

## **Theoretical study of conformational properties and the anomeric effect study of the 2- phosphinanes**

**Javad Azizian<sup>a,\*</sup>, Mahdieh Entezari<sup>b</sup>, Hossein Anaraki Ardakani<sup>b</sup>, Shahab Zomorodbakhsh<sup>b</sup>**

*<sup>a</sup>Department of chemistry, Science and Reaserch branch, Islamic azad university, Tehran, Iran, Corresponding author E-mail address: [j-azizian@cc.sbu.ac.ir](mailto:j-azizian@cc.sbu.ac.ir)*

*<sup>b</sup>Department of chemistry, , Mahshahr branch, Islamic azad university, Mahshahr, Iran*

### **Abstract**

Ab initio HF/6-31G\* Methode was employed to calculate the bond length in 2- phosphinanes when electronegative groups was at C-2 tend axial and equatorial positions. The magnitude of the anomeric effect depends on the nature of the substituent, the effect of the substituent can be seen by comparing the bond length in 2-chloro and 2-boromo substituted phosphinanes. The effect of anomeric effect have been effected on the bond length in 2- phosphinanes.

**Keywords:** anomeric effect; 2- phosphinane; bond length; axial and equatorial position; Ab initio calculations

### **Introduction**

The discussion about the origin of the anomeric effect is very old [1,6]. An important feature of the stereochemistry of tetrahydropyrans and other reduced oxygen and sulphur heterocycles is that electronegative groups at C-2 tend to preferentially occupy an axial position even though this sterically more hindered. The X-ray crystal structures of several heterocycles of these types bearing 2-halo substituents have been determined and those axial halogen groups have bonds that shortened [7].

Several structural factors have been considered as possible causes of the anomeric effect. In localized valence bond terminology, it can be recognized that there will be a dipole-dipole repulsion between the polar bonds at the anomeric carbon in the equatorial conformation. This dipole-dipole interaction is reduced in the axial conformation.

From the molecular orbital viewpoint, the anomeric effect is described as resulting from an interaction between the lone-pair electrons on the hetero atom and the  $\sigma^*$  orbital associated with the bond to the electronegative C-2 substituent [8]. when the C-X bond is axial, an interaction between an occupied lone-pair electrons and the anti bonding  $\sigma^*$  orbital of the C-X bond combination is possible. This permits delocalization of the lone-pair electrons and would be expected to shorten and strengthen the C-O bond while lengthening and weakening the C-X bond.

Due to the biological interest associated with the six membered cyclic phosphates, phosphorinane and phosphinanes systems have become an important structural moiety [9,11].

One aspect of 2-phosphinanes chemistry is determination of anomeric effect, we reported a detailed Ab initio study on the bond-length in axial and equatorial conformers and reported the effect of anomeric effect on them.

### Computational details

Ab initio Hartree-Fock calculations were carried out using GASSIAN 98 program with the standard 6-31G\* basis set [12].

### Results and Discussion

2-phosphinanes can exist in two chair conformations in which the electronegative group on 2-phosphinanes is either axial (**1A**) and equatorial (**1E**) (Fig. 1).

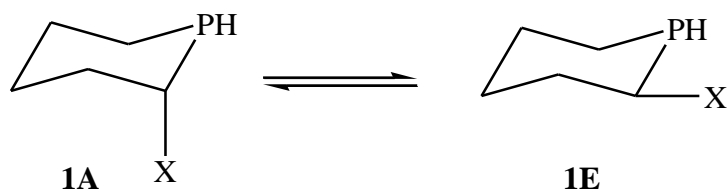


Fig. 1. X in axial and equatorial position

The bond length of the 2-phosphinanes (Fig. 2) are calculated and determined (Table1).

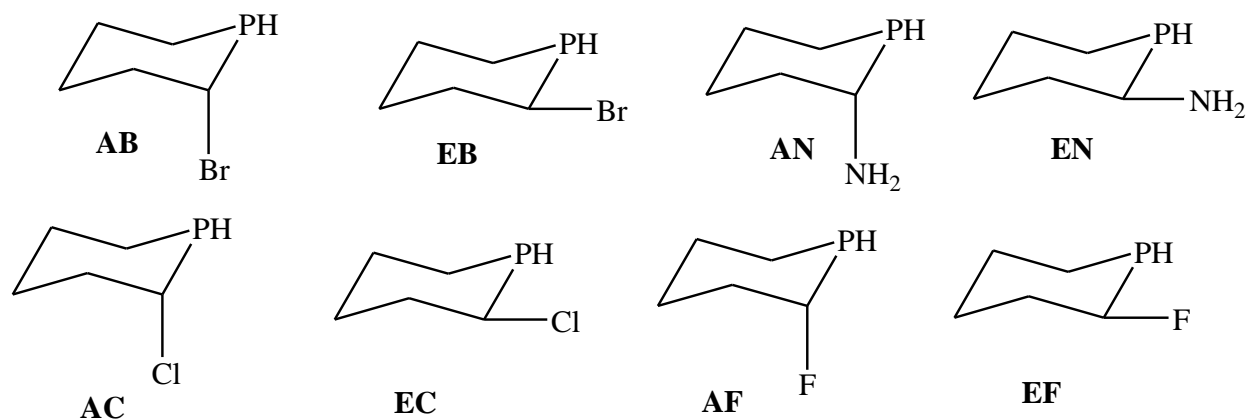


Fig. 2. 2-Phosphinanes with an electronegative group in 2-phosphinanes

Table1. Bond length and dipole moment of 2-Phosphinanes

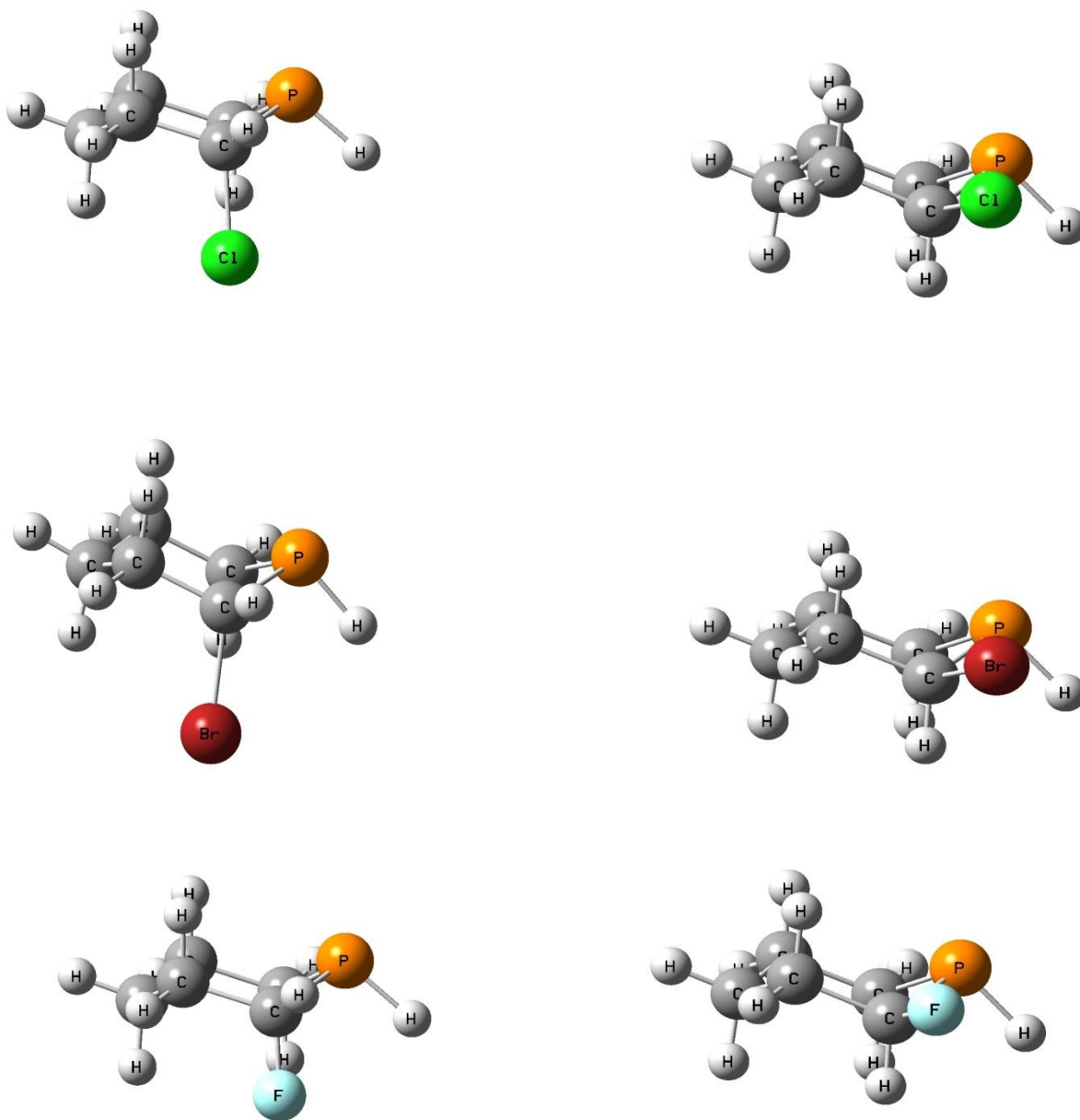
Name	rC-P A <sup>0</sup>	rC-X A <sup>0</sup>	Dipole moment
<b>AB</b>	1.860	1.9868	1.72
<b>EB</b>	1.861	1.970	3.43
<b>AC</b>	1.865	1.817	1.75
<b>EC</b>	1.866	1.804	3.47
<b>AF</b>	1.384	1.861	1.19
<b>EF</b>	1.393	1.872	3.34
<b>AN</b>	1.883	1.458	1.327
<b>EN</b>	1.870	1.460	2.627

The difference of energy between axial and equatorial conformers in 2-Phosphinanes are studied (Table2).

Table 2.  $\Delta E$  between axial and equatorial conformers

Name group	$\Delta E$ (Kcal mol <sup>-1</sup> )
Br	0.542167776
Cl	0.153112196
F	0.134286926
NH <sub>2</sub>	0.067331716

The HF/6-31G\* optimized structures of 2-Phosphanane conformers are existed ( Fig.3).



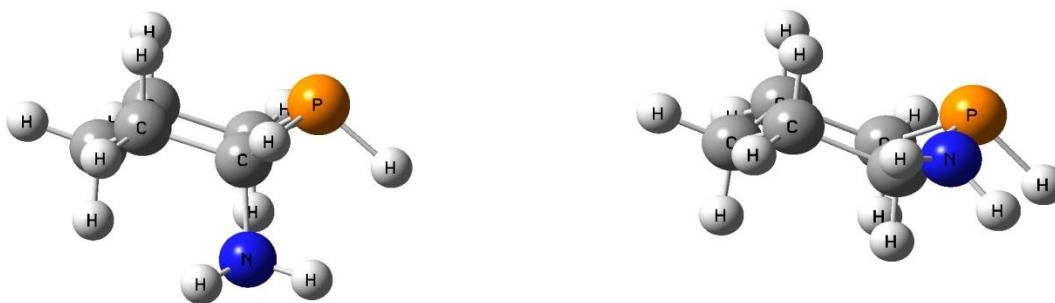


Fig. 3. HF/6-31G\* optimized pictures of 2-Phosphinane conformers

The C-P bond length in the phosphinanes with X group in axial position are shorter than those with X group in equatorial position.

The dipole moment in phosphinanes with X group in axial position are shorter than those with X group in equatorial position.

The  $\Delta E$  in phosphinanes were explained that phosphinanes with high electronegativity groups in axial position are more stable.

The results are determined that in 2-phosphinanes with X group in axial position, the transfer of electron density from the lone pair to the  $\sigma^*$  orbital, the introduction of some  $\pi$ -bonding character to the C-P bond, That is strengthened, and weakening of the C-X bond.

## Conclusion

Thus the anomeric effect in 2-phosphinanes is existed and the electronegative groups in axial position act as electrons acceptors, But the anomeric effect in tetrahydro-2H-pyranes and tetrahydro-2H-thiopyranes is much stronger because is existed a spatial interaction between phosphour and X group in axial position.

## Acknowledgments

The author(s) would like to acknowledge the support provided by the Research Council of Islamic Azad University, Science and Research Branch and Mahshahr branch.

## References

- [1] C.L, Perrin, K. B, Armstrong, M. A, Fabian: *J. Am. Chem. Soc.* 116, 1994, pp. 715-722.
- [2] Chu N, J. Ph.D Thesis, university of Ottawa, 1959.
- [3] R. U, Lemieux, Chu, N. J. Abstracts of papers, 133th national meeting of the American Chemical society; Washington, DC, 1958, Abstr. 31N.
- [4] E, Juaristi; G, Cuevas: *Tetrahedron* 48 (1992) 5019.
- [5] A. J Kirby: Springer Verlag, Berlin, (1983).
- [6] R. U, Lemieux. In *Molecular Rearrangement*; P. De Mayo, Ed: Interscience, New York, (1964), pp. 723.
- [7] W. A. Szarek, D. Horton, the anomeric effect: Origin and Consequences, ACS Symposium series no. 87, American Chemical Society, Washington D.C, (1979).
- [8] S. Wolfe, A. Rauk, L. M. Tel, I. G. Csizmaida, *J. Chem. Soc. B*: 136 (1971). Eisenstein, W. J. Hehre, L. salem, R. Hoffmann: *J. Am. Chem. Soc.*: 95 (1973) 306.
- [9] M J. Gallager, phosphorus 31-NMR spectroscopy in *Stereochemical Analysis*, edited by J G. Verkade , L D. Quin, 1987, Chapter9.
- [10] W. E. McEwen , K. D. Berlin, *Organophosphorus stereochemistry part I, Orgins and p (III and IV) compounds*, 1975.
- [11] Allinger N L & von Voithenberg H: *Tetrahedron*, 34 (1978) 627.
- [12] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Jr. Burant, S Dapprich., J. Millam, V. Barone, M. Cossi, R. Cammi, B. Mennucci C. Pomelli, C. Adamo, S. Clifford, j. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, j. Cioslowski, J. V. Ortiz, B. tefanovb, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A Al-Laham. C. Y.

Peng, A Nanayakkara., C. Gonzalez, M. Challacombe, P. M. W. Gill, B .Johnson, W.Chen, M. W.Wong, J. L Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, GAUSSIAN 98 (Revision A. 3) Gaussian Inc., Pittsburgh, PA, (1998).