Research article

Chlorates and perchlorates as potential high-energy materials: chlorate- and perchlorate-substituted methanes

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A B S T R A C T

The structures and properties of thirty-three of the thirty-four possible chlorato-*Cl*-, chlorato-*O*- and perchlorato-derivatives of methane have been computed using the range-separated hybrid generalized gradient approximation density functional method ωB97X-D with the 6-311+G(2d,p) basis set. These results indicate that the chlorato-*O*-substituent confers more stability to a molecule than does the chlorato-*Cl*-substituent; the perchlorato-substituent is approximately intermediate in this regard when decomposition energies are calculated. The C–Cl bond lengths in the chlorato-*Cl*-substituents generally elongate and the C–O distances in the chlorato-*O*- and perchlorato-substituents tend to shorten as the number of chlorate/perchlorate substituents increases. In addition, as the C–O bond shortens, the CO–Cl bond lengthens. The calculated Mulliken and Löwdin bond orders for these bonds exhibit the opposite of the trends exhibited by the bond lengths, as expected: As the bond lengthens, the bond order decreases, and vice versa. The single molecule that could not be optimized as a stable methane derivative, (chlorato-*Cl*-)tris(chlorato-*O*-)methane, rearranged during all optimization attempts to an isomer of the neutral Cl_2O_5 molecule and a hitherto unknown molecule, bis(chlorato-*O*-)carbonyl, $(O_2ClO)_2C=O$.

1. Introduction

The concept of high-energy materials generally involves molecules that, either experimentally or computationally, are shown to undergo highly exothermic decomposition or rearrangement reactions. Previously, somewhat unusually-bound nitrate-containing systems — nitratoxycarbons — were computationally investigated and found to have the potential to act as high-energy materials [1]. Following this report, two additional articles pertaining to these molecules were also published [2, 3]. Could a chlorate or perchlorate anion also participate in bonding to a methyne carbon atom in a manner similar to that of the nitrate group in a nitratoxycarbon? Before a computational answer to this question could be formulated, a related computational investigation of all possible chlorate and perchlorate derivatives of methane was necessary to delineate the potential bonding trends these anions might undergo when acting as a substituent on methane.

The high-level computational work of Brunswick and Ball [4, 5] has provided a baseline and much needed initial information on the structures and properties of methyl chlorate and perchlorate [4] as well as on the structures and properties of dichloratomethane and bis(perchlorato) methane [5]. (The chlorate group was investigated as both a

chlorine-bound, chlorato-*Cl*-, and an oxygen-bound, chlorato-*O*-, substituent. The di-substituted methanes investigated were the symmetrical isomers. None of the unsymmetrically-di-substituted molecules, or any molecules with higher numbers of substituents, were investigated in those reports.) Based on theoretical decomposition reactions in which the molecules were presumed to decompose to gaseous carbon dioxide, water, hydrogen chloride and dioxygen, $\Delta E_{decomposition}$ values were calculated based on results from both the G2 and G3 computational methods.

As detailed by Brunswick and Ball [4, 5], chlorates are often fragile — explosive — compounds, but similar compounds or derivatives may be able to be developed as more robust high-energy compounds. Herein is reported the density functional computational investigation of the structures and properties of all thirty-four possible combinations of chlorato-*Cl*-, chlorato-*O*-, and perchlorato-methane species. This database of the structures and properties of these novel species may inspire new areas of research in the search for robust high-energy compounds or novel explosives. In addition, the novel bonding arrangements identified for these species may serve to provide a comprehensive database with which to compare other organo-chlorate and organo-perchlorate systems.

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2. Theory/calculation

All calculations were performed using the *Spartan '16* and *'18* programs [6] with the range-separated hybrid generalized gradient approximation density functional method ωB97X-D [7]. Initially, each molecule was calculated from an initial trial geometry using the 6-31G* basis set. In those instances in which that basis set resulted in a bound structure with all real vibrational frequencies, calculations were then extended to the 6-311+G(2d,p) basis set, which includes diffuse functions on all non-hydrogen atoms and polarization functions on all atoms. Only the results from these latter calculations using the larger basis set are reported herein. In all cases, vibrational frequencies were calculated to verify that a stable minimum on the relevant potential energy surface had been attained. Molecules chosen as decomposition products or identified as rearrangement products were also calculated using the ωB97X-D density functional method and the 6-311+G(2d,p) basis set.

3. Results and discussion

Due to the moderately large number of molecules investigated, a simplified labeling system to substitute for the somewhat cumbersome IUPAC names of the molecules was developed in the hope of allowing the reader to quickly identify the molecule under discussion. This labeling system is detailed in Table 1. Essentially, as all of these molecules are substituted methanes with chlorato-*Cl*-, chlorato-*O*-, or perchlorato-substituents, the molecules are designated by the number and kind of substituents present, followed by **m**. The chlorato-*Cl*-substituent is designated **C**, the chlorato-*O*-substituent, **O**, and the perchlorato-substituent, **P**. Thus, the more complicated name of bis(chlorato-*Cl*-)(perchlorato-)methane becomes, simply, **C$_2$P-m**.

The decomposition energies, $\Delta E_{\text{decomposition}}$, of **C-m**, **O-m**, and **P-m**, and **C$_2$-m**, **O$_2$-m**, and **P$_2$-m**, the mono- and symmetrically-di-substituted methane derivatives of the chlorato-*Cl*-, chlorato-*O*-, and perchlorato-groups, as calculated by Brunswick and Ball [4, 5], were re-examined at the ωB97X-D/6-311+G(2d,p) level of theory. In addition, calculations were extended to all possible chlorato-*Cl*-, chlorato-*O*-, and perchlorato-substituted methane molecules; all of these results are listed in Table 2 along with the presumed decomposition products for each molecule. The method of calculation of $\Delta E_{\text{decomposition}}$ in the present study differs from that of Brunswick and Ball [4, 5], however. In this present work, $\Delta E_{\text{decomposition}}$ is calculated by subtracting the optimized electronic energy of the chlorate or perchlorate molecule from the sum of the optimized electronic energies of the arbitrarily-chosen decomposition products while ignoring any basis set superposition error effects. The chemical and mathematical equations below demonstrate the process of the determination of $\Delta E_{\text{decomposition}}$ for gaseous **O-m** decomposing to gaseous carbon dioxide, hydrogen chloride, and water.

$$O_2ClO\text{–}CH_3(g) \rightarrow CO_2(g) + HCl(g) + H_2O(g)$$
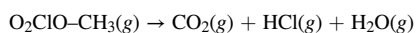
$$\Delta E_{\text{decomposition}} = [E_{\omega B97X\text{-}D}(CO_2) + E_{\omega B97X\text{-}D}(HCl) + E_{\omega B97X\text{-}D}(H_2O)] - [E_{\omega B97X\text{-}D}(O_2CO\text{–}CH_3)]$$

$$\Delta E_{\text{decomposition}} = [-188.585154 \text{ a.u.} + -460.816316 \text{ a.u.} + -76.387070 \text{ a.u.}] - [-725.530901 \text{ a.u.}]$$

$$\Delta E_{\text{decomposition}} = -0.257639 \text{ a.u.} \ (-676.43 \text{ kJ/mol})$$

All of the molecules in Table 2 exhibit highly exothermic calculated $\Delta E_{\text{decomposition}}$ values per mole, save for one, **CO$_3$-m**. That single molecule could not be optimized as a bound system, despite multiple optimization attempts using different initial trial geometries (ITGs) and variations in initial conformations. The use of constraints during early partial optimizations in an attempt to locate a potentially shallow minimum for the molecule was also unsuccessful. (The sequential removal of constraints during consecutive partial optimizations ultimately resulted in rearrangement failure during, or prior to, the final optimization step,

Table 1
Master list of molecules investigated, with corresponding simplified labels

Molecule	Label
(chlorato-*Cl*-)methane	**C-m**
(chlorato-*O*-)methane	**O-m**
(perchlorato-)methane	**P-m**
bis(chlorato-*Cl*-)methane	**C$_2$-m**
bis(chlorato-*O*-)methane	**O$_2$-m**
(chlorato-*Cl*-)(chlorato-*O*-)methane	**CO-m**
(chlorato-*Cl*-)(perchlorato-)methane	**CP-m**
(chlorato-*O*-)(perchlorato-)methane	**OP-m**
bis(perchlorato-)methane	**P$_2$-m**
tris(chlorato-*Cl*-)methane	**C$_3$-m**
tris(chlorato-*O*-)methane	**O$_3$-m**
(chlorato-*Cl*-)bis(chlorato-*O*-)methane	**CO$_2$-m**
bis(chlorato-*Cl*-)(chlorato-*O*-)methane	**C$_2$O-m**
bis(chlorato-*Cl*-)(perchlorato-)methane	**C$_2$P-m**
bis(chlorato-*O*-)(perchlorato-)methane	**O$_2$P-m**
(chlorato-*Cl*-)(chlorato-*O*-)(perchlorato-)methane	**COP-m**
(chlorato-*Cl*-)bis(perchlorato-)methane	**CP$_2$-m**
(chlorato-*O*-)bis(perchlorato-)methane	**OP$_2$-m**
tris(perchlorato-)methane	**P$_3$-m**
bis(chlorato-*Cl*-)bis(chlorato-*O*-)methane	**C$_2$O$_2$-m**
(chlorato-*Cl*-)tris(chlorato-*O*-)methane	**CO$_3$-m**
tris(chlorato-*Cl*-)(chlorato-*O*-)methane	**C$_3$O-m**
tetrakis(chlorato-*Cl*-)methane	**C$_4$-m**
tetrakis(chlorato-*O*-)methane	**O$_4$-m**
(chlorato-*Cl*-)bis(chlorato-*O*-)(perchlorato-)methane	**CO$_2$P-m**
bis(chlorato-*Cl*-)(chlorato-*O*-)(perchlorato-)methane	**C$_2$OP-m**
tris(chlorato-*Cl*-)(perchlorato-)methane	**C$_3$P-m**
tris(chlorato-*O*-)(perchlorato-)methane	**O$_3$P-m**
(chlorato-*Cl*-)(chlorato-*O*-)bis(perchlorato-)methane	**COP$_2$-m**
bis(chlorato-*Cl*-)bis(perchlorato-)methane	**C$_2$P$_2$-m**
bis(chlorato-*O*-)bis(perchlorato-)methane	**O$_2$P$_2$-m**
(chlorato-*Cl*-)tris(perchlorato-)methane	**CP$_3$-m**
(chlorato-*O*-)tris(perchlorato-)methane	**OP$_3$-m**
tetrakis(perchlorato-)methane	**P$_4$-m**

by which point all remaining constraints had been removed.) Rather, the **CO$_3$-m** "molecule" always rearranged to two independent moieties. These were a dichlorine pentoxide isomer, μ-oxo-bis(dioxochlorine-*Cl*), $O_2ClOClO_2$, and $(O_2ClO)_2C$=O, a molecule which may be considered as either a derivative of formaldehyde, bis(chlorato-*O*-)carbonyl, or of carbonic acid, bis(dioxochlorine-*Cl*-)carbonate. The former rearrangement product is known computationally, but the peroxo-bridged isomer, $ClOOClO_3$, is reported to be the more stable system [8, 9, 10, 11]. Calculations at the ωB97X-D/6-311+G(2d,p) level of theory reproduce this result: The peroxo-bridged molecule is 31.63 kJ/mol more stable than the symmetrical oxo-bridged system at this level of theory.

Bis(chlorato-*O*-)carbonyl has not yet been reported in the literature. (For the calculated structures of all three compounds, see Fig. 1.) The calculated C=O distance in this molecule is 119.5 pm, which compares well with the C=O distance in F_2CO, 117.2 pm [12]. Formaldehyde itself exhibits a C=O distance of 123.0 pm [12]. Acetone, with slightly electron-donating methyl groups, exhibits a C=O distance of 122.2 pm [13]; both fluorine and the chlorato-*O*-group are strongly electron-withdrawing.

While specific structural data for μ-oxo-bis(dioxochlorine) are not available — although the electronic energy of the molecule has been calculated at various levels of theory [8, 9, 10, 11] — the calculated structure of μ-oxo-(perchlorato-)chlorine has been reported [9]. At the current level of density functional theory, the molecule adopts a *gauche*-structure with respect to rotation about the O–O bond, while a *trans*-structure was reported for the molecule when calculations were carried out with the MP2(Full)/6-31G(d) level of theory [9]. (No *trans*-conformer could be located at the ωB97X-D/6-311+G(2d,p) level of theory.)

The current DFT results provide an O_3Cl–O distance of 178.1 pm, an O–O distance of 135.7 pm, and an O–Cl distance of 173.4 pm, while the MP2(Full)/6-31G(d) results [9] provide distances of 186.7 pm, 139.4 pm,

Table 2

Density functional computational results for the chlorate- and perchlorate-substituted methane gas-phase species.

Molecule	Energy[a]	$\Delta E_{\text{decomposition}}$				Decomposition products[b]
		G2[4,5][c]	G3[4,5][c]	ωB97X-D[c]	ωB97X-D[d]	
C-m	–725.484195	–886.1	–877.9	–799.06	–8.114	$CO_2(g)$, $HCl(g)$, $H_2O(g)$
O-m	–725.530901	–784.3	–786.4	–676.43	–6.868	"
P-m	-800.487124	–804.9	–797.3	–1148.24	–10.030	$CO_2(g)$, $\frac{1}{2}O_2(g)$, $HCl(g)$, $H_2O(g)$
C$_2$-m	–1410.422940	–756.1	–756.5	–888.86	–4.913	$CO_2(g)$, $2O_2(g)$, $2HCl(g)$
O$_2$-m	–1410.556395	–1024.0	–1047.0	–538.48	–2.976	"
CO-m	–1410.502749	—	—	–697.32	–3.584	"
CP-m	–1485.627592	—	—	–708.42	–3.597	$CO_2(g)$, $2\frac{1}{2}O_2(g)$, $2HCl(g)$
OP-m	–1485.692064	—	—	–539.15	–2.738	"
P$_2$-m	–1560.824446	–812.7	–794.3	–548.46	–2.576	$CO_2(g)$, $3O_2(g)$, $2HCl(g)$
C$_3$-m	–2095.346129	—	—	–1017.12	–3.862	$CO_2(g)$, $Cl_2(g)$, $3\frac{1}{2}O_2(g)$, $HCl(g)$
O$_3$-m	–2095.572815	—	—	–421.95	–1.602	"
CO$_2$-m	–2095.522559	—	—	–553.90	–2.103	"
C$_2$O-m	–2095.445796	—	—	–755.44	–2.868	"
C$_2$P-m	–2170.566236	—	—	–756.10	–2.706	$CO_2(g)$, $Cl_2(g)$, $4O_2(g)$, $HCl(g)$
O$_2$P-m	–2170.709625	—	—	–419.63	–1.502	"
COP-m	–2170.648684	—	—	–579.63	–2.075	"
CP$_2$-m	-2245.767925	—	—	–623.44	–2.111	$CO_2(g)$, $Cl_2(g)$, $4\frac{1}{2}O_2(g)$, $HCl(g)$
OP$_2$-m	–2245.836683	—	—	–442.92	–1.500	"
P$_3$-m	–2320.969885	—	—	–450.07	–1.445	$CO_2(g)$, $Cl_2(g)$, $5O_2(g)$, $HCl(g)$
C$_2$O$_2$-m	–2780.459686	—	—	–645.56	–1.867	$CO_2(g)$, $2Cl_2(g)$, $5O_2(g)$
CO$_3$-m	[failure to converge — rearranges (see text)]					
C$_3$O-m	–2780.382454	—	—	–848.34	–2.453	"
C$_4$-m	–2780.263515	—	—	–1160.61	–3.356	"
O$_4$-m	–2780.599994	—	—	–277.18	–0.802	"
CO$_2$P-m	–2855.657841	—	—	–482.18	–1.333	$CO_2(g)$, $2Cl_2(g)$, $5\frac{1}{2}O_2(g)$
C$_2$OP-m	–2855.596688	—	—	–642.74	–1.776	"
C$_3$P-m	–2855.486858	—	—	–931.10	–2.573	"
O$_3$P-m	–2855.725024	—	—	–305.79	–0.845	"
COP$_2$-m	–2930.791791	—	—	–487.37	–1.290	$CO_2(g)$, $2Cl_2(g)$, $6O_2(g)$
C$_2$P$_2$-m	–2930.700069	—	—	–728.19	–1.927	"
O$_2$P$_2$-m	–2930.858514	—	—	–312.19	–0.826	"
CP$_3$-m	–3005.906959	—	—	–541.87	–1.376	$CO_2(g)$, $2Cl_2(g)$, $6\frac{1}{2}O_2(g)$
OP$_3$-m	–3005.986952	—	—	–331.85	–0.843	"
P$_4$-m	–3081.112523	—	—	–359.03	–0.876	$CO_2(g)$, $2Cl_2(g)$, $7\,O_2(g)$

[a] All electronic energies were calculated at the ωB97X-D/6-311+G(2d,p) level of theory in a.u.

[b] The gas phase ωB97X-D/6-311+G(2d,p) energies of the decomposition products (CO_2, Cl_2, O_2, HCl, and H_2O) are provided in Table S1 of the Supplementary Data.

[c] kJ/mol.

[d] kJ/g.

and 175.3 pm, respectively for the lower energy, $ClOOClO_3$, isomer. The DFT results for the higher energy isomer, μ-oxo-bis(dioxochlorine), indicate that the molecule has C_2-symmetry with an O_2Cl–O bond length of 178.6 pm and Cl–O bond lengths of 143.7 and 144.4 pm. The ωB97X-D/6-311+G(2d,p) energies of these molecules are provided in Table S2 of the Supplementary Data.

Interestingly, the homo-substituted methanes, *i.e.*, **C-m**, **C$_2$-m**, **C$_3$-m**, and **C$_4$-m**; **O-m**, **O$_2$-m**, **O$_3$-m**, and **O$_4$-m**; and **P-m**, **P$_2$-m**, **P$_3$-m**, and **P$_4$-m**, exhibit contrary patterns in $\Delta E_{\text{decomposition}}$ per mole. For the chlorato-*Cl*-system, $\Delta E_{\text{decomposition}}$ per mole becomes increasingly more exoergic from **C-m** to **C$_4$-m**, with **C$_4$-m** exhibiting the most negative $\Delta E_{\text{decomposition}}$ per mole in the group. The reverse is true for both the chlorato-*O*- and perchlorato-systems, with **O-m** and **P-m** exhibiting the most negative

$\Delta E_{\text{decomposition}}$ per mole and **O$_4$-m** and **P$_4$-m** exhibiting the least exoergic $\Delta E_{\text{decomposition}}$ per mole. In addition, molecules containing the chlorato-*O*-substituent, perhaps because of lessened steric interactions, appear to be generally more stable (less exoergic $\Delta E_{\text{decomposition}}$ values) than molecules containing either the chlorato-*Cl*- or perchlorato-systems. For the chlorato-*Cl*-containing systems, the C–Cl bond brings the oxygen moieties of adjacent substituents closer together than in the chlorato-*O*- or perchlorato-system. Note, however, that the $\Delta E_{\text{decomposition}}$ values *per gram* all become less negative as more substituents are added to the homo-substituted methane systems.

Structurally, the mono-substituted molecules (Fig. 2) optimized to structures essentially identical to the structures reported by Brunswick and Ball [4], with only slight variations in bond lengths (Table 3). The
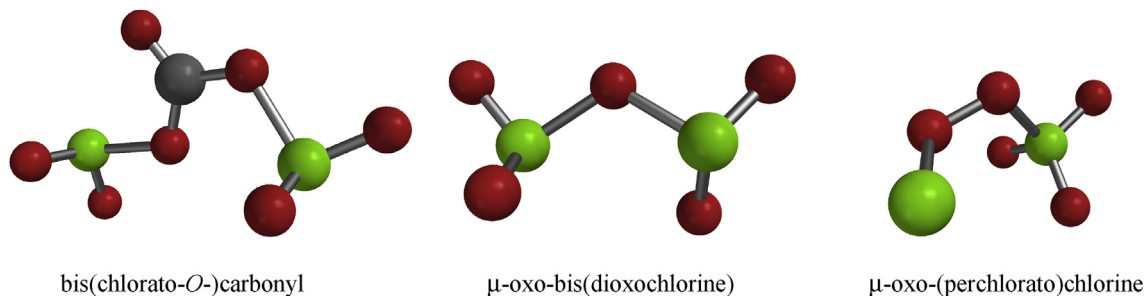

μ-oxo-bis(dioxochlorine)   bis(chlorato-*O*-)carbonyl   μ-oxo-(perchlorato)chlorine

Fig. 1. The calculated structures of the rearrangement products found during the attempted optimization of the carbon atom is depicted in dark gray; chlorine atoms, green; and oxygen atoms, red.
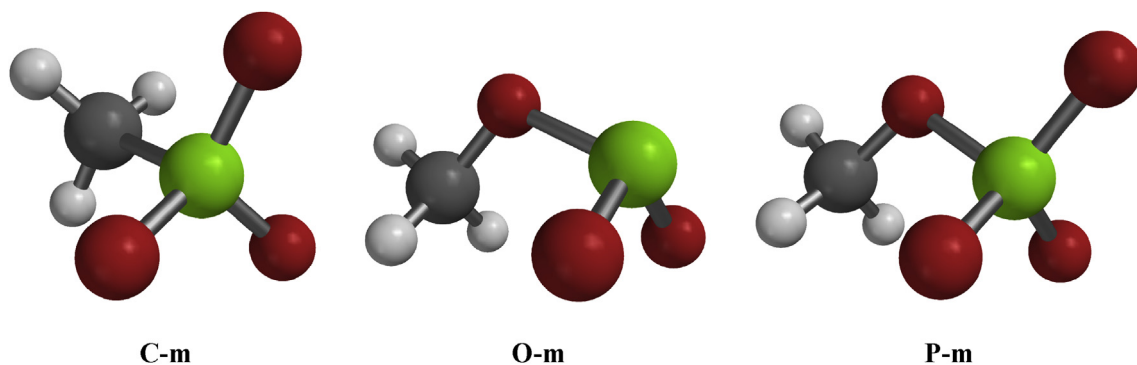
Fig. 2. The ωB97X-D-calculated structures of (chlorato-*Cl*-)methane, **C-m**, left, (chlorato-*O*-)methane, **O-m**, center, and (perchlorato-)methane, **P-m**, right. Hydrogen atoms are depicted in light gray; carbon atoms, dark gray; chlorine atoms, green; and oxygen atoms, red.

Table 3
Selected bond lengths in the optimized chlorate- and perchlorate-substituted methane molecules.

Molecule[a]	Bond length (pm)[b]				
	Cl–C	Cl^O–OC	Cl^{O}O–C	Cl^P–OC	Cl^{P}O–C
C-m	179.9				
	178.6 [4]				
O-m		171.5	142.7		
		177.2 [4]	*143.5* [4]		
P-m				167.2	143.6
				168.6 [4]	*144.6* [4]
C$_2$-m	182.8				
	182.5 [5]				
O$_2$-m		177.5	139.3		
		177.9	139.9		
		188.3 [5]	*140.0* [5]		
CO-m	189.1	187.1	133.4		
CP-m	186.3			174.3	136.1
OP-m		181.7	137.1	166.3	143.6
P$_2$-m				169.5	140.5
				169.6	140.4
				174.7 [5]	*141.4* [5]
C$_3$-m	187.0				
O$_3$-m		175.6	141.4		
		179.3	138.6		
		180.6	137.9		
CO$_2$-m	197.3	187.2	133.8		
		189.8	132.4		
C$_2$O-m	190.5	196.1	128.6		
	191.8				
C$_2$P-m	188.5			179.6	132.1
	189.6				
O$_2$P-m		181.8	137.0	165.9	145.3
		182.8	136.4		
COP-m	198.4	197.0	130.5	174.4	137.4
CP$_2$-m	192.2			175.5	135.8
				177.2	135.6
OP$_2$-m		187.7	135.3	168.5	142.9
				170.5	141.2
P$_3$-m				170.4	140.0
				170.5	140.4
				173.3	138.5
C$_2$O$_2$-m	200.3	199.6	129.0		
	200.4	199.7	129.0		
CO$_3$-m	[failure to converge — rearranges (see text)]				
C$_3$O-m	196.1	224.7	121.8		
	197.0				
	204.6				
C$_4$-m	191.7				
O$_4$-m		183.7	138.6		
		183.8	138.8		
		184.4	138.4		

(continued on next page)

Table 3 (*continued*)

Molecule[a]	Bond length (pm)[b]				
	Cl–C	Cl^O–OC	Cl^{O}O–C	Cl^P–OC	Cl^{P}O–C
		185.0	138.3		
CO$_2$P-m	206.5	200.1	130.6	170.8	141.1
		200.3	130.6		
C$_2$OP-m	201.0	217.2	124.8	179.9	132.8
	203.1				
C$_3$P-m	193.8			193.9	127.1
	196.4				
	197.1				
O$_3$P-m		182.8	138.5	170.9	142.8
		184.8	136.8		
		187.0	137.2		
COP$_2$-m	202.7	199.7	130.1	176.2	135.7
				177.9	137.1
C$_2$P$_2$-m	195.8			181.2	132.7
	199.8			186.3	131.0
O$_2$P$_2$-m		186.2	136.4	172.2	141.6
		188.0	136.0	172.4	141.1
CP$_3$-m	197.8			177.3	135.5
				178.1	135.4
				179.9	135.2
OP$_3$-m		188.2	134.8	173.1	139.4
				173.1	140.1
				173.2	141.0
P$_4$-m				173.9	139.1
				174.4	138.7
				174.9	138.7
				175.3	138.5

[a] Final optimized atomic coordinates for all molecules are provided in Tables S3 through S5 in the Supplimentary Data.
[b] The superscript O refers to the chlorato-*O*-group and the superscript P refers to the perchlorato-group. When distances share the same line, the distances refer to bonds within the same substituent. Values in italics are taken from the work of Brunswick and Ball [4, 5].

C-m structure is staggered, as previously reported, but, as was also reported by Brunswick and Ball, in **O-m** and **P-m** the hydrogen atoms on carbon are eclipsed with respect to the oxygen atoms on chlorine. Attempts to locate other minima in which the hydrogen atoms and oxygen atoms are staggered (or, in the case of **O-m**, rotated about the Cl–OC bond into an "anti" position) were unsuccessful. [Note: Illustrations of all molecules investigated are provided in Fig. S1 through S6.]

The structures of the three symmetrically di-substituted methanes are illustrated in Fig. 3. While the structures of **C$_2$-M** (approximate C_{2v}-symmetry; actual C_2-symmetry) and **P$_2$-m** (C_2-symmetry) were similar to the results of Brunswick and Ball [5], the DFT-calculated structure of **O$_2$-m** did not contain a C_2-axis and, rather, displayed C_1-symmetry. No lower energy structures could be located despite calculating these molecules from different ITGs and with different initial conformations.

The three symmetrically tri-substituted chlorates and perchlorate are illustrated in Fig. 4. Continuing the bond length trend seen in Table 3, in which C–Cl bonds elongate when additional chlorato-*Cl*-groups are added, the C–Cl bonds in **C$_3$-m** are 187.0 pm, longer than the C–Cl bonds

in **C$_2$-m**, 182.8 pm, and longer than the C–Cl bond in the monosubstituted **C-m**, 179.9 pm. An additional trend is observed in the chlorato-*O*- and perchlorato-containing molecules: As the O$_2$Cl–O or O$_3$Cl–O bond increases in length, the O–C bond decreases in length. The bond lengths in the tetra-substituted systems, Fig. 5, exhibit similar bond length changes.

Both Mulliken and Löwdin bond orders exhibit trends that are the reverse of the observed bond length trends, as expected. As the C–Cl bond lengthens, the bond order decreases, and the C–O bond and CO–Cl bonds follow similar patterns: As the C–OCl bond shortens, the bond order increases, and conversely for the CO–Cl bonds, as the bond length increases, the bond order decreases.

While direct comparisons cannot be made between all molecules because the energies of molecules with different numbers and kinds of atoms cannot be directly compared, evaluations can be made for those smaller groups of molecules that do contain the same numbers and kinds of atoms. Referring to the data in Table 2, molecules containing the chlorato-*O*-substituent are significantly more stable than those
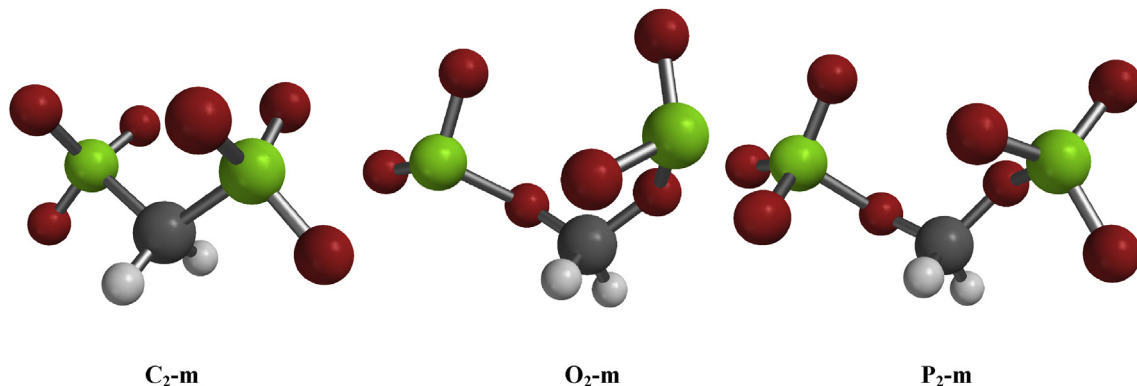

Fig. 3. The calculated structures of bis(chlorato-*Cl*-)methane, **C$_2$-m**, left, bis(chlorato-*O*-)methane, **O$_2$-m**, center, and bis(perchlorato-)methane, **P$_2$-m**, right. Hydrogen atoms are depicted in light gray; carbon atoms, dark gray; chlorine atoms, green; and oxygen atoms, red.
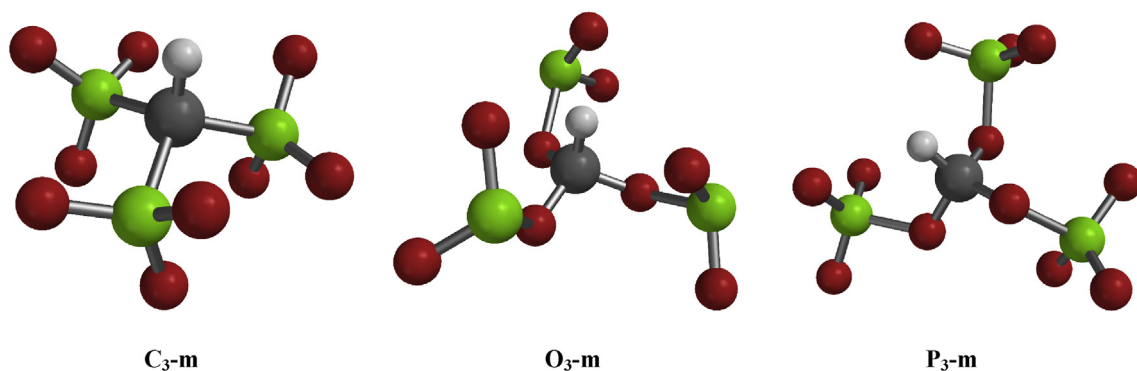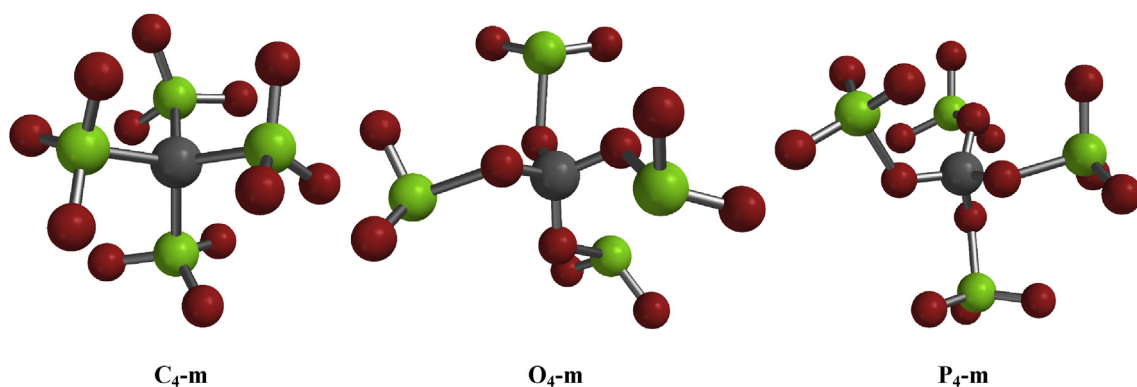
Fig. 4. The calculated structures of tris(chlorato-*Cl*-)methane, **C₃-m**, left, tris(chlorato-*O*-)methane, **O₃-m**, center, and tris(perchlorato-)methane, **P₃-m**, right. Hydrogen atoms are depicted in light gray; carbon atoms, dark gray; chlorine atoms, green; and oxygen atoms, red.

Fig. 5. The calculated structures of tetrakis(chlorato-*Cl*-)methane, **C₄-m**, left, tetrakis(chlorato-*O*-)methane, **O₄-m**, center, and tetrakis(perchlorato-)methane, **P₄-m**, right. Carbon atoms are depicted in dark gray; chlorine atoms, green; and oxygen atoms, red. could be located despite calculating these molecules from different ITGs and with different initial conformations.

containing the chlorato-*Cl*-substituent. Further, in general, more chlorato-*O*-substituents confer greater comparative stabilities. This observation, unfortunately, makes the inability to locate a stable minimum for **CO₃-m** less explicable, especially as a stable minimum could be located for a similar molecule in which a perchlorato-group has been substituted for the chlorato-*O*-group, **CP₃-m**. This discrepancy may require additional investigation.

4. Conclusions

The chlorato-*Cl*-, chlorato-*O*-, and perchlorato-derivatives of methane all exhibit significant exoergic decomposition energies, and for that property alone these molecules are expected to be exceptionally fragile and potentially explosive. However, the presence of the chlorato-*Cl*-group appears to *decrease* the stability of the molecules, while the chlorato-*O*-group appears to *increase* the stability of the molecules. While these molecules may be difficult to synthesize and handle safely, such highly exoergic molecules, or their derivatives, may hold great promise as novel high-energy materials.

Declarations

Author contribution statement

Robert W Zoellner: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Amelia G McArthur: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

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The authors declare no conflict of interest.

Additional information

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