Article Title

Geometric and energetic data from *ab initio* calculations of haloethene, haloimine, halomethylphosphine, haloiminophosphine, halodiazene, halodiphosphene and halocyclopropane

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Abstract

This article presents theoretical data on geometric and energetic features of halogenated compounds of cyclopropane (Δ) and ethene (C=C), imine (C=N), methylphosphine (C=P), iminophosphine (N=P), diazene (N=N) and diphosphene (P=P). The data were obtained from *ab initio* geometric optimization and frequency calculations at HF, B3LYP, MP2 and CCSD levels of theory on 6-311++G(d,p) basis set. Input structures were generated by shell scripts and run by Q-Chem quantum chemical package. The output files were processed to extract geometric and energetic information by Wolfram Mathematica.

Keywords

cis effect, haloethene, haloimine, halomethylphosphine, haloiminophosphine, halodiazene, halodiphosphene, halocyclopropane

Specifications Table

Subject area	Chemistry
More specific subject area	Physical and Theoretical Chemistry/Spectroscopy
Type of data	Tables/Q-Chem output files
How data was acquired	Quantum chemical computation
Data format	Both raw and analyzed
Parameters for data collection	HF/6-311++G(d,p), B3LYP/6-311++G(d,p), MP2/6-311++G(d,p) and CCSD/6-311++G(d,p)
Description of data collection	Q-Chem 5.1, Developer Version
Data source location	Thailand
Data accessibility	With the article

Value of the Data

- Systematic and high-quality quantum chemical results in this article can be used by scientists to understand the nature of chemical bonding in these compounds and to explore special phenomena such as the *cis* effect [1].
- General/trivial trends and some anomalies can be observed in both geometric and energetic data of the compounds. Experimental results are currently very limited and these trends can provide further insights into development of future experiments.
- Provided source codes can be modified for uses in other classes of compounds.

Data

In this data set, we present the theoretical results from a combinatorial investigation of substituted cyclopropane and double-bonded (a combination of C, N and P) compounds. The data in this paper were generated and optimized in vacuum by *ab initio* quantum chemical calculations at HF/6-311++G(d,p), B3LYP/6-311++G(d,p), MP2/6-311++G(d,p) and CCSD/6-311++G(d,p) levels of calculations.

- The geometric data include all the available bond lengths of A_1=A_2 and A_1-a, all bond angles of a-A_1-b and a-A_1-A_2, and dihedral angles of a-A_1-A_2-b, where A_1/A_2 and a/b refer to the central and peripheral atoms respectively.
- The energetic data include electronic energy (E_{elec}), thermal correction to enthalpy (H_{corr}), enthalpy (H), entropy (S), and Gibbs free energy at 298.15 K (G).
- The data are available in tables (.xlsx files) along with other associated Unix shell scripts (as text files) and Wolfram Mathematica notebooks (.nb files) are provided in the supplementary information.
- Output files which include vibrational spectrum are also available and can be viewed in IQmol.[2]

Here we include geometric and energetic data of the halogenated forms of seven classes of compounds: ethene (C=C), imine (C=N), methylphosphine (C=P), iminophosphine (N=P), diazene (N=N), diphosphene (P=P) and cyclopropane (Δ) where substitutions are via halogenation (including F, Cl, Br and I) with all degrees of substitution from mono- to tetra-substitution. The total numbers of all possible compounds are as follows: 175 for C=C (Table 1), 125 for C=N (Table 2), 125 for C=P (Table 3), 50 for N=P (Table 4), 30 for N=N (Table 5), 30 for P=P (Table 6) and 315 for Δ (Table 7). The total number of structures are summarized in Table 8. The dataset described in this paper is the most comprehensive compared to other previously published results on these compounds [3-6].

Table 1 List of 175 structures for haloethene (C=C)

Empirical Formula	Number of Empirical Formula	Isomer/Formula	Total number of structures
$C_2\alpha\beta\gamma\delta$	$\binom{5}{4} = 5$	αβC=Cγδ (*E*/*Z*) αγC=Cβδ (*E*/*Z*) αδC=Cβγ (*E*/*Z*)	5 × 6 = 30
$C_2\alpha_2\beta\gamma$	$\binom{5}{1}\binom{4}{2} = 30$	αβC=Cαγ (*E*/*Z*) α_2C=Cβγ	30 × 3 = 90
$C_2\alpha_2\beta_2$	$\binom{5}{2} = 10$	αβC=Cβα (*E*/*Z*) α_2C=Cβ_2	10 × 3 = 30
$C_2\alpha_3\beta$	$\binom{5}{1}\binom{4}{1} = 20$	α_2C=Cαβ	20 × 1 = 20
$C_2\alpha_4$	$\binom{5}{1} = 5$	α_2C=Cα_2	5 × 1 = 5

Table 2 List of 125 structures for haloimine (C=N)

Empirical Formula	Number of Empirical Formula	Isomer/Formula	Total number of structures
$CN\alpha_3$	$\binom{5}{1} = 5$	α_2C=Nα	5 × 1 = 5
$CN\alpha_2\beta$	$\binom{5}{1}\binom{4}{1} = 20$	α_2C=Nβ αβC=Nα (*E*/*Z*)	20 × 3 = 60
CNαβγ	$\binom{5}{3} = 10$	αβC=Nγ (*E*/*Z*) αγC=Nβ (*E*/*Z*) βγC=Nα (*E*/*Z*)	10 × 6 = 60

Table 3 List of 125 structures for halomethylphosphine (C=P)

Empirical Formula	Number of Empirical Formula	Isomer/Formula	Total number of structures
$CP\alpha_3$	$\binom{5}{1} = 5$	α_2C=Pα	5 × 1 = 5
$CP\alpha_2\beta$	$\binom{5}{1}\binom{4}{1} = 20$	α_2C=Pβ αβC=Pα (*E*/*Z*)	20 × 3 = 60
CPαβγ	$\binom{5}{3} = 10$	αβC=Pγ (*E*/*Z*) αγC=Pβ (*E*/*Z*) βγC=Pα (*E*/*Z*)	10 × 6 = 60

Table 4 List of 50 structures for haloiminophosphine (N=P)

Empirical Formula	Number of Empirical Formula	Isomer/Formula	Total number of structures
$NP\alpha_2$	$\binom{5}{1} = 5$	αN=Pα (*E*/*Z*)	5 × 2 = 10
NPαβ	$\binom{5}{2} = 10$	αN=Pβ (*E*/*Z*) βN=Pα (*E*/*Z*)	10 × 4 = 40

Table 5 List of 30 structures for halodiazene (N=N)

Empirical Formula	Number of Empirical Formula	Isomer/Formula	Total number of structures
$N_2\alpha_2$	$\binom{5}{1} = 5$	αN=Nα (*E*/*Z*)	5 × 2 = 10
$N_2\alpha\beta$	$\binom{5}{2}$ = 10	αN=Nβ (*E*/*Z*)	10 × 2 = 20

Table 6 List of 30 structures for halodiazene (N=N)

Empirical Formula	Number of Empirical Formula	Isomer/Formula	Total number of structures
$P_2\alpha_2$	$\binom{5}{1} = 5$	αP=Pα (*E*/*Z*)	5 × 2 = 10
$P_2\alpha\beta$	$\binom{5}{2}$ = 10	αP=Pβ (*E*/*Z*)	10 × 2 = 20

Table 7 List of 315 structures for halocyclopropane (Δ)

Empirical Formula	Number of Empirical Formula	Isomer/Formula	Total number of structures
$(CH_2)C_2\alpha\beta\gamma\delta$	$\binom{5}{4}$ = 5	αβΔγδ (*E*/*Z*, *R*/*S*) αγΔβδ (*E*/*Z*, *R*/*S*) αδΔβγ (*E*/*Z*, *R*/*S*)	5 × 12 = 60
$(CH_2)C_2\alpha_2\beta\gamma$	$\binom{5}{1}\binom{4}{2}$ = 30	αβΔαγ (*E*/*Z*, *R*/*S*) α_2Δβγ (*R*/*S*)*	24 × 6 = 144 (α is not H.) 6 × 5 = 30 (α is H.)
$(CH_2)C_2\alpha_2\beta_2$	$\binom{5}{2} = 10$	$\alpha_2\Delta\beta_2$ αβΔαβ (*E*, *R*/*S*) αβΔαβ (*Z*, *ME*)	10 × 4 = 40
$(CH_2)C_2\alpha_3\beta$	$\binom{5}{1}\binom{4}{1} = 20$	α_2Δαβ (*R*/*S*)*	16 × 2 = 32 (α is not H.) 4 × 1 = 4 (α is H.)
$(CH_2)C_2\alpha_4$	$\binom{5}{1} = 5$	$\alpha_2\Delta\alpha_2$	5 × 1 = 5

* If α is H there is no *R*/*S* and the number of total isomers must be calculated separately for this case.

Table 8 A summary of all data in this paper

system	Number of isomers				HF/6-311++G** B3LYP/6-311++G** MP2/6-311++G**		CCSD/6-311++G**	
	E	*Z*	other	total	opt	freq	opt	freq
N=N (diazene)	15	15	0	30	all	all	all	all
P=P (diphosphene)	15	15	0	30	all	all	all	all
N=P (iminophosphine)	25	25	0	50	all	all	all	all
C=N (imine)	50	50	25	125	all	all	all	all
C=P (methylphosphine)	50	50	25	125	all	all	all	all
C=C (ethene)	55	55	65	175	all	all	all	30
Δ (cyclopropane)	100	110	115	325	all*	all*	all*	20*

* Excluding enantiomers, † opt and freq refer to geometry optimization and frequency calculation respectively

Experimental Design, Materials, and Methods

Q-Chem input files (.inp) were generated using shell scripts previously described elsewhere [7-9]. The *ab initio* calculations were performed using the Q-Chem 5.1 program package [10] to optimize the structures at HF, B3LYP, MP2 and CCSD levels of theory on 6-311++G(d,p) basis set. The rationale behind the choosing of this basis set is the availability of iodine, which was used as a part to fulfill all possible halogenation in this combinatorial investigation. Frequency calculations confirm that structures are minima on the electronic potential energy surface for all HF, B3LYP and MP2 jobs and some CCSD jobs where possible. The output files were processed using Wolfram Mathematica [11] to extract relevant geometric and energetic data of all the seven classes of compounds.

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