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An *ab initio* investigation of structure and inversion barrier of triisopropylamine and related amines and phosphines

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Summary. The equilibrium geometry and barrier to pyramidal inversion of triisopropylamine, $N(CH(CH_3)_2)_3$, is computed at SCF level of theory. For comparison, results for ammonia NH_3 (including a near HF calculation), trimethylamine $N(CH_3)_3$ and the three analogous phosphine compounds PH_3, $P(CH_3)_3$ and $P(CH(CH_3)_2)_3$ are presented as well.

Key words: Triisopropylamine – Phosphines – Amines – Pyramidal inversion

1. Introduction

Within a recent experimental study of the equilibrium structure of triisopropylamine [1], it was suggested that the size of this molecule combined with the relatively small barrier height as derived from semi-empirical calculations might be prohibitive for an accurate theoretical treatment by *ab initio* methods even at the SCF level of theory. We will demonstrate in this study that by application of the direct SCF method [2], including the exploitation of molecular symmetry, one can in fact obtain reliable information about both the equilibrium structure and the height of the barrier to inversion for this molecule which confirm and complement experimental information. Of course, this compound deserves theoretical interest in itself since the nitrogen atom adopts a nearly planar configuration.

A theoretical determination of the inversion barrier in amine or phosphine compounds requires the proper identification of the transition structure(s) corresponding to a first order saddle point on the energy hypersurface. In the special case of the NX_3 or PX_3 molecules (where X represents a single atom like hydrogen or fluorine), symmetry arguments lead to a transition structure with at least C_s and at most D_{3h} symmetry. If one assumes that replacing atom X by a methyl or isopropyl group does not alter the planar configuration of the central atom (which is either nitrogen or phosphorus) and its bond partners within the transition state and fixes this structure using symmetry restrictions, one is led to a transition structure with either C_{3h} or C_s symmetry. In the following, the possibility that the lowest energy transition structure does not possess any symmetry will not be considered. Instead, we will restrict ourselves to the C_{3h} and C_s like structures as displayed in Fig. 1. Whenever possible – i.e. with two

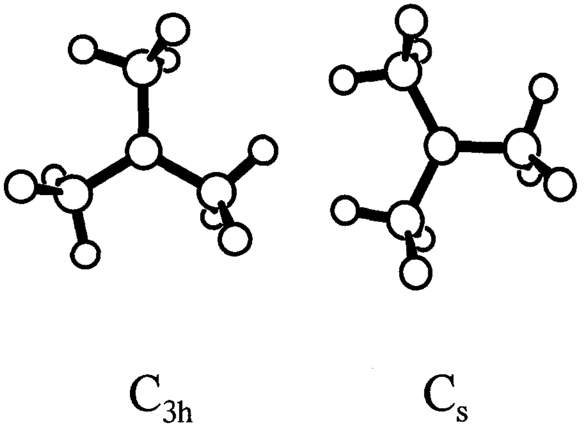

Fig. 1. C_{3h} and C_s symmetry transition structures of $A(CR_3)_3$ molecules ($A = N, P$)

exceptions – force field calculations are performed to confirm minimum or saddle point characteristics.

The computational methods, especially the basis sets employed, will be described in the next section. In the following section we describe and discuss our results; the last section provides conclusions.

2. Computational methods and basis sets

The geometry optimizations have been performed using the TURBOMOLE package of programs [3] which is based on a direct SCF procedure [2] that allows for the exploitation of symmetry. Most of the calculations have been performed on a HP9000/835 workstation.

We have employed two types of basis sets denoted A and B_X ($X = N, P$) which are displayed in Table 1.

Basis set A corresponds to a split valence plus polarization basis set for nitrogen or phosphorus and an STO-3G [5] basis set for carbon and hydrogen. Basis set B_N, used for describing the amines, consists of a $(9s5p1d)/[5s3p1d]$ triple zeta quality plus polarization basis set for nitrogen and carbon and a $(5s1p)/[3s1p]$ triple zeta plus polarization basis set for hydrogen. The sp-basis sets have been taken from the compilation of Huzinaga [6]. Basis set B_P, used for

Table 1. Definition of CGTO basis sets

Basis set	Atom	GTO/CGTO basis	Contraction scheme	Ref.
A	N	(7, 4, 1)/[3, 2, 1]	421/31/1	[4]
	P	(9, 6, 1)/[4, 3, 1]	4311/411/1	[4]
	C	(6, 3)/[2, 1]	33/3	[5]
	H	(3)/[1]	3	[5]
B_N	N	(9, 5, 1)/[5, 3, 1]	51111/311/1	[6]
	C	(9, 5, 1)/[5, 3, 1]	51111/311/1	[6]
	H	(5, 1)/[3, 1]	311/1	[6]
B_P	P	(9, 6, 1)/[4, 3, 1]	4311/411/1	[4]
	C	(7, 4, 1)/[3, 2, 1]	421/31/1	[4]
	H	(4)/[2]	31	[7]

description of the phosphines, consists of a split valence plus polarization basis set for phosphorus and carbon [4] and a Huzinaga (4*s*)/[2*s*] double zeta basis set for the hydrogen atoms [7]. The split valence basis sets have been derived from the 43/4 Huzinaga single zeta basis set for carbon [4] and from the 432/42 Huzinaga single zeta basis set for phosphorus [4]. A split valence contraction scheme then yields the final (7*s*4*p*)/[3*s*2*p*] and (9*s*6*p*)/[4*s*3*p*] *sp*-basis sets. In all cases reported, exponents of the polarization functions have been optimized simultaneously with the geometry optimization. Orbital exponents thus obtained are documented in Tables 2 and 4–8 presented below. The relatively small basis set A has been introduced to allow for a normal coordinate analysis of the triisopropyl compounds which would not have been possible with basis set B on the computer facilities available to us. Since it will be clear from the context whether the basis set B_N or B_P is referred to, the subscript will be dropped in the following.

3. Results and discussion

3.1. Ammonia vs. phosphine

Ammonia and phosphine were treated mainly to assess the basis set quality. The results using basis sets A and B are summarized in Tables 2 and 4.

The computed barrier to pyramidal inversion of ammonia (A: 26.8 kJ/mol, B: 18.0 kJ/mol) are in error by less than 25% compared to the experimental value of 24.2 kJ/mol [9]. From calculations with different types of *sp*-basis sets and polarization functions we have obtained values between 18 and 30 kJ/mol which demonstrates the pronounced basis set dependence of the computed barrier height [11]. We have therefore decided to perform a definitive SCF calculation for the inversion barrier of ammonia. The basis set chosen for this purpose is (15*s*10*p*2*d*1*f*;7*s*2*p*1*d*)/[9*s*7*p*2*d*1*f*;4*s*2*p*1*d*]. The nitrogen 15*s*10*p* primitive basis was fully optimized for ^4S state of nitrogen. The SCF energy

Table 2. Computed vs. experimental geometry, inversional barrier and vertical ionization potential for ammonia NH_3

Symmetry	Basis set[a]	η_d (N) η_p (H)	E_{SCF} [a.u.]	N–H [pm]	HNH	ϵ_{HOMO} [eV]
C_{3v}[b]	A	0.754	−56.102892	101.5	106.8°	11.66
D_{3h}[c]	A	1.015	−56.092666	99.8	120.0°	10.65
		$\Rightarrow \Delta E_{inv} = 26.8$ kJ/mol				
C_{3v}[b]	B_N	0.858 (N) 1.100 (H)	−56.211472	99.9	108.4°	11.43
D_{3h}[c]	B_N	1.310 (N) 1.137 (H)	−56.204600	98.5	120.0°	10.53
		$\Rightarrow \Delta E_{inv} = 18.0$ kJ/mol				

Exp.: N–H = 101.5 pm, ∠HNH = 106.6° [8]

$\Delta E_{inv} = 24.2$ kJ/mol [9], $IE^v = 10.85$ eV [10]

[a] See text and Table 1 for description of basis sets

[b] Local minimum structure

[c] Transition structure

Table 3. Comparison of near HF limit calculations for ammonia NH_3

Reference	Barrier [kJ/mol]	E_{SCF} (C_{3v}) [a.u.]	N–H (C_{3v}) [pm]	HNH (C_{3v})	E_{SCF} (D_{3h}) [a.u.]	N–H (D_{3h}) [pm]
this work[a]	19.7	−56.224785	99.8	108.2	−56.217278	98.4
RR[b]	21.8	−56.22333	99.9	107.7	−56.21504	98.4
RAC[c]	21.2	−56.22191	100.0	107.1	−56.21382	98.4
S[d]	24.7	−56.22113	100.1	106.2	−56.21173	98.5

[a] large basis as explained in text [b] Rodwell and Radom [13]
[c] Rauk, Allen and Clementi [14] [d] Stevens [15]

$E_{SCF}(N, {}^4S) = -54.400914$ a.u. is just 10 μH higher than the STO value of Clementi and Roetti [12]. The 7*s* basis for hydrogen has been taken from Huzinaga tables [7]. The orbital exponents for polarization functions were fully optimized (in the order 2*d*1*f*; 2*p*1*d*):

$$C_{3v}\colon\ 2.07, 0.62, 0.87; 1.54, 0.30, 1.88$$

$$D_{3h}\colon\ 2.56, 0.88, 1.05; 1.73, 0.42, 1.79$$

The results are given in Table 3 in comparison with extended gaussian basis treatments of Rodwell and Radom [13] and Rauk, Allen and Clementi [14] as well as the Slater-type calculation of Stevens [15].

Whereas different basis sets cause minor deviations (about 0.1 pm) in the N–H bond length there is a more pronounced change in the HNH angle of the pyramidal structure (variation between 106.2° and 108.2°). The present result for the inversion barrier of 19.7 kJ/mol, which we estimate to be accurate to about 0.5 kJ/mol, indicates a 10% error in the so far best calculations [13, 14, 15]. The deviation of the present result and the result of Rodwell and Radom [13] is almost exclusively due to the additional *f*-set for N and *d*-set for H. Since we have no reason to doubt the experimental result of 24.2 kJ/mol [9] we can safely conclude that correlation effects (including changes of equilibrium structure

Table 4. Computed vs. experimental geometry, inversional barrier and vertical ionization potential for phosphine PH_3

Symmetry	Basis set[a]	η_d (P)	E_{SCF} [a.u.]	P–H [pm]	HPH	ϵ_{HOMO} [eV]
C_{3v}[b]	*A*	0.424	−342.049919	140.1	95.8°	10.10
D_{3h}[c]	*A*	0.499	−341.991419	137.1	120.0°	7.93
		$\Rightarrow \Delta E_{inv} = 153.6$k J/mol				
C_{3v}[b]	B_P	0.498	−342.064134	141.0	95.4°	10.40
D_{3h}[c]	B_P	0.553	−342.001453	137.4	120.0°	8.02
		$\Rightarrow \Delta E_{inv} = 164.6$ kJ/mol				

Exp.: P–H = 143.7 ± 0.4 pm [16]
P–H = 142.1 ± 0.5 pm, ∠HPH = 93.5° [17, 18]
$IE^v = 9.97$ eV [19]
[a] See text and Table 1 for description of basis sets
[b] Local minimum structure
[c] Transition structure

constants) amount to 4.5 kJ/mol, which contradicts the conclusion of Stevens [15] based on small basis set calculations.

For the phosphine molecule there exists only a rough estimate for the inversion barrier of 132 kJ/mol [20]. The results obtained employing either basis set *A* ($\Delta E_{inv} = 154$ kJ/mol) or *B* ($\Delta E_{inv} = 165$ kJ/mol) are in good agreement with the theoretical value of 155 kJ/mol [21, 22] and 151 kJ/mol [23] obtained from SCF calculations and the near HF limit value of 153.6 kJ/mol [24]. Correlation effects will reduce the barrier height by about 10 kJ/mol as has been concluded from PNO-CI [25] and CI(SD) [24] calculations.

In both cases, a normal coordinate analysis reveals that the D_{3h} structure corresponds to a true transition structure (i.e., a first order saddle point). By the same method, the C_{3v} structures turn out to be proper local minima as was to be expected.

3.2. Trimethylamine vs. trimethylphosphine

A normal coordinate analysis shows that the C_{3v} structure corresponds to a local minimum for both systems if the methyl groups adopt a staggered conformation with respect to the nitrogen-carbon bonds, the so called LEM form. The other possible C_{3v} structure (the so called CALDER form) is less stable and not even a local minimum. For trimethylamine it was checked that there is no further stabilization when rotating one or two of the methyl groups by 180 degrees, thereby reducing the symmetry to C_s. We also have checked for both molecules that there is relaxation into C_{3v} symmetry when starting from C_3 symmetry, which has been derived from C_{3v} by conrotatory motion of the methyl groups. The global minimum structure of trimethylamine and trimethylphosphine may thus be safely assumed to exhibit C_{3v} symmetry which is in accord with earlier findings [26].

The substitution of hydrogen atoms by methyl groups poses the problem that there are at least two candidates for a possible transition structure. Depending on the relative orientation of the methyl groups, the molecular symmetry is either a C_{3h} or a C_s structure as depicted in Fig. 1. There are more short-distance hydrogen-hydrogen interactions for the C_{3h} structure, but the C_s structure should induce the shortest hydrogen-hydrogen distance at all. Thus it is difficult to make a prediction which of these structures will be more stable.

The results for trimethylamine and trimethylphosphine employing basis sets *A* and *B* are summarized in Tables 5 and 6, respectively. The deviation of present computed and experimental structure constants of $N(CH_3)_3$ (as given in Table 9) amounts to 0.5 pm for N–C, 1.5 pm for C–H and at most 1.2° for angles which is about twice the experimental errors. The situation is similiar for $P(CH_3)_3$ (as given in Table 10).

Let us first consider the transition state of trimethylamine. Here, the C_{3h} and C_s structures differ by about 1–2 kJ/mol. A normal coordinate analysis of these structures reveals that the C_{3h} structure is not a proper transition structure since two imaginary frequencies occur. The second imaginary frequency disappears if one of the methyl groups is rotated by 180 degrees, which results in the C_s geometry which is thus shown to be a 'true' transition structure within the method employed. The present results (*A*: 38.4 kJ/mol, *B*: 36.0 kJ/mol) may be compared with values obtained more or less directly from experimental information: 25.1 kJ/mol [22], 31.4 kJ/mol [29] and 34.7 kJ/mol [30]. The quite low

Table 5. Computed vs. experimental geometry, inversional barrier and vertical ionization potential for trimethylamine $N(CH_3)_3$

Symmetry	Basis set[a]	η_d (N, C) η_p (H)	E_{SCF} [a.u.]	N–C[d] [pm]	CNC[d]	ϵ_{HOMO} [eV]
C_{3v}[b]	A	0.860 (N)	−171.816395	148.3	111.3°	8.75
C_{3h}	A	1.047 (N)	−171.801269	147.0	120.0°	7.66
C_s[c]	A	1.048 (N)	−171.801760	146.9	120.0°	7.68
		⇒ ΔE_{inv}	= 38.4 kJ/mol			
C_{3v}[b]	B_N	0.921 (N) 0.802 (C) 1.312 (H_v) 1.259 (H)	−173.317524	144.6	111.8°	9.49
C_{3h}	B_N	1.067 (N) 0.808 (C) 1.217 (H_s) 1.286 (H)	−173.303073	143.3	120.0°	8.51
C_s[c]	B_N	1.069 (N) 0.809 (C) 1.215 (H_s) 1.286 (H)	−173.303812	143.2	120.0°	8.54
		⇒ ΔE_{inv}	= 32.9 kJ/mol			

H_v = hydrogen lying in σ_v; H_s = hydrogen lying in σ_s plane

Exponents cited for the C_s structure have been averaged

Exp.: N–C = 145.1 ± 0.3 pm, ∠CNC = 110.9° ± 0.6° [27]

ΔE_{inv} = 25.1 kJ/mol [28]/31.4 kJ/mol [29]/34.7 kJ/mol [30], IE^v = 8.44 eV [10]

[a] See text and Table 1 for description of basis sets

[b] Local minimum structure

[c] Transition structure

[d] Average values are given for the C_s structure, individual values are given in Table 9

'experimental' value of 25.1 kJ/mol proposed in a review of inversion barrier heights in amines and phosphines [22] lacks reliability since it had simply been transferred from experimental information for dimethylbenzylamine [28]. The value of 34.7 kJ/mol was obtained by a theoretical model calculation fit to fluorescene data [30]. In a previous theoretical calculation on the inversion barrier of trimethylamine a value of 40.2 kJ/mol was obtained on the basis of PRDDO geometries [33].

There is a similar state of affairs for the trimethylphosphine molecule with the minor exception of the calculations employing basis set A predicting both C_{3h} and C_s structures to be 'true' transition structures. For all calculations, there is no significant change in the HOMO's orbital energy when going from the C_{3h} to the C_s structure, so the change in total energy should mainly reflect the difference in intramolecular hydrogen-hydrogen interactions. The computed inversion barrier (A: 186 kJ/mol, B: 203 kJ/mol) is larger than an experimental estimate (149 kJ/mol [22, 32]), but it has to be considered that this value was obtained for cyclohexyl-methyl-*n*-propylphosphine and thus is not reliable. A recent *ab initio* SCF study on the inversion barrier in phosphine, trimethylphosphine and triphenylphosphine [23] yields a value of 198.7 kJ/mol which comes very close to our results. The computed increase of the barrier height when comparing to

Table 6. Computed vs. experimental geometry, inversional barrier and vertical ionization potential for trimethylphosphine $P(CH_3)_3$

Symmetry	Basis set[a]	η_d (P, C) η_p (H)	E_{SCF} [a.u.]	P–C[d] [pm]	CPC[d]	ϵ_{HOMO} [eV]
C_{3v}[b]	A	0.496 (P)	−457.802513	185.3	100.9°	7.99
C_{3h}[c]	A	0.527 (P)	−457.731820	185.3	120.0°	5.60
C_s[c]	A	0.528 (P)	−457.731823	185.2	120.0°	5.60
		⇒ ΔE_{inv} = 185.6 kJ/mol				
C_{3v}[b]	B_P	0.558 (P) 0.820 (C)	−459.033481	184.7	100.1°	8.93
C_{3h}	B_P	0.570 (P) 0.800 (C)	−458.955894	183.2	120.0°	6.37
C_s[c]	B_P	0.570 (P) 0.801 (C)	−458.956112	183.2	120.0°	6.37
		⇒ ΔE_{inv} = 203.1 kJ/mol				

Exp.: P–C = 184.6 ± 0.3 pm, ∠CPC = 98.6° ± 0.3° [31]

ΔE_{inv} = 149 kJ/mol [32], obtained for cyclohexyl-methyl-*n*-propylphosphine

[a] See text and Table 1 for description of basis sets

[b] Local minimum structure

[c] Transition structure

[d] Average values are given for the C_s structure, individual values are given in Table 10

phosphine correlates with the observation [23] that the lone pair of the phosphorus atom in trimethylphosphine is more strongly destabilized during planification than in phosphine as is apparent from the change of the corresponding orbital energy (see Tables 4 and 6 for the HOMO's orbital energy ϵ_{HOMO}) in phosphine, we have $\Delta\epsilon_{HOMO} = 2.38$ eV compared to $\Delta\epsilon_{HOMO} = 2.56$ eV in trimethylphosphine (basis set B)).

3.3. *Triisopropylamine vs. triisopropylphosphine*

The results for triisopropylamine and triisopropylphosphine employing basis sets A and B are summarized in Tables 7 and 8, respectively. Detailed information about the equilibrium geometries obtained with basis set B has been compiled in Tables 11 and 12.

Normal coordinate analyses were feasible for the basis set A calculations only. For both molecules it turns out that the C_3 structure is a local minimum, whereas the C_{3h} structure corresponds to a first order saddle point and thus a possible transition state of the inversion process.

The barrier height in triisopropylamine amounts to 3.4 kJ/mol (or 285 cm^{-1}) with basis set A and to 0.7 kJ/mol (or 25 cm^{-1}) with basis set B. The difference in the computed barrier height reflects the fact that basis set A yields a smaller CNC angle of 117.8° compared to the value of 118.9° for basis set B. Concludingly, thermal averaging should suffice for observing effectively a planar structure. The agreement between theoretical and experimental structure parameters – at least for those available – is satisfying as can be seen from Table 11. There is some deviation with respect to those parameters which involve the single hydrogen atom of the isopropyl group as is exemplified by the torsional

Table 7. Computed vs. experimental geometry, inversional barrier and vertical ionization potential for triisopropylamine $N(CH(CH_3)_2)_3$

Symmetry	Basis set[a]	η_d (N, C) η_p (H)	E_{SCF} [a.u.]	N–C [pm]	CNC	ϵ_{HOMO} [eV]
C_3[b]	A	0.893 (N)	−403.289592	149.5	117.8°	7.63
C_{3h}[c]	A	0.975 (N)	−403.288292	148.7	120.0°	7.35
		⇒ ΔE_{inv} = 3.4 kJ/mol				
C_3[b]	B_N	1.050 (N) 0.787 (C) 0.871 (C) 0.872 (C) 1.243 (H)	−407.574033	145.6	118.9°	8.59
C_{3h}[c]	B_N	1.015 (N) 0.788 (C) 0.872 (C) 1.245 (H)	−407.573749	145.2	120.0°	8.46
		⇒ ΔE_{inv} = 0.7 kJ/mol				

Exp. [1]: N–C = 146.0 pm, ∠CNC = 119.2°

ΔE_{inv} = 5.9 kJ/mol (MNDO), IE^v = 7.18 eV

[a] See text and Table 1 for description of basis sets

[b] Local minimum structure

[c] Transition structure

Table 8. Computed vs. experimental geometry, inversional barrier and vertical ionization potential for triisopropylphosphine $P(CH(CH_3)_2)_3$

Symmetry	Basis set[a]	η_d (P, C) η_p (H)	E_{SCF} [a.u.]	P–C [pm]	CPC	ϵ_{HOMO} [eV]
C_3[b]	A	0.455 (P)	−689.258491	188.7	106.6°	7.33
C_{3h}[c]	A	0.488 (P)	−689.205352	187.6	120.0°	5.41
		⇒ ΔE_{inv} = 139.5 kJ/mol				
C_3[b]	B_P	0.581 (P) 0.716 (C) 0.823 (C) 0.827 (C)	−692.924701	187.9	106.2°	8.39
C_{3h}[c]	B_P	0.592 (P) 0.709 (C) 0.825 (C)	−692.870159	185.6	120.0°	6.45
		⇒ ΔE_{inv} = 143.2 kJ/mol				

Exp. [34]: P–C = 185.9 pm, ∠CPC = 104.5°

[a] See text and Table 1 for description of basis sets

[b] Local minimum structure

[c] Transition structure

angle ∠CNCH, which is 5° from experiment and – depending on the carbon atoms involved in the definition of the torsional angle – 14° or 6°, respectively, from the calculation employing basis set *B*. Due to the difficulties and approximations inherent in the experimental structure determination [1], this deviation may be regarded as less significant. Nevertheless, our calculations show that it is

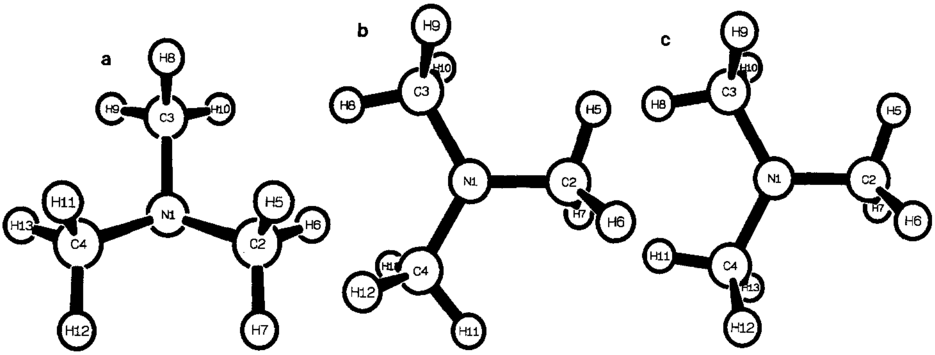

Fig. 2a–c. Equilibrium and transition structures of trimethylamine (SCF, basis set *B*): **a** C_{3v}-, **b** C_{3h}-, **c** C_s-symmetry

Table 9. Structural parameters for trimethylamine $N(CH_3)_3$ (basis set B_N)

	Distances [pm]		Bond angles		Dihedral angles	
C_{3v}	N(1)-C(2)	144.6	C(3)-N(1)-C(2)	111.8°		
Fig. 2a	C(2)-H(5)	109.4	N(1)-C(2)-H(5)	112.9°	C(3)-N(1)-C(2)-H(5)	63.1°
	C(2)-H(6)	108.2	N(1)-C(2)-H(6)	109.9°	C(3)-N(1)-C(2)-H(6)	−57.6°
			H(5)-C(2)-H(6)	108.1°		
			H(6)-C(2)-H(7)	107.9°		
C_{3h}	N(1)-C(2)	143.3	C(3)-N(1)-C(2)	120.0°		
Fig. 2b	C(2)-H(5)	108.2	N(1)-C(2)-H(5)	109.5°		
	C(2)-H(6)	108.9	N(1)-C(2)-H(6)	112.6°	C(3)-N(1)-C(2)-H(6)	119.2°
			H(5)-C(2)-H(6)	107.2°		
			H(6)-C(2)-H(7)	107.5°		
C_s	N(1)-C(2)	143.1	C(3)-N(1)-C(2)	119.8°		
Fig. 2c	C(2)-H(5)	108.2	N(1)-C(2)-H(5)	110.0°		
	C(2)-H(6)	109.0	N(1)-C(2)-H(6)	112.1°	C(3)-N(1)-C(2)-H(6)	119.6°
			H(5)-C(2)-H(6)	107.5°		
			H(6)-C(2)-H(7)	107.3°		
	N(1)-C(3)	143.3	C(4)-N(1)-C(3)	122.9°		
	C(3)-H(8)	108.1	N(1)-C(3)-H(8)	109.8°		
	C(3)-H(9)	108.9	N(1)-C(3)-H(9)	112.4°	C(4)-N(1)-C(3)-H(9)	119.3°
			H(8)-C(3)-H(9)	107.2°		
			H(9)-C(3)-H(10)	107.5°		
	N(1)-C(4)	143.1	C(2)-N(1)-C(4)	117.3°		
	C(4)-H(11)	108.1	N(1)-C(4)-H(11)	110.3°		
	C(4)-H(13)	109.0	N(1)-C(4)-H(13)	112.1°	C(2)-N(1)-C(4)-H(12)	119.7°
			H(11)-C(4)-H(13)	107.5°		
			H(13)-C(4)-H(12)	107.1°		
Exp. [27]	N-C	145.1 ± 0.3	C-N-C	110.9° ± 0.6°		
C_{3v}	C-H_v	110.9 ± 0.8	N-C-H_v	111.7° ± 0.4°		
	C-H	108.8 ± 0.8	N-C-H	110.1° ± 0.5°		
			H_v-C-H	108.1° ± 0.7°		
			H-C-H′	108.6° ± 0.8°		

H_v = hydrogen atoms lying in the σ_v plane

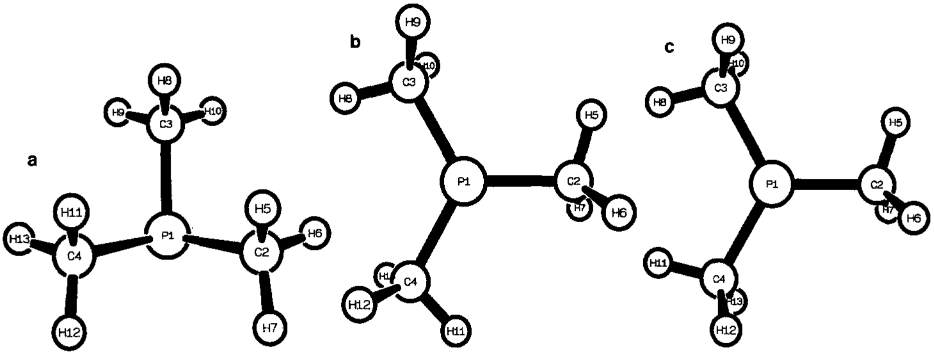

Fig. 3a–c. Equilibrium and transition structures of trimethylphosphine (SCF, basis set *B*): **a** C_{3v}-, **b** C_{3h}-, **c** C_s-symmetry

Table 10. Structural parameters for trimethylphosphine $P(CH_3)_3$ (basis set B_P)

	Distances [pm]		Bond angles		Dihedral angles	
C_{3v}	P(1)–C(2)	184.7	C(3)–P(1)–C(2)	100.1°		
Fig. 3a	C(2)–H(5)	109.2	P(1)–C(2)–H(5)	112.8°	C(3)–P(1)–C(2)–H(5)	51.2°
	C(2)–H(6)	109.1	P(1)–C(2)–H(6)	109.8°	C(3)–P(1)–C(2)–H(6)	−69.9°
			H(5)–C(2)–H(6)	108.5°		
			H(6)–C(2)–H(7)	107.4°		
C_{3h}	P(1)–C(2)	183.2	C(3)–P(1)–C(2)	120.0°	C(3)–P(1)–C(2)–H(6)	117.8°
Fig. 3b	C(2)–H(5)	109.1	P(1)–C(2)–H(5)	106.2°		
	C(2)–H(6)	109.0	P(1)–C(2)–H(6)	113.1°		
			H(5)–C(2)–H(6)	107.6°		
			H(6)–C(2)–H(7)	108.9°		
C_s	P(1)–C(2)	183.0	C(3)–P(1)–C(2)	120.0°	C(3)–P(1)–C(2)–H(6)	118.0°
Fig. 3c	C(2)–H(5)	109.1	P(1)–C(2)–H(5)	106.7°		
	C(2)–H(6)	109.0	P(1)–C(2)–H(6)	112.8°		
			H(5)–C(2)–H(6)	107.6°		
			H(5)–C(2)–H(7)	108.9°		
	P(1)–C(3)	183.4	C(4)–P(1)–C(3)	119.9°		
	C(3)–H(8)	109.0	P(1)–C(3)–H(8)	106.4°		
	C(3)–H(9)	109.0	P(1)–C(3)–H(9)	113.0°	C(4)–P(1)–C(3)–H(9)	117.9°
			H(8)–C(3)–H(9)	107.6°		
			H(9)–C(3)–H(10)	108.9°		
	P(1)–C(4)	183.2	C(2)–P(1)–C(4)	120.2°	C(2)–P(1)–C(4)–H(12)	118.2°
	C(4)–H(11)	108.9	P(1)–C(4)–H(11)	107.0°		
	C(4)–H(13)	109.6	P(1)–C(4)–H(13)	112.8°		
			H(11)–C(4)–H(13)	107.7°		
			H(13)–C(4)–H(12)	108.8°		
Exp. [31]	P–C	184.6 ± 0.3	C–P–C	98.6° ± 0.3°		
C_{3v}	C–H	109.1 ± 0.6	P–C–H	110.7° ± 0.5°		

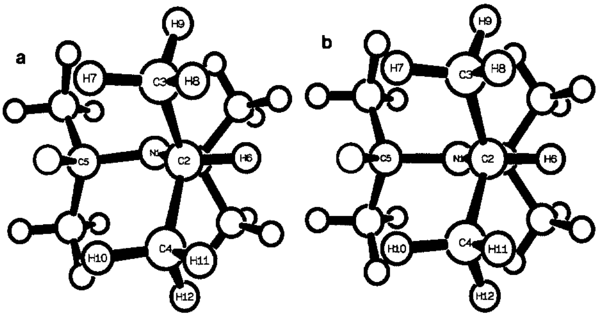

Fig. 4a,b. Equilibrium and transition structures of triisopropylamine (SCF, basis set *B*): **a** C_3-, **b** C_{3h}-symmetry

Table 11. Structural parameters for triisopropylamine $N(CH(CH_3)_2)_3$ (basis set B_N)

	Distances [pm]		Bond angles		Dihedral angles	
C_3	N(1)-C(2)	145.6	C(2)-N(1)-C(5)	118.9°		
Fig. 4a	C(2)-H(6)	108.1	N(1)-C(2)-H(6)	106.2°	C(5)-N(1)-C(2)-H(6)	173.5°
	C(2)-C(3)	153.3	N(1)-C(2)-C(3)	111.7°	C(5)-N(1)-C(2)-C(3)	−71.1°
	C(2)-C(4)	153.7	N(1)-C(2)-C(4)	115.1°	C(5)-N(1)-C(2)-C(4)	55.9°
			C(3)-C(2)-H(6)	106.2°		
			C(4)-C(2)-H(6)	106.5°		
			C(3)-C(2)-C(4)	110.4°		
	C(3)-H(9)	108.2	C(2)-C(3)-H(9)	110.3°	N(1)-C(2)-C(3)-H(9)	−54.8°
	C(3)-H(7)	108.4	C(2)-C(3)-H(7)	111.8°	N(1)-C(2)-C(3)-H(7)	65.4°
	C(3)-H(8)	108.5	C(2)-C(3)-H(8)	110.7°	N(1)-C(2)-C(3)-H(8)	185.1°
			H(9)-C(3)-H(7)	108.0°		
			H(9)-C(3)-H(8)	108.5°		
			H(7)-C(3)-H(8)	107.5°		
	C(4)-H(10)	108.4	C(2)-C(4)-H(10)	111.8°	N(1)-C(2)-C(4)-H(10)	−65.7°
	C(4)-H(11)	108.4	C(2)-C(4)-H(11)	110.1°	N(1)-C(2)-C(4)-H(11)	175.1°
	C(4)-H(12)	108.2	C(2)-C(4)-H(12)	111.3°	N(1)-C(2)-C(4)-H(12)	55.3°
			H(12)-C(4)-H(10)	108.1°		
			H(12)-C(4)-H(11)	108.0°		
			H(10)-C(4)-H(11)	107.4°		
C_{3h}	N(1)-C(2)	145.2	C(2)-N(1)-C(5)	120.0°		
Fig. 4b	C(2)-H(6)	108.1	N(1)-C(2)-H(6)	106.3°		
	C(2)-C(3)	153.5	N(1)-C(2)-C(3)	113.3°	C(5)-N(1)-C(2)-C(3)	−63.6°
			C(3)-C(2)-H(6)	106.4°		
			C(3)-C(2)-C(4)	111.7°		
	C(3)-H(7)	108.4	C(2)-C(3)-H(7)	111.8°	N(1)-C(2)-C(3)-H(7)	65.1°
	C(3)-H(8)	108.5	C(2)-C(3)-H(8)	110.6°	N(1)-C(2)-C(3)-H(8)	184.8°
	C(3)-H(9)	108.2	C(2)-C(3)-H(9)	110.6°	N(1)-C(2)-C(3)-H(9)	−55.3°
			H(7)-C(3)-H(8)	107.5°		
			H(7)-C(3)-H(9)	108.0°		
			H(8)-C(3)-H(9)	108.3°		
Exp.[a]	N-C	146.0	C-N-C	119.2°	C-N-C-H	5.0°
C_3 [1]	C-C	154.1	N-C-H	109.5°		
	C-H	109.4	N-C-C	112.4°		
			C-C-C	108.7°		

[a] Internal coordinates have been equivalenced [1]

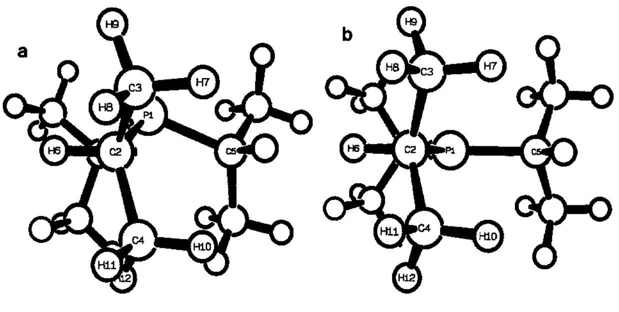

Fig. 5a,b. Equilibrium and transition structures of triisopropylphosphine (SCF, basis set B): **a** C_3-, **b** C_{3h}-symmetry

Table 12. Structural parameters for triisopropylphosphine $P(CH(CH_3)_2)_3$ (basis set B_P)

	Distances [pm]		Bond angles		Dihedral angles	
C_3	P(1)-C(2)	187.9	C(2)-P(1)-C(5)	106.2°		
Fig. 5a	C(2)-H(6)	109.5	P(1)-C(2)-H(6)	103.6°	C(5)-P(1)-C(2)-H(6)	205.6°
	C(2)-C(3)	153.7	P(1)-C(2)-C(3)	108.5°	C(5)-P(1)-C(2)-C(3)	92.3°
	C(2)-C(4)	153.3	P(1)-C(2)-C(4)	119.6°	C(5)-P(1)-C(2)-C(4)	−34.4°
			C(4)-C(2)-H(6)	107.8°		
			C(3)-C(2)-H(6)	106.8°		
			C(3)-C(2)-C(4)	109.7°		
	C(3)-H(9)	108.9	C(2)-C(3)-H(9)	111.5°	P(1)-C(2)-C(3)-H(9)	54.2°
	C(3)-H(8)	109.2	C(2)-C(3)-H(8)	110.5°	P(1)-C(2)-C(3)-H(8)	174.7°
	C(3)-H(7)	109.2	C(2)-C(3)-H(7)	111.3°	P(1)-C(2)-C(3)-H(7)	−66.0°
			H(9)-C(3)-H(8)	108.3°		
			H(9)-C(3)-H(7)	107.7°		
			H(8)-C(3)-H(7)	107.5°		
	C(4)-H(10)	109.0	C(2)-C(4)-H(10)	111.4°	P(1)-C(2)-C(4)-H(10)	64.4°
	C(4)-H(11)	109.2	C(2)-C(4)-H(11)	109.6°	P(1)-C(2)-C(4)-H(10)	182.9°
	C(4)-H(12)	108.6	C(2)-C(4)-H(12)	112.8°	P(1)-C(2)-C(4)-H(12)	−57.4°
			H(10)-C(4)-H(11)	107.2°		
			H(10)-C(4)-H(12)	108.1°		
			H(11)-C(4)-H(12)	107.5°		
C_{3h}	P(1)-C(2)	185.6	C(2)-P(1)-C(5)	120.0°		
Fig. 5b	C(2)-H(6)	109.4	P(1)-C(2)-H(6)	102.1°		
	C(2)-C(3)	153.4	P(1)-C(2)-C(3)	113.8°	C(5)-P(1)-C(2)-C(3)	64.1°
			C(3)-C(2)-H(6)	107.8°		
			C(3)-C(2)-C(4)	110.8°		
	C(3)-H(7)	109.1	C(2)-C(3)-H(7)	111.1°	P(1)-C(2)-C(3)-H(7)	−63.9°
	C(3)-H(8)	109.3	C(2)-C(3)-H(8)	110.5°	P(1)-C(2)-C(3)-H(8)	176.8°
	C(3)-H(9)	108.8	C(2)-C(3)-H(9)	111.2°	P(1)-C(2)-C(3)-H(9)	56.2°
			H(9)-C(3)-H(8)	108.6°		
			H(9)-C(3)-H(7)	107.8°		
			H(8)-C(3)-H(7)	107.5°		
Exp.[a]	P-C	185.9	C-P-C	104.5°		
[34]	C-C	152.8	P-C-H	102.4°		
	C-H(*ipso*)	110.0	P-C-C	114.2°		
	C-H(methyl)	108.6	C-C-C	110.0°		
			C-C-H	111.2°		
			H-C-H	107.6°		

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[a] Internal coordinates have been averaged
Data for molecular complex $H_5Ir(P(i\text{-}Pr)_3)_2$

justified to assume local C_s symmetry for the isopropyl groups and local C_{3v} symmetry for the methyl groups.

Let us consider briefly barrier heights for inversion and equilibrium bond angles at N for NH_3, $N(CH_3)_3$ and $N(CH(CH_3)_2)_3$. In $N(CH_3)_3$ one finds a larger bond angle than in NH_3, 111.8° vs. 108.4° (Tables 5 and 2; results obtained with basis set *B*), which probably reflects the larger sterical requirements of methyl groups as compared to hydrogen. Although $N(CH_3)_3$ is closer to the planarity than NH_3 we find the larger barrier, 32.9 kJ/mol vs. 18.0 kJ/mol (basis set *B*, Tables 5 and 2). This trend, which may be unexpected at first sight, can be rationalized by the larger polarizability of CH_3 as compared to H, which leads to a more pronounced stabilization of the polar C_{3v} structure. For triisopropylamine the near planarity is clearly enforced by steric requirements.

The inversion barrier in triisopropylphosphine of about 140 kJ/mol turns out to be slightly (i.e., by about 10 kJ/mol) smaller than that in phosphine. The sterical strain induced by the bulky isopropyl groups does not suffice to enforce a nearly planar configuration around phosphorus, but at least leads to a significant increase with respect to the CPC angle from about 100° in trimethylphosphine to about 106° in triisopropylphosphine.

4. Conclusions

It has been shown that no serious difficulties hamper the application of *ab initio* methods to the determination of the equilibrium geometry and inversion barrier of triisopropylamine at least at the SCF level of theory. The barrier to inversion is predicted to be in the order of 1 kJ/mol, which means that at room temperature thermal averaging should result in observing a planar structure.

For all species it has been assumed that in the transition state, the planar configuration around the central atom is fixed by symmetry requirements. By application of normal coordinate analysis it has been confirmed that the symmetry of a possible transition state for the triisopropyl compounds is C_{3h} in contrast to the trimethyl compounds where it turned out to be C_s.

Since we are not aware of more elaborate theoretical studies than the present one and considering the difficulties to obtain experimental information, we consider the barrier heights obtained for trimethylamine, trimethylphosphine, triisopropylamine and triisopropylphosphine to be the most reliable available to date.

The agreement between computed and experimental structure parameters is as expected for applications of the SCF method to compounds of the first and second row elements [35]. Bond distances and bond angles are in error by less than 2 pm and 2 degrees, respectively.

The decrease in the vertical ionization potentials when going through the series AH_3, AMe_3, $A(i\text{-Pr})_3$ ($A = N, P$) as obtained from Koopmans theorem is in accord with the experimental data as far as those are available. The computed values are always too large which is to be expected from the neglect of electronic relaxation effects inherent to the approximation made.

Within the series AH_3, AMe_3, $A(i\text{-Pr})_3$ ($A = N, P$), the largest barrier to inversion occurs for the methyl compound, which is in agreement with experiment (there are no data available for the triisopropyl compounds, however).

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