SHORT
COMMUNICATIONS

Theoretical Conformational Analysis of 1,3,2-Benzodioxaphosphinan-4-ones

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We previously [1] studied the structure of 1,3,2-benzodioxaphosphinan-4-ones by X-ray analysis, by IR spectroscopy, and by measuring their dipole moments. Regardless of the aggregate state, the phosphorus-containing heteroring with planar fragments exists preferentially in a *flattened sofa* conformation and that the exocyclic substituent occupies axial ($N=C=O$, NEt_2) or equatorial (Cl) position. In the present work we performed theoretical conformational analysis of 1,3,2-benzodioxaphosphinan-4-ones **I–IV** by nonempirical B3LYP/6-31G(*d*) quantum-chemical calculations.
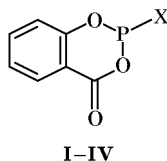
I, X = H; **II**, X = Cl; **III**, X = N=C=O; **IV**, X = NEt₂.

According to the calculation results, the preferential conformation of all compounds **I–IV** is that with axial orientation of the X substituent. This is seen most clearly with compound **I** as an example: the energy difference ΔE between the conformers with axial and equatorial orientation of the substituent on the phosphorus atom is as large as 19.80 kJ/mol. The corresponding difference for diethylamino derivative **IV** is considerably smaller, 1.27 kJ/mol, but the tendency for the axial conformer to prevail is retained. The global minima on the potential energy surfaces for compounds **II** and **III** correspond to conformers with axial orientation of the chlorine atom (**II**) or isocyanato group (**III**). It should be noted that our nonempirical calculations predict no equatorial con-

formers for compounds **II** and **III**. The calculations satisfactorily describe the polarities of compounds **II–IV**. Below are given the calculated and experimental dipole moments:

Compound no.	**II**	**III**	**IV**
μ_{calc}, D	4.23	3.87	4.14
μ_{exp}, D (CCl₄)	3.80	–	3.88
μ_{exp}, D (C₆H₆)	4.02	4.23	4.17

Thus, the calculated data well explain the experimental results obtained in [1] for compounds **III** and **IV** but contradict those for compound **II**, according to which the chlorine atom therein occupies equatorial position. Presumably, we should recognize that the chlorine atom in **II** is also axial, in keeping with the assumption [1] that the observed dipole moment exaltation ($\Delta\mu$ 0.76 to 0.98 D) indicates strong intramolecular electronic interactions. According to the X-ray diffraction data [2], the fluorine atom in structurally related 2-chloro-1,3,2-benzodiazaphosphinan-4-one occupies axial position.

All calculations were performed with the aid of Gaussian 98 software [3] in terms of the density functional theory (B3LYP) using the 6-31G(*d*) basis set [each internal orbital is described by six Gauss-type functions (GTO), valence 2*s* orbital, by three functions, and valence *p*-AO, by one function; also, polarizational *d*-GTO is added to each *p*-function]. Stationary points on the potential energy surface were identified by calculation of the second derivatives.

REFERENCES

1. Ishmaeva, E.A., Vereshchagina, Ya.A., Yarkova, E.G., Burnaeva, L.M., Litvinov, I.A., Krivolapov, D.B., Gubaidullin, A.T., Mironov, V.F., and Fattakhova, G.R., *Russ. J. Gen. Chem.,* 2002, vol. 72, no. 8, p. 1195.

2. Neda, I., Kaukorat, T., Schmutzler, R., Niemeyer, U., Kutscher, B., Pohl, J., and Engel, J., *Phosphorus, Sulfur, Silicon,* 2000, vol. 162, no. 1, p. 81.

3. Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Zakrzewski, V.G., Montgomery, J.A., Stratmann, R.E., Jr., Burant, J.C., Dapprich, S., Millam, J.M., Daniels, A.D., Kudin, K.N., Strain, M.C., Farkas, O., Tomasi, J., Barone, V., Cossi, M., Cammi, R., Mennucci, B., Pomelli, C., Adamo, C., Clifford, S., Ochterski, J., Petersson, G.A., Ayala, P.Y., Cui, Q., Morokuma, K., Malick, D.K., Rabuck, A.D., Raghavachari, K., Foresman, J.B., Cioslowski, J., Ortiz, J.V., Baboul, A.G., Stefanov, B.B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Gomperts, R., Martin, R.L., Fox, D.J., Keith, T., Al-Laham, M.A., Peng, M.A., Nanayakkara, A., Gonzalez, C., Challacombe, C., Gill, P.M.W., Johnson, B., Chen, W., Wong, M.W., Andres, J.L., Head-Gordon, M., Replogle, E.S., and Pople, J.A., *Gaussian 98,* Pittsburgh, PA: Gaussian, 1998.