

3,3,6,6,9,9-Hexaethyl-1,2,4,5,7,8-hexaoxacyclononane at 296 K

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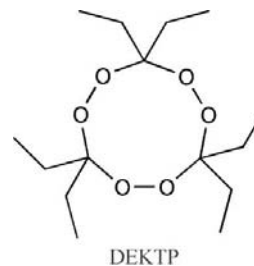
The title molecule (diethyl ketone triperoxide, DEKTP), C₁₅H₃₀O₆, is a cyclic triperoxide closely related to triacetone triperoxide (TATP), one of the most unstable explosives known. However, the stability of DEKTP is *ca* 20–50 times greater than that of TATP. DEKTP crystallizes with two molecules in the asymmetric unit, with virtually identical geometry. The cyclononane core is stabilized in a twisted boat–chair conformation (approximate *D*₃ symmetry), very close to that previously described for TATP. The explanation for the safe thermal behaviour of DEKTP compared with TATP should thus not be sought in the molecular dimensions, but rather in the thermal decomposition kinetics.

Comment

Cyclic *gem*-peroxides with three peroxidic functions are formed readily from the acid-catalyzed oxidation of carbonyl compounds with hydrogen peroxide to form a mixture of open-chain and cyclic peroxides, the latter arising from the former. The unusual reactivity of peroxides is generally attributed to the weakness of the O–O bond linkage (the reactive site) and hence the ease with which it is homolytically cleaved. Many studies have reported the thermal decomposition rate reaction constants (Cañizo, 2006; Eyler, 2006; Iglesias *et al.*, 2009) for diethyl ketone triperoxide (DEKTP) and triacetone triperoxide (TATP). These reports showed that it is possible to compare the thermal solution behaviour for both compounds, and concluded that DEKTP has a higher thermal solution decomposition stability than TATP.

Cyclic peroxide derivatives have been studied mainly for two reasons. Firstly, they are potentially useful radical initiators, for example, in the bulk polymerization of styrene (Cerna *et al.*, 2002) or for controlled-rheology polypropylene (Pucci *et al.*, 2004). In this application, their performance is similar to

that presented by a multifunctional initiator, giving rise to high molecular weight polystyrene at a high reaction rate. Secondly, some members of this family are also interesting from a conformational point of view, since large rings including only *sp*³-hybridized atoms can be stabilized in different conformations, sometimes affording separable conformers. A classic example is TATP, a well known peroxide-based explosive material with a power close to that of TNT. A comprehensive study showed that the explosion of this product involves an entropic burst, which is the result of the formation of four gaseous compounds from one molecule of TATP in the solid state (Dubnikova *et al.*, 2005). The X-ray structure of TATP has been established (Groth, 1969; Dubnikova *et al.*, 2005; Jensen *et al.*, 2009), showing that a single conformer is stabilized in the solid state, where the nine-membered cycle adopts a twisted boat–chair conformation with a local symmetry close to *D*₃. However, some reports claim that two TATP conformers related by a flip-flop interconversion mechanism may exist at room temperature. Computational and experimental evidence supports this claim. For instance, it was found that the C₂-TATP conformer is only 1.85 kcal mol⁻¹ (1 kcal mol⁻¹ = 4.184 kJ mol⁻¹) less stable than the *D*₃ conformer. On the other hand, the barrier for interconversion, at least in the gas phase, is sufficiently high to allow the two conformers to be separated (Denekamp *et al.*, 2005).



A direct strategy for assessing the conformational flexibility of TATP is to synthesize and characterize closely related compounds. However, very few cyclic triperoxide derivatives bearing a cyclononane core have been X-ray characterized to date (Denekamp *et al.*, 2005; Terent'ev *et al.*, 2007), and all presented a *D*₃ conformation. The present work deals with the room-temperature solid-state structure of the title compound, DEKTP, where all the methyl groups of TATP are formally substituted by ethyl groups. It should be emphasized that, although the compound is difficult to handle at room temperature, low-temperature data collection was not attempted because the room-temperature structure is the one of interest regarding the relationship with the peculiar properties of the compound. On the other hand, these systems are known to be prone to polymorphism, as recently reported for TATP, for which an exceptional series of five new polymorphs were characterized at *T* = 180–200 K (Reany *et al.*, 2009).

DEKTP crystallizes as well-shaped colourless crystals with a rather low melting point (m.p. 332–333 K) and a strong unpleasant smell. Although the crystals are air-stable for several months, they slowly volatilize in the X-ray beam, as previously observed in the case of TATP (Dubnikova *et al.*, 2005). Depending on the crystal size and power of irradiation,

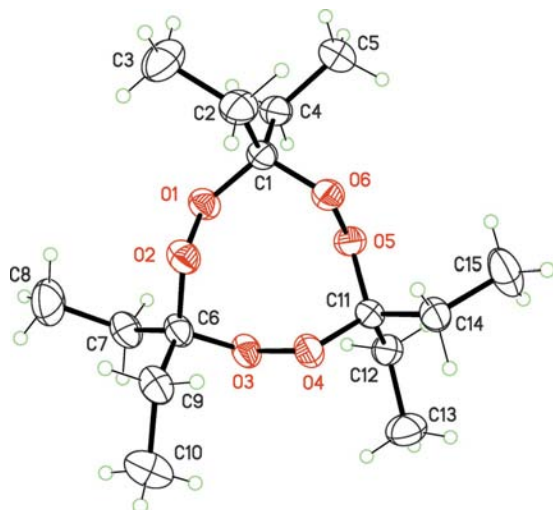


Figure 1

The structure of the first independent molecule of DEKTP, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

ca 75% diffraction decay is observed after 40 h of data collection. Four partial diffraction patterns with overlapping layers were thus measured, using four crystals, which afforded a complete scaled data set for structure refinement (see *Experimental*).

The crystal structure of DEKTP has no unexpected features. Molecules display a globular shape with a hydrophobic external surface, and are thus well separated in the crystal. The resulting packing index is rather low at 0.63 (*PLATON*; Spek, 2009), although no significant voids are detected in the crystal structure.

In contrast with TATP, the title peroxide has two molecules in the asymmetric unit, both located on general positions (Figs. 1 and 2). The two independent molecules have quite similar conformations: an overlay (*Mercury*; Macrae *et al.*, 2006) between both molecules computed with all non-H atoms affords an r.m.s. deviation of 0.115 Å. The largest differences arise from the peripheral ethyl groups, which are potentially free to rotate about their σ C–C bonds, providing that the C atoms in the cyclononane rings retain a tetrahedral geometry (Fig. 2, inset). The largest deviation of 0.348 Å corresponds to the pair of fitted atoms C10/C30. Each molecule displays the same twisted boat–chair conformation, similar to that found for TATP. Total puckering amplitudes (Cremer & Pople, 1975) are similar in both independent molecules, *viz.* 1.3232 (13) and 1.3220 (13) Å for the O1- and O21-rings, respectively. Departures from ideal D_3 symmetry for the cyclononane cores are small, as reflected in the range of the C–O–O–C torsion angles in the cycles from -134.54 (14) to -136.54 (14)°. The bond lengths for the O–O groups also span a very narrow range [1.4711 (16)–1.4775 (17) Å] and compare well with those found in TATP [average 1.470 (2) Å at 180 K].

In conclusion, a comparison between the molecular structures of TATP and DEKTP clearly shows that substitution of methyl by ethyl groups does not introduce additional strain in the cyclononane ring system. Assuming a similar thermal

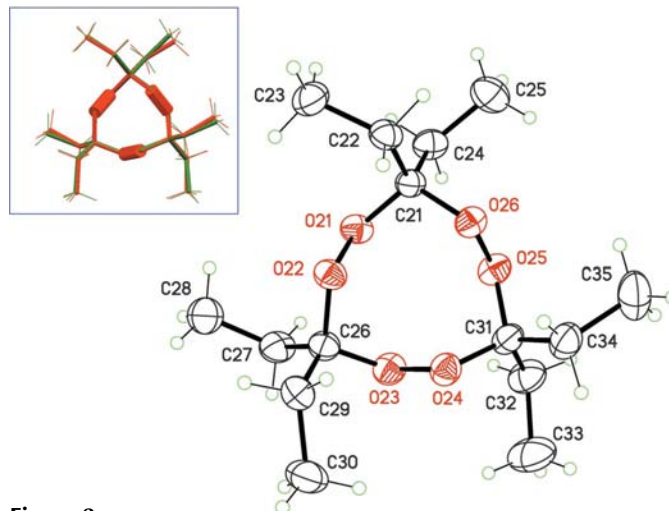


Figure 2

The structure of the second independent molecule of DEKTP, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. The inset is an overlay of the non-H atoms between the two molecules.

decomposition pathway for both molecules, we can then suggest that DEKTP is not as sensitive to impact or temperature changes as TATP, because some products of the decomposition process have higher molecular weights. For instance, acetone, the main product of TATP decomposition, should be diethyl ketone in the case of DEKTP decomposition. In the same way, methyl acetate as a product of decomposition of TATP is replaced by ethyl propanoate for DEKTP (see scheme 2 in Dubnikova *et al.*, 2005).

Experimental

Caution: normal safety precautions for the handling of peroxide materials should be observed. It is generally known that peroxides can be detonated by shock. DEKTP was obtained in a simple and efficient one-step procedure using the acid-catalyzed oxidation reaction of diethyl ketone by hydrogen peroxide (Eyler *et al.*, 1993). Over a period of 1 h, diethyl ketone (50 mmol, 5.6 ml) was added dropwise to a mixture of hydrogen peroxide (4.6 ml) and sulfuric acid (7.3 ml, 70% *v/v*). The reaction is exothermic and was conducted at low temperature (263 K). After addition, the slurry was stirred for 2 h at low temperature. Subsequently, the organic and aqueous phases were allowed to separate. The organic layer was isolated, neutralized with a saturated ammonium sulfate aqueous solution, and re-extracted with petroleum ether (333 K). This phase was dried over anhydrous sodium sulfate for 12 h, filtered, and the solvent removed under reduced pressure. The crude product was crystallized from methanol, affording colourless crystals of DEKTP (m.p. 332–333 K; yield 80%).

Crystal data

$C_{15}H_{30}O_6$
 $M_r = 306.39$
 Monoclinic, $P2_1/c$
 $a = 10.4545$ (12) Å
 $b = 10.859$ (3) Å
 $c = 32.168$ (5) Å
 $\beta = 91.796$ (10)°

$V = 3650.0$ (12) Å³
 $Z = 8$
 Mo $K\alpha$ radiation
 $\mu = 0.09$ mm⁻¹
 $T = 296$ K
 $0.6 \times 0.4 \times 0.3$ mm

Data collection

Siemens P4 diffractometer	$R_{\text{int}} = 0.045$
17260 measured reflections	3 standard reflections
6424 independent reflections	every 97 reflections
4356 reflections with $I > 2\sigma(I)$	intensity decay: >50%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$	392 parameters
$wR(F^2) = 0.112$	H-atom parameters constrained
$S = 1.03$	$\Delta\rho_{\text{max}} = 0.15 \text{ e } \text{\AA}^{-3}$
6424 reflections	$\Delta\rho_{\text{min}} = -0.15 \text{ e } \text{\AA}^{-3}$

Because of the intrinsic instability of DEKTP under X-ray irradiation, four crystals of quite similar sizes were used for data collection. In order to minimize damage, the beam shutter was left closed during dead times, ensuring noncontinuous irradiation. Different parts of reciprocal space were measured for each crystal, with a common layer in each pair of crystals. Raw data were corrected for crystal decay, using the intensity of three standard reflections. The index range and decay for each crystal were as follows. Crystal 1: $h -12 \rightarrow 3$ and decay $1 \rightarrow 0.23$; crystal 2: $h -12 \rightarrow -6$ and decay $1 \rightarrow 0.66$; crystal 3: $h -1 \rightarrow -3$ and decay $1 \rightarrow 0.72$; crystal 4: $h -3 \rightarrow 5$ and decay $1 \rightarrow 0.65$. Finally, a data set scaling by least-squares fitting of common reflections was used to produce a suitable intensities file (*XPREP*; Bruker, 1997). Scale factor and R_{int} indices for each contributing crystal in the final data set were as follows. Crystal 1: $K = 1$ and $R_{\text{int}} = 0.066$; crystal 2: $K = 0.09$ and $R_{\text{int}} = 0.061$; crystal 3: $K = 0.60$ and $R_{\text{int}} = 0.041$; crystal 4: $K = 0.34$ and $R_{\text{int}} = 0.025$.

Methylene H atoms were placed in idealized positions and refined as riding on their parent C atoms, with C–H = 0.97 Å. Methyl H atoms were placed in calculated positions, with C–H = 0.96 Å, and the CH₃ groups considered as rigid groups free to rotate about their C–C bonds. For all H atoms, $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for methylene groups or $1.5U_{\text{eq}}(\text{C})$ for methyl groups.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics:

SHELXTL (Sheldrick, 2008) and *Mercury* (Version 2.0; Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: UK3010). Services for accessing these data are described at the back of the journal.

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