This article presents theoretical data on geometric and energetic features of halogenated compounds of cyclopropane (\(\Delta\)) 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.
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 \textit{ab initio} quantum chemical calculations at HF/6-31++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 \( A_1 - A_2 - b \), where \( A_1/A_2 \) and \( a/b \) refer to the central and peripheral atoms respectively.
- The energetic data include electronic energy \( (E_{\text{elec}}) \), thermal correction to enthalpy \( (H_{\text{corr}}) \), 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 \((\text{C}=\text{C})\), imine \((\text{C}=\text{N})\), methylphosphine \((\text{C}=\text{P})\), iminophosphine \((\text{N}=\text{P})\), diazene \((\text{N}=\text{N})\), diphosphene \((\text{P}=\text{P})\) and cyclopropane \((\Delta)\) 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 \( \text{C}=\text{C} \) (Table 1), 125 for \( \text{C}=\text{N} \) (Table 2), 125 for \( \text{C}=\text{P} \) (Table 3), 50 for \( \text{N}=\text{P} \) (Table 4), 30 for \( \text{N}=\text{N} \) (Table 5), 30 for \( \text{P}=\text{P} \) (Table 6) and 315 for \( \Delta \) (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 \((\text{C}=\text{C})\) |
|-----------------|-----------------|-----------------|-----------------|
| Empirical Formula | Number of Empirical Formula | Isomer/Formulas | Total number of structures |
| \( \text{C}_{2}\alpha\beta\gamma\delta \) | \( \binom{5}{4} = 5 \) | \( \alpha\beta\gamma\delta = E/Z \) | \( 5 \times 1 = 5 \) |
| \( \text{C}_{2}\alpha\beta\gamma \) | \( \binom{5}{1} \binom{4}{1} = 30 \) | \( \alpha\beta\gamma = E/Z \) | \( 5 \times 3 = 15 \) |

| Table 2 List of 125 structures for halominine \((\text{C}=\text{N})\) |
|-----------------|-----------------|-----------------|-----------------|
| Empirical Formula | Number of Empirical Formula | Isomer/Formulas | Total number of structures |
| \( \text{C}_{2}\alpha\beta \) | \( \binom{5}{1} \binom{4}{1} = 20 \) | \( \alpha\beta = E/Z \) | \( 5 \times 1 = 5 \) |
| \( \text{C}_{2}\alpha\beta \) | \( \binom{5}{1} \binom{4}{1} = 10 \) | \( \alpha\beta = E/Z \) | \( 5 \times 1 = 5 \) |

| Table 3 List of 125 structures for halomethylphosphine \((\text{C}=\text{P})\) |
|-----------------|-----------------|-----------------|-----------------|
| Empirical Formula | Number of Empirical Formula | Isomer/Formulas | Total number of structures |
| \( \text{C}_{2}\alpha\beta \) | \( \binom{5}{1} \binom{4}{1} = 20 \) | \( \alpha\beta = E/Z \) | \( 5 \times 1 = 5 \) |
| \( \text{C}_{2}\alpha\beta \) | \( \binom{5}{1} \binom{4}{1} = 10 \) | \( \alpha\beta = E/Z \) | \( 5 \times 1 = 5 \) |
Table 4 List of 50 structures for haloiminophosphine (N=P)

| Empirical Formula | Number of Empirical Formula | Isomer/Formula | Total number of structures |
|------------------|-----------------------------|----------------|--------------------------|
| NPα₂             | \( \binom{5}{1} = 5 \)     | αN=Pa (E/Z)    | 5 × 2 = 10               |
|                  |                             | βN=Pa (E/Z)    |                          |
| NPαβ             | \( \binom{5}{2} = 10 \)    | αN=PB (E/Z)    | 10 × 4 = 40              |
|                  |                             | βN=Pa (E/Z)    |                          |

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

| Empirical Formula | Number of Empirical Formula | Isomer/Formula | Total number of structures |
|------------------|-----------------------------|----------------|--------------------------|
| N₂α₂             | \( \binom{5}{1} = 5 \)     | αN=Na (E/Z)    | 5 × 2 = 10               |
|                  |                             | βN=Na (E/Z)    |                          |
| N₂αβ             | \( \binom{5}{2} = 10 \)    | αN=Nβ (E/Z)    | 10 × 2 = 20              |
|                  |                             | βN=Na (E/Z)    |                          |

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

| Empirical Formula | Number of Empirical Formula | Isomer/Formula | Total number of structures |
|------------------|-----------------------------|----------------|--------------------------|
| P₂α₂             | \( \binom{5}{1} = 5 \)     | αP=Pa (E/Z)    | 5 × 2 = 10               |
|                  |                             | βN=Pa (E/Z)    |                          |
| P₂αβ             | \( \binom{5}{2} = 10 \)    | αP=PB (E/Z)    | 10 × 2 = 20              |
|                  |                             | βN=Pa (E/Z)    |                          |

Table 7 List of 315 structures for halocyclopropane (Δ)

| Empirical Formula | Number of Empirical Formula | Isomer/Formula | Total number of structures |
|------------------|-----------------------------|----------------|--------------------------|
| (CH₂)Cαβγδ       | \( \binom{5}{1} \binom{4}{2} = 5 \) | αβγδ (E/Z, R/S) | 5 × 12 = 60 |
|                  |                             | αγβδ (E/Z, R/S) |                          |
|                  |                             | αδβγ (E/Z, R/S) |                          |
| (CH₂)Cααβγ       | \( \binom{5}{1} \binom{4}{2} = 30 \) | αβαγ (E/Z, R/S) | 24 × 6 = 144 (α is not H.) |
|                  |                             | ααβγ (E/Z, R/S) | 6 × 5 = 30 (α is H.) |
| (CH₂)Cααβα       | \( \binom{5}{2} = 10 \)    | ααβα (E, R/S)   | 10 × 4 = 40              |
|                  |                             | ααβα (Z, ME)    |                          |
| (CH₂)Cααβ        | \( \binom{5}{1} \binom{4}{1} = 20 \) | ααβα (R/S)      | 16 × 2 = 32 (α is not H.) |
|                  |                             | ααβα (α is H.)  | 4 × 1 = 4 (α is H.)     |
| (CH₂)Cααα        | \( \binom{5}{1} = 5 \)     | ααα (E/Z)       | 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 | all |
| P=P (diphosphene) | 15 | 15 | 0 | 30 | all | all | all | all | all |
| N=P (iminophosphine) | 25 | 25 | 0 | 50 | all | all | all | all | all |
| C=N (imine)       | 50 | 50 | 25 | 125 | all | all | all | all | all |
| C=P (methylphosphine) | 50 | 50 | 25 | 125 | all | all | all | all | all |
| C=C (ethene)      | 55 | 55 | 65 | 175 | all | all | all | 30 |
| \( \Delta \) (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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References

[1] R.C. Bingham, The stereochemical consequences of electron delocalization in extended π systems. An interpretation of the cis effect exhibited by 1,2-disubstituted ethylenes and related phenomena, Journal of the American Chemical Society 98 (1976) 535-540.

[2] A.T.B. Gilbert, IQmol, iqmol.org, 2019.

[3] J.B.P. da Silva, M.N. Ramos, R.E. Bruns, Vibrational intensities and directions of the dipolar derivatives of the trans-C2H2X2 (XF or Cl), Journal of molecular structure 482 (1999) 585-589.

[4] J.B.P. da Silva, M.N. Ramos, R.E. Bruns, Effects of wave function modifications on calculated C-H vibrational frequencies and infrared intensities of the dihaloethylenes, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 53 (1997) 733-747.

[5] J.B.P. da Silva, Application of factorial design for the ab initio study of cis-and trans-1, 2 dihaloethylene stabilities, Journal of the Brazilian Chemical Society 11 (2000) 219-223.

[6] S. Vogt-Geisse, H.F. Schaefer, Reducing and Reversing the Diphosphene–Diphosphinylidene Energy Separation, Journal of Chemical Theory and Computation 8 (2012) 1663-1670.

[7] T. Limpanuparb, P. Roongruangsree, C. Areekul, A DFT investigation of the blue bottle experiment: E∘half-cell analysis of autooxidation catalysed by redox indicators, Royal Society Open Science 4 (2017) 170708.

[8] T. Limpanuparb, R. Noorat, Y. Tantirungrotechai, In silico investigation of mitragynine and 7-hydroxymitragynine metabolism, BMC Research Notes 12 (2019) 451.

[9] T. Limpanuparb, W. Lorpaiboon, K. Chinsukserm, In silico investigation of menthol metabolism, PLoS ONE 14 (2019) e0216577.

[10] Y. Shao, Z. Gan, E. Epifanovsky, A.T. Gilbert, M. Wormit, J. Kussmann, A.W. Lange, A. Behn, J. Deng, X. Feng, Advances in molecular quantum chemistry contained in the Q-Chem 4 program package, Molecular Physics 113 (2015) 184-215.

[11] Wolfram Research Inc, Mathematica, Champaign, Illinois, 2019.
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