MINDO/3 AND MNDO CALCULATIONS OF PHOSPHINES: CONFORMATIONAL ENERGIES, ROTATIONAL BARRIERS, BOND LENGTHS AND BOND ANGLES

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MINDO/3 and MNDO derived heats of formation data are reported for all low-energy, unique conformations of PH_3, PH_2Me, PH_2Et, PH_2-i-Pr, PH_2-t-Bu, PH_2Ph, $PHMe_2$, PHMeEt, $PHEt_2$, $PH(i-Pr)_2$, PMe_3, PMe_2Et, $PMeEt_2$, PEt_3, and PMe_2Ph. In general, the computational methods predict similar stability orders for the conformations of each molecule. The conformational energies, as well as calculated rotational barriers, bond lengths and bond angles, are compared to previously reported computational and experimental data.

INTRODUCTION

Steric effects of coordinated phosphorus ligands, especially phosphines in transition metal catalysts, are currently of considerable interest and can account for the course of asymmetric syntheses,[1–3] reaction rates,[4] and product distributions.[5–6] To quantify ligand size, Tolman introduced the concept of cone angles.[7] Recently, we have expanded upon his ideas and used computational data (from MINDO/3) to illustrate the importance of ligand conformations in cone angle determinations.[8]

Even though phosphorus-ligand conformations dictate ligand size, little supporting experimental or computational data are available. As a part of our continuing interest in this area, we report herein the results from treating fifteen phosphines with the semi-emperial molecular orbital methods, MINDO/3[9] and MNDO.[10]

The theoretical differences between MINDO/3 and MNDO and their ramifications have been described in some detail by Thiel.[11] Recently, Frenking, Marschner and Goetz have compared heat of formation data, ionization potentials, dipole moments, bond angle and bond length data computed by the two programs for a variety of phosphorus compounds including the phosphines PH_3, PH_2Me, $PHMe_2$, PMe_3, PH_2Et, $PHEt_2$, PEt_3, and PH_2Ph.[12]

In this paper, however, is a discussion of the utility of MINDO/3 and MNDO for conformational studies of phosphines by comparisons to the available experimental data. It expands upon the results reported by Frenking, Marschner and Goetz[12] by considering multiple conformations and rotational barriers.
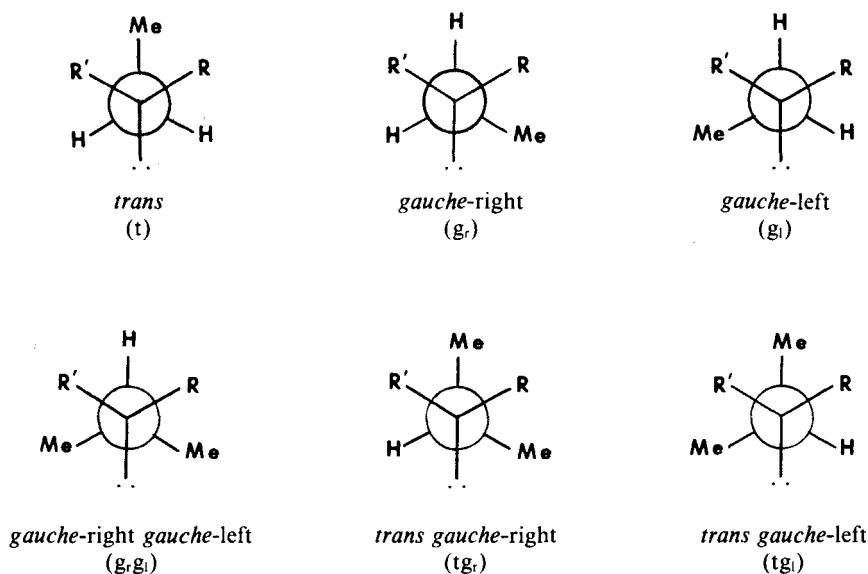
METHODS

MINDO/3 and MNDO calculations were performed on all potentially low-energy conformations of 15 phosphorus ligands. The compounds and conformers consid-

12   J. A. MOSBO *et al.*

TABLE I

MINDO/3 and MNDO Derived Heats of Formation of All Phosphine Conformers

Compound	Unique Conformers Contributing Conformers[a]	No.	ΔH_f (kcal/mol) MINDO/3	MNDO
PH_3	—	—	2.52^b	3.94
PH_2Me	—	—	-10.01^b	-14.65
PH_2Et	t	1	-4.74^b	-21.03
	g_r; g_l	2	-4.78^b	-21.39
PH_2-i-Pr	tg_r; tg_l	1	10.43^b	-24.47
	g_r,g_l	2	10.38^b	-24.62
PH_2-t-Bu	—	—	34.56^b	-23.96
PH_2Ph	s	1	52.52^b	16.20
	e	2	53.57^b	15.95
$PHMe_2$	—	—	-19.73^b	-32.05
$PHMeEt$	t	1	-14.21	-37.74
	g_r	2	-14.39	-38.29
	g_l	3	-14.60	-38.42
$PHEt_2$	t,t	1	-8.34^b	-42.78
	t,g_l; g_r,t	2	-8.70^b	-43.73
	t,g_r; g_l,t	3	-8.91^b	-44.18
	g_l,g_r	4	-9.37^b	-44.75
	g_l,g_l; g_r,g_r	5	-9.13^b	-44.47
	g_r,g_l	6	-8.75^b	-43.88
$PH(i-Pr)_2$	tg_l,tg_r	1	22.85^b	
	tg_r,tg_l	2	23.09^b	-45.84
	tg_r,tg_r; tg_l,tg_l	3	22.98^b	-48.48
	tg_r,g_rg_l; g_rg_l,tg_l	4	22.58^b	-47.82
	tg_l,g_rg_l; g_rg_l,tg_r	5	22.44^b	-49.37
	g_rg_l,g_rg_l	6	22.57^b	-48.15
PMe_3	—	—	-27.05^b	-48.23
PMe_2Et	t	1	-21.22	-53.02
	g_r; g_l	2	-21.50	-53.97
$PMeEt_2$	t,t	1	-15.17	-56.75
	t,g_l; g_r,t	2	-15.52	-58.58
	t,g_r; g_l,t	3	-15.62	-58.84
	g_l,g_r	4	-15.94	-59.43
	g_l,g_l; g_r,g_r	5	-15.88	-59.54
	g_r,g_l	6	-15.68	-46.30
PEt_3	t,t,t	1	-8.68^b	-58.27
	t,t,g_r; t,t,g_l; t,g_r,t; t,g_l,t; g_r,t,t; g_l,t,t	2	-9.42^b	-62.16
	t,g_l,g_r; g_r,t,g_l; g_l,g_r,t	3	-9.88^b	-63.84
	t,g_r,g_r; t,g_l,g_l; g_r,t,g_r; g_l,t,g_l; g_r,g_r,t; g_l,g_l,t	4	-9.91^b	-64.15
	t,g_r,g_l; g_l,t,g_r; g_r,g_l,t	5	-9.66^b	-63.90
	g_r,g_r,g_r; g_l,g_l,g_l	6	-10.20^b	-65.16
	g_r,g_l,g_l; g_l,g_r,g_r; g_r,g_r,g_l; g_l,g_l,g_r; g_r,g_l,g_r; g_l,g_r,g_l	7	-9.95^b	d
PMe_2Ph	s	1	36.70^b	-12.47
	e	2	37.59^b	-15.49

[a] See Methods for description.
[b] From Ref. 8.
[c] Input conformation was not maintained. See Methods.
[d] Convergence was not attained. See Methods.

ered are contained in Table I; symmetry-related, energetically identical conformations are listed together as one unique conformation. For each of the ligands PH_3, PH_2Me, $PHMe_2$, PMe_3, and PH_2-t-Bu a single conformation was used with staggered hydrogens on methyl substituents and staggered methyls on the *tert*-butyl group. Three conformations were considered for ethyl and isopropyl substituents. They are represented below (phosphorus

| *trans* (t) | *gauche*-right (g_r) | *gauche*-left (g_l) |

| *gauche*-right *gauche*-left ($g_r g_l$) | *trans gauche*-right (tg_r) | *trans gauche*-left (tg_l) |

is the front atom) and named according to the system cited by Hanack,[13] where *trans* and *gauche* refer to the relationship between the back-carbon substituent and the phosphorus lone pair electrons. For a phenyl group the staggered (s) and eclipsed (e) conformations

| staggered (s) | eclipsed (e) |

were used. In Table I, the individual substituent orientations of a given ligand conformation are separated by commas and listed in counterclockwise order as viewed from the phosphorus lone pair. The symmetry-related, equal-energy conformations are separated by semicolons.

Input data for MINDO/3 and MNDO were initial approximate bond lengths (P—H = 1.4 Å, P—C = 1.8 Å, C—C (alkyl) = 1.5 Å, C—C (aryl) = 1.4 Å, C—H = 1.1 Å), bond angles (R—P—R' = 109.5°, R—C—R' (alkyl) = 109.5°, R—C—R' (aryl) = 120°), and idealized twist angles (staggered groups for alkyl substit-

uents, staggered and eclipsed for aryl substituents). All atom positions were allowed to optimize. For conformer 2 of PMe_2Ph with MNDO this required over 3 hr of CPU time (DECsystem 1020).

Maxima for P—C (alkyl) bond rotations were approximated by treating the twist angle defined by the bond of interest as a reaction coordinate and allowing all bond lengths and angles, and the other twist angles to optimize. Values for the maxima plus or minus the increment differed by no more than 0.02 kcal/mole. The locations of P—C (aryl) rotational maxima were not attempted because of the extensive CPU time required for geometry optimizations of phenyl groups.

RESULTS AND DISCUSSION

Conformations

All of the conformations that constitute the unique conformations used as input geometries for the fifteen phosphines are defined in the Methods section and listed in Table I. These conformations were essentially maintained upon geometry optimization by MINDO/3 and MNDO with two notable exceptions from MNDO: conformer 1 of $PH(i\text{-}Pr)_2$ rotated to conformer 5, and convergence was not attained for conformer 7 of PEt_3 despite several attempts and approaches.

Conformational energies

Computed heats of formation data are listed in Table I. Values for PH_3, PH_2Me, PH_2Et, PEt_3 and PH_2Ph are comparable to those reported by Frenking, Marschner and Goetz,[12,14] although conformers were not specified for the latter four compounds. For PMe_3, however, the MINDO/3 computed heat of formation reported here and in our earlier paper[8] is over 10 kcal/mol lower than the previous value. The reason for this discrepancy is not known, since we apparently used the same parameters.

There is a general, qualitative similarity between relative conformational energies computed by MINDO/3 and MNDO (e.g., the six unique conformations of $PHEt_2$ are in the same stability order for both). Noteworthy exceptions occur with conformer 6 of $PMeEt_2$, which is unusually large (in a positive sense) from MNDO, and with the conformers of PH_2Ph and PMe_2Ph. Reported differences in the phenyl-substituted phosphines should be viewed with caution, however. In most cases the MNDO program had considerable difficulty with phenyl groups, requiring over three hours of CPU time for conformer 2 of PMe_2Ph. In light of these time requirements, for this study we did not feel justified in undertaking a definitive, systematic investigation of the causes of the difficulty. It appeared, however, that the computed energy surface for the compounds was very flat and/or contained several shallow, local minima. Consequently, the heat of formation data for PH_2Ph and PMe_2Ph listed in Table I may not represent global minima.

There are some experimental data reported for relative conformational energies of phosphines to which the results described here can be compared. Durig and Cox[15] have reported microwave, infrared and Raman data for PH_2Et from which the *trans* conformer (1) was concluded to be more stable by 0.56 kcal/mole. The MINDO/3 and MNDO results, however, predict the *gauche* geometry (conformer 2) to be more stable by 0.04 and 0.36 kcal/mole, respectively. Durig and Li have also reported microwave data for $PH_2\text{-}i\text{-}Pr$ and found no experimental evidence for conformer 1.[16]

Consistent with these results, MINDO/3 and MNDO predict conformer 2 to be more stable by 0.05 and 0.15 kcal/mole, respectively, but when conformational multiplicity is also considered, both predict greater mole fractions for conformer 1. (See Ref. 8 for a method of computing mole fractions.) Although definitive, quantitative experimental data are lacking, based on infrared and Raman studies, Crocker and Goggin[17] have concluded that: (1) for PMe_2Et the stable conformer is 2 in the solid, whereas both conformers are present in the liquid; (2) the solid forms of $PMeEt_2$ are probably 4 and 5, while the liquid probably contains conformations 2 or 3 as well; and (3) the solid form of PEt_3 is conformer 6 with 3 and/or 4 also present in the liquid. The MINDO/3 and MNDO heats of formation data are generally consistent with these conclusions.

Parr[18] has reported that ab initio (STO-3G) calculations predict conformer 1 ($\theta = 42°$ in the drawing below) to be the most stable for PH_2Ph and that a maximum 1.12 kcal/mol higher occurs
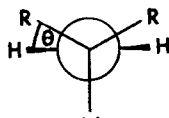
at $\theta = 135°$. Similarly, from CNDO calculations that included conjugative interruption between the phenyl and the PH_2 groups, Schmidt et al.[19] concluded the stable conformation to be that with $\theta = 40°$ (relative energy of zero kcal/mol) and the maximum to be at $\theta = 130°$ (~1.8 kcal/mol). Results from MINDO/3 and MNDO are similar, but two minima were found for each at $\theta = 38°$ and 128°, and 64° and 126°, respectively. In contrast to PH_2Ph, the CNDO calculations of PMe_2Ph showed a minimum at 52° (relative energy of zero kcal/mol), a pseudominimum at 80° (~1.1 kcal/mol), a maximum at 40° (~2.4 kcal/mol) and a pseudomaximum at 95° (~1.2 kcal/mol).[19] The MINDO/3 and MNDO calculations of PMe_2Ph provided minima at 22° and 116°, and 42° and 124°, respectively.

Rotational barriers

Computational and experimental data for P—C (alkyl) bond rotations are presented in Table II. Those for both MINDO/3 and MNDO are too small by factors exceeding 6 and 3, respectively, differences that are probably too great to be ascribed to the technique used for locating the maxima (see Methods sections).

Bond lengths and angles

As originally described by Frenking, Marschner and Goetz,[12] P—C and P—H bond lengths computed by MINDO/3 are longer and closer to experimental values than those from MNDO. Conversely, H—P—H, H—P—C and C—P—C bond angles are relatively poorly predicted by MINDO/3, being considerably too large.[12]

Additional information pertinent to the use of MINDO/3 and MNDO for conformational studies are the P—C—H and P—C—C angles. Table III contains a compilation of these data from other computational and experimental sources. Both MINDO/3 and MNDO predict greater angles for substituents trans to the phosphorus lone pair. This tilting of groups toward the lone pair is consistent with

J. A. MOSBO et al.

TABLE II

Rotational Barriers of P—C (alkyl) Bonds[a]

Compound	MINDO/3	MNDO	Other semi-emprical	ab initio	Experimental
PH_2Me	0.38	0.62	0.79[b], 1.32[c] 1.78[d], 2.92[e]	1.71[f], 1.83[g]	1.96[h]
$PHMe_2$	0.30	0.73			2.22[i]
PMe_3	0.34	0.93	3.0[i], 3.1[j]		2.6[k], 3.58[j]
PH_2Et	0.32[m]	0.72[m]			1.82[m,o]
	0.66[n]	0.59[n]			2.70[n,o]

[a] In kcal/mol.
[b] CNDO/2, SP with optimized geometry, Ref. 22.
[c] INDO with optimized geometry, Ref. 23.
[d] CNDO/2, SPD′ with optimized geometry, Ref. 22.
[e] CNDO/2, SPD with optimized geometry, Ref. 22.
[f] (95/52/3) GTO with fixed geometry, Ref. 24.
[g] (951/52/3) GTO with fixed geometry, Ref. 24.
[h] Ref. 25.
[i] Ref. 21.
[j] CNDO/2, two different fixed geometries, Ref. 26.
[k] Ref. 27.
[l] Ref. 28.
[m] Barrier height for gauche → gauche rotation relative to energy of gauche conformer.
[n] Barrier height for trans → gauche rotation relative to energy of trans conformer.
[o] Ref. 15.

TABLE III

P—C—H and P—C—C Bond Angles[a]

Compound	MINDO/3 trans	MINDO/3 gauche	MNDO trans	MNDO gauche	Other trans	Other gauche
PH_2Me	118.9	115.0	113.9	108.8	112.7[b]	109.2[b]
$PHMe_2$	118.6	114.8	114.3	108.3		
PMe_3	118.5	114.8	114.1	108.2	111.4[c]	109.8[c]
PH_2Et	129.4	126.6	118.8	112.6	115.2[d]	110.1[d]

[a] In degrees; trans and gauche refer to the orientation with respect to the phosphorus lone pair of electrons.
[b] Calculation, CNDO/2 SPD′ with geometry optimization, Ref. 22.
[c] Experimental, Ref. 20.
[d] Experimental, Ref. 15.

experimental data.[20,21] Both sets of angles, trans and gauche, are too large by both techniques, however, and are particularly poor for MINDO/3.

Bond lengths are not very sensitive to substituent orientations. The trans hydrogens in the methylphosphine series are about 0.03 Å longer than the gauche from MINDO/3, but differ insignificantly with MNDO. Experimental data for PMe₃ suggest the trans hydrogen to be about 0.02 Å longer.[20] The MINDO/3 and MNDO computed C—C bond lengths of PH₂Et are unaffected by the ethyl group orientation.

ACKNOWLEDGMENTS

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