THIOACETONE ANALOGS OF CYCLIC DIACETONE DIPEROXIDE (DADP), TRIACETONE TRIPEROXIDE (TATP) AND TETRAÄCETONE TETRAPEROXIDE (4A4P): STRUCTURES AND PROPERTIES FROM DENSITY FUNCTIONAL CALCULATIONS

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Abstract

Density functional computational investigations at the ωB97X-D/6-311++G**and M06-2X/6-311++G** levels of theory are reported for the cyclic thioacetone analogs of diacetone diperoxide (DADP), triacetone triperoxide (TATP), and tetraäcetone tetraperoxide (4A4P). These hitherto unreported cyclic systems contain –C–S–O–C– linkages rather than –C–O–O–C– linkages; the parent compounds are known and utilized for their explosive properties as well as in other reactions. The exoergic or endoergic nature of the hypothetical decomposition reactions of the thioacetone analogs (to thioacetone and dioxygen) compared to the parent molecules (to acetone and dioxygen) are reported; the calculated hypothetical decomposition reactions of dithioacetone diperoxide (DtADP), trithioacetone triperoxide (TtATP), and tetrathioacetone tetraperoxide (4tA4P) are calculated to be significantly endoergic, while the decompositions of the parent compounds are calculated to be exoergic.

Introduction

Cyclic peroxide oligomers of acetone, $[-C(CH_3)_2-O-O-]_n$, n=2–6, are sensitive materials known to explode when subjected to friction[1] even when wet. Diacetone diperoxide (DADP), n=2 (3,3,6,6-tetramethyl-1,2,4,5-tetraoxane), was first synthesized[2] in 1893 via the reaction of acetone with hydrogen peroxide. The well-known trimeric peroxide oligomer of acetone is triacetone triperoxide (TATP), n=3 (3,3,6,6,9,9-hexamethyl-1,2,4,5,7,8-hexoxonane), and was first described[3] in 1899, while the cyclic tetramer, tetraäcetone tetraperoxide (4A4P), n=4 (3,3,6,6,9,9,12,12-octamethyl-1,2,4,5,7,8,10,11-octaoxacyclo-dodecane), may not have been unequivocally synthesized[4] until 1999. Both pentaäcetone pentaperoxide (n=5) and hexaäcetone hexaperoxide (n=6) were relatively recently synthesized[5] as by-products during the attempted hydrogen peroxide oxidation of platinum complexes using acetone as the solvent.

Organic peroxides are used as polymerization accelerators[6], as hardening and curing agents[7], and possess explosive properties, the latter because of the relative weakness of the O–O peroxide bond[8] and the stability of dioxygen. Many organic peroxides are also utilized in the polymer industry as cross-linking agents[9] and for their bleaching[10] and antibacterial[11] properties, but DADP and TATP have gained significant notoriety in criminal and extremist activities due to their ease of synthesis[12,13] and explosive[14] properties. Despite their potential utility as organic peroxides, DADP and TATP are not often utilized for civilian or military purposes[14] due to their particularly unstable and volatile nature.

While a large body of published work exists concerning these cyclic peroxide oligomers of acetone, little work appears to have been reported concerning the potential for altering the molecular properties of these materials through elemental substitution. That is, studies to determine whether the replacement of specific atoms in these molecules might result in synthesizable molecules exhibiting better stability (with or without explosivity) or which would alter other properties of the cyclic peroxides, making the molecules better suited as starting materials for other syntheses, have not been found.

Persulfur analogs of the cyclic acetone peroxides are extremely rare: Only one system of the $[-C(CH_3)_2-S-S-]_n$ type, where n=2, has been reported, and this molecule was likely[15,16] first synthesized[17] in 1887. Analogs of the cyclic peroxides in which half of the oxygen atoms have been replaced by sulfur atoms, *i.e.*, cyclic systems of the $[-C(CH_3)_2-S-O-]_n$ type, are presently unknown. These novel latter molecules can be envisioned as being formally derived from the oxidative cyclization of propanethione — thioacetone — with hydrogen peroxide, although that synthetic pathway is unlikely to be viable due to the rapid cyclization and polymerization[18] of the thioacetone monomer. The thioacetone analogs of DADP, TATP, and 4A4P are, for simplicity and for reference to their parent molecules, termed dithioacetone diperoxide (DtADP), trithioacetone triperoxide (TtATP), and tetrathioacetone tetraperoxide (4tA4P), even though these molecules no longer contain peroxide (–O–O–) linkages. Given this cavity in the published literature, a density functional theory computational project was initiated with the purpose of investigating the calculated structures and properties of DtADP, TtATP, and 4tA4P and, for comparison, of DADP, TATP, and 4A4P themselves. Herein are presented the results of the computational study of the $[-C(CH_3)_2-S-O-]_n$ systems, n=2–4, using the M06-2X/6-311++G** and ωB97X-D/6-311++G** levels of density functional theory.

Computational methods

The *Spartan '18* computational package[19] was used for all calculations, and the density functional methods ωB97X-D/6-311++G** and M06-2X/6-311++G** were each used for all molecules. The former[20] performs well for thermochemistry and covalent and non-covalent systems, while the latter also performs well in the computational investigation of sulfur-containing[21] molecules. Although the possible conformers of each molecule were readily determined without recourse to computational methods (using the "up-down" method, *vide infra*), conformational analyses on each

molecule were performed using the MMFF method, followed by the examination of each potential conformer for similarity using the PM3 semi-empirical method. As predicted, only two conformers each were identified for DADP, DtADP, TATP, and TtATP, and four each were identified for 4A4P and 4tA4P. Multiple initial trial geometries (ITGs) were employed for each conformer — varying bond lengths and angles — to better ascertain whether an energy minimum for the conformer had been identified. Throughout the investigation of differing ITGs, no interconversions between conformers were observed. Vibrational analyses were performed on all lowest energy conformers at both levels of theory to determine that a stable minimum on the potential energy surface had been found.

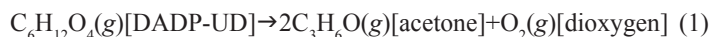## Results and Discussion

Thioacetone analogs of DADP

Computational results for the thioacetone analogs of DADP at the ωB97X-D/6-311++G** and M06-2X/6-311++G** levels of density functional theory are listed in Table 1, along with results for the reference molecules dioxygen, acetone, thioacetone, and DADP itself at the same levels of theory. As seen in Figure 1, two conformers of DADP and the thioacetone analog (DtADP) were identified. In the figures, only the structures of molecules calculated at the ωB97X-D level of theory are shown; molecules calculated at the M06-2X level of theory are essentially identical. The conformers may be identified by describing the orientation — "up" and "down" — of the oxygen atoms, in sequence, in the ring. For example, as seen in Figure 1, the conformers of DADP can be redundantly described as "up-down-down-up" ("UD" for short, identifying every other oxygen atom in the ring) and "up-down-up-down" ("UU"). The DADP-UD conformer was determined to be more stable at both levels of theory, as was DtADP-UD. Overall, calculations at both the ωB97X-D and M06-2X levels of theory indicated that DADP-UD is more stable than DADP-UU by 13.3 kJ/mol and 13.7 kJ/mol, respectively, while for DtADP, DtADP-UD was determined to be more stable than DtADP-UU by 5.9 kJ/mol and 6.5 kJ/mol, respectively. The larger size of and longer bonds to the sulfur atom are likely to contribute to the smaller energy differences between the conformers of DtADP compared to those of DADP.

The relative exoergic (or endoergic) nature of the decomposition of DADP and DtADP may be estimated and compared through the following hypothetical equations, where the molecules decompose to acetone or thioacetone and dioxygen:
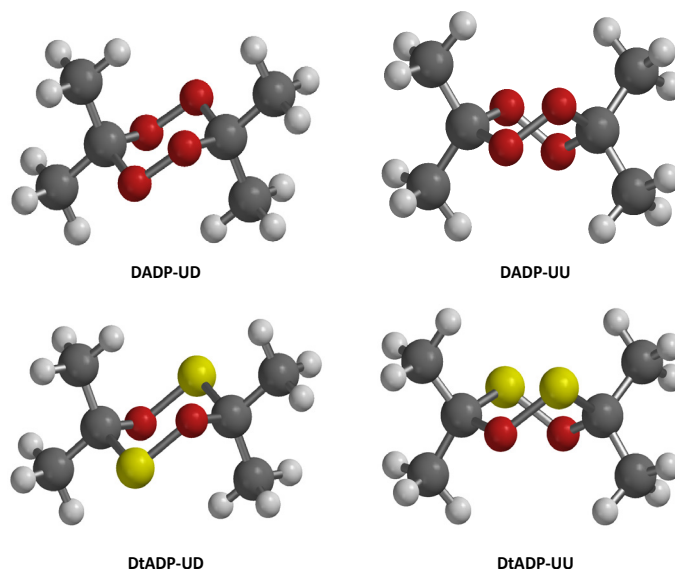
$$C_6H_{12}O_4(g)[\text{DADP-UD}] \rightarrow 2C_3H_6O(g)[\text{acetone}] + O_2(g)[\text{dioxygen}] \quad (1)$$

$$C_6H_{12}O_2S_2(g)[\text{DtADP-UD}] \rightarrow 2C_3H_6S(g)[\text{thioacetone}] + O_2(g)[\text{dioxygen}] \quad (2)$$

(All calculations were carried out assuming isolated gas-phase molecules.) Using the calculated energies from Table 1, at the ωB97X-D and M06-2X levels of theory and the more stable conformers, the decomposition of DADP-UD via reaction (1) results in an energy change for the reaction of -107.6 kJ/mol and -62.6 kJ/mol, respectively; calculational results[8] at the G4 level of theory with the same decomposition reaction report a value of -68.5 kJ/mol. Similarly, using reaction (2), the decomposition of DtADP-UD via reaction (2) results in a calculated energy change for the reaction of +290.3 kJ/mol and +337.6 kJ/mol, using the ωB97X-D and M06-2X levels of theory, respectively. The thioacetone analog of DADP, DtADP-UD, is calculated to exhibit an *endoergic* hypothetical decomposition while the decomposition of DADP-UD is *exoergic*. The M06-2X result for DADP aligns more closely to the result at the G4 level of theory than does the ωB97X-D result.

The sulfur–oxygen single bond lengths in these molecules vary over a small range, from ~167 pm to ~169 pm. Such bonds are about 20 pm longer than inorganic[22] S–O bonds, but are in line with computational results[23] on molecules such as $H_3C–S–O–CH_3$.
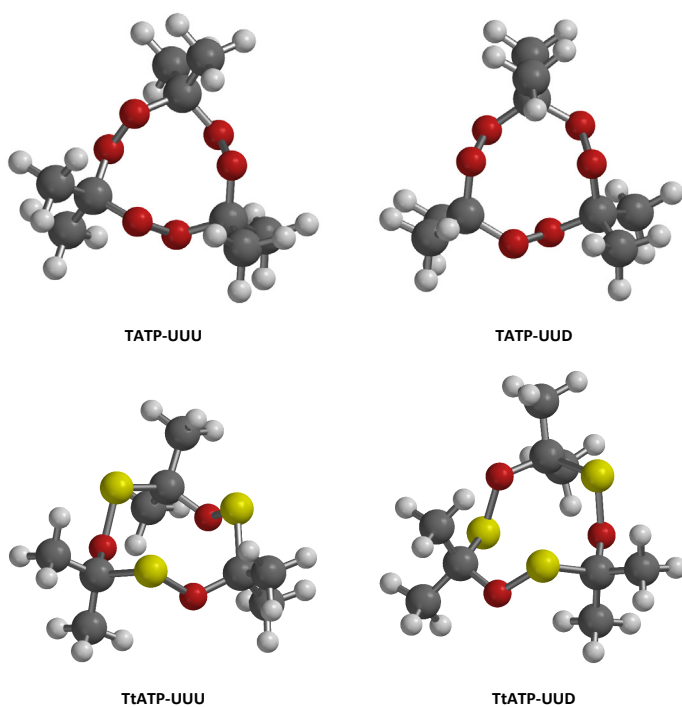
Thioacetone analogs of TATP

Conformational analyses indicated that two TATP and two TtATP conformers exist, and these conformers are illustrated in Figure 2. Again, the conformers may be described by the relative orientation of the oxygen (or sulfur) atoms: The more stable TtATP conformer, TtATP-UUU ("up-down-up-down-up-down"), exists with all sulfur atoms on the same "side" of the molecule, while TtATP-UUD ("up-down-up-down-down-up") has two sulfur atoms on one side of the molecule and the third sulfur atom on

Table 1. Selected electronic and structural properties of dioxygen, acetone, thioacetone, and reference DADP molecules and the thioacetone analogs of DADP at the ωB97X-D/6-311++G** (normal font) and M06-2X/6-311++G** (*italic font*) levels of density functional theory

molecule	electronic energy (au)	dipole moment (D)	HOMO	LUMO	difference[a]	O–O	S–O	C–O	C–S
dioxygen[b]	-150.318782	0.00	-10.98	4.45	15.43	119.6			
	-150.308613	*0.00*	*-10.93*	*2.99*	*13.92*	*118.9*			
acetone	-193.149386	3.18	-9.20	0.99	10.19			120.7	
	-193.119597	*3.13*	*-8.86*	*-0.19*	*8.67*			*120.5*	
thioacetone	-516.106540	3.06	-8.18	-0.19	7.99				162.6
	-516.068346	*2.90*	*-7.53*	*-1.07*	*6.46*				*162.2*
DADP-UD[c]	-536.576554	0.00	-9.67	1.16	10.83	142.7		142.4	
	-536.523969	*0.00*	*-9.38*	*-0.04*	*9.34*	*142.6*		*142.3*	
DADP-UU[c]	-536.571473	0.00	-9.52	1.16	10.68	141.7		143.1	
	-536.518762	*0.00*	*-9.25*	*-0.04*	*9.21*	*141.7*		*143.1*	
DtADP-UD[c]	-1182.642421	0.00	-8.48	1.01	9.49		168.5	143.4	184.1
	-1182.573905	*0.00*	*-7.85*	*-0.05*	*7.80*		*168.6*	*143.2*	*183.6*
DtADP-UU[c]	-1182.640166	0.55	-8.18	1.01	9.19		167.5	143.4	186.0
	-1182.571417	*0.54*	*-7.57*	*-0.06*	*7.51*		*167.7*	*143.3*	*185.5*

[a] $E_{LUMO} - E_{HOMO}$. [b] Calculated as a ground state triplet. [c] See Figure 1 for these structures.

Figure 1. Structures of the diacetone diperoxide (DADP) and dithioacetone diperoxide (DtADP) conformers at the ωB97X-D level of theory.

the "opposite" side. Structures of the two TATP conformers are similar to those of TtATP.

Computational results for the thioacetone analogs of TATP at the ωB97X-D/6-311++G** and M06-2X/6-311++G** levels of density functional theory are listed in Table 2, along with results for the TATP reference molecules. Interestingly, the more stable conformers of TATP and TtATP are the "UUU" conformers, while for DADP and DtADP, the more stable conformers were found to exhibit the "UD" arrangement. Overall, calculations at the ωB97X-D and M06-2X levels of theory indicated that TATP-UUU is more stable than TATP-UUD by 7.6 kJ/mol and 9.4 kJ/mol, respectively, while for TtATP, the UUU conformer was determined to be more stable than the UUD conformer by 3.2 kJ/mol and 4.1 kJ/mol, respectively. The calculated values for the O–O, S–O, C–O, and S–O bond lengths in TATP and TtATP are

similar to those of DADP and DtADP, perhaps indicating that the six-membered rings of the latter and the nine-membered rings of the former do not exhibit significant steric or ring strain which might force bond length changes in the smaller rings in comparison to the larger rings.

In a similar fashion to the determination of the relative exoergic/endoergic nature of the decomposition of DADP and DtADP, the exoergic or endoergic nature of the decomposition of TATP and TtATP may be estimated through equations (3) and (4), respectively.

$$C_9H_{18}O_6(g)[\text{TATP}] \rightarrow 3C_3H_6O(g)[\text{acetone}]+1.5O_2(g)[\text{dioxygen}] \quad (3)$$

$$C_9H_{18}O_3S_3(g)[\text{TtATP}] \rightarrow 3C_3H_6S(g)[\text{thioacetone}]+1.5O_2(g)[\text{dioxygen}] \quad (4)$$

(Again, all calculations were carried out assuming isolated gas-phase molecules.) Using the calculated energies from Tables 1 and 2 and the more stable conformer, the decomposition of TATP-UUU via reaction (3) results in an energy change at the ωB97X-D and M06-2X levels of theory for the reaction of -135.1 kJ/mol and -60.5 kJ/mol, respectively; calculational results[8] at the G4 level of theory with the same decomposition reaction yield a value of -78.6 kJ/mol. Again, as noted for DADP, the M06-2X result for TATP aligns more closely to the G4 result than does the ωB97X-D result. As was observed with DtADP, the decomposition of TtATP-UUU via reaction (4) results in an *endoergic* energy change for the reaction of +443.0 kJ/mol and +519.0 kJ/mol, at the ωB97X-D and M06-2X levels of theory, respectively.

As expected, the hypothetical decomposition of TATP was calculated to be exoergic, in line with the known sensitive and explosive nature of the molecule, but the analogous decomposition of TtATP was calculated to be significantly *endoergic*. An obvious culprit for this reversal may be the presence of the sulfur atoms in the ring: The larger size of the sulfur atoms and the longer bonds to the sulfur atoms may allow greater flexibility and lowered steric interferences in the ring, and this is supported by the smaller differences in the stability of the conformers of TtATP in comparison to those of TATP, thus allowing the TtATP molecule to be more stable with respect to decomposition to thioacetone and dioxygen. (The actual decomposition of TATP[8] does not produce only acetone and dioxygen, nor would the decomposition of TtATP be expected to produce only thioacetone and dioxygen; many other products would likely be observed.) Further, the decomposition of TATP experimentally results in (among a myriad of other products) the production of dioxygen, which may be hampered in the decomposition of TtATP, which does not contain adjacent oxygen atoms in the ring. With such an endoergic hypothetical decomposition reaction, TtATP, like DtADP, may not be an explosive, while both TATP and DADP most definitely are predicted to decompose exoergically.

Figure 2. Structures of the triacetone triperoxide (TATP) and trithioacetone triperoxide (TtATP) conformers at the wB97X-D level of theory.
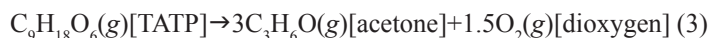
Table 2. Selected electronic and structural properties of reference TATP molecules and the thioacetone analogs of TATP at the ωB97X-D/6-311++G** (normal font) and M06-2X/6-311++G** (*italic font*) levels of density functional theory

Molecule[a]	electronic energy (au)	dipole moment (D)	molecular orbital energies (eV)			mean bond distances (pm)			
			HOMO	LUMO	difference[b]	O–O	S–O	C–O	C–S
TATP-UUU	-804.874882	0.00	-9.25	1.14	10.39	142.6		141.4	
	-804.798672	*0.00*	*-9.06*	*-0.06*	*9.00*	*142.4*		*141.4*	
TATP-UUD	-804.872005	0.16	-8.84	1.15	9.99	142.6		141.6	
	-804.795094	*0.20*	*-8.64*	*-0.06*	*8.58*	*142.5*		*141.6*	
TtATP-UUU	-1773.966528	0.03	-8.15	1.12	9.27		168.0	142.4	183.4
	-1773.865650	*0.13*	*-7.52*	*-0.06*	*7.46*		*168.3*	*142.2*	*183.2*
TtATP-UUD	-1773.965313	0.43	-7.92	1.11	9.03		167.9	143.2	183.5
	-1773.864078	*0.52*	*-7.31*	*-0.07*	*7.24*		*168.1*	*143.0*	*183.1*

[a] See Figure 2 for these structures. [b] $E_{LUMO} - E_{HOMO}$.

Thioacetone analogs of 4A4P

An "up-down" analysis of tetraäcetone tetraperoxide (4A4P) and the thioacetone analogs (4tA4P) of 4A4P indicate that four conformers of each molecule should exist: UUUU, UUUD, UUDD, and UDUD. Conformational analyses confirm this conjecture; the four conformers of each molecule are illustrated in Figure 3. Save for the longer S–O and C–S bonds, the structures of the four 4A4P

conformers are similar to the four conformers of 4tA4P.

Computational results for the four conformers of 4tA4P at the ωB97X-D/6-311++G** and M06-2X/6-311++G** levels of density functional theory are listed in Table 3, along with results for the parent 4A4P reference molecules. The most stable conformers of 4A4P and 4tA4P are the "UUUU" conformers, and the relative ordering of the 4A4P and 4tA4P conformers are the same. For the former, the ordering, with the most stable conformer first (energy differences in parentheses; ωB97X-D results in normal font, M06-2X results in *italic font*), is 4A4P-UUUU (20.9 kJ/mol; *21.8 kJ/mol*) < 4A4P-UUUD (2.8 kJ/mol; *2.9 kJ/mol*) < 4A4P-UUDD (21.1 kJ/mol; *18.8 kJ/mol*) < 4A4P-UDUD. The conformers of the latter are, with the most stable conformer first (energy differences in parentheses; ωB97X-D results in normal font, M06-2X results in *italic font*), in the order 4tA4P-UUUU (6.3 kJ/mol; *8.8 kJ/mol*) < 4tA4P-UUUD (7.8 kJ/mol; *4.3 kJ/mol*) < 4tA4P-UUDD (8.9 kJ/mol; *8.9 kJ/mol*) < 4tA4P-UDUD. As was observed for the cyclic trimers and cyclic dimers, the calculated mean values for the O–O, S–O, C–O, and S–O bond lengths in 4A4P and 4tA4P do not vary significantly with those in DADP, DtADP, TATP, and TtATP.

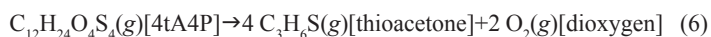The relative exoergic/endoergic nature of the decomposition
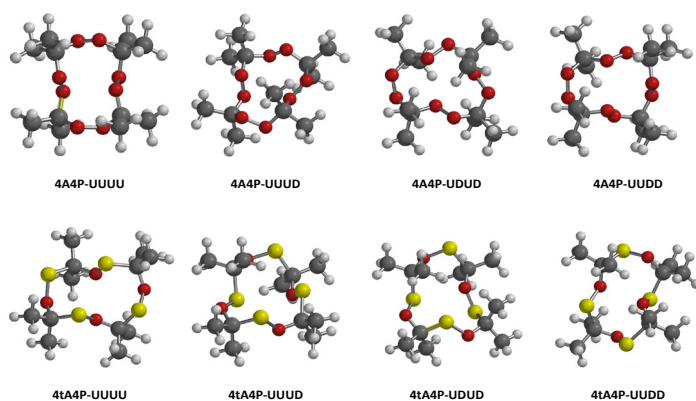
Figure 3. Structures of the tetraäcetone tetraperoxide (4A4P) and tetrathioacetone tetraperoxide (4tA4P) conformers at the wB97X-D level of theory.

Table 3. Selected electronic and structural properties of reference 4A4P molecules and the thioacetone analogs of 4A4P at the ωB97X-D/6-311++G** (normal font) and M06-2X/6-311++G** (*italic font*) levels of density functional theory

molecule[a]	electronic energy (au)	dipole moment (D)	molecular orbital energies (eV)			mean bond distances (pm)			
			HOMO	LUMO	difference[b]	O–O	S–O	C–O	C–S
4A4P-UUUU	-1073.165914	0.01	-8.87	1.11	9.98	142.9		141.1	
	-1073.064021	*0.01*	*-8.67*	*-0.11*	*8.56*	*142.6*		*141.2*	
4A4P-UUUD	-1073.157938	1.32	-8.69	1.10	9.79	142.9		141.6	
	-1073.055712	*1.35*	*-8.52*	*-0.12*	*8.40*	*142.6*		*141.6*	
4A4P-UDUD	-1073.148862	1.81	-8.73	1.08	9.81	142.7		142.3	
	-1073.047440	*1.92*	*-8.57*	*-0.14*	*8.43*	*142.4*		*142.3*	
4A4P-UUDD	-1073.156886	1.39	-8.70	1.10	9.80	143.0		141.5	
	-1073.054605	*1.36*	*-8.52*	*-0.12*	*8.40*	*142.7*		*141.6*	
4tA4P-UUUU	-2365.288957	0.31	-7.61	1.09	8.70		168.4	142.4	183.6
	-2365.155856	*0.23*	*-6.99*	*-0.11*	*6.88*		*168.4*	*142.4*	*183.2*
4tA4P-UUUD	-2365.286539	1.01	-7.82	1.05	8.87		168.3	143.2	183.2
	-2365.152486	*0.95*	*-7.25*	*-0.13*	*7.12*		*168.4*	*143.0*	*183.0*
4tA4P-UDUD	-2365.281123	2.57	-7.92	0.94	8.86		168.3	143.5	184.9
	-2365.147475	*2.58*	*-7.32*	*-0.21*	*7.11*		*168.5*	*143.4*	*184.4*
4tA4P-UUDD	-2365.283582	1.12	-7.77	1.04	8.81		168.3	142.8	184.2
	-2365.150863	*0.93*	*-7.21*	*-0.13*	*7.08*		*168.2*	*142.6*	*184.3*

[a] See Figure 3 for these structures. [b] $E_{LUMO} - E_{HOMO}$.

of 4A4P and 4tA4P may be estimated through equations (5) and (6), respectively, with all molecules in the gas phase.

$$C_{12}H_{24}O_8(g)[4A4P] \rightarrow 4\ C_3H_6O(g)[acetone] + 2\ O_2(g)[dioxygen]\quad (5)$$

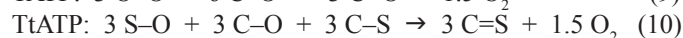$$C_{12}H_{24}O_4S_4(g)[4tA4P] \rightarrow 4\ C_3H_6S(g)[thioacetone] + 2\ O_2(g)[dioxygen]\quad (6)$$
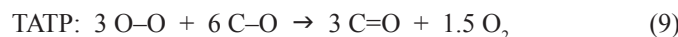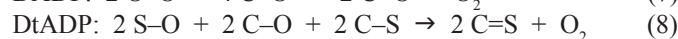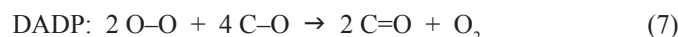
Using the calculated energies from Tables 1 and 3 and the more stable conformer, the hypothetical decomposition of 4A4P-UUUU via reaction (5) results in an energy change for the reaction of -181.7 kJ/mol and -82.9 kJ/mol at the ωB97X-D and M06-2X levels of theory, respectively. (No comparison for the decomposition energy of 4A4P exists in the published literature.) The decomposition of 4tA4P-UUUU via reaction (6) again is seen to result in an *endoergic* energy change for the reaction of +591.3 kJ/mol and +696.4 kJ/mol at the ωB97X-D and M06-2X levels of theory, respectively.

As was observed for the decompositions of DADP and TATP, the decomposition of 4A4P was calculated to be exoergic, but the decomposition of 4tA4P was calculated to be slightly *more endoergic* than that observed for TtATP. While, as stated earlier, the decomposition of these molecules containing –C–S–O–C– linkages may not occur in the simplistic fashion of equations (2), (4), and (6), all three sulfur-containing molecules are likely to be synthesized and be stable, if appropriate methodologies can be found.

The relationship of bond dissociation energies to the decomposition reactions

An estimate of the energy change in the decomposition reactions may also be derived from the bond dissociation energies for the O–O, S–O, C–O, C=O, C–S, C=S, and O_2 (dioxygen) bonds, as these are the bonds that break or form during the decomposition reactions. Assuming that all other bond dissociation energies in the molecules remain approximately constant, the relevant equations are as follows:

DADP: $2\ O–O + 4\ C–O \rightarrow 2\ C=O + O_2$ (7)
DtADP: $2\ S–O + 2\ C–O + 2\ C–S \rightarrow 2\ C=S + O_2$ (8)

TATP: $3\ O–O + 6\ C–O \rightarrow 3\ C=O + 1.5\ O_2$ (9)
TtATP: $3\ S–O + 3\ C–O + 3\ C–S \rightarrow 3\ C=S + 1.5\ O_2$ (10)

4A4P: $4\ O–O + 8\ C–O \rightarrow 4\ C=O + 2\ O_2$ (11)
4tA4P: $4\ S–O + 4\ C–O + 4\ C–S \rightarrow 4\ C=S + 2\ O_2$ (12)

The bond dissociation energies[24] for the bonds in equations (9) through (12), in kJ/mol, are as follows:

O–O 142 C–O 358 C=O 743 O_2 494
S–O 522 C–S 259 C=S 573
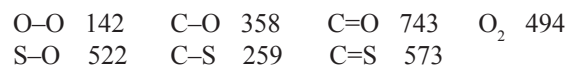
(The value for the bond dissociation energy of dioxygen, O_2, is taken from the experimental bond dissociation energy[25] of dioxygen from spectroscopic measurements.) Based on endothermic bond breaking and exothermic bond formation during the hypothetical decomposition reactions, the following values, in kJ/mol, can be determined for the overall decomposition energies of reactions (7) through (12):

(7)	-264	(9)	-396	(11)	-528
(8)	+638	(10)	+957	(12)	+1276

The signs, if not the magnitudes (the decomposition energies from bond dissociation energies are approximately double the energies calculated from electronic energies, *vide supra*), of the values parallel the decomposition energies calculated from the electronic energies of the molecules.

Comparison of ωB97X-D and M06-2X Results

Structurally, both the ωB97X-D and M06-2X density functional methods result in essentially equivalent molecules with regard to bond lengths and overall appearance. The only significant differences appear in the energies of the highest occupied and lowest unoccupied molecular orbitals, wherein this difference is calculated to be ~1.5 eV greater with the ωB97X-D density functional method. However, the differences in highest occupied and lowest unoccupied molecular orbitals, regardless of how large or small, are unlikely to be predictive[26] of the explosive nature of a molecule. The M06-2X method appears to reproduce the G4 results[8] more closely than does the ωB97X-D method. However, as the hypothetical decomposition reactions used in the G4 calculations[8] are, like the results reported herein, unrealistic with respect to the actual complex decomposition reactions; whether these values have any relevance to the actual decompositions of these molecules is unknown.

Conclusions

Although rational syntheses from thioacetone and dioxygen of dithioacetone diperoxide (DtADP), trithioacetone triperoxide (TtATP), and tetrathioacetone tetraperoxide (4tA4P) are unlikely, the molecules are calculated to be stable, based on calculations at the ωB97X-D and M06-2X levels of density functional. Further, in the cases of all three molecules and the hypothetical decomposition reactions to thioacetone and dioxygen, the decomposition reactions are predicted to be significantly endoergic. The molecules exhibit cyclic structures that, based on the energy differences of identified conformers, would be expected to be flexible and interconvert readily. Substitution of sulfur atoms for alternating oxygen atoms in DADP, TATP, and 4A4P may be an invitation to the preparation of safer explosives or, perhaps, simply stable, non-explosive, molecules containing –C–S–O–C– linkages.

All calculations concerning these molecules were carried out under circumstances in which the molecules exist as isolated systems with no molecule-to-molecule interactions, *i.e.*, in the "gas-phase" with infinite separation from any other molecules. However, just as DADP, TATP, and 4A4P are solids at room temperature, DtADP, TtATP, and 4tA4P are also expected to be solids at room temperature. Unfortunately, the determination of the properties of the solid-state structures of these molecules, or of their properties in solution, is beyond the scope of the present study.

Acknowledgements

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