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Two Separable Conformers of TATP and Analogues Exist at Room Temperature

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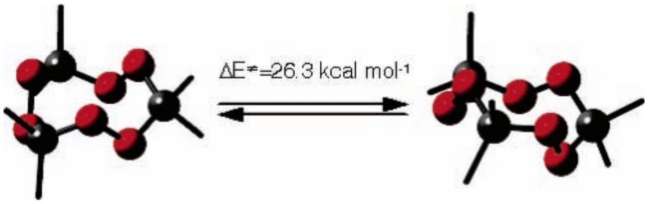
ABSTRACT



TATP gives rise to two separable conformations because the barrier for interconversion between them is relatively high at room temperature. This kind of behavior is rare in cyclic organic systems and is the result of poor overlap in the "flip-flop" transition state. The crystal structure of the analogous tricyclohexanone triperoxide also indicates the presence of two conformers.

Cycloalkanes, including cyclononane, are known to have several conformers that equilibrate rapidly at room temperature.[1,2] Therefore, we were surprised by the indications that triacetone triperoxide (TATP)[3] might exist at room temperature in the form of two separable conformers. We and others have recently noticed that TATP exhibits two distinctive peaks with the same mass in both GC/MS and HPLC/MS analyses.[4,5] Crowson and co-workers had proposed that these two peaks might correspond to C_2- and D_3-conformers of the TATP nine-membered ring based on temperature-dependent NMR studies.[6] However, their proposal is also based on AM1 semiempirical calculations by Yavari et al.,[7] and these authors concluded that the barrier for the interconversion of these two conformers (via a flip-flop motion) is 3.4 kcal mol^{-1} (14.4 kJ mol^{-1}). Since such a low barrier cannot account for the observation of two separable conformers, the authors have made no claim for separable conformers.[7]

Here we show, on the basis of both experimental and computational evidence, that the two conformers of TATP, as well as those of a TATP analogue, are indeed kinetically stable at room temperature.

TATP and other cyclic peroxides have attracted increasing interest because these readily available compounds are extensively used by terrorist organizations worldwide for manufacturing of improvised explosive devices. The physical properties of these cyclic peroxides are of particular interest because the lack of any nitrogen functionality in the molecule

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makes their detection and identification by standard explosive detectors an extremely difficult task.[4,5]

As found by Yavari et al.[7] and more recently by Keinan, Zeiri, and co-workers,[3] the most stable conformer of TATP adopts a D_3 conformation (**1-D$_3$** in Figure 1).

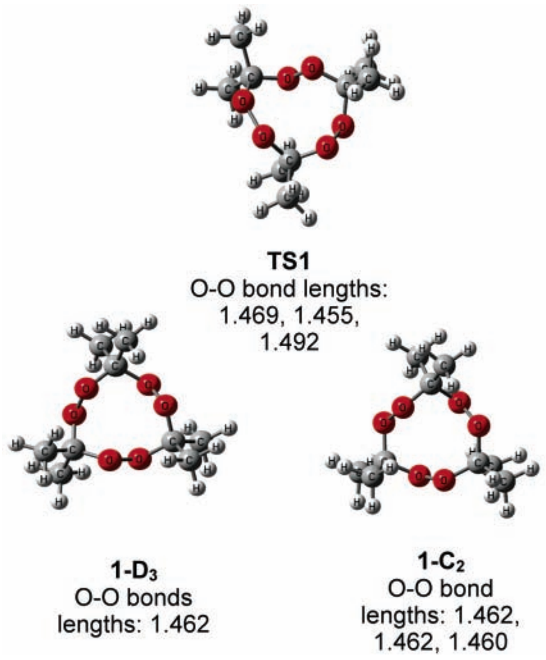

Figure 1. Structures of calculated D_3 and C_2 conformers of TATP **1** and transition state for the conversion between them (B3LYP/6-31G*).

In the present work it is found that the other conformer, **1-C$_2$**, is only 1.85 kcal mol^{-1} (ZPE total energies) less stable than **1-D$_3$**.[8] A transition state (**TS1**) was located (Figure 1) that was shown to connect the two conformers by carrying out an intrinsic reaction coordinate (IRC) calculation,[9] in which the imaginary mode for the transition state is followed in both the forward and reverse directions. The interconversion between the two conformers is a flip-flop movement of one of the three oxygen atom pairs and the energy of this transition state, **TS1**, is 26.3 kcal mol^{-1} higher than the most stable conformer **1-D$_3$** and 24.4 kcal mol^{-1} higher than **1-C$_2$**. The dihedral angle C−O−O−C that involves this isomerization is 133.8° in **1-D$_3$**, −127.4° in **1-C$_2$**, and −16.3° in **TS1**. Indeed, this high barrier justifies the presence of two separable conformers in the gas phase (i.e., GC). Figure 2 illustrates the HOMO-1 and HOMO-2 orbitals of **1-C$_2$** and **TS1**. The high energy required for isomerization in the case of TATP can be rationalized by the poor overlap in the molecular orbitals of the transition state in comparison with the ground-state structure **1-C$_2$** in which stabilizing interactions between C−O bonds and adjacent oxygen atoms are possible. The HOMO orbitals of both structures (**1-C$_2$** and **TS1**) are the nonbonding *p*-orbitals of the oxygen atoms and are therefore not informative.

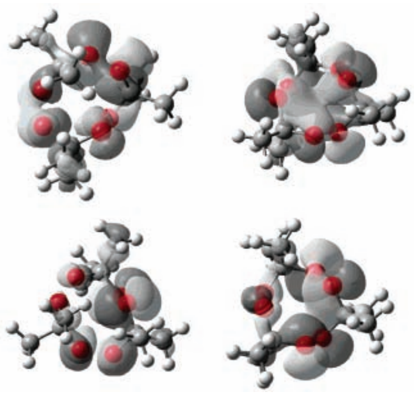

Figure 2. HOMO-1 (bottom) and HOMO-2 (top) orbitals of **1-C$_2$** (right side) and **TS1** (left side).

Evidently, however, slow equilibration occurs in solution,[6] and it is therefore proposed that the barrier for transformation between the two conformers is reduced in the presence of protic solvents. To support this suggestion, the geometries and energies of **TS1-2H$_2$O** and **1-C$_2$-2H$_2$O** structures with two interacting water molecules (Figure 3) were calculated. Two water molecules were introduced in order to retain the C_2 symmetry. However, the transition state in this case, **TS1-2H$_2$O**, is 24.0 kcal mol^{-1} above the corresponding **1-C$_2$-2H$_2$O** minimum, indicating a very small reduction in activation energy for isomerization (∼0.4 kcal mol^{-1}).[10]

As the effective acidity of water might be presented better by the interaction with a hydronium ion, the structure and energy of **C$_2$-H$_3$O$^+$** has also been calculated. However, the calculated geometry of **1-C$_2$-H$_3$O$^+$** (Figure 3) indicates an extremely elongated O−C bond upon H_3O^+ cationization (2.350), and the resulting structure is almost an open ring structure.

This suggests that the **1-C$_2$−1-D$_3$** equilibration, in solution, occurs through ring opening and re-closure. Alternatively, the flip-flop barrier can be lowered by protonation and C−O bond elongation, without a ring-opening step; however, we

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(8) Calculations were carried out using Gaussian 98 package of programs at the B3LYP/6-31G* level of theory: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*; Gaussian, Inc.: Pittsburgh, PA, 1998.

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(10) This is the most stable complex between TATP and two water molecules however there are several possible complexes that correspond to higher energies.

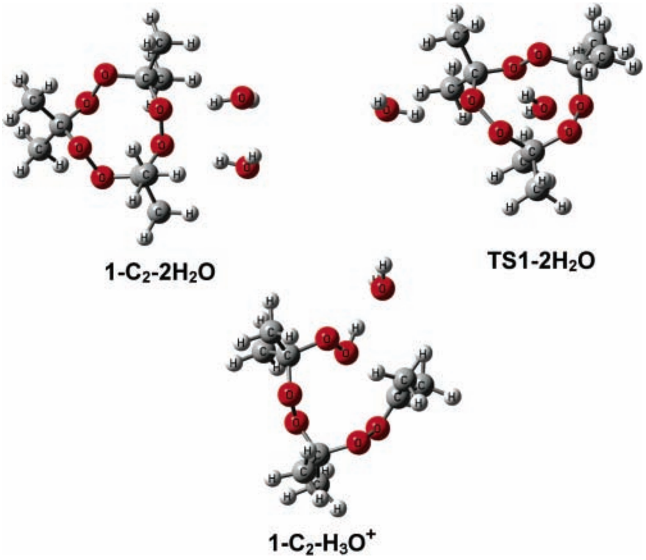

Figure 3. **1-C_2** with two water molecules (top); flip-flop transition state in TATP 1 interacting with two water molecules (middle); **1-C_2** with interacting with an hydronium ion (bottom).

were unable to locate such a transition state. As stated above, acid-catalyzed equilibration is supported by the work of Crowson et al., who reported that a solution of the separated conformers reequilibrate after a few days of storage at 0 °C in a mixture of solvents containing ammonium acetate.

Table 1. Geometrical Parameters from the Crystal Structure and Calculations (B3LYP/6-31G*) of the Conformers of 2

	2-pseudo-C_3		**2**-pseudo-C_2
property	exptl	calcd	calcd
C−O	1.4176 (18), 1.418 (2), 1.4271 (19)	1.417	1.422
		1.417	1.423
		1.420	1.429
O−C	1.4284 (18), 1.431 (2), 1.4187 (18)	1.419	1.424
		1.419	1.423
		1.416	1.419
O−O	1.4747 (14), 1.475 (2), 1.4678 (15)	1.464	1.465
		1.465	1.468
		1.466	1.465
O−C−O	112.76 (12)	113.0	112.2
	112.76 (12)	113.2	112.0
	112.05 (11)	113.0	112.1
C−O−O−C	135.0	134.0	124.7
	136.2	133.5	124.4
	134.0	134.7	−126.6

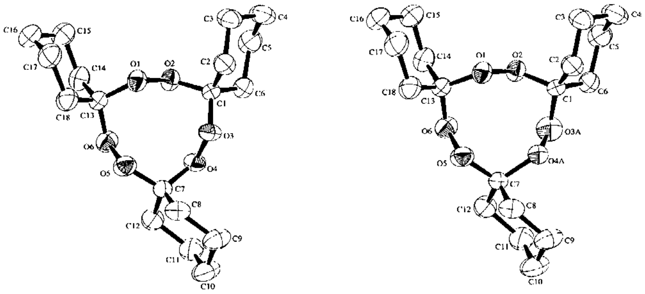

Figure 4. Crystal structure of **2-C_3** (94%, left) and the minor conformer **2-C_2** (6%, right).

The same phenomenon was observed in tricyclohexanone triperoxide (TC6TP)[11] **2** during HPLC analysis. An accompanying chromatographic peak which could be attributed to a minor conformer was observed in 3−5% yield. However, attempts to change the ratio of isomers by interconverting the conformers in acidic solution failed. Fortunately, conclusive evidence for the existence of two conformers in the solid state was obtained from the crystal structure of **2** (Table 1, Figure 4). A colorless crystal of **2** with the dimensions 0.39 × 0.39 × 0.24 mm^3 indicated an orthorhombic, *Pbca* cell with the following geometrical parameters: $a = 11.7390(2)$ Å, $b = 9.9400(2)$ Å, $c = 31.9930(6)$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90$, $V = 369.7(2)$ Å^3 and $\rho = 1.331$ g cm^{-3}. Some bond lengths and angles are given in Table 1. The diffraction of crystalline molecule **2** shows a disordered electron density pattern, which could only be interpreted as follows: 94% of the cells contain the pseudo-C_3 conformer **2-C_3**, whereas the rest of the cells, with the same cell dimensions, contain the pseudo-C_2 conformer **2-C_2** (Figure 5).[12]

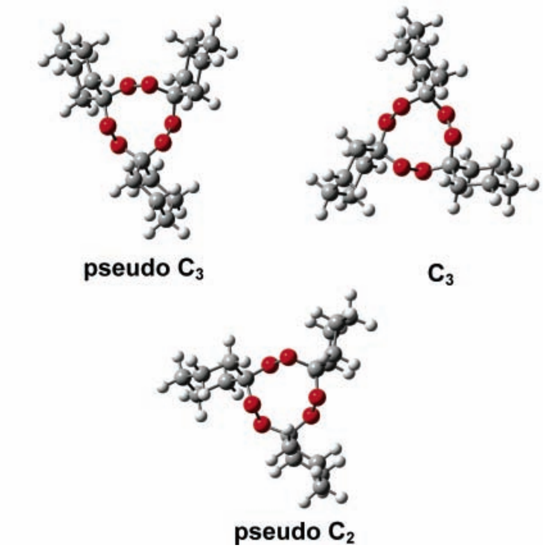

Figure 5. Structures of calculated **2-C_3** and **2-C_2** conformers of **2** (B3LYP/6-31G*).

The barrier for transformation between **2-C_3** and **2-C_2** was not calculated due to the size of the system. However, the C−O−O−C angle in **2-C_3** is 134.0, comparable with the

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[11] Tricyclohexanone triperoxide (TC6TP) was prepared according to Sanderson et al. (Sanderson, J. R.; Paul, K.; Story, P. R. *Synthesis* **1975**, 275−275) in 45% yield after two crystallizations from methanol and then from acetone, mp 89−92 °C (lit. 87−90 °C).

[12] The symmetry of **2** cannot be D_3 and since the three cyclohexyl rings can exist in two chair conformations there are several pseudo-C_3 or -C_2 conformers with similar energies.

C−O−O−C dihedral angle in **1-D_3**, which is 133.8. It is reasonable to assume that the barrier for flip-flop in **2** is comparable to the one found in **1**. The difference in energy between the **2-C_3** and **2-C_2** conformers is 1.9 kcal mol^{-1}, favoring **2-C_3**, as expected.

In summary, we have shown here that contrary to what is known for the conformers of cycloalkanes, TATP and its analogues have two separable conformers at room temperature. These kinetically stable conformers can interconvert through a high barrier, in the gas phase. Consequently, these cyclic peroxides are expected to show two isobaric peaks in either HPLC/MS or GC/MS analyses.

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Supporting Information Available: CIF file for the X-ray structure of **2** and Cartesian coordinates for all calculated structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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