. The B rings are similarly disposed at $x = ^1/_4, ^3/_4$. This arrangement suggests that correlation of the motions of rings A, and perhaps also of rings B, may be important for adjacent molecules. Extrapolation from the values measured at 100 and 150 K implies that $\langle \Omega_A^2 \rangle$ would be *at least* 125 deg² at room temperature. The root-mean-square displacement amplitude of some of the phenyl H atoms would then be more than 0.4 Å. It is hard to imagine this large a motion of neighboring groups that is *not* correlated.[43] As normally used, the program WMIN assumes that the motions of all symmetry-related molecules are in phase, i.e., the space-group symmetry is preserved. The eigenvalues and their frequencies correspond to the totally symmetric irreducible representation of the space group at $q = 0$ (where q is the wave vector). Some calculations for other irreducible representations

(42) Cyvin, S. J. "Molecular Vibrations and Mean Square Amplitudes"; Elsevier: Amsterdam, 1968.

(43) Disorder can probably be ruled out since the individual U tensors for ring A and also the value of $\langle \Omega_A^2 \rangle^{1/2}$ show the same temperature dependence as those for the rest of the molecule and for the other crystal phase.

were attempted, but no structure having a significantly lower energy and corresponding to a true minimum of the energy surface was found.

More work needs to be done on the interpretation of these experimental results. To model this system properly we would need to do lattice-dynamical calculations allowing for four (for the monoclinic phase) or eight (for the orthorhombic phase) linear combinations of the molecular motions within a unit cell and for integration over the Brillouin zone. This would present problems since available programs[44] do not seem adequate for the task.

(44) (a) Pawley, G. S. *Phys. Status Solidi* **1967,** *20,* 347–360. (b) Filippini, G.; Gramaccioli, C. M.; Simonetta, M.; Suffritti, G. B. *J. Chem. Phys.* **1973,** *59,* 5088–5101.

Carbon Acidity. 66. Equilibrium Ion Pair Acidities of Substituted Diphenylmethanes in Cyclohexylamine[1]

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Abstract: The pK_{CsCHA} values are reported for a number of symmetrically meta- and para-substituted diphenylmethanes. The pK_{CsCHA} values for the meta series (Me, 33.8; OMe, 32.7; F, 29.9; CF$_3$, 28.9; Ph, 32.3; H, 33.4) give a normal Hammett plot with ρ = 9.69. The para series (Me, 35.1; OMe, 37.6; Ph, 30.8; NMe$_2$, 38.6; SPh, 28.8; CN, 23.0; SO$_2$Me, 22.4) do not fit attempted correlations with σ^-, the Yukawa–Tsuno modification, or dual substituent parameter approaches. Electron-donating groups are more anion destabilizing than in other reference systems. "Amphoteric" substituents, those that stabilize both anions and cations (phenyl, thio, etc.), cause special problems in generalized correlations.

Interest in substituent effects and in Hammett-type linear free energy relationship (LFER) continues undiminished as judged by recent reviews,[2-9] undoubtedly because of the general success of such approximations in correlating a range of chemical phenomena and their utility in studies of reaction mechanism. Limitations of the original Hammett $\rho\sigma$ scheme in situations of high electron demand or supply have resulted in modification either by the use of "enhanced" σ values (e.g., σ^+ or σ^-)[3,10,11] or by extensions to additional parameters such as σ_R, σ_R^+, or σ_R^-.[7,12,13] Substituent effects in situations of high electron demand, as in carbocation systems, have been amply documented by many studies in strong acidic media. The chemistry of high electron

supply, however, is not as well documented and is restricted mostly to substituted anilines and phenols. Few studies of substituent effects in carbanions are presently available.

Equilibrium acidities of substituted 9-phenylfluorenes are available in aqueous dimethyl sulfoxide (Me$_2$SO),[14] but in these systems the phenyl group is twisted by steric effects with respect to the fluorenyl anion and the change of conjugative electron supply is limited. Similarly, equilibrium acidities are available for ring-substituted fluorenes,[15,16] but substituent effects in these systems are complicated by the different modes of conjugation available in the fluorenyl system; e.g., the 3-position is conjugated directly (para) to the fluorenyl 9-position but the 2-position (meta) is also conjugated via the second benzene ring. More recently, Bordwell has summarized the results of a number of carbanion substituent effects in Me$_2$SO.[17-19] These results will be discussed below.

In the present paper we report the equilibrium ion pair acidities on the cesium cyclohexanamide (CsCHA) scale, pK_{CsCHA}, for a series of symmetrically substituted diphenylmethanes. The examples include several compounds whose acidities are too low to measure in Me$_2$SO or related polar media, but the established correlation[20] between ionic pK_{Me_2SO} and ion pair pK_{CsCHA} for highly

(1) Paper 65 in this series: Streitwieser, A., Jr.; Bors, D. A.; Kaufman, M. J. *J. Chem. Soc., Chem. Commun.* **1983,** 1394. Paper 64: Streitwieser, A., Jr.; Swanson, J. T. *J. Am. Chem. Soc.* **1983,** *105,* 2502.
(2) Hammett, L. P. "Physical Organic Chemistry"; McGraw-Hill: New York, 1940; Chapter 7.
(3) Jaffe, H. H. *Chem. Rev.* **1953,** *53,* 191.
(4) Wells, P. R. "Linear Free Energy Relationships"; Academic Press, Inc.: New York, 1968.
(5) Johnson, C. D. "The Hammett Equation"; Cambridge University Press: London, Great Britain, 1973.
(6) Shorter, J. "Correlation Analysis in Organic Chemistry"; Oxford University Press: London, Great Britain, 1973.
(7) Ehrenson, S.; Brownlee, R. T. C.; Taft, R. W. *Prog. Phys. Org. Chem.* **1973,** *10,* 1.
(8) Chapman, N. B.; Shorter, J. "Correlation Analysis in Chemistry"; Plenum Press: New York, 1978.
(9) Charton, M. *Prog. Phys. Org. Chem.* **1981,** *13,* 119.
(10) Brown, H. C.; Okamoto, Y. *J. Am. Chem. Soc.* **1958,** *80,* 4979.
(11) (a) Exner, O. "Advances in Linear Free Energy Relationships"; Plenum Press: London, 1972; Chapter 1. (b) Reference 8, Chapter 10, from ref 11a.
(12) Taft, R. W. "Steric Effects in Organic Chemistry"; Newman, M. S., Ed.; Wiley: New York, 1956; Chapter 13.
(13) Taft, R. W. *J. Phys. Chem.* **1960,** *64,* 1805.

(14) Cockerill, A. F.; Lamper, J. E. *J. Chem. Soc. B* **1971,** 503.
(15) Bowden, K.; Cockerill, A. F. *J. Chem. Soc. B* **1970,** 173.
(16) Bowden, K.; Cockerill, A. F.; Gilbert, J. R. *J. Chem. Soc. B* **1970,** 179.
(17) Bordwell, F. G.; Algrim, D.; Vanier, N. R. *J. Org. Chem.* **1977,** *42,* 1817–9.
(18) Algrim, D.; Bares, J. E.; Branca, J. C.; Bordwell, F. G. *J. Org. Chem.* **1978,** *43,* 5024–6.
(19) Bordwell, F. G.; McCallum, R. J.; Olmstead, W. N. *J. Org. Chem.* **1984,** *49,* 1424–7.
(20) Streitwieser, A., Jr.; Juaristi, E.; Nebenzahl, L. L. "Comprehensive Carbanion Chemistry"; Buncel, E., Durst, T., Eds.; Elsevier: New York, 1980; Chapter 7.