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An ab initio study of the structure and methyl rotational barriers of methylphosphonic dihalides

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Abstract

The molecular structure and the barriers to methyl rotation of symmetric methylphosphonic dihalides (CH_3POX_2, $X=F$, Cl, Br) and of the corresponding non-halogenated molecule (methyl phosphine oxide, $X=H$) were determined through ab initio calculations at the MP2/6-31+G(2d,p) level. The four molecules adopt the staggered conformation, with skeletal angles decreasing in the order $\widehat{OPC} > \widehat{OPX} > \widehat{XPC} > \widehat{XPX}$. The strong electron-withdrawing effect of the halogen atoms decreases the electron density on the oxygen atom, and increases the double bond character of the phosphoryl group. This, in turn, leads to an increase of the hyperconjugative interactions between this group and the two C–H bonds lying out of the OPC plane, and results in a slight lengthening of these bonds relative to the in-plane C–H bond. Methyl rotations were followed by means of intrinsic reaction coordinate calculations (IRC), and the calculated energy barriers were 1.61, 2.41, 2.77 kcal/mol for the difluoride, dichloride and dibromide, respectively, and 2.01 kcal/mol for methyl phosphine oxide. Structural evidences suggest that hyperconjugation stabilizes the transition structure for methyl rotation in the difluoride molecule, which explains the comparatively low value of its rotational barrier.

Keywords: Methylphosphonic dihalides; Structure; Methyl rotational barrier; Intrinsic reaction coordinate; Hyperconjugation

1. Introduction

Methylphosphonic dihalides (CH_3POXY, $X,Y=F$, Cl) attracted considerable attention from chemists during World War II and subsequent decades, due to their military application in the synthesis of chemical warfare agents (CWA) [1–4]. In fact, the products of the reaction of these molecules with some specific alcohols are powerful acetylcholinesterase inhibitors, and their detection [5], biomonitoring [6], mechanism of action [7,8], poisoning treatment [9,10], prophylaxis [11,12], decontamination and destruction [13–15] are the subject of intense research until our days. However, theoretical studies on these CWA are relatively scarce [16], and the same holds for their precursors.

In a recent paper [17], we described our investigations into the structure, vibrational spectrum and methyl rotational barrier of methylphosphonic difluoride ($X=Y=F$). It was demonstrated that ab initio calculations at MP2 level with the inclusion of two d-type polarization functions in the basis set for each of the heavy atoms show a good agreement with experimental data. Herein, an extension of the aforementioned work concerning the symmetric methylphosphonic dihalides (CH_3POX_2, $X=F$, Cl, Br) is presented. It is our intention to evaluate the influence of the halogen atom on the structure and methyl rotational barrier of these molecules. Therefore, the corresponding non-halogenated molecule (methyl phosphine oxide, $X=H$) is also included for comparison.

2. Theoretical methods

Ab initio molecular orbital calculations have been performed at the MP2/6-31+G(2d,p) level, using

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the PC-UNIX GAMESS v. 2003 (R2) program [18]. The appropriate point group symmetry (C_s) was maintained in all minimizations, but no symmetry constraints were imposed in the search for transition structures. The convergence criterion for stationary point location runs was taken as tight as possible, and the resulting points were confirmed either as minima or saddle points by frequency calculations.

Vibrational frequencies and the corresponding normal modes of vibration were obtained numerically. Corrections for zero-point vibrational energy were estimated from the harmonic frequencies (scaled by the factor 0.9608). Intrinsic reaction coordinates (IRC) for methyl rotations were calculated using the Runge-Kutta algorithm available in the PC-UNIX GAMESS package. The Molden package [19] was used to draw the relevant structures and the normal mode displacement vectors.

3. Results and discussion

3.1. Minimum energy conformations

The calculated structural parameters and total energies of the most stable conformation of each molecule are shown in Table 1. The four molecules assume a staggered conformation (Fig. 1), with skeletal angles decreasing in the order $\widehat{OPC} > \widehat{OPX} > \widehat{XPC} > \widehat{XPX}$. The angles involving the P=O bond are considerably larger, due to its partial double bond character.

Taking the non-halogenated molecule (methyl phosphine oxide, X = H) as reference, one can see that the halogen atoms act mainly via inductive effect, by shortening the P = O bonds from 1.4970 to 1.4635–1.4785 Å, shortening the P–C bonds from 1.8110 to 1.7855–1.7996 Å, and decreasing the Mulliken and Lowdin electron populations on the oxygen atom (Table 2). Accordingly, the double bond character of the phosphoryl bond increases in the order H (1.585) < Br (1.634) < Cl (1.666) < F (1.756), as shown by the bond order analysis [20,21] in Table 3.

A subtle yet important feature in the calculated structures of these molecules is that the three C–H bonds do not have the same length. In fact, C–H7 and C–H8 bonds are slightly longer than C–H6 in all the three halides, and the reverse occurs in methyl phosphine oxide. In order to verify that this small difference did not occur by pure chance, as well as that it is not a peculiarity of the level of theory/basis set adopted, the following precautions were taken: (a) the tightest convergence criterion was used; (b) the values of these bond lengths were seen to agree up to the sixth decimal figure in the last three iterations of the minimization processes; (c) all of our previous calculations for X = F in several levels of theory/basis sets [17] were seen to confirm this feature; (d) minimizations were also performed in MP2/6-311+G(2d,p) for X = H, F, Cl, and in DFT-B3LYP/6-31+G(2d,p) for X = H, F, Cl, Br, and the structural feature in question was observed in all these calculations.

A similar phenomenon was recently reported by Jalbout et al. [22] for the minimum energy conformation of the acetone molecule. Their calculations, in a variety of levels of theory/basis sets, showed that the C–H bonds which do not lie in the O=C–C plane (C–H_{opl}) are longer than those lying in that plane (C–H_{ipl}). A natural

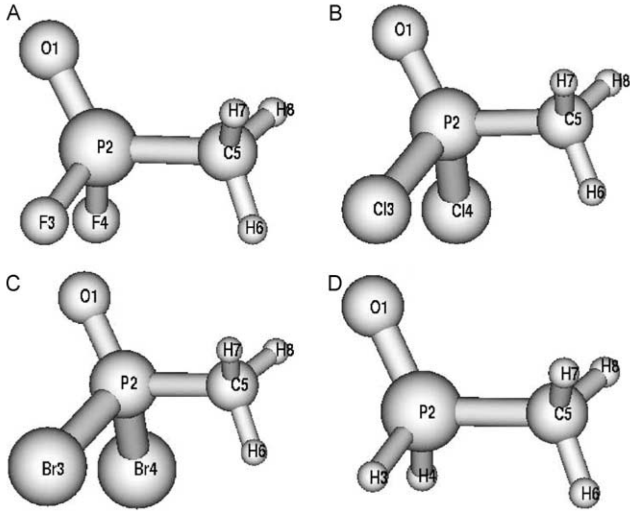

Fig. 1. Minimum energy conformations of the CH_3POX_2 molecules. (A) X = F; (B) X = Cl; (C) X = Br; (D) X = H.

Table 1
Geometrical parameters and energies for the minimum energy conformations of CH_3POX_2

	X = F	X = Cl	X = Br	X = H
Bond lengths (Å)				
PO	1.4635	1.4748	1.4785	1.4970
PX	1.5820	2.0488	2.2072	1.4029
PC	1.7855	1.7974	1.7996	1.8110
CH6	1.0881	1.0880	1.0883	1.0914
CH7/ CH8	1.0887	1.0899	1.0903	1.0892
Bond angles (deg.)				
OPC	119.17	116.98	117.04	116.54
OPX	115.09	114.30	114.41	115.60
XPC	103.26	103.72	103.26	103.06
XPX	98.16	102.06	102.67	100.83
H6CP	110.10	110.61	110.11	110.15
H7CP/ H8CP	108.52	107.67	107.79	109.15
Dihedral angle (deg.)				
OPCH6	180.00	180.00	180.00	180.00
Total energy (hartrees)				
E	−655.120420	−1375.049549	−5596.157406	−456.887870

Table 2
Mulliken and Lowdin atomic charges in the oxygen atom of CH_3POX_2 molecules

	X = F	X = Cl	X = Br	X = H
Mulliken	−0.619	−0.594	−0.638	−0.712
Lowdin	−0.581	−0.622	−0.627	−0.742