

THE EFFECT OF SUBSTITUENTS ON THE HYPOTHETICAL DECOMPOSITION ENERGIES OF TRIACETONE TRIPEROXIDE (TATP) DERIVATIVES: STRUCTURES AND PROPERTIES FROM DENSITY FUNCTIONAL CALCULATIONS

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Abstract

Density functional computational investigations at the ω B97X-D/6-311++G** level of theory are reported for derivatives of triacetone triperoxide (TATP) based on hypothetical ketone precursors to the substituted-TATP molecules. The exoergic or endoergic nature of the hypothetical decomposition reactions (to the parent ketone and dioxygen) of the substituted-TATP molecules are compared to the analogous decomposition of the parent TATP molecule. Of the substituted-TATP molecules investigated, only the substituted-TATP molecule derived from cyclopropanone was calculated to undergo an endoergic decomposition. With the exceptions of the methoxy- and *spiro*-cyclopropano-substituted derivatives, the UUU (“up-down-up-down-up-down”, based on the relative positions of the oxygen atoms in the nine-membered ring) conformers of the substituted-TATP molecules were more stable than the UUD (“up-down-up-down-down-up”) conformers, as was observed for TATP itself.

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Introduction

A recent article¹ reported the density functional theory calculational results of an investigation of derivatives of diacetone diperoxide (DADP), triacetone triperoxide (TATP), and tetraacetone tetraperoxide (4A4P) which contained –C–S–O–C– linkages rather than the peroxide –C–O–O–C– linkages of the parent molecules. In that study, the thioacetone analogs — dithioacetone diperoxide (DtADP), trithioacetone triperoxide (TtATP), and tetrathioacetone tetraperoxide (4tA4P) — were determined to be *endoergic* with respect to the hypothetical decomposition reactions to thioacetone and dioxygen. The parent molecules, known² to be explosive, were, as expected, calculated to decompose to acetone and dioxygen exoergically, thus corresponding to the known properties of DADP, TATP, and 4A4P themselves. With those results in hand, the effect of substituents formally derived from symmetrically-substituted acetone or other ketone precursors on the energy of the hypothetical decomposition reactions of TATP derivatives became of interest.

Substituted derivatives of TATP have not been synthesized or otherwise studied. In fact, ketones, other than acetone, apparently do not form cyclic peroxides when treated³ with hydrogen peroxide, perhaps posing challenges to the experimental syntheses of derivatives of TATP such as are described herein. However, to address the void of information concerning substituted derivatives of TATP, herein are reported the computational results for substituted TATP molecules formally derived from their putative ketone precursors. These ketone precursors contain either fluoro-, methyl-, nitro-, or methoxy- substituents, or the cyclic substituents derived from cyclohexanone or cyclopropanone, *i.e.*, pentane-1,5-diyl- and ethane-1,2-diyl-substituents. These data were calculated at the ω B97X-D/6-311++G** level of density functional theory and decomposition energies were determined from the hypothetical decomposition reactions to the ketone precursors and dioxygen.

Computational methods

The *Spartan* '18 computational package⁴ was used for all

calculations, and the density functional method ω B97X-D/6-311++G** was used for all molecules. This method reportedly⁵ performs well for investigations of thermochemistry and for covalent and non-covalent systems. (No attempts were made to determine whether the inclusion of diffuse functions was necessary for these investigations; such determinations were beyond the scope of these investigations.)

As previously¹ reported, the structures of TATP molecules can be described using an “up-down” nomenclature: Each TATP derivative will have only two cyclic conformers with respect to the carbon- and oxygen-containing ring. These conformers are thus designated “up-down-up-down-up-down” (briefly, “UUU”) and “up-down-up-down-down-up” (“UUD”) with respect to the relative positions of the oxygen atoms in the nine-membered ring.

Multiple initial trial geometries were employed for each conformer in which variations in bond lengths and angles determined the starting points for each calculation to better ascertain whether an energy minimum for the conformer had been identified. Only symmetrically-substituted ketone precursors were included to eliminate the possibility of unsymmetrically-substituted TATP molecules and limit the number of isomers to be investigated. Vibrational analyses were performed on all lowest energy conformers at the ω B97X-D/6-311++G** level of theory to ensure that a stable minimum on the potential energy surface had been located.

Results and Discussion

For the sake of brevity, and to uniquely identify the TATP derivatives and the ketones from which the derivatives are formally derived, Table 1 lists the putative parent ketones and the substituted-TATP molecules herein described along with the numbering scheme for them.

Formal ketone precursors

Computational results for the ketone precursors to the TATP derivatives at the ω B97X-D/6-311++G** level of density functional theory are listed in Table 2. In addition, previously-report-

ed¹ results for the reference molecules dioxygen and acetone have been included at the same level of theory, as the electronic energies of these precursors to the cyclic trimer triperoxides are essential to the determination of the hypothetical decomposition energies of the substituted-TATP molecules and TATP itself. The ketones in Table 2 have been the subject of other investigations, and various properties, whether experimentally or computationally determined, have been reported.

Of the symmetrically-substituted acetones with electronegative fluoro-substituents, the conformational equilibrium of [1a] has been determined⁶ through infrared spectroscopy supplemented by calculations at the B3LYP/6-311++G(2df,2p) level of theory. The dipole moment of [1a] has also been experimentally measured⁷ using microwave spectroscopy, and determined to be 2.54 ± 0.03 D, slightly lower than the value, 2.76 D, calculated herein at the ω B97X-D/6-311++G** level of theory. (The accuracy of dipole moments derived from calculations are often⁸ significantly method-dependent.) Somewhat less information has been reported concerning the properties of [2a], but the structure has been calculated at the comparatively low-level STO-3G/6-31G* level of theory as part of an investigation⁹ primarily focused on electron affinities and ionization potentials. For [3a], the experimental structure¹⁰ of the molecule has been determined by gas-phase electron diffraction and the dipole moment¹¹ by microwave spectroscopy. In this case, the measured dipole moment of 0.3949 ± 0.0018 D compares well with the calculated value of 0.41 D. In the gas-phase electron diffraction structure, a C–F bond length of 133.5 pm and a C=O bond length of 124.6 pm (converted from the Ångstrom units of the article) were reported; the C–F bond length compares well, while the C=O bond is calculated herein to be shorter than the

experimental value.

The 1,3-disubstituted-acetone, [4a], containing two electron-withdrawing¹² nitro groups, has been computationally investigated¹³ at the M06-2X/6-311++G(d,p) level of theory using *Gaussian 03*, which is equivalent to the M06-2X/6-311++G** method used herein, as part of a study of “green, energetic oxidants.” Molecule A2 in that report is 1,3-dinitroacetone, [4a], and was calculated to have a heat of formation of +302.93 kJ/mol. While no structural information was reported in the primary article, Cartesian coordinates were provided in the supplementary material. From these coordinates, the following bond lengths were calculated: C=O, 119.7 pm; mean C–N, 149.3 pm; and mean N–O, 121.4 pm. These values are in reasonable agreement with the results reported herein. On the other hand, [5a], 1,3-dimethoxyacetone, containing electron-donating¹² methoxy groups, has no reported experimental or computational structural data, despite being synthesized¹⁴ as early as 1939. The data herein appear to be the first reported — albeit computational — structural data for [5a]; the structure of [5a] is depicted in Figure 1.

Molecules [6a], [7a], and [8a] are alkyl-substituted ketones; alkyl groups are known¹² to be marginally electron-donating. The gas-phase electron diffraction structure¹⁵ of 2-butanone, [6a], “diethyl ketone,” has been reported and were best interpreted with two conformers, the more-stable *trans-trans* and the less-stable *trans-gauche*; the experimental C=O bond distance of 121.7 pm is somewhat longer than the value calculated herein.

Both cyclohexanone, [7a], and cyclopropanone, [8a], have been the subject of many computational and experimental investigations. The calculated structures described herein are carried out as if for an isolated molecule in the gas phase; gas-phase electron diffraction structures are the experimental analog of such calculations. For [7a], such a structure¹⁶ has been reported, resulting in an experimental C=O distance of 122.9 pm, slightly longer than calculated, and a C1–C2 distance of 150.3 pm, slightly shorter than calculated herein. For [8a], the experimental structure based on the microwave spectrum¹⁷ yielded a C=O distance of 119.1 pm, a C1–C2 distance of 147.5 pm, and a C2–C3 distance of 157.5 pm, are in reasonable agreement with the current calculational results.

Table 1. Key to the substituted-TATP molecules and the ketone precursors

substituted-ketone precursor	substituted-TATP
[1a] 1,3-difluoroacetone	[1b] 3,3,6,6,9,9-hexa(fluoromethyl)-1,2,4,5,7,8-hexoxonane
[2a] 1,1,2,3-tetrafluoroacetone	[2b] 3,3,6,6,9,9-hexa(difluoromethyl)-1,2,4,5,7,8-hexoxonane
[3a] hexafluoroacetone	[3b] 3,3,6,6,9,9-hexa(trifluoromethyl)-1,2,4,5,7,8-hexoxonane
[4a] 1,3-dinitroacetone	[4b] 3,3,6,6,9,9-hexa(nitromethyl)-1,2,4,5,7,8-hexoxonane
[5a] 1,3-dimethoxyacetone	[5b] 3,3,6,6,9,9-hexa(methoxymethyl)-1,2,4,5,7,8-hexoxonane
[6a] 3-pentanone	[6b] 3,3,6,6,9,9-hexa(ethyl)-1,2,4,5,7,8-hexoxonane
[7a] cyclohexanone	[7b] 3,6,9-tris(pentane-1,5-diyl)-1,2,4,5,7,8-hexoxonane
[8a] cyclopropanone	[8b] 3,6,9-tris(ethane-1,2-diyl)-1,2,4,5,7,8-hexoxonane

Table 2. Selected electronic and structural properties of the putative ketone precursors to the substituted-TATP molecules at the ω B97X-D/6-311++G** level of density functional theory

molecule	electronic energy (au)	dipole moment (D)	molecular orbital energies (eV)	mean bond distances (pm)
			E_{LUMO} E_{HOMO} difference ²	C–O X–Y ³
dioxygen ^{c,d}	-150.318782	0.00	-10.98 4.45 15.43	119.6 ^d
acetone ^d	-193.149386	3.18	-9.20 0.99 10.19	120.7
1,3-difluoroacetone [1a]	-391.611729	2.76	-9.98 0.59 10.57	119.9 137.8 ^{c,f}
1,1,3,3-tetrafluoroacetone [2a]	-590.095419	2.24	-10.68 -0.65 10.03	119.3 135.2 ^{c,f}
Hexafluoroacetone [3a]	-788.598054	0.41	-11.47 -1.20 10.27	118.6 133.0 ^{c,f}
1,3-dinitroacetone [4a]	-602.119720	0.17	-10.80 -1.01 9.79	119.8 150.3 ^{c,h} 121.1 ^{h,i}
1,3-dimethoxyacetone [5a]	-422.166029	2.10	-8.81 0.92 9.73	120.4 139.6 ^{o,CH2} 141.2 ^{o,CH3}
3-pentanone [6a]	-271.773955	2.98	-9.03 0.97 10.00	120.8
cyclohexanone [7a]	-309.881866	3.48	-8.89 0.89 9.78	120.8 151.7 ^{c,h2}
cyclopropanone [8a]	-191.871885	3.08	-8.93 0.78 9.71	119.2 146.7 ^{c,h2} 156.9 ^{h2,h2}

^a $E_{\text{LUMO}} - E_{\text{HOMO}}$

^b Superscripts denote X-Y atom types.

^c Calculated as a ground state triplet.

^d From reference 1.

Substituted-TATP systems — structures

Table 3 lists the calculated properties of the substituted-TATP molecules, each of which is novel and has not been reported in the literature. The “UUU” conformer is the more stable conformer for all of these molecules with the [5b] and [8b], formally derived from 1,3-dimethoxyacetone and from cyclopropanone, respectively, for which the “UUD” conformer is the more stable. Figure 2

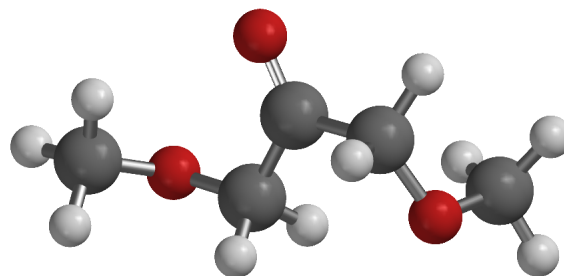


Figure 1. The calculated structure of 1,3-dimethoxyacetone [5a].

depicts the “UUU” and “UUD” conformers for those molecules in which the “UUU” conformer is more stable, and Figure 3 depicts the “UUU” and “UUD” conformers for molecules [5b] and [8b] in which the “UUD” conformer is more stable.

The reasons for the reversal of stability from “UUU” to

“UUD” for [5b] and [8b] are difficult to discern from only two examples; more research may be needed to fully answer this question. The methoxy-substituted TATP system appears to exhibit the greatest substituent mobility of any of the substituents investigated; the “UUD” conformer may allow better “inter-substituent” relaxation than can be attained in the “UUU” conformer. However,

Table 3. Selected electronic and structural properties of the conformers of TATP and substituted-TATP molecules at the ω B97X-D/6-311++G** level of density functional theory

molecule ^a	electronic energy (au) ^b	dipole moment (D)	molecular orbital energies (eV)			reaction energy (kJ/mol) ^d	mean bond distances (pm)		
			HOMO	LUMO	difference ^c		O–O	C–O	X–Y ^e
TATP-UUU ^f	-804.874882 {7.55}	0.00	-9.25	1.14	10.39	-135.1	142.6	141.4	
TATP-UUD ^f	-804.872005	0.16	-8.84	1.15	9.99		142.6	141.6	
[1b]-UUU	-1400.256262 {8.57}	4.19	-10.34	0.92	11.26	-149.9	142.6	140.2	137.8 ^{C-F}
[1b]-UUD	-1400.252999	3.89	-9.99	0.94	10.93		142.9	140.5	137.8 ^{C-F}
[2b]-UUU	-1995.717960 {12.13}	2.17	-11.20	0.49	11.69	-122.0	142.5	139.4	134.8 ^{C-F}
[2b]-UUD	-1995.713341	2.30	-10.87	0.40	11.27		142.7	139.8	134.8 ^{C-F}
[3b]-UUU	-2591.213292 {21.57}	0.00	-11.92	-0.14	11.78	-155.0	142.4	138.9	132.7 ^{C-F}
[3b]-UUD	-2591.205075	0.14	-11.48	-0.23	11.25		142.5	139.3	132.7 ^{C-F}
[4b]-UUU	-2031.766095 {13.87}	4.29	-10.81	-1.02	9.79	-187.0	142.3	140.2	150.4 ^{C-N}
[4b]-UUD	-2031.760814	7.25	-10.82	-1.28	9.54		142.4	140.6	150.4 ^{C-N}
[5b]-UUU	-1491.920348 {-13.77}	4.37	-8.78	0.94	9.72		142.7	140.5	140.0 ^{O-CH2}
[5b]-UUD	-1491.925593	2.92	-9.24	0.94	10.18	-133.0	143.1	140.9	140.0 ^{O-CH2}
[6b]-UUU	-1040.739253 {8.27}	0.29	-9.19	1.11	10.30	-159.6	142.5	141.2	
[6b]-UUD	-1040.736104	0.40	-8.78	1.09	9.87		142.6	141.6	
[7b]-UUU	-1155.080227 {5.30}	0.48	-9.11	1.10	10.21	-114.3	142.7	141.1	152.8 ^{C-CH2}
[7b]-UUD	-1155.078207	0.42	-8.77	1.10	9.87		142.8	141.4	152.9 ^{C-CH2}
[8b]-UUU	-801.101075 {-14.37}	0.01	-9.36	1.32	10.68		144.8	137.8	149.2 ^{C-CH2}
[8b]-UUD	-801.106550	0.08	-9.26	1.32	10.58	+33.4	145.5	137.7	149.4 ^{C-CH2}

^a See Table 2 for the identity of the numbered molecules; for the description of the UUU and UUD conformer designations, see text.

^b Numbers in curly brackets are the energy differences, $E_{\text{UUD}} - E_{\text{UUU}}$, between the UUU and UUD conformers in kJ/mol.

^c $E_{\text{LUMO}} - E_{\text{HOMO}}$.

^d Energy of the hypothetical decomposition reaction of the more stable conformer to the precursor ketone and dioxygen; see text.

^e Superscripts denote X–Y atom types.

^f From reference 1.

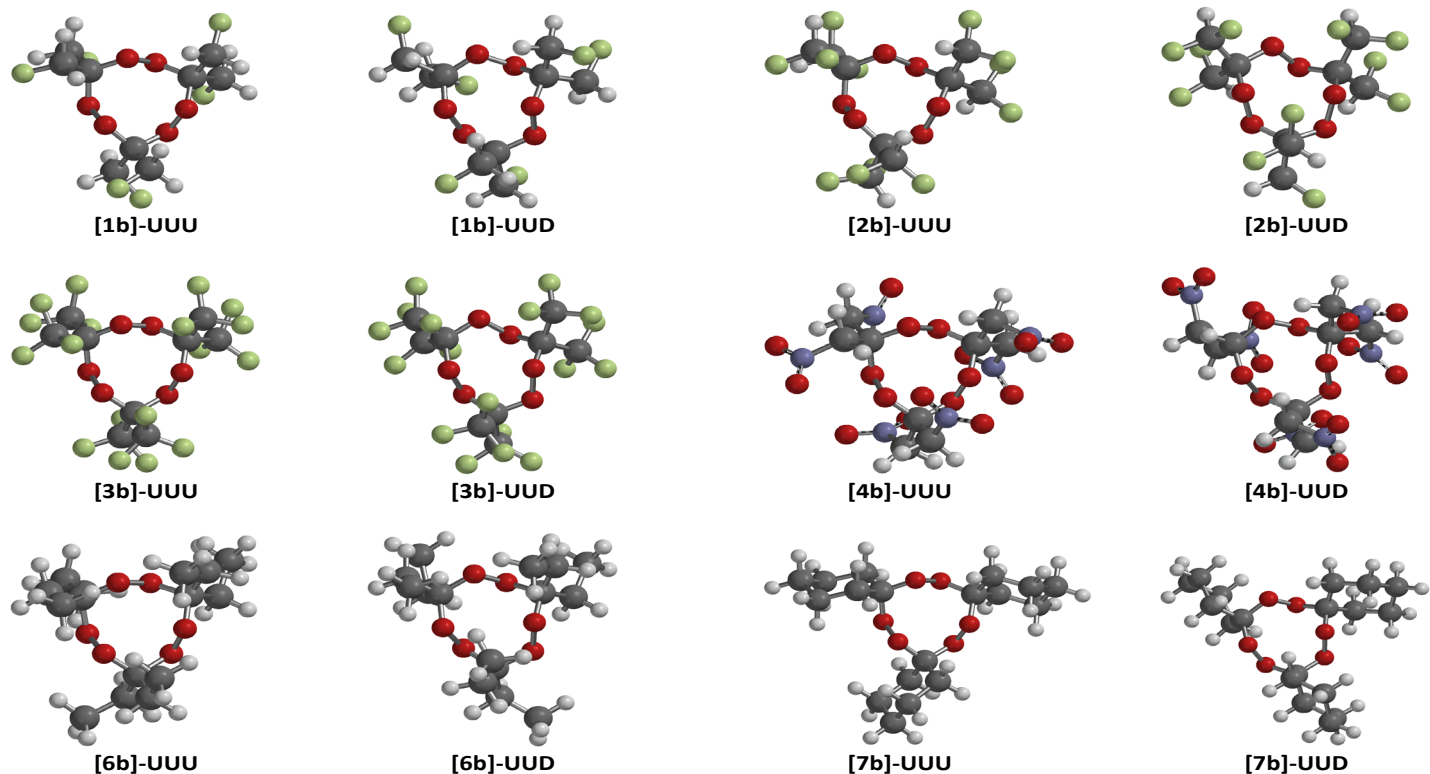


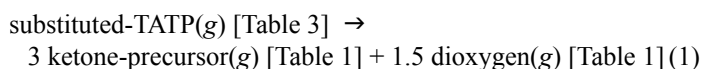
Figure 2. Substituted-TATP molecules in which the “UUU” conformer is more stable than the “UUD” conformer. See Table 1 for molecular identification.

this is purely speculative; additional molecules containing the methoxy substituents in both the “UUU” and “UUD” conformations were investigated starting from different initial trial geometries, yet a “UUD” conformer was always found to be the lowest energy conformer.

On the other hand, **[8b]**, containing *spiro*-fused cyclopropane groups, may have the completely opposite problem: lack of substituent relaxation potential. The *spiro*-fused cyclopropane moieties are forced to be more rigid than any other substituent. (The *spiro*-fused cyclohexane substituents in **[7b]** are all in the chair conformation, but can interconvert from one chair conformation to another, while the *spiro*-fused cyclopropane substituents are fixed and rigid.) In this case, the “UUD” conformer might be conjectured to allow for lowered steric interactions than is possible for the “UUU” conformer. However, such a conclusion does not seem to be supported when the **[8b]** conformers are viewed “edge-on,” as depicted in Figure 3.

Substituted-TATP systems — decomposition

The hypothetical energies of decomposition of the substituted-TATP molecules may be estimated through the use of generic equation (1) and the calculated electronic energies from Tables 1 and 3:



The reaction energies calculated from equation (1) are listed in Table 3; all calculations were carried out assuming only gas-phase molecules. (The investigation of these molecules in other than the gas phase was beyond the scope of this study.) For all of the substi-

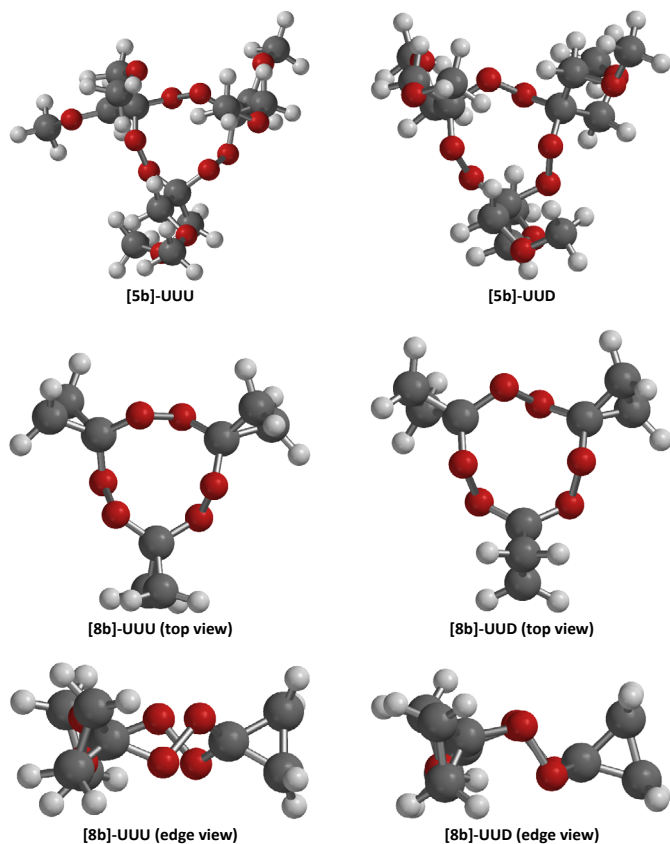


Figure 3. Substituted-TATP molecules in which the “UUD” conformer is more stable than the “UUU” conformer. See Table 1 for molecular identification.

tuted-TATP molecules, save for **[8b]**, the decomposition energies are *exoergic*; only **[8b]** demonstrates an *endoergic* hypothetical decomposition. The decomposition of **[8b]** may be an aberration, as the molecule contains three highly-ring-strained *spiro*-fused cyclopropane rings. Thus, **[8b]** may simply be less strained than **[8a]** due to the rearrangement of the carbonyl group containing a C=O double bond in the ketone precursor into two C–O single bonds in the substituted-TATP system.

Because of reaction (1), each hypothetical decomposition, regardless of ketone involved, occurs with the conversion of three C–O bonds to three C=O bonds and scission of three C–O and three O–O bonds so as to form 1.5 dioxygen molecules. Thus, even though the reactions appear to be disparate, the reaction energies can be compared. However, the decomposition reaction must be emphasized as hypothetical; the actual decomposition of these molecules is expected to be as complicated as that¹⁸ of TATP itself, wherein the major products are acetone and carbon dioxide, while other products include methyl acetate and acetic acid. That being noted, the least exoergic decomposition (save for **[8b]**) is for **[7b]**, containing three *spiro*-fused cyclohexane rings. Thus, future research to investigate more stable or less exoergically reactive TATP derivatives may involve other *spiro*-fused systems.

Conclusion

Structurally, the UUU conformation was found to be more stable than the UUD conformation for all molecules, with the exceptions of the methoxy- and *spiro*-fused-cyclopropane-substituted systems, **[5b]** and **[8b]**. The reasons for this reversal are not straightforward: In **[5b]**, the substituent mobility of the methoxy-groups may allow the UUD conformer more opportunities for relaxation and, hence, greater stability than is possible in the UUU conformer, but with only one example, such a conclusion is tentative in the extreme. On the other hand, for **[8b]**, the *spiro*-fused cyclopropane moieties allow essentially no substituent mobility, yet the UUD conformer in this case is calculated to be more stable than the UUU conformer. Steric interactions do not appear to explain this reversal for **[8b]**, and with the information currently in hand, no conclusion as to the reason for this reversal can be made at this time.

Of the eight substituted-TATP derivatives investigated, only **[8b]**, containing three *spiro*-fused cyclopropane rings, exhibited an exoergic hypothetical decomposition reaction. This result may be ascribed to the conversion of three highly-strained cyclopropane molecules to the three *spiro*-fused cyclopropane moieties in which the C=O group has been replaced by two C–O bonds, thus reducing ring strain in the cyclopropane rings. The lowest exoergic decomposition reaction was determined to be for **[7b]**, with three *spiro*-fused cyclohexane rings. All other decomposition reactions were similar to, or more exoergic than, the decomposition of TATP itself.

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