Substituent Effect on the Aromaticity of Phosphazene

Selçuk Gümüş* and Ayşegül Gümüş

Van Yuzuncu Yil University, Department of Chemistry, Van, Turkey

gumuss@gmail.com

Abstract: Important information about the possible reactions and other propeties of a molecule can be determined by the aromaticity. Therefore, measurement of aromaticity is very important. Although there are a few applications for the determination of aromaticity, Nucleus Independent Chemical Shift (NICS) calculations provide the easiest computation and best approach to the discussion. Phosphazene is a nonaromatic material with structural resemblance to benzene. Phosphazenes nonaromatic character can be modified by subtitution of the hydrogen atoms on phosphorous atoms with electron donating or withdrawing groups.

Keywords

Aromaticity, Nucleus Independent Chemical Shift, Phosphazene, 6-31+G(d,p)

1. Introduction

Aromaticity has still been considered as an actively investigated area of chemistry. There are a few criterion for monocyclic compounds to be promoted as aromatic; they possess uncut conjugation in the main circle with the proper number of π-electrons (i.e., the Hückel rule). While this criteria work sufficiently to predict the aromaticity of neutral and charged ring systems, it can not be an obvious indicator of aromaticity for more complex structures.

Aromaticity is described by a combination of properties in cyclic conjugated compounds. Generally, aromaticity has been expressed in terms of energetic, structural and magnetic criteria (Minkin, Glukhovtsev & Simkin, 1994; Schleyer & Jiao, 1996; Glukhovtsev, 1997; Krygowski, Cyranski, Czarnocki, Hafelinger & Katritzky, 2000; Schleyer, 2001; Cyranski, Krygowski, Katritzky & Schleyer, 2002). In 1996, Schleyer introduced an easy but an efficient way for definition aromaticity: Nucleus-independent chemical shift (NICS) (Schleyer, Maerker, Dransfeld, Jiao & Hommes, 1996), which is the calculated value of the negative magnetic shielding at some selected point in space, usually, at center of a ring or cage. Negative NICS data indicate aromaticity (-11.4 for naphthalene) and positive NICS data mean antiaromaticity (28.8 for cyclobutadiene) while small values of

NICS are accepted as an indicator for nonaromaticity (-3.1 for 1,3-cyclopentadiene). NICS might be a useful indicator of aromaticity that often correlates well with the other energetic, structural and magnetic criteria for aromaticity (Jiao & Schleyer, 1998; Schleyer, Kiran, Simion & Sorensen, 2000; Quinonero, et al. 2002; Patchkovskii & Thiel, 2002). Resonance energies and magnetic susceptibilities can be used to define the overall aromaticity of a polycyclic compound, but do not provide information about the individual rings. However, NICS is an effective probe for local aromaticity of separate rings of polycycles.

In order to enlighten the effect of substitution on the phosphazene skeleton, we have applied NICS calculations using Density Functional Theory. The computed NICS values have been used to compare the stabilities of the structures.

2. Method of calculation

The ground state optimizations of phosphazene derivatives leading to minimum energy geometry were achieved by using MM2 method followed by semi-empirical PM3 self-consistent field molecular orbital (SCF MO) method (Stewart, 1989; Stewart, 1989) at the restricted level (Leach, 1997). Then, further optimizations were done within the application of density functional theory (DFT, B3LYP) (Kohn & Sham, 1965; Parr & Yang, 1989) at the level of 6-31G(d,p) (restricted closed-shell) (Stewart, 1989). The hybrid functional term of B3LYP is a combination of hybrid Hartree–Fock and local spin density (LSD) exchange functions with Becke’s gradient correlation to LSD exchange (Becke, 1988). B3LYP is formed by Vosko, Wilk, Nusair (VWN3) local correlation functional (Vosko, Vilk & Nusair, 1980) and Lee, Yang, Parr (LYP) correlation correction functional (Lee, Yang & Parr, 1988). The BLYP method shows a better improvement over the SCF-HF results. Its predictions are in quite good agreement with experiment (Scuseria, 1992; Sosa & Lee, 1993; Wilson, Amos & Handy, 2000).

The normal mode analysis for each structure did not yield any imaginary frequencies for the 3N-6 vibrational degrees of freedom, where N is the number of points in the system. This shows that the structure of each optimized structure corresponds to at least a local minimum on the potential energy surface.

Absolute NMR shielding values (Pulay, Hinton & Wolinski, 1993) were computed using the Gauge-Independent Atomic Orbital method (Hehre, Radom, Schleyer & Pople, 1986) with the restricted closed shell formalism applying 6-31+G(d,p) basis set over B3LYP/6-31+G(d,p) geometry optimized structures. NICS values were obtained by calculating absolute NMR shielding at the ring centers, NICS(0).

The ground state geometry optimizations and NICS computations of all the compounds have been performed by the use of Gaussian 09 package program (Frisch et al., 2010).

3. Results and Discussion

Investigation of the effect of substitution of an electron donating or electron withdrawing groups with the hydrogens connected to the parent circle of well-known aromatic or nonaromatic compounds has been attractive scientists for both theoretical and experimental studies. In this work, phosphazenes aromaticity has been tried to increase with substitution with NO_2, Ph and OMe groups theoretically, by the application of B3LYP/6-31+G(d,p) level of theory in order to judge their ground state stabilities and aromaticities.

The first step of the current study was obtaining the ground state geometries of all the compounds using B3LYP/6-31+G(d,p) level of theory. The geometry optimized structures of phosphazenes can be seen in Figure 1.

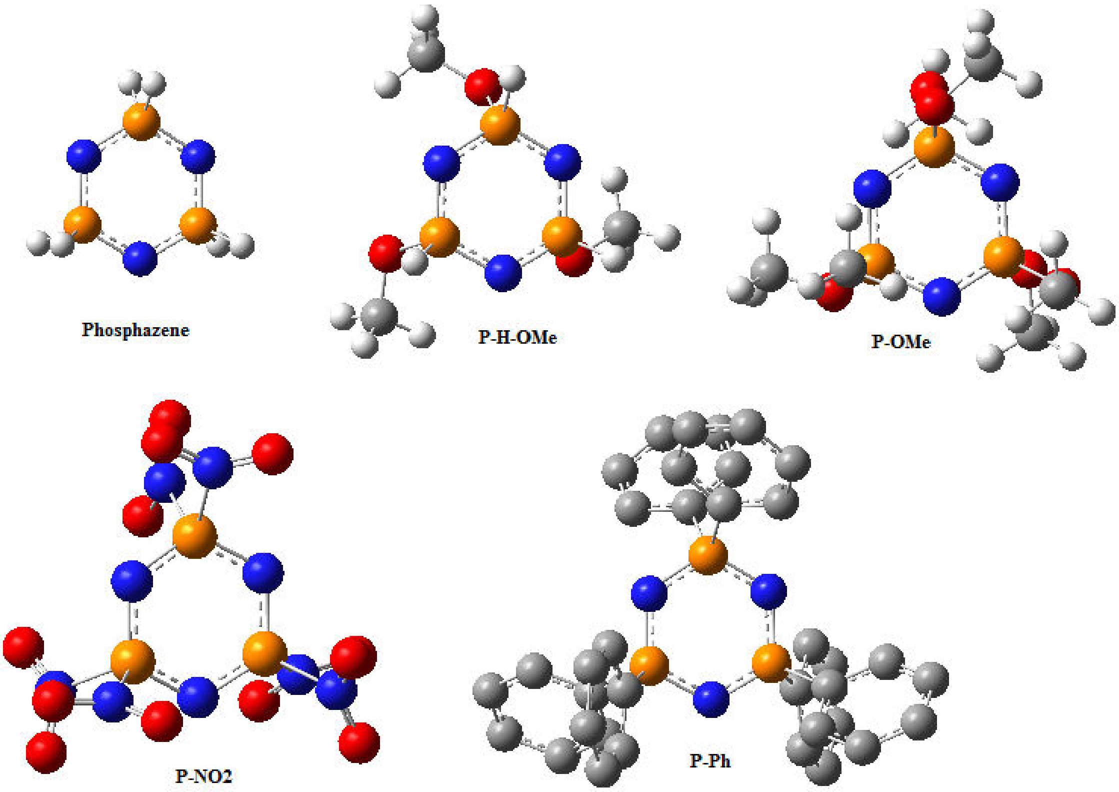

Figure 1. Geometry optimized structures of Phosphazene derivatives

Table 1. NICS data for phosphazene derivatives (ppm).

Structure	**NICS**
Phosphazene	-1.04
P-H-OMe	-2.53
P-OMe	-5.64
P-Ph	-1.35
P-NO_2	-4.59

In Table 1, the NICS data for the present systems are tabulated. **Phosphazene** itself is a nonaromatic compound with a NICS data of -1.04 ppm. The aromaticity of the parent system is slightly increased by replacement of one of the hydrogens on each phosphorous (**P-H-OMe**) by methoxy groups. Electron donating ability of methoxy groups of **P-OMe** made the phosphazene system almost an aromatic compound by enhancing the NICS data up to -5.64 ppm. Phenyl substitution (**P-Ph**) on the other hand, had no effect on the aromaticity of the parent compound. The nonplanar alignment of the phenyl groups has been thoughout to be responsible for this behaviour. Finally, a very strong electron withdrawing NO_2 groups were substituted by the hydrogens by the idea that they could pull the electrons towards themselves so that electrons located on nitrogens have been gained by the π-system of the ring. **P-NO_2** molecule showed an enhanced aromaticity as expected (Table 1).

4. References

Becke, A.D. (1988). Density-functional exchange-energy approximation with correct asymptotic behavior. Phys. Rev. A 38, 3098-3100.

Brogli, F., Heilbronner, E., Kobayashi, T. (1972). Photoelectron spectra of azabenzenes and azanaphthalenes, II. A reinvestigation of azanaphthalenes by high-resolution photoelectron spectroscopy. Helv. Chim. Acta 55, 274-288.

Cyranski, M.K., Krygowski, T.M., Katritzky, A.R., Schleyer, P.R. (2002). To What Extent Can Aromaticity Be Defined Uniquely? J. Org. Chem. 67, 1333-1338.

Frisch et al., M.J. Gaussian 09, Gaussian Inc., Wallingford, CT, 2010.

Ghiasi, R. (2005). The mono- and di-silanaphthalene: structure, properties, and aromaticity. J. Mol. Struct. (Theochem) 718, 225-233.

Glukhovtsev, M.N. (1997). Aromaticity today: energetic and structural criteria. J. Chem. Educ. 74, 132-136.

Gümüş, S. (2011). The aromaticity of substituted diazanaphthalenes. Comput. Theor. Chem. 963, 263-267.

Gümüş, S. (2011). A computational study on substituted diazabenzenes. Turk. J. Chem. 35, 803-808.

Hehre, W.J., Radom, L., Schleyer, P.R., Pople, J.A. Ab Initio Molecular Orbital Theory, Wiley, New York, 1986.

Heinis, T., Chowdhury, S., Kebarle, P. (1993). Electron Affinities of Naphthalene, Anthracene and Substituted Naphthalenes and Anthracenes. Org. Mass Spectrom. 28, 358-365.

Jiao, H., Schleyer, P.R. (1998). Aromaticity of pericyclic reaction transition structures: magnetic evidence. J. Phys. Org. Chem. 111, 655-662.

Kaim, W., Tesmann, H., Bock, H. (1980). Me_3C-, Me_3Si-, Me_3Ge-, Me_3Sn- und Me_3Pb-substituierte benzol- und naphthalin-derivate und ihre radikalanionen. Chem. Ber. 113. 3221-3234.

Kitagawa, T. (1968). Stark Spectroscopy of Molecular Crystals. J. Mol. Spectrosc. 26, 1-23.

Klasinc, L., Kovac, B., Gusten, H. (1983). Photoelectron spectra of acenes. Electronic structure and substituent effects. Pure Appl. Chem. 55, 289-298.

Kohn, W., Sham, L.J. (1965). Self-Consistent Equations Including Exchange and Correlation Effects. Phys. Rev. 140, A1133-A1138.

Krygowski, T.M., Cyranski, M.K., Czarnocki, Z., Hafelinger, G., Katritzky, A.R. (2000). Aromaticity: a Theoretical Concept of Immense Practical Importance. Tetrahedron 56, 1783-1796.

Lardin, H.A., Squires, R.R., Wenthold, P.G. (2001). Determination of the electron affinities of alpha- and beta- naphthyl radicals using the kinetic method with full entropy analysis. The C-H bond dissociation energies of naphthalene. J. Mass Spectrom. 36, 607-615.

Leach, A.R. Molecular Modelling, Longman, Essex, 1997.

Lee, C., Yang, W., Parr, R.G. (1988). Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. Phys. Rev. B 37, 785-789.

Meot-Ner, M., Liebman, J.F., Kafafi, S.A. (1988). Ionic Probes of Aromaticity in Annelated Rings. J. Am. Chem. Soc. 110, 5937-5941.

Meylan, W.M., Howard, P.H. (1991). Bond contribution method for estimating Henry's law constants. Environ. Toxicol. Chem. 10, 1283-1293.

Minkin, V.I., Glukhovtsev, M.N., Simkin, B.Y. Aromaticity and Antiaromaticity: Electronic and Structural Aspects, New York, Wiley, 1994.

Parr, R.G., Yang, W. Density Functional Theory of Atoms and Molecules, Oxford University Press, London, 1989.

Patchkovskii, S., Thiel, W. (2002). Nucleus–Independent Chemical Shifts from Semiempirical Calculations. J. Mol. Model. 6, 67-75.

Pulay, P., Hinton, J.F., Wolinski, K. Nuclear magnetic shieldings and molecular structure, in: Tossel, J.A. (Ed.), NATO ASI Series C, vol. 386, Kluwer, The Netherlands, 1993. pp. 243.

Quinonero, D., Garau, C., Frontera, A., Ballester, P., Costa, A., Deya, P.M. (2002). Quantification of aromaticity in oxocarbons: the problem of the fictitious “nonaromatic” reference system. Chem. Eur. J. 8, 433-438.

Schafer, W., Schweig, A., Markl, G., Heier, K.H. (1973). Zur elektronenstruktur der λ3- und λ5-phosphanaphthaline - ungewöhnlich grosse mo destabilisierungen. Tetrahedron Lett. 3743-3746.

Schafer, W., Schweig, A., Vermeer, H., Bickelhaupt, F., Graaf, H.D. (1975). On the nature of the “free electron pair” on phosphorus in aromatic phosphorus compounds: The photoelectron spectrum of 2-phosphanaphthalene. J. Electron Spectrosc. Relat. Phenom. 6, 91-98.

Schiedt, J., Knott, W.J., Barbu, K.L., Schlag, E.W., Weinkauf, R. (2000). Microsolvation of similar-sized aromatic molecules: Photoelectron spectroscopy of bithiophene–, azulene–, and naphthalene–water anion clusters. J. Chem. Phys. 113, 9470-9478.

Schleyer, P.R. (2001). Introduction: aromaticity. Chem. Rev. 101, 1115-1118.

Schleyer, P.R., Jiao, H. (1996). What is aromaticity? Pure Appl. Chem. 68, 209-218.

Schleyer, P.R., Kiran, B., Simion, D.V., Sorensen, T.S. (2000). Does Cr(CO)3 complexation reduce the aromaticity of benzene? J. Am. Chem. Soc. 122, 510-513.

Schleyer, P.R., Maerker, C., Dransfeld, A., Jiao, H., Hommes, N.J.R.E. (1996). Nucleus independent chemical shifts: a simple and efficient aromaticity probe. J. Am. Chem. Soc. 118, 6317-6318.

Scuseria, G.E. (1992). Comparison of coupled-cluster results with a hybrid of Hartree–Fock and density functional theory. J. Chem. Phys. 97, 7528-7530.

Song, J.K., Han, S.Y., Chu, I.H., Kim, J.H., Kim, S.K., Lyapustina, S.A., Xu, S.J., Nilles, J.M., Bowen, K.H. (2002). Photoelectron spectroscopy of naphthalene cluster anions. J.Chem. Phys. 116, 4477-4481.

Sosa, C., Lee, C. (1993). Density functional description of transition structures using nonlocal corrections. Silylene insertion reactions into the hydrogen molecule. J. Chem. Phys. 98, 8004-8011.

Spedaletti, C.A., Estrada, M.R., Zamarbide, G.N., Garro, J.C., Ponce, C.A., Vert, F.T. (2005). Theoretical study on hydration of two particular diazanaphthalenes. J. Mol. Struct. (Theochem) 723, 211-216.

Stewart, J.J.P. (1989). Optimization of parameters for semiempirical methods I. Method. J. Comput. Chem. 10, 209-220.

Stewart, J.J.P. (1989). Optimization of parameters for semiempirical methods. 2. Applications. J. Comput. Chem. 10, 221-264.

Takeda, N., Shinohara, A., Tokitoh, N. (2002). Synthesis and Properties of the First 1-Silanaphthalene. Organometallics 21, 4024-4026.

Vosko, S.H., Vilk, L., Nusair, M. (1980). Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis. Can. J. Phys. 58, 1200-1211.

Wang, L., Wang, H. (2007). Planar mono-, di- aza- and phospha-naphthalene: Structure and aromaticity. Int. J. Quantum Chem. 107, 1846-1855.

Wilson, P.J., Amos, R.D., Handy, N.C. (2000). Density functional predictions for metal and ligand nuclear shielding constants in diamagnetic closed-shell first-row transition-metal complexes. Phys. Chem. Chem. Phys. 2, 187-194.

Yencha, A.J., El-Sayed, M.A. (1968). Lowest ionization potentials of some nitrogen heterocyclics. J. Chem. Phys. 48, 3469-3475.