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Dramatic Structural Effects of a Single Hydrogen Atom in $HNPBu^t_3$

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The molecular structure of tri-*tert*-butylphosphine imide has been re-determined using the recently developed DYNAMITE method, which allows all assumptions about local symmetry to be removed without increasing the number of refining structural parameters excessively. The imide hydrogen causes the $NPBu^t_3$ group to deviate hugely from local C_3 symmetry, with N–P–C angles returned as 99.2(9), 110.9(7), and 111.5(11)°, while the C–P–C angles also deviate from symmetry, being 109.8(8), 110.5(9), and 113.9(9)°, so that the NPC_3 fragment is close to C_s rather than C_3 symmetry. The application of the DYNAMITE method to $HNPBu^t_3$ also allows the methyl groups to be asymmetric, which has been shown to be important by ab initio methods. The re-determination of this structure using these more sophisticated methods has also resulted in a much shorter P–N bond than was previously determined, and is consistent with the molecule being regarded as $HN{=}PBu^t_3$, rather than $HN^-{-}P^+Bu^t_3$.

Introduction

Small, simple changes to the chemical formula of a molecule can result in dramatic changes to its structure. For example, $OPMe_3$ adopts a fully staggered C_{3v} structure (Figure 1a), shown by both gas electron diffraction (GED)[1] and by computational methods. However, when the oxygen is replaced by the isoelectronic NH or CH_2 groups to give the imide or ylide, dramatic structural effects are observed. $HNPMe_3$ has been shown by theory to have a C_s structure, with the imidic hydrogen sitting exactly staggered between two methyl groups (Figure 1b). This results in the P−C bonds for the gauche methyl groups being approximately 2.5 pm longer than the anti P−C bond. The N−P−C angles are also greatly affected, with the gauche angles being 119.0°, while the anti angle is 107.0°. These are huge effects to be imposed by just one hydrogen atom. The effects are even greater when the NH group is replaced by a CH_2 group, with the ylidic protons staggered (C_s symmetry, Figure 1c).[2] In this case a 3.5 pm variation in P−C bond length and a 14° variation in CPC bond angles are observed. With these dramatic changes for relatively small, simple molecules, are the effects so pronounced for phosphines with larger, more bulky, substituents?

The original molecular structure determination of tri-*tert*-butylphosphine imide was reported in 1985.[3] Given the limitations of the methodology available at the time, it was necessary to make many symmetry assumptions about the molecule to allow the investigation to proceed. Also, parameters relating to the position of the imide hydrogen were fixed. It was thought that this hydrogen would have little structural effect, and the large size of $HNPBu^t_3$ made it necessary to make assumptions about local symmetry to reduce the refining parameters to a manageable number. However, we have demonstrated that this can lead to a misplacement of atomic positions in the refined structure of a molecule, as compensation even for inadequately modeled hydrogen atoms is made by displacement of carbon atoms.[4] The DYNAMITE method has recently been developed in Edinburgh to deal with this problem.[4] This method involves the DYNAMic Interaction of Theory and Experiment, to allow as many structural parameters as possible to refine, while allowing a molecule to be truly asymmetric if required. This is achieved by incorporating theoretical data, which are continually updated, into the least-squares refinement procedure. To do this we have linked a molecular mechanics procedure to our refinement program to calculate the positions of the light atoms, in this case hydrogen, dynami-

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(1) Wilkins, C. J.; Hagen, K.; Hedberg, L.; Shen, Q.; Hedberg, K. *J. Am. Chem. Soc.* **1975**, *97*, 6352.

(2) (a) Ebsworth, E. A. V.; Fraser, T. E.; Rankin, D. W. H. *Chem. Ber.* **1977**, *110*, 3494. (b) Mitzel, N. W.; Brown, D. H.; Parsons, S.; Brain, P. T.; Pulham, C. R.; Rankin, D. W. H. *Angew. Chem., Int. Ed.* **1998**, *37* (12), 1670.

(3) Rankin, D. W. H.; Robertson, H. E.; Seip, R.; Schmidbaur, H.; Blaschke, G. *J. Chem. Soc., Dalton Trans.* **1985**, 827.

(4) Hinchley, S. L.; Haddow, M. F.; Rankin, D. W. H. *Dalton Trans.* **2004**, 384.

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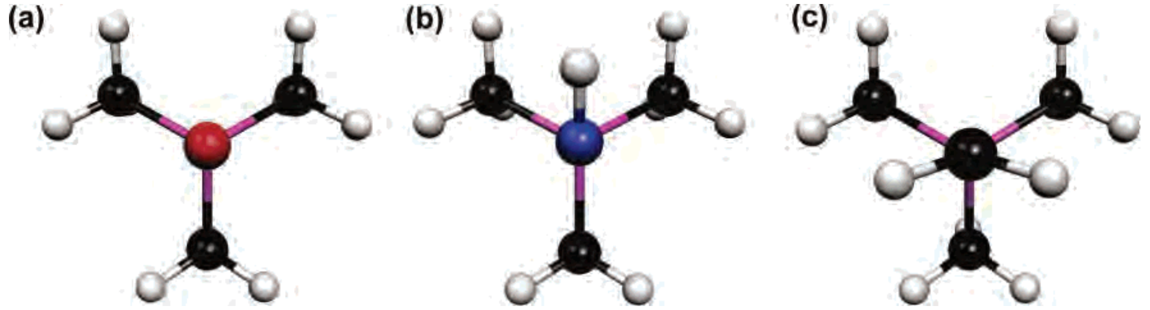

Figure 1. Molecular structures of $OPMe_3$ (C_3, left), $HNPMe_3$ (C_s, middle), and H_2CPMe_3 (C_s, right), viewed along the X−P bonds (X = O, N, C).

cally during the refinement process. Although ideally one would use a computational method of higher quality, computing time considerations enforce the use of a fast method at this stage. This procedure removes the necessity to make assumptions about the symmetry of the methyl groups and therefore allows the *tert*-butyl groups to be completely asymmetric if they require to be so. Although molecular mechanics will calculate the differences between the light-atom parameters (bond lengths, angles, and torsions) reasonably accurately, it will not calculate the absolute values well. The values are therefore scaled relative to refining reference parameters to allow the structural parameters to reproduce the experimental scattering intensities accurately.

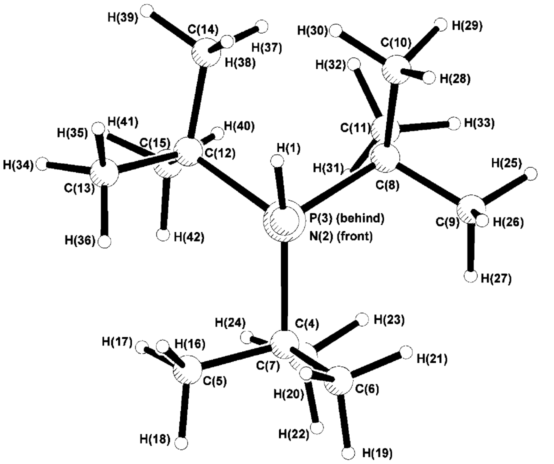

Figure 2. Lowest energy molecular structure of HNPBu$^t_3$, viewed along the N−P bond.

DYNAMITE was developed using tri-*tert*-butylphosphine oxide, which, while possessing *tert*-butyl groups with C_1 local symmetry, had overall C_3 symmetry. This allowed the method to be developed on a molecule that was sterically crowded but still only required a small number of refining parameters to describe the structure. The determination of this structure using DYNAMITE allowed a much more sophisticated analysis of the molecular structure than was originally performed. Following the successful implementation of DYNAMITE for OPBu$^t_3$, we have now applied it to HNPBu$^t_3$. Initial ab initio investigations indicated that this structure has C_1 symmetry, with large differences between C−P−C and N−P−C angles at the central phosphorus atom. By applying the more sophisticated DYNAMITE method, we have removed the large number of symmetry assumptions that were necessary for the original structural determination.

Experimental Section

Theoretical Methods. Geometry optimizations and frequency calculations were performed on a dual-processor Pentium III 1000 MHz workstation using the Gaussian 98 program.[5] All MP2 calculations were frozen core [MP2(fc)]. For the DYNAMITE optimizations the TINKER[6] molecular mechanics package with the MM3 parameter set was used. An extensive search of the torsional potential of HNPBu$^t_3$ was undertaken at the HF level with the 3-21G* basis set[7−9] to locate all minima. Only one conformer, of C_1 symmetry, was located and further geometry optimizations were undertaken at the HF and MP2 levels using the standard 6-31G* basis set,[10−12] and at the MP2 level using the 6-311G* basis set.[13,14] The lowest energy structure of HNPBu$^t_3$ is shown in Figure 2, with the atom numbering scheme. Analytic second derivatives of the energy with respect to nuclear coordinates calculated at the HF/6-31G* level for HNPBu$^t_3$ gave the force field, which was used to provide estimates of the amplitudes of vibration (u) for use in the gas electron diffraction (GED) refinements. The force field was also used to calculate the frequencies for the optimized structure, which in turn provided information about the nature of the stationary point on the potential energy surface. All calculated frequencies were positive, indicating that the structure is a minimum on the potential energy surface.

Gas Electron Diffraction Data. Original digital molecular intensity scattering data[3] for HNPBu$^t_3$ were reintroduced directly

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(5) Gaussian 98, Revision A.7. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E., Jr.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1998.

(6) Ponder, J. W. TINKER Molecular Mechanics Freeware Package, Version 3.8; St. Louis, MO, 2000.

(7) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939.

(8) Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* **1982**, *104*, 2797.

(9) Pietro, W. J.; Francl, M. M.; Hehre, W. J.; DeFrees, D. J.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* **1982**, *104*, 5039.

(10) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257.

(11) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(12) Gordon, M. S. *Chem. Phys. Lett.* **1980**, *76*, 163.

(13) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639.

(14) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.

into the new Edinburgh electron diffraction refinement program ed@ed[15] without further modification. The scattering factors of Ross et al. were used in the refinements.[16]

Gas Electron Diffraction Model. With the DYNAMITE method, positions of all the atoms are defined independently. There are $3N - 6 = 120$ parameters ($N = 42$). Of these possible 120 parameters, 81 relate to the 27 methyl hydrogen atoms (leaving 39 parameters to describe the rest of the molecule). However, differences between distance, angle, and dihedral angle parameters for the methyl hydrogen atoms are set and updated by the computational (in this case molecular mechanics) method. Therefore, of the potential 81 parameters required, only 1 distance, 1 angle, and 9 torsion parameters are needed. This reduces the total number of independent parameters to 50 (11 + 39). This was further reduced to 42 by treating all C−C distances as equal, an assumption justified by the ab initio calculations. Although in principle there are three different C−C distances within a butyl group, the ab initio calculations showed that the differences are insignificantly small. Our experience has shown that in such cases, if two additional parameters are used to describe the differences, the values and standard deviations returned exactly match those of the restraints placed on them, so there is no benefit at all in using more than the one parameter. The 42 parameters comprised seven bond lengths and differences, 22 bond angles and differences, and 13 torsion parameters (Table 1; atom numbering shown in Figure 2). The bond-length parameters were N−H (p_1), the average and difference of C−C and P−N bond lengths (p_{2-3}), and the average and two differences for the three P−C bond lengths (p_{4-6}). Independent bond-angle parameters included three average and difference parameters for the P−C−C angles of each *tert*-butyl group, with two associated C−C−C angles (p_{7-21}). The third C−C−C angle for each *tert*-butyl group was thus a dependent parameter. For the first group, the average of ∠P(3)−C(4)−C(5), ∠P(3)−C(4)−C(6), and ∠P(3)−C(4)−C(7) was used (p_7), as well as two difference parameters [∠P(3)−C(4)−C(5) − ∠P(3)−C(4)−C(6) and ∠P(3)−C(4)−C(5) − ∠P(3)−C(4)−C(7) (p_{8-9})]. ∠C(5)−C(4)−C(6) (p_{10}) and ∠C(5)−C(4)−C(7) (p_{11}) were used to complete the placement of the methyl groups. Equivalent sets of parameters define the geometries of the second and third butyl groups, with carbon atoms 8−11 and 12−15 replacing 3−7. The average N−P−C angle (p_{22}) and two difference parameters [N(2)−P(3)−C(4) − N(2)−P(3)−C(8) and N(2)−P(3)−C(4) − N(2)−P(3)−C(12)] (p_{23-24}) were also used, as were ∠C(4)−P(3)−C(8) and ∠C(4)−P(3)−C(12) (p_{25-26}) and ∠P−N−H (p_{27}). The torsion parameters included the following three *tert*-butyl group torsions: ϕN(2)−P(3)−C(4)−C(5), ϕN(2)−P(3)−C(8)−C(9), and ϕN(2)−P(3)−C(12)−C(13) (p_{28-30}) and ϕH−N−P−C(4) (p_{31}). Finally, parameters to describe the starting positions of the hydrogen atoms were included. These were the mean C−H bond length (p_{32}), mean C−C−H bond angle (p_{33}), and nine parameters to describe the torsions of the three methyl groups about their adjacent C−C bonds (p_{34-42}). The meanings of $p_{32} - p_{42}$ changed according to the type of refinement being performed. For example, for the initial SARACEN refinement,[17] all C−H bonds were of equal length. In the subsequent DYNAMITE refinement,[4] they were different, so p_{32} then represented the mean distance.

Results

Theoretical Methods. The structure of HNPBu$^t_3$ was investigated ab initio. In a thorough potential energy surface search, involving rotation of the *tert*-butyl groups around the P−C bonds and the amide hydrogen about the N−P bond, only one conformer of HNPBu$^t_3$ was found. The molecular geometry of HNPBu$^t_3$ at the MP2(fc)/6-311G* level is given in Table 2, along with those calculated at the HF/6-31G* and MP2(fc)/6-31G* levels, to compare the effects of improving basis set and level of theory on the structural parameters, particularly the N−P bond length. The variation within the structure of the C−H bond distances, C−C−H bond angles, and P−C−C−H torsion angles is of importance for the DYNAMITE investigation, and values from the MP2(fc)/6-311G* calculation are listed in Table 3. The coordinates from the highest level calculation are given in Supporting Information Table S1.

It can be seen from Table 3 that, at the highest level of theory and basis set investigated (MP2(fc)/6-311G*), the C−C−H angles range from 107.8 to 114.1°, a variation of over 6°. Failure to model this correctly in the electron diffraction refinement has been shown previously to lead to error in some of the heavy-atom parameter values as they compensate for the light-atom positions.[4] Allowance for this variation must therefore be made in the GED refinement. Another observation from this calculation is that the three P−C−C−H torsion angles [e.g., ϕPCCH(16/17/18)] within a methyl group do not differ uniformly by 120°. This is another assumption that is made when local C_{3v} symmetry is assigned to the groups during the electron diffraction refinement.

Table 2 demonstrates how the inclusion of electron correlation and increasing the size of the basis set used during the calculations affects the observed molecular structure. Most of the parameters listed vary little upon the inclusion of electron correlation via the MP2 method, or upon the increase in basis set from 6-31G* to 6-311G*. However, the H−N and N−P bonds are sensitive to the inclusion of electron correlation, with the H−N bond length increasing by over 2 pm from HF/6-31G* to MP2(fc)/6-31G*, while the N−P distance increases by 2.3 pm. The H−N−P bond angle is also sensitive to both electron correlation effects and basis set size, with a decrease of 2.4° from HF to MP2, and an increase of 1.5° from 6-31G* to 6-311G*. Therefore this parameter cannot be said to have converged, as its value is still changing substantially at the limit of the calculations performed [MP2(fc)/6-311G*]. However, we would expect that change beyond this basis set size/level of theory to be small, and as most other parameters have converged further calculations were not performed.

Gas Electron Diffraction Refinement. The starting parameters for the refinement were taken from the theoretical geometry optimized at the MP2(fc)/6-311G* level. A theoretical (HF/6-31G*) Cartesian force field was obtained and

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(15) Rankin, D. W. H.; Turner, A. R. *ed@ed Refinement Program*; University of Edinburgh: Edinburgh, U.K. http://www.ged.chem.ed.ac.uk/edated (accessed May 14, 2004).

(16) Ross, A. W.; Fink, M.; Hilderbrandt, R. *International Tables for Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Dordrecht 1992; Vol. C, p 245.

(17) Blake, A. J.; Brain, P. T.; McNab, H.; Miller, J.; Morrison, C. A.; Parsons, S.; Rankin, D. W. H.; Robertson, H. E.; Smart, B. A. *J. Chem. Phys.* **1996**, *100*, 12280. Brain, P. T.; Morrison, C. A.; Parsons, S.; Rankin, D. W. H. *J. Chem. Soc., Dalton Trans.* **1996**, 4589.

Table 1. Refined and Calculated Geometric Parameters for $HNPBu^t_3$ (Distances in pm, Angles in deg) from the Original GED Study,[a] the SARACEN Study, and the DYNAMITE Study[b,c]

	parameter	MP2(fc)/6-311G* (r_e)	original (r_a)	SARACEN (r_{h1})	DYNAMITE (r_{h1})	restraint
			Independent			
p_1	N−H	101.0	102.0(fixed)	101.1(10)	101.1(6)	101.0(5)
p_2	C−C/P−N *av*[d]	156.3		155.9(2)	156.0(2)	
p_3	C−C/P−N *d*[d]	5.0		5.4(5)	5.4(5)	5.0(5)
p_4	P−C *av*	189.8	191.3(6)	190.4(4)	191.2(4)	
p_5	P−C *d1*	−2.4		−2.4(5)	−2.4(5)	−2.4(5)
p_6	P−C *d2*	−2.7		−2.7(5)	−2.5(5)	−2.7(5)
p_7	P−C−C *av* (gp 1)	110.9		110.9(8)	111.2(8)	110.9(10)
p_8	P−C−C *d1* (gp 1)	0.6		−0.2(10)	−0.4(10)	0.6(10)
p_9	P−C−C *d2* (gp 1)	−6.0		−5.5(10)	−5.1(10)	−6.0(10)
p_{10}	C(5)−C(4)−C(6)	108.4	107.8(5)[e]	108.0(10)	107.9(10)	108.4(10)
p_{11}	C(5)−C(4)−C(7)	105.4		105.1(10)	105.6(10)	105.4(10)
p_{12}	P−C−C *av* (gp 2)	111.1		112.5(10)	111.7(10)	
p_{13}	P−C−C *d1* (gp 2)	0.9		1.6(10)	1.0(10)	0.9(10)
p_{14}	P−C−C *d2* (gp 2)	−8.3		−8.3(10)	−8.0(10)	−8.3(10)
p_{15}	C(9)−C(8)−C(10)	104.7		104.6(10)	104.8(10)	104.7(10)
p_{16}	C(9)−C(8)−C(11)	108.6		108.5(10)	108.5(10)	108.6(10)
p_{17}	P−C−C *av* (gp 3)	111.3		109.6(11)	106.7(9)	
p_{18}	P−C−C *d1* (gp 3)	−1.3		−0.9(10)	−1.4(10)	−1.3(10)
p_{19}	P−C−C *d2* (gp 3)	−8.1		−8.4(10)	−8.7(10)	−8.1(10)
p_{20}	C(13)−C(12)−C(14)	105.2		105.4(10)	106.3(10)	105.2(10)
p_{21}	C(13)−C(12)−C(15)	109.1		109.6(10)	110.2(10)	109.1(10)
p_{22}	N−P−C *av*	109.8	109.6(7)	107.3(3)	107.2(3)	
p_{23}	N−P−C *d1*	10.3		9.9(13)	11.8(14)	10.3(15)
p_{24}	N−P−C *d2*	0.8		0.7(15)	−0.8(15)	0.8(15)
p_{25}	C(4)−P(3)−C(8)	109.7		109.7(9)	110.5(9)	109.7(10)
p_{26}	C(4)−P(3)−C(12)	109.8		110.1(8)	109.8(8)	109.8(10)
p_{27}	P−N−H	115.7	114.0(fixed)	115.8(11)	115.8(10)	115.7(10)
p_{28}	ϕN(2)−P(3)−C(4)−C(5)	73.8	18.5(14)[d]	74.3(21)	72.2(20)	73.8(25)
p_{29}	ϕN(2)−P(3)−C(8)−C(9)	67.6		67.2(19)	66.5(20)	67.6(25)
p_{30}	ϕN(2)−P(3)−C(12)−C(13)	−36.3		−34.7(20)	−39.3(20)	−36.3(25)
p_{31}	H−N−P−C	−172.9	160.0(fixed)	−172.9(11)	−172.9(11)	−172.9(10)
p_{32}	C−H	109.2	110.7(3)	114.5(3)	114.9(3)	
p_{33}	C−C−H	107.6	111.1(14)	108.6(8)	110.4(8)	
p_{34}	ϕP(3)−C(4)−C(5)−H(16)	72.6	−8.9(25)[d]	70.9(26)	71.4(27)	72.6(25)
p_{35}	ϕP(3)−C(4)−C(6)−H(19)	175.9		176.4(26)	176.2(27)	175.9(25)
p_{36}	ϕP(3)−C(4)−C(7)−H(22)	70.2		69.4(26)	69.5(27)	70.2(25)
p_{37}	ϕP(3)−C(8)−C(9)−H(25)	73.8		73.1(26)	73.5(27)	73.8(25)
p_{38}	ϕP(3)−C(8)−C(10)−H(28)	68.0		67.3(26)	67.8(27)	68.0(25)
p_{39}	ϕP(3)−C(8)−C(11)−H(31)	175.4		175.3(27)	175.4(27)	175.4(25)
p_{40}	ϕP(3)−C(12)−C(13)−H(34)	50.6		50.4(26)	50.0(27)	50.6(25)
p_{41}	ϕP(3)−C(12)−C(14)−H(37)	51.9		53.3(26)	52.4(27)	51.9(25)
p_{42}	ϕP(3)−C(12)−C(15)−H(40)	176.2		177.4(26)	176.7(27)	176.2(25)
	butyl tilt		−2.3(11)[d]			
R_G			0.120	0.072	0.067	
			Dependent			
dp_1	N(2)−P(3)	158.8	165.2(11)[c]	158.6(4)	158.7(4)	
dp_2	C−C *av*	153.8	153.2(2)[c]	153.2(2)	153.3(2)	
dp_3	P(3)−C(4)	188.1		188.7(5)	189.6(5)	
dp_4	P(3)−C(8)	190.5		191.1(6)	192.0(6)	
dp_5	P(3)−C(12)	190.8		191.4(6)	192.1(6)	
dp_6	N(2)−P(3)−C(4)	103.2		100.9(9)	99.2(9)	
dp_7	N(2)−P(3)−C(8)	112.7		110.1(10)	111.5(11)	
dp_8	N(2)−P(3)−C(12)	113.5		110.8(8)	110.9(7)	
dp_9	P(3)−C(4)−C(5)	109.2		109.1(9)	109.3(9)	
dp_{10}	P(3)−C(4)−C(6)	108.5		114.5(11)	114.4(11)	
dp_{11}	P(3)−C(4)−C(7)	115.2		109.2(11)	109.7(11)	
dp_{12}	P(3)−C(8)−C(9)	108.6		110.3(11)	109.4(11)	
dp_{13}	P(3)−C(8)−C(10)	107.7		108.7(13)	108.3(13)	
dp_{14}	P(3)−C(8)−C(11)	116.9		118.6(12)	117.4(11)	
dp_{15}	P(3)−C(12)−C(13)	108.0		106.4(12)	103.3(11)	
dp_{16}	P(3)−C(12)−C(14)	109.4		107.4(13)	104.7(12)	
dp_{17}	P(3)−C(12)−C(15)	116.2		114.8(13)	112.0(12)	
dp_{18}	C(8)−P(3)−C(12)	107.9		114.3(10)	113.9(9)	

[a] Ref 3. [b] Figures in parentheses are the estimated standard deviations of the last digits. [c] See text for parameter definitions. [d] P−N and C−C parameters were defined separately in the original refinement. [e] As the original model had high symmetry, only one C−C−C angle, one methyl torsion, and one *tert*-butyl torsion were included in the original study. A butyl tilt included in the original investigation was not needed in the current study because of the different parameter definitions.

converted into a force field described by a set of symmetry coordinates using SHRINK[18] which provided both the amplitudes of vibration and the curvilinear corrections for the interatomic distances. All geometric parameters (r_{h1}) were then

Table 2. Molecular Geometry of $HNPBu^t_3$ at the HF/6-31G*, MP2(fc)/6-31G*, and MP2(fc)/6-311G* Levels[a,b]

parameter	HF/6-31G*	MP2(fc)/ 6-31G*	MP2(fc)/ 6-311G*
	Bond Distances		
H(1)−N(2)	100.1	102.2	101.6
N(2)−P(3)	157.1	159.4	158.8
P(3)−C(4)	189.9	188.6	188.1
P(3)−C(8)	191.7	191.2	190.5
P(3)−C(12)	192.0	191.6	190.8
	Bond Angles		
H(1)−N(2)−P(3)	116.6	114.2	115.7
N(2)−P(3)−C(4)	103.9	103.0	103.2
N(2)−P(3)−C(8)	111.8	112.7	112.7
N(2)−P(3)−C(12)	112.2	113.5	113.5
P(3)−C(4)−C(5)	110.0	108.9	109.2
P(3)−C(4)−C(6)	108.9	108.7	108.5
P(3)−C(4)−C(7)	115.4	115.2	115.2
P(3)−C(8)−C(9)	109.6	108.2	108.6
P(3)−C(8)−C(10)	108.3	107.8	107.7
P(3)−C(8)−C(11)	116.7	117.0	116.9
P(3)−C(12)−C(13)	108.3	107.9	108.0
P(3)−C(12)−C(14)	110.5	109.1	109.4
P(3)−C(12)−C(15)	116.1	116.3	116.2
	Bond Torsions		
H(1)−N(2)−P(3)−C(4)	−174.0	−173.4	−172.9
N(2)−P(3)−C(4)−C(5)	73.2	73.8	73.8
N(2)−P(3)−C(8)−C(9)	68.6	67.2	67.6
N(2)−P(3)−C(12)−C(13)	−37.3	−36.3	−36.3
energy[c]	−865.8303	−867.7261	−867.9261

[a] Distances in pm, angles in deg. [b] See Figure 2 for atom numbering. [c] Energies in Hartrees, not corrected for zero-point energy.

Table 3. C−H Bond Lengths, C−C−H Bond Angles, and P−C−C−H Bond Torsions for $HNPBu^t_3$ Calculated at the MP2(fc)/6-311G* Level[a,b]

parameter	rC−H	∠C−C−H	ϕP−C−C−H
P−C(4)−C(5)−H(16)	109.0	113.0	72.6
P−C(4)−C(5)−H(17)	109.2	111.0	−51.0
P−C(4)−C(5)−H(18)	109.6	107.9	−169.2
P−C(4)−C(6)−H(19)	108.8	113.4	−70.2
P−C(4)−C(6)−-H(20)	109.1	110.3	51.6
P−C(4)−C(6)−H(21)	109.6	107.8	170.9
P−C(4)−C(7)−H(22)	109.6	108.1	−175.9
P−C(4)−C(7)−H(23)	109.0	112.7	65.9
P−C(4)−C(7)−H(24)	109.1	113.0	−57.3
P−C(8)−C(9)−H(25)	108.9	113.2	73.8
P−C(8)−C(9)−H(26)	109.6	108.1	−167.7
P−C(8)−C(9)−H(27)	109.2	111.1	−49.5
P−C(8)−C(10)−H(28)	109.3	110.5	54.9
P−C(8)−C(10)−H(29)	109.6	108.2	172.6
P−C(8)−C(10)−H(30)	108.7	114.1	−68.0
P−C(8)−C(11)−H(31)	109.0	112.9	66.2
P−C(8)−C(11)−H(32)	109.7	108.5	−175.3
P−C(8)−C(11)−H(33)	109.2	112.6	−56.7
P−C(12)−C(13)−H(34)	108.7	113.4	−71.1
P−C(12)−C(13)−H(35)	109.6	108.2	169.7
P−C(12)−C(13)−H(36)	109.2	111.2	50.6
P−C(12)−C(14)−H(37)	109.4	111.9	−51.9
P−C(12)−C(14)−H(38)	109.6	108.0	−169.6
P−C(12)−C(14)−H(39)	108.9	113.3	71.8
P−C(12)−C(15)−H(40)	109.1	113.0	−57.3
P−C(12)−C(15)−H(41)	109.7	108.5	−176.2
P−C(12)−C(15)−H(42)	109.1	112.3	65.6
Δ range	1.0 pm	6.3°	6.0°[c]

[a] Distances in pm, angles in deg. [b] See Figure 2 for atom numbering. [c] Defined as the range of differences between dihedral angles for adjacent hydrogen atoms.

refined. The DYNAMITE method was then activated as described previously[4] and the final refinement was performed.

In total all 42 geometric parameters and 10 groups of vibrational amplitudes were refined. Flexible restraints were employed during the refinements using the SARACEN method.[17] Altogether, 35 geometric and 6 amplitude restraints were employed. These are listed in Tables 1 and S2.

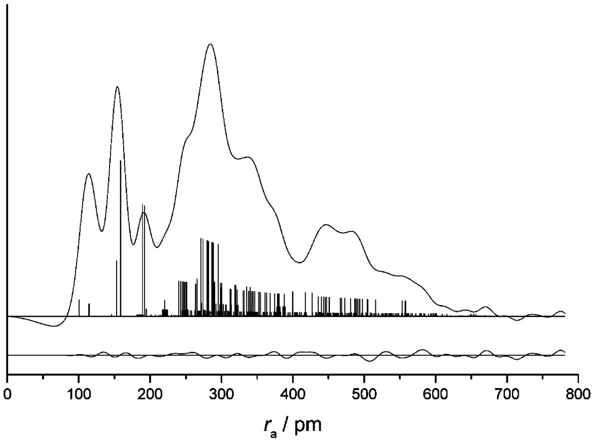

Figure 3. Experimental and difference (experimental − theoretical) radial-distribution curves, $P(r)/r$, from the DYNAMITE refinement of $HNPBu^t_3$. Before Fourier inversion the data were multiplied by $s \cdot \exp(-0.00002s^2)/(Z_C - f_C)/(Z_P - f_P)$.

In the final refinement R factors were $R_G = 0.072$ ($R_D = 0.097$) for the SARACEN refinement and $R_G = 0.067$ ($R_D = 0.096$) for the DYNAMITE refinement. The radial distribution curve is shown in Figure 3, while the molecular scattering intensity curves are shown in Supporting Information Figure S1. Final refined parameters are listed in Table 1, interatomic distances and the corresponding amplitudes of vibration are in Table S2, with the least-squares correlation matrix shown in Table S3. Experimental coordinates from the DYNAMITE GED analysis are given in Table S4.

Discussion

The molecular structure of tri-*tert*-butylphosphine imide has been reexamined using a new gas electron diffraction refinement method that has been developed in Edinburgh.[4] The original determination of the gas-phase molecular structure[3] required the use of many symmetry constraints for the refinement to proceed. This refinement was performed before the introduction of the SARACEN[17] and DYNAMITE[4] methods of structure determination, which use the power of computational chemistry to aid the refinement process. The SARACEN method uses flexible restraints determined from a series of calculations to allow previously unrefinable structural parameters to refine. The DYNAMITE method goes one step further and actually incorporates real-time calculated atomic positions into the gas-phase electron diffraction refinement program. The dynamic interaction of theory (at this time a molecular mechanics method) and experiment allows all atomic positions to be determined individually, rather than having to use symmetry constraints to allow the structure to be refined. This is important because if light-atom positions are constrained by symmetry in sterically crowded systems, then the associated heavy-atom positions may be artificially distorted to accommodate the constrained atoms.

The ab initio molecular structure investigation of $HNPBu^t_3$ has shown that the methyl groups of each *tert*-butyl group

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(18) Sipachev, V. A. *J. Mol. Struct. (THEOCHEM)* **1985**, *121*, 143.

are quite asymmetric. From Table 3 it can be seen that, at the MP2(fc)/6-311G* level of theory and basis set, the C−H bond distances vary from 108.7 to 109.7 pm, while the C−C−H bond angles vary from 107.8 to 114.1°, an enormous range of 6.3°. The bond torsions also indicate that the P−C−C−H dihedral angles for any one methyl group do not vary from each other by a uniform 120.0° but rather that the groups are distorted in this sense as well, again with a scatter of 6°. Such distortions are an inevitable consequence of steric crowding. A far more unexpected observation from the ab initio methods is the large distortion of the HNPC$_3$ fragment. The P−C bonds indicate a pseudo C_s structure for this fragment, with one bond length returned at 188.1 pm, while the other two are 190.5 and 190.8 pm. The shorter bond is that anti to the N−H bond, with the two longer bonds in gauche positions relative to the imido proton. Even more dramatic differences are observed for the N−P−C bond angles. The angle anti to the N−H bond is very narrow, 103.2° at the MP2(fc)/6-311G* level, but the two gauche N−P−C angles are 112.7° and 113.5°. When compared to the MP2(fc)/6-311G* calculated structure of the closely related OPBu$^t_3$ at the same level and basis,[4] it can be seen that this has a C_3-symmetric OPC$_3$ fragment, with O−P−C bond angles of 109.1°, hardly distorted from tetrahedral (109.5°). Therefore the effect of replacing the oxygen with the N−H group is a massive distortion of the whole molecule, caused by the imido proton. That such a small change in structure should have such a large effect is quite remarkable, and the asymmetry must be modeled within the gas electron diffraction refinement for a reliable gaseous structure to be determined.

The original gas-phase structure determination of HNPBu$^t_3$ used thirteen parameters to describe the structure, with local 3-fold symmetry for the methyl groups, the *tert*-butyl groups, and the NPC$_3$ fragment. In addition, parameters relating to the N−H group (N−H distance and P−N−H angle) could not be refined, because there is little information relating to the hydrogen atom in the gas electron diffraction data. The problems associated with refining the imido parameters and of including the asymmetry of the NPBu$^t_3$ fragment can be solved using the SARACEN method, while the asymmetry in the methyl groups can be included via the DYNAMITE method.

The original data were reanalyzed, using 42 parameters and a calculated force field, with the SARACEN and DYNAMITE methods, with the results listed in Table 1. It can be seen that the inclusion of asymmetry via the SARACEN method results in a large improvement to the goodness-of-fit parameter (0.072 for R_G compared to 0.120 for the original refinement). Allowing the methyl groups to be asymmetric resulted in even more improvement in the R factor (to 0.067). Thus the experimental data are fully in agreement with the markedly asymmetric structure predicted by the ab initio calculations. In general, the esds improved and there were significant changes to some of the heavy-atom parameters, indicating that the inclusion of asymmetry for the methyl groups is important. All the P−C bond lengths increase by approximately 0.8 pm upon the inclusion of DYNAMITE. All the C−C−C angles within the *tert*-butyl groups get slightly smaller, implying that the methyl carbon atoms were compensating for the symmetry imposed upon the methyl hydrogen atoms. In the *tert*-butyl group anti to the imido proton [with C(4) at the center], the P−C−C angles hardly change with the introduction of DYNAMITE. However, in the other two *tert*-butyl groups, gauche to the imido proton, there are some large changes, with the P−C(8)−C angles all decreasing by ∼1°, while the P−C(12)−C angles all decrease by ∼3°. The N−P−C angles also display changes, with the trans ∠N−P−C(4) becoming even more acute [from 100.9(9) to 99.2(9)°], while ∠N−P−C8) increases from 110.1(10) to 111.5(11)°. The N−P−C(12) angle hardly changes. Therefore, all the rearrangement in the *tert*-butyl groups has had the effect of pushing the anti group toward the nitrogen atom and one of the gauche groups away from it.

The low-temperature neutron and X-ray diffraction structures of another sterically encumbered phosphorane were reported in 1998.[19] The data for imino(triphenyl)phosphorane (HNPPh$_3$) were collected at 150(2) K for the X-ray structure and 20(1) K for the neutron diffraction structure. The aim of the study was to elucidate the nature of the P−N bond in iminophosphoranes. The P−N bond length was returned at 158.2(2) pm and the P−N−H angle was 115.0(2)° from the neutron study. These compare well with those determined for the gaseous structure of HNPBu$^t_3$, 158.7(4) pm and 115.8(10)° respectively. The angles around phosphorus were also found to vary by about 6°, ranging from 109.1(1) to 115.6(1)°. This is not as wide a range as is observed in HNPBu$^t_3$ [99.2(9) − 111.5(11)°] but is still significant. Unfortunately, the authors were unable to draw any firm conclusions regarding the nature of the P−N bond in HNPPh$_3$ from their investigations.

One reason for analyzing the gaseous data was to reinvestigate the nature of the P−N bond. The original investigation concluded that, as the P−N bond was so long [165.2(11) pm] it should be regarded as single and so the molecule was considered as ionic HN$^-$−P$^+$Bu$^t_3$, rather than covalent HN=PBu$^t_3$.[3] However, there should still be electrostatic attraction which would also shorten the P−N distance. A parallel conclusion was also originally reached for the structure of OPBu$^t_3$.[3] Upon reanalysis of the data for OPBu$^t_3$[4] it was found that, in fact, the O−P bond was approximately 9 pm shorter than originally thought. The same trend is revealed in the current investigation of the P−N bond for HNPBu$^t_3$. The P−N distance was calculated [MP2(fc)/6-311G*] to be 158.8 pm, and determined by the DYNAMITE method to be 158.7(4) pm, 6.5 pm shorter than the original value of 165.2(11) pm.[3] Therefore the distance is consistent with this bond being double and therefore covalent, although, as mentioned above, the influence of electrostatic forces could result in a short ionic bond. Ligand sphere asymmetry could also account for the shorter bond length, which is why a sophisticated structural analysis using

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(19) Davidson, M. G.; Goeta, A. E.; Howard, J. A. K.; Lehmann, C. W.; McIntyre, G. M.; Price, R. D. *J. Organometallic Chem.* **1998**, *550*, 449.

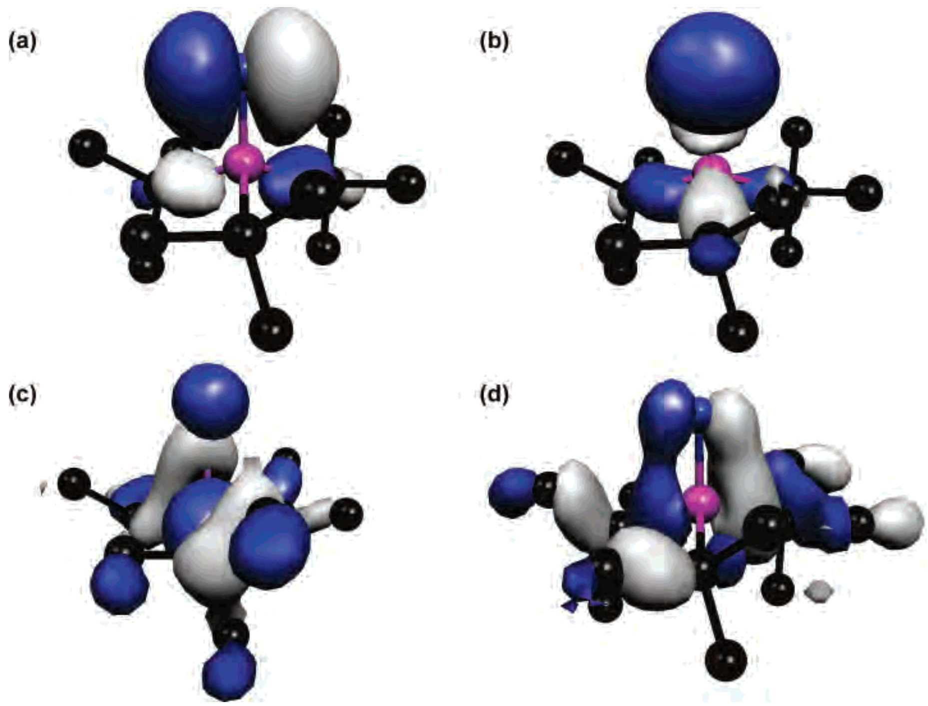

Figure 4. Four highest occupied molecular orbitals (a = HOMO, d = HOMO − 3) at the MP2(fc)/6-311G* level for $HNPBu^t_3$.

DYNAMITE is important. The overall radii of the ligands has been shown to affect bond lengths of other substituents attached to the central atom,[20] and they should not simply be considered as symmetric spheres. Another point to note is that neither of the initial investigations accounted adequately for the close proximity of the C−C and P−N/O bonds under the same peak in the radial distribution curve, which led to the P−N/O bond lengths being overestimated, while the C−C bond lengths were underestimated.

Examination of the four highest occupied molecular orbitals (HOMOs) at the MP2(fc)/6-311G* level also reveals interesting information about the nature of the P−N bond. The four HOMOs shown in Figure 4 are all involved with P−N bonding. The orbitals shown in 4a and d both indicate significant π-bonding character. While the calculation of electron density is accurate, the graphical representation of the molecular orbitals is somewhat arbitrary and dependent on the package used. However, the results do serve to reinforce the conclusion from the GED and ab initio investigations that the P−N bond can be regarded primarily as a covalent double bond, rather than as an ionic single bond.

The re-determination of the molecular structure of tri-*tert*-butylphosphine imide has revealed that the original assumptions of local symmetry for the methyl, *tert*-butyl, and NPC_3 groups were invalid. Reexamination of the structure using the DYNAMITE method has shown that the use of a fully asymmetric model provides a better fit to the data than the original model and gives more realistic esds than when the SARACEN method is used. The structure is highly asymmetric, and when compared to the relatively symmetric $OPBu^t_3$ it can be seen that the imide hydrogen has an enormous effect on the overall structure. This finding completely opposes the original supposition that the NH group would have little effect on the structure. This investigation has also led to the finding that the P−N bond can be regarded as covalent rather than ionic.

Acknowledgment. We thank the EPSRC for grant GR/N24407/01.

Supporting Information Available: Listings of coordinates (Å) for $HNPBu^t_3$ from the MP2(fc)/6-311G* geometry calculation, interatomic distances (r_a/pm) and amplitudes of vibration (u/pm) for the DYNAMITE GED structure of $HNPBu^t_3$, least squares correlation matrix (× 100) for the DYNAMITE GED refinement of $HNPBu^t_3$, experimental gas-phase coordinates (Å) from the DYNAMITE refinement of $HNPBu^t_3$, and experimental and final weighted difference (experimental − theoretical) molecular-scattering intensities from the DYNAMITE refinement of $HNPBu^t_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

IC049467R

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[20] Gillespie, R. J.; Bytheway, I.; Robinson, E. A. *Inorg. Chem.* **1998**, *37*, 2811.