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Calculation of Phosphororganic Compounds by MINDO/3.

1. Parametrization of the P-C Bond

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Abstract: The original parameters α_{XY} and B_{XY} for the core repulsion and the resonance integrals in MINDO/3 were found to be incorrect in case of the P-C bonding. New parameters were determined based on true experimental data.

The semiempirical method MINDO/3 was developed by Dewar et al.¹ Calculations in a wide field of chemical compounds showed good results. It is our aim to apply MINDO/3 systematically for phosphororganic compounds which has been done for only a small number of molecules by Dewar et al.² The parameters α_{XY} for the core repulsion and B_{XY} for the resonance integrals were only given for P-C, P-P, and P-H bonding. When we recalculated the molecules reported by Dewar et al.² we could not reproduce the same results in the case of P-C bonding; a complete optimization of all independent geometrical parameters gave much lower values for the heat of formation. This is shown in Table I. Therefore we found it necessary to determine new values for α_{XY} and B_{XY} for P-C bonding. Furthermore, we found the experimental values used by Dewar et al. not very reliable. The only true experimental value used for the parametrization was that for trimethylphosphine (M_3), whereas the other values of dimethylphosphine (M_2), methylphosphine (M_1), and the ethylphosphines (E_1 and E_2) were determined by calculations using an increment method based upon the values for M_3 and PH_3 .³ The reported experimental value for the heat of formation of

triethylphosphine (E_3)⁴ shows the values for the ethylphosphines to be in error.

We based our parametrization only on experimental values, that is M_3 , E_3 , and the value for tri-*n*-butylphosphine.⁴ The results are shown in Table I. The new values for α_{XY} and B_{XY} are 0.8700 and 0.5000, respectively. Table II shows the calculated ionization potentials, that is the negative eigenvalue of the HOMO, in comparison to experimental values and Dewar's results. In Table III the geometrical data are presented, together with experimental values. In all cases, the deviation from Dewar's results is not strong and the agreement with experimental results is good.

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Note Added by M. J. S. Dewar and G. P. Ford: We have checked the calculations for phosphorus compounds and confirmed that the results listed in ref 2 do not follow from the parameters listed in ref 1. We have also repeated calculations

Table I. Calculated and Observed Heats of Formation in kcal/mol

	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>
CH ₃ PH ₂	-8.3	-15.4	-9.8	
(CH ₃) ₂ PH	-16.6	-30.6	-19.5	
(CH ₃) ₃ P	-21.9	-43.2	-16.6	-23.5
C ₂ H ₅ PH ₂	-11.7	-16.4	-3.2	
(C ₂ H ₅) ₂ PH	-23.9	-31.6	-8.1	
(C ₂ H ₅) ₃ P		-41.1	-7.3	-11.8
PhPH ₂	30.4	30.0	53.1	
HCP	3.7	-10.9	-8.0	
CH ₂ PH	5.2	-5.8	-1.1	
(<i>n</i> -Bu) ₃ P		-60.0	-20.9	-13.0

^a Values reported by Dewar et al.² ^b Calculated results using Dewar's values for α_{XY} and B_{XY} with complete optimization of all independent geometrical parameters. ^c Calculated with our values for α_{XY} (0.8700) and B_{XY} (0.5000). ^d Experimental values.⁴ The value for tri-*n*-butylphosphine ((*n*-Bu)₃P) was determined with an extrapolated heat of vaporization of 15 kcal/mol.

Table II. Calculated and Experimental Ionization Potentials in eV

	<i>a</i>	<i>b</i>	<i>c</i>
CH ₃ PH ₂	9.41	9.31	9.62 ^d
(CH ₃) ₂ PH	8.91	8.87	9.08 ^d
(CH ₃) ₃ P	8.58	8.52	8.60 ^d
C ₂ H ₅ PH	9.27	9.32	
(C ₂ H ₅) ₂ PH	9.00	8.92	
(C ₂ H ₅) ₃ P		8.49	8.28 ^d
PhPH ₂	8.36	8.40	8.70; ^e 8.47 ^f
HCP	10.69	10.75	10.73 ^g
CH ₂ PH	9.52	9.53	
(<i>n</i> -Bu) ₃ P		8.43	8.00 ^h

^a Dewar's values.² ^b Our values with new parameters. ^c Experimental values. ^d Reference 5. ^e Reference 6. ^f Reference 7. ^g Reference 8. ^h Reference 9.

for the other third-period elements and have found similar but smaller errors in the results for Si and S. Some examples are shown in Table IV. The values for Cl are correct. It would appear that an earlier set of parameters for Si, P, and S was inadvertently included in the final computer program and hence in the published list of parameters in ref 1. These errors went undetected since we have not ourselves been carrying out MINDO/3 calculations for these elements.

In this connection, it should be noted that parameters for Si, P, S, and Cl (without 3d AO's) are now available in the MNDO method, which is superior to MINDO/3 and has the advantage of allowing calculations for all combinations of atoms. A paper regarding this is being submitted for publication.

Table III. Calculated (Observed)^a Bond Lengths (ab, Å) and Bond Angles (abc)

CH ₃ PH ₂	PH, 1.420 (1.423, 1.414); PC, 1.824 (1.858, 1.863); HPH, 100.0° (93.4°)
(CH ₃) ₂ PH	PH, 1.422 (1.445); PC, 1.831 (1.853); CPC, 113.0° (99.2°):
(CH ₃) ₃ P	PC, 1.838 (1.846, 1.841); CPC, 112.9° (98.6°, 99.1°)
C ₂ H ₅ PH	PH, 1.420; PC, 1.868; HPC, 104.5°; HPH, 100.0°
(C ₂ H ₅) ₂ PH	PH, 1.423; PC, 1.877; HPC, 105.2°; CPC, 112.1°
(C ₂ H ₅) ₃ P	PC, 1.882; CPC, 112.5°
PhPH ₂	PH, 1.421; PC, 1.884; HPH, 101.0°; HPC, 105.1°
HCP	CP, 1.502 (1.542); CH, 1.096 (1.067)
CH ₂ PH	PH, 1.421; PC, 1.632; CPH, 108.2°; HCP, 129.1°
(<i>n</i> -Bu) ₃ P	PC, 1.885; CPC, 112.1°

^a Reference 2 and cited literature therein.

Table IV. Heats of Formation (kcal/mol)

compd	personally ² reported	value using published parameters ¹	difference
HC≡P	3.7	-10.9	-14.6
H ₂ C=PH	5.2	-5.9	-11.1
H ₃ CPH ₂	-8.3	-15.2	-6.9
H ₂ S	-1.9	-2.9	-1.0
CH ₃ SH	-6.1	-8.3	-2.2
CS ₂	27.2	27.0	-0.2
CH ₃ SCH ₃	-8.3	-12.0	-3.7
Thiophene	34.4	32.5	-1.9
SiH ₄	8.7	8.2	-0.5
HC≡SiH	45.0	38.1	-6.9
H ₂ S=SiH ₂	17.6	11.8	-5.8
H ₂ Si=SiH ₂	49.2	48.1	-1.2

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