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Conformational Analysis of the Triphenylphosphine Molecule in the Free and Solid States*

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A conformational analysis study of the triphenylphosphine molecule, $P(C_6H_5)_3$, as it exists in the free and solid states has been carried out in order to assess the influence of crystallization on molecular geometry. A semi-empirical energy minimization procedure has been used in which the strain energy of the molecule is taken as the sum of valence bond and angle deformation terms and of repulsive and van der Waals interactions between non-bonded atoms; the energy is then minimized by varying the atomic positions. In order to simplify the problem, the phenyl rings were treated as rigid bodies having D_{6h} symmetry. Calculations were made both for the isolated molecule and for triphenylphosphine in the experimentally determined unit cell. The molecular conformation resulting from this latter refinement closely reproduced that found by X-ray diffraction. Similar bond distances and angles were calculated in the free and solid states, showing that crystallization has little effect on these parameters. However, while the rotations of the phenyl rings in the solid state are fixed, it is found that in the free state there are a number of conformations of similar energy which differ only in the rotations of the three rings about their respective phosphorus–carbon bonds.

Introduction

The structures of small and medium-sized molecules, as specified by their bond distances and angles, may be precisely determined by spectroscopic and diffraction techniques. The structural parameters thus obtained reflect not only the bonding properties of the atoms in the molecule, but the steric interactions between non-bonded atoms in the molecule as well. For molecules studied in the solid state, interactions with adjacent molecules may also be important. In trying to understand the significance of the geometry of a molecule it is important to understand the relative importance of these factors.

Calculational techniques for predicting molecular geometry have been successfully developed, particularly for organic molecules (Williams, Stang & Schleyer, 1968). These calculations are based on a mechanical model in which the molecule is treated as a system of masses held together by classical forces. The force field is parameterized, and the molecular conformation of minimum energy found. Information is obtained not only about the types of distortions apt to be seen, but also about the distribution of energy between the internal coordinates. Comparisons with the experimentally determined structure reveal the extent to which the assumed force field can account for the observed molecular geometry.

In this type of calculation the energy minimized is the strain energy, that is, the energy in excess of some hypothetical strain-free state. The hypothesis of such a state implies that all the strain in a molecule arises from the non-bonded atomic repulsions, and that the final conformation reflects a distribution of this energy throughout the internal coordinates. The strain energy of the molecule is expressed as the sum of contributions from bond stretching, angle bending, and non-bonded interactions. In this summation the strain energy is divided into terms dependent on the individual internal coordinates and the non-bonded distances. This latter group leads to a large number of interactions; rather than taking the summation over all the interatomic distances, the series is truncated at some arbitrary limit beyond which it is assumed that the non-bonded energy will have little effect on the equilibrium geometry. The expressions for the individual energy terms are derived from classical models of atomic motion. For bond and angle deformation terms harmonic potentials are used, while non-bonded interactions are usually represented by either the Lennard-Jones (6–12) or the Buckingham (exp-6) potentials.

The triphenylphosphine molecule is often used as a ligand in complexes of transition metals. It is usually the most bulky part of the molecule and consequently the conformations of the rings determine the shape of the complex and the manner in which it is packed into the unit cell upon crystallization. It is therefore of interest to study the possible conformations of the phenyl groups and to assess the influence which crystallization has on them.

The $P(C_6H_5)_3$ species should be a good molecule to study. The non-bonded contacts are almost exclusively between carbon and hydrogen atoms; potential functions for these interactions have been extensively investigated. Also, since it is the inter-ring contacts which determine the conformation, the atoms involved are not held in close proximity by valence forces, nor

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are 1,3-non-bonded terms, which may be directionally dependent, particularly important. The interactions should therefore be well represented by standard potential functions. It is unlikely that the phenyl rings would be distorted by steric forces. Rather, rotation about the phosphorus–carbon bond should occur to relieve crowding. Therefore, the phenyl groups may be treated as rigid bodies of D_{6h} symmetry, the position and orientation of each being specified by three translations and three rotations. This idealization reduces the number of variables considerably and makes the problem tractable.

By energy minimization techniques the most stable conformation may be found for both the isolated molecule and for the molecule within the crystal. Comparison of these two should give some indication of the types of constraints imposed by the solid state and the kinds of molecular deformations that may be found as a result of crystallization. Since the crystal structure of triphenylphosphine is known (Daly, 1964), these two calculated conformations may be compared with the experimentally determined one in order to determine how well the force field used reproduces the observed structure.

Description of the calculations

All calculations were performed using Busing's (1970) Fortran program *WMIN*. This program combines calculation of molecular strain energy with the possibility of summation of the non-bonded contributions to the energy (van der Waals, repulsive, and Coulombic) over the crystal lattice. A number of options are available within the program, including variation by Newton's method of the atomic positions to minimize the strain energy, determination by least-squares methods of those force-field parameters which best reproduce a given molecular geometry, and mapping of the energy as a function of up to three structural or force-field parameters. The majority of the computations were carried out on the Northwestern CDC 6400 and University of Kentucky IBM 360/65 computers. Those calculations which involved summations over the crystal lattice required more central memory than is available on these machines. Such calculations were carried out by remote transmission to the Lawrence Berkeley Laboratory CDC 7600 computer via the Northwestern CDC 200 Series User Terminal. Geometrical analysis of the calculated conformations was made using Busing, Martin & Levy's *ORFFE* program and parts of the X-RAY 70 system.

Initial parameters describing the force field of the molecule were taken from literature values. The potential functions employed to describe the energy of deformation of valence bonds and angles were the usual harmonic expressions:

$$E(r)=\tfrac{1}{2}k_r(r-r_0)^2$$
$$E(\theta)=\tfrac{1}{2}k_\theta(\theta-\theta_0)^2,$$

where k_r and k_θ are the stretching and bending force constants, and r_0 and θ_0 are the hypothetical strain-free bond lengths and angles, respectively. The value of k_r for the P–C bond was taken from vibrational work on a series of substituted phosphines (Smit & van der Maas, 1967) and is given in Table 1 along with all other parameters used to describe the force field. The strain free C(1)–P–C(1) bond angle was taken to be 90° reflecting the observed lack of hybridization in phosphorus compounds. Values for the angle-bending force constant k_θ and the hypothetical strain-free P–C bond length r_0 were found by a least-squares fit of these two parameters to the experimentally determined geometry of the triphenylphosphine molecule. The final values of these two parameters (Table 1) are physically reasonable.

Table 1. *Potential function parameters used for triphenylphosphine*

Bond and angle deformation :

P–C	$k_r=3{\cdot}00$ mdyne Å^{-1}	$r_o=1{\cdot}71$ Å
∠C–P–C	$k_\theta=0{\cdot}188$	$\theta_o=90{\cdot}00°$

Non-bonded potentials:

Set I (Williams, 1967, Potential IV)

P	$A=1{\cdot}877$ Å	$B=0{\cdot}1381$ Å	$C=37{\cdot}8$ (kcal Å^6/mole)$^{1/2}$
C	1·752	0·1389	23·8
H	1·230	0·1337	5·22

Set II (Alternate functions for carbon and hydrogen atoms)

C	1·579	0·141	22·64
H	1·336	0·146	4·94

A non-bonded potential developed for argon···argon interactions from data on gases (Mason & Kreevoy, 1955) and used successfully to reproduce the structure of orthorhombic sulfur (Giglio, Liquori & Mazzarella, 1968) was used for the phosphorus atom. Two sets of carbon and hydrogen atom non-bonded potentials were tested. The first set was taken from those developed by Williams to reproduce the intermolecular distances in a series of crystals of alkyl and aryl hydrocarbons (Williams, 1967). A second, alternate set was used in order to compare the effects of interactions arising from carbon and hydrogen atoms. The parameters for the attractive part of this second potential set were taken from the literature (Williams, 1970). Parameters for the repulsive part, however, were chosen so that this second potential set represented a more repulsive H···H interaction and a less repulsive C···C interaction than did the first set. In this way it was possible to test the sensitivity of the preferred conformation to the potential parameters used, and correlate the energy barriers between conformations with either C···C or H···H interactions. The parameters for both potential sets are given in Table 1. The form of the Buckingham expression for the non-bonded interaction between two atoms i and j used is (Gilbert, 1968):

$$E(nb) = (B_i + B_j) \exp [(A_i + A_j - r_{ij})/(B_i + B_j)] - (C_iC_j)/r_{ij}^6 .$$

This expression requires that the geometric-mean combining law be used for the mixed interactions; therefore, the C···H potential is a combination of the C···C and H···H potentials.

In all calculations the phenyl rings were treated as rigid bodies of D_{6h} symmetry with $d_{C-C} = 1{\cdot}40$ Å and $d_{C-H} = 1{\cdot}08$ Å, the orientation of the ring being specified by three translations and three rotations. Energy terms involving atoms belonging to the same rigid body were omitted.

Two series of calculations were carried out. In the first, the molecule was originally assumed to have C_3 symmetry with the P–C bond length of 1·828 Å and the C–P–C angle of 103·0° equal to the averages of the values found in the crystal structure (Daly, 1964). These restrictions were gradually relaxed as various maps of the energy as a function of the structural parameters were made and refinements leading to the energy minima were performed. Also, tests were made of the sensitivity of the depth and position of these minima to the exact parameters of the potential functions. The rhombohedral coordinate system used for these calculations was defined by the three P–C bonds of the original C_3 model, coordinates being expressed in Å.

Fractional coordinates based on the monoclinic unit cell, space group $P2_1/c$, found by Daly for the crystals of triphenylphosphine were used for the second set of computations. Energy minimization using Williams's carbon and hydrogen non-bonded potential functions was carried out both on the isolated molecule and on the molecule within the framework of the crystal lattice. The starting coordinates for both refinements were taken from the results of the crystal structure determination after idealization of the phenyl rings. In all cases, refinement was carried out until root-mean-square shifts in translations and rotations of the rigid bodies were less than 0·01 Å and 0·005 rad (0·3°) respectively.

The summation made during the energy calculations included contributions from all bond lengths and angles and from all non-bonded interactions between atoms less than 5 Å apart. In the mapping procedures, however, all such distances up to 8 Å were included. A table of the non-bonded contacts is generated only once during each execution of the mapping segment of the program; the higher limit was used to ensure that non-bonded terms which might become important after large rotations of the rings would not be neglected. In the refinement in the crystal lattice the summation was extended to 6 Å in order to include all important intermolecular terms. Repulsive interactions are negligible beyond this distance, and convergence errors in calculating van der Waals terms for the lattice are virtually eliminated by use of the Ewald–Bertaut–Williams method (Bertaut, 1952; Williams, 1971). In both of these cases, the position of the minimum was not changed by increasing the summation limit past 5 Å, although the energy varied by several kcal mole^{-1} as more interactions were included.

Results and discussion

In order to compare the possible conformations of triphenylphosphine, the geometries must be specified by descriptive structural parameters. A picture of the molecule as observed by Daly showing the numbering of the atoms is given for reference in Fig. 1; the distances and angles describing this structure are found in Table 2. To characterize the coordination about the phosphorus atom, the P–C(1) bond distance and the C(1)–P–C(1) angles are given. The angle between the P–C(1) bond and the plane of the three C(1) atoms provides an alternative description. If the molecule is constrained to have C_3 symmetry, the number of degrees of freedom needed to specify the geometry of the PC_3 portion of the molecule is reduced from six to two.

Description of the triphenylphosphine molecule is completed by specification of the three orientation angles of each of the phenyl rings. The number of degrees of freedom required to designate the positions of the rings is reduced from nine to three if C_3 symmetry is imposed on the molecule. If the P–C(1)–C(4) bond angle is required to be linear, the number of independent rotations is also reduced by a factor of three. For the case in which both C_3 symmetry and P–C(1)–C(4) linearity are maintained, the orientations of the phenyl rings are determined by a single variable. This one

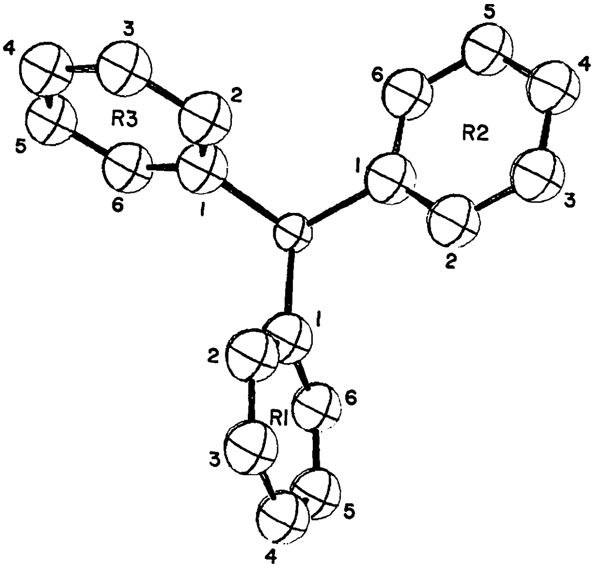

Fig. 1. Triphenylphosphine molecule as observed in the crystal structure determination. In this and the following figures hydrogen atoms are omitted for the sake of clarity.

Table 2. *Results of refinements of triphenylphosphine*

Distances are in Å, angles in °, and energy is in kcal mole^{-1}.

Refinement	P–C(1)	C(1)–P–C(1)	P···C(2)	P···C(6)	P–C(1)–C(4)	[C(1), C(1), C(1)] [C(1), C(4), C(6)]*	C(6)–C(1)–P–LP†	[C(1), C(1), C(1)] P–C(1)‡	Calculated energy
1. Daly crystal structure	1·822	103·6	2·86	2·74	174·9	67·8	24·8	64·6	
	1·831	102·1	2·86	2·76	173·4	36·5	61·8	64·7	44·84
	1·831	103·3	2·86	2·74	176·3	64·8	28·0	64·7	
2. Isolated, idealized molecule. Only rotations about C(1)–C(4) varied	1·828§	103·0§	2·804	2·804§	180·0§	55·6	38·6	64·6	47·25
						55·6	38·6	64·6	
						55·6	38·6	64·6	
3. Isolated molecule starting from C_3 symmetry	1·829	103·4	2·867	2·736	175·1	59·3	34·4	65·1	
	1·829	103·6	2·868	2·736	175·1	57·3	36·7	65·1	44·75
	1·829	103·6	2·869	2·735	175·0	58·1	35·8	65·1	
4. Isolated molecule starting from Daly coordinates	1·828	104·5	2·866	2·736	175·3	70·5	21·7	65·0	
	1·830	102·5	2·869	2·738	174·9	41·0	56·2	65·0	44·70
	1·830	103·2	2·863	2·742	174·9	61·0	32·7	65·0	
5. Molecule in crystal lattice	1·829	104·4	2·872	2·731	174·7	69·9	22·0	64·8	
	1·828	102·6	2·861	2·742	175·2	39·2	58·6	64·7	44·75 ‖
	1·826	102·3	2·857	2·741	175·8	65·1	27·8	64·7	

* Angle between plane of the three C(1) atoms and plane of each of the phenyl rings.
† Conformation angle defined by C(6), C(1), P, and the idealized position of the lone pair (LP).
‡ Angle between plane of the three C(1) atoms and each of the P–C(1) vectors.
§ Values held fixed in the refinement.
‖ Energy does not include intermolecular contacts.

parameter may be given in several ways. The first is the dihedral angle between the ring and the basal plane of the three C(1) atoms. This angle is 90° when the rings are parallel to the C_3 axis of the molecule and decreases as the rings are rotated. After rotation by 90°, when the ring is in the flattest position possible, this angle is the complement of the angle between the P–C(1) vector and the plane of the three C(1) atoms. These two extremes will be referred to as the parallel and flat positions respectively. A second description of this parameter is the torsion, or conformation, angle defined by C(6)–C(1)–P–LP, where the lone-pair electrons (LP) are assumed to lie on a line perpendicular to the plane of the three C(1) atoms and passing through the P atom. This number gives the degrees of twist around the C(1)–P bond necessary to bring C(6) into the plane defined by the other three atoms. The parallel and flat positions correspond to values of this angle of 0° and 90°, respectively.

In the more general case, in which C_3 symmetry and P–C(1)–C(4) linearity are not maintained ,the orientation of each ring is specified by the angles of rotation about the C(1)–C(4) vector and about two axes normal to this vector and passing through the center of the ring. Since P–C(1) is no longer necessarily parallel to C(1)–C(4), the molecular conformation is no longer completely described by the angles discussed in the preceding paragraph. However, the deviations from linearity of P–C(1)–C(4) that are observed are small, and the dihedral or conformation angles do provide an adequate description of the molecular geometry. Deviations from linearity, that is tilt of the rings relative to the P–C(1) bond, can be judged from the nonbonded distances between the phosphorus and α-carbon atoms of the rings, C(2) and C(6), and from the P–C(1)–C(4) angle.

Since the triphenylphosphine molecule may display C_3 symmetry, initial investigation of possible conformations proceeded from this idealized geometry. In addition, the P–C(1)–C(4) angle was required to be linear. The energy of the molecule was calculated as a function of the rotation of the rings about the P–C(1)–C(4) axis in increments of 0·04 rad (2·3°), C_3 symmetry being maintained. This calculation need only be made over 90°. The symmetry of the rings limits the unique values to a range of 180°, and since conformations differing only in their chiral sense have equal energies, the number of unique rotations is reduced by a second factor of two.

This map of the energy surface is shown in Fig. 2. Since the energy is referred to an arbitrary zero, only the energy differences between conformations are significant. More favorable conformations are identified with lower energies. The two curves correspond to the two different sets of carbon and hydrogen non-bonded potential functions of Table 1. Graphs of the nonbonded energy as a function of interatomic separation are given for these two sets of functions in Fig. 3. The two potential sets differ considerably, the C···C interaction being softer and the H···H interaction harder in the alternate set of functions than in the corresponding Williams expressions. Even so, the general features of the map are the same indicating that at least in this case the exact parameters of the potential functions are not crucial to the determination of the most stable geometry. The single minimum corresponds to a rotation of 39 ± 2° about the P–C(1)–C(4) axis away from the parallel position. The two maxima are found as expected at the parallel and flat positions, the latter barrier being of higher energy. When the rings are all flat, or the molecule is in the 'inverted umbrella' conformation, the inter-ring interactions between the α-carbon and the attached hydrogen atoms are very large. In the parallel position, the contacts between the hydrogen atoms of the α-carbon atoms are again important, but only one per ring is involved. Thus the barrier is lower. Since the maximum at the flat position is higher using the alternate set of functions, it may be concluded that the H···H interactions are predominant. Conversely, the C···C, and perhaps C···H, contacts are more important in the parallel position since the higher barrier is correlated with the more repulsive potentials of Williams.

Kitaigorodskii found that the preferred rotation angle of the rings in the molecules $M(C_6H_5)_4$, M = C, Si, Sn, and Pb, differed with the M–C bond length which varied from 1·50 to 2·29 Å over the series (Ahmed & Kitaigorodskii, 1972). By mapping techniques, however, we find that the position of the rings giving the minimum energy for $P(C_6H_5)_3$ is not dependent on the exact length of the P–C(1) bond. Over the much smaller range of 0·15 Å, the optimum rotation angle

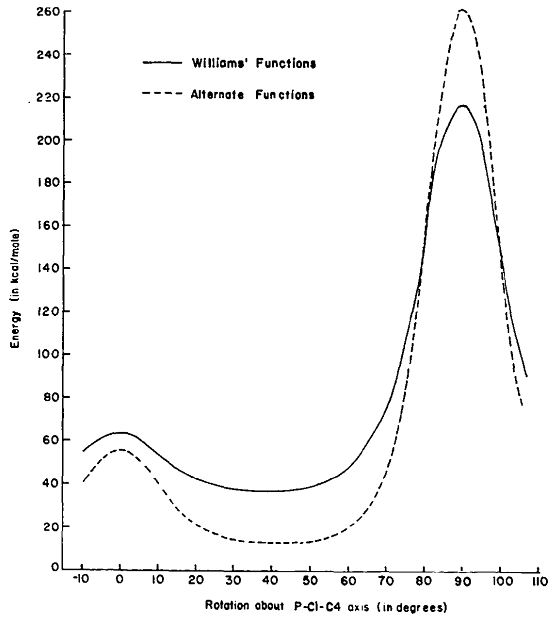

Fig. 2. Map of the energy of the triphenylphosphine molecule constrained to have C_3 symmetry as a function of the rotation of the phenyl rings.

was the same to within the size of the grid (*ca.* 2°), while the depth of the minimum varied by only several kcal mole^{-1}. Thus the exact values of the P–C(1) bond lengths, and hence of the bond-stretching potential constants, are not critical to the results. Kitaigorodskii also found that the constants of the non-bonded potential for the Group IV metal had little effect on the final geometry of the molecule. We find a similar insensitivity to the phosphorus atom potential.

Refinement of the individual rotations of the three rings about their P–C(1)–C(4) axes using Williams's functions located the minimum more exactly at 38·6°. The C_3 symmetry was maintained without imposing constraints. Results of this and subsequent refinements are given in Table 2. It should be noted that the energy of the minimum of the symmetric conformation is higher than that of the structure found by Daly. Bond and angle deformation terms are approximately equal for the two conformations; the difference arises from the more important repulsions in the symmetric one.

The next series of calculations involved refinement of all the degrees of freedom of the three phenyl rings of the molecule. Refinement starting from the geometry observed by Daly led to very small shifts in the ring translations and rotations. Such small changes would be expected since the force field describing the potential energy of the molecule had been chosen to fit this model. The refined structure did differ from the one found by Daly in that the three P–C(1) bond lengths and three C(1)–P–C(1) bond angles showed much smaller deviations from their mean values than did the corresponding distances and angles in the experimentally determined structure.

A similar refinement starting from the symmetric minimum found previously led to the same results with respect to the phosphorus–carbon bond distances and angles. The observed values were again reproduced, but with smaller deviations from the mean values than found in the crystal structure. The conformations of the rings in the refinement starting from C_3 geometry, however, were very different from those in the structure of Daly. The conformation observed in the crystal has two rings which are rotated significantly towards the parallel position, and one ring which is in a relatively flat position. The C_3 refinement, though, converges to another minimum in which the threefold axis is almost exactly maintained; the three rings are rotated equally. This conformation of the molecule is shown in Fig. 4. Note that the energy of the molecule for this refinement is 2·5 kcal mole^{-1} lower than for the refinement in which the P–C(1)–C(4) bond angles were required to be linear, and the only degree of freedom was the rotation of the ring around the P–C(1)–C(4) axes. As is observed in the crystal structure, the α-carbon atoms of the rings in the latter refinement are not symmetrically disposed with respect to the phosphorus atom. Rather, the C(6) atom, which is closer to the lone pair of the phosphorus than is the C(2) atom, is also closer to the phosphorus atom. Inter-ring repulsions involving C(2) atoms and the attached hydrogen atoms evidently tip the ring towards the lone pair. The angle P–C(1)–C(4) then deviates from 180° by about 5°, again in a

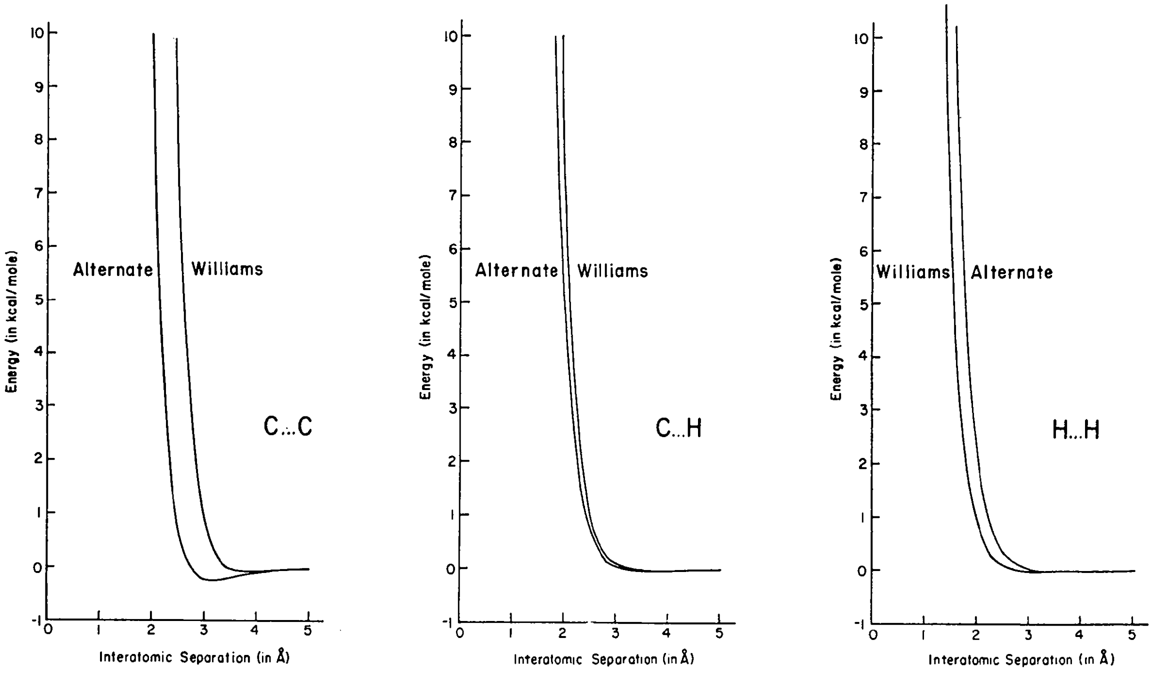

Fig. 3. Graphs of the non-bonded potential functions for the carbon and hydrogen atoms.

manner similar to that observed in the crystal structure.

Since there appear to be at least two equal minima differing only in the conformation of the rings, it seemed advisable to investigate further the shape of the potential energy surface as a function of the rotations of the rings. As before, the P–C(1) distance and the C(1)–P–C(1) angles were taken to be equal to the averages from the crystal structure, and the P–C(1)–C(4) angle was required to be 180°. The rotations of the three rings about this P–C(1)–C(4) axis, however, were varied independently, so that C_3 symmetry was no longer imposed on the molecule. The step size for calculating the map was 0·2 rad (11·5°). Again each ring need be rotated through only 90° owing to the symmetry of the ring and the energetic equivalence of the right-and left-handed conformations of the molecule. It was assumed that all three rings would have the same chiral sense; reversal of one of them would lead to large non-bonded interactions with the others. The number of unique energy values is further reduced by considering the threefold axis of the molecule. This map showed a large range of conformations having energies close to the minimum value. Furthermore, these conformations are all interconnected along one valley in the potential energy surface. The C_3 conformation mentioned above is similar to that at the one end of this long minimum, while the structure observed experimentally corresponds to an intermediate position. Throughout the valley the energy varies by less than 2 kcal mole^{-1}.[*]

The prediction of the existence of a number of equally probable conformations is in agreement with the generalizations drawn from a compilation of 26 structures of molecules containing the coordinated triphenylphosphine ligand given by Horrocks & Greenberg (1971). They found an approximately symmetric distribution for the conformation angles of the rings, the intermediate values being considerably more prevalent than those close to 0 or 90°. Since the data are for the solid state, while the map was for an isolated molecule, it is possible that crystal packing requirements favor the intermediate values. Some bias of the distribution towards higher conformation angles is seen, with the maximum in the 50 to 55° range. In the maps calculated for the C_3 model for triphenylphosphine, however, the favored conformation angle has a value of 35° to 40°. This discrepancy may reflect the difference between the free and coordinated states. Upon coordination, bond lengths and angles in the molecule do not change significantly. Interactions between the C(6) atoms, the associated hydrogen atoms, and the acceptor species become important, however. Positions of the rings close to the parallel position may therefore be less probable. The actual conformation observed out of the wide range of possibilities probably depends on a complex interplay of intra- and intermolecular factors. Entropy considerations favoring the asymmetric structure may also be important (Scheraga, 1971).

In order to determine the effect of the crystal lattice on the observed conformation, the refinement was carried out including contacts with the adjacent molecules and summing the van der Waals energy over the entire crystal lattice. In agreement with expectations, the crystal lattice does not significantly affect the bond distances and angles of the molecule. As in the isolated molecule, the valence bond distances and angles of the experimental structure are closely reproduced; conformation angles are also very similar to those found by Daly (Table 2). The observation that the geometry of minimum energy is very similar in the crystal and the free state indicates that at least in this case the process of crystallization changes the molecular conformation very little. In the free state there is a large range of possible conformations of the rings having a probability distribution function reflecting their relative energies. Which one of these conformations will be found in a particular crystal probably depends on the exact nature of the species, if any, to which the triphenylphosphine is complexed. The selection will depend both on what ring conformations are compatible with the rest of the complex and what the packing requirements of the lattice may be. The important point is, however, that the conformation found in the solid state is probably the same as one of the conformations that would be found in the free state or in solution.

A final question concerns the degree to which the refinement in the lattice reproduces the experimentally determined crystal structure. This agreement measures the suitability of the potential functions used. After refinement to root-mean-square (r.m.s.) shifts of 0·004

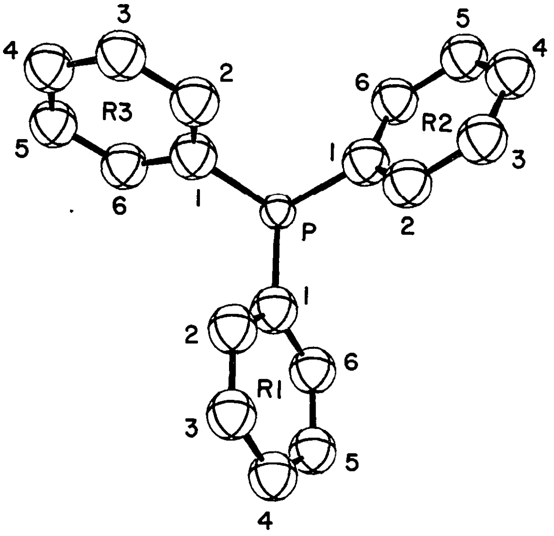

Fig. 4. Minimum-energy conformation of the triphenylphosphine molecule as refined from C_3 geometry.

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[*] There do appear to be shallow local minima in this valley which are different from either of the two conformations previously described. These minima are several kcal mole^{-1} higher in energy than the more important minima, but it is possible to converge to them if the refinement is carefully monitored and damping factors are applied to the shifts.

Å and 0·003 rad (0·2°) in the final cycle, the r.m.s. average of the translations of the rigid bodies totaled over all the rings is 0·082 Å. The same average over the rotations is 0·029 rad (1·7°). A second measurement of the similarily between the observed and calculated structures is the r.m.s. displacement of the atoms. Since the phenyl rings were refined as rigid bodies, the comparison must be made between the final atomic coordinates of the calculated structure and the idealized coordinates based on Daly's work. The r.m.s. displacements between the atoms of the two structures are then 0·174, 0·117 and 0·195 Å, respectively, for the three phenyl rings. The phosphorus atom is translated by 0·147 Å, and the total r.m.s. displacement over all the atoms is 0·165 Å. These shifts are small; the experimental structure appears to be well reproduced.

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The Crystal Structure of $Bi_2(MoO_4)_3$

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The crystal structure of $Bi_2(MoO_4)_3$ has been determined by Patterson and Fourier methods. Refinement was carried out by a block-matrix least-squares method, with 1902 Mo $K\alpha$ intensity data. The final R is 3·7%. The space group is $P2_1/c$ with lattice constants $a=7{\cdot}685$ (6), $b=11{\cdot}491$ (16), $c=11{\cdot}929$ (10) Å, $\beta=115{\cdot}40$ (2)°. There are four molecules per unit cell. Distorted tetrahedra of oxygen ions surround the molybdenum ions and occur in pairs. The bismuth ions have eight oxygen neighbours and the Bi–O distances can be divided into two distinct groups.

Introduction

During the last ten years, bismuth molybdates have been successfully applied as catalysts to the oxidation of propene and butene and the ammoxidation of propene, yielding respectively acrolein, butadiene and acrylonitrile. Although in the recent literature many efforts have been made to relate the activity and the selectivity of these mixed oxide catalysts to their physical and chemical characteristics, the crystal structures of some bismuth molybdates were still unknown or had not been determined with great accuracy. Therefore, as part of an investigation into the possible dependence of the catalytic properties of bismuth molybdates on the atomic arrangement in these catalysts, the crystal structure of $Bi_2(MoO_4)_3$ was determined.

Experimental

Very pure $Bi_2(MoO_4)_3$ was prepared by coprecipitation of bismuth nitrate with a very large excess of molybdic acid, as described by Batist, Bouwens & Schuit (1972). From the powder thus obtained, single crystals were grown by zone-melting in an open quartz-glass vessel.

The compound was analysed X-ray spectrographically from the intensity of the emitted Bi $L\alpha$ and Mo $K\alpha$ radiation. The ratio Bi:Mo was 2:2·85 between the limits 2:2·80 and 2:2·93. It was not possible to detect