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(6Z,8Z)-2,4,6-Trimethyl-8-phenyl-7-oxa-2,4-diazabicyclo[4.2.0]octane-3,5-dione

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Abstract

The title compound, $C_{14}H_{16}N_2O_3$, is a model of the crucial intermediate in a postulated mechanism for the enzyme (6–4) photoproduct photolyase, which repairs a particular form of UV-light induced DNA damage. The dihedral angle of the two oxetane ring H atoms is 143.5°, which means the bulky phenyl ring is *exo* to the pyrimidine ring.

Comment

Ultraviolet (UV) light is responsible for many forms of damage to DNA, which includes strand breaks, formation of abasic sites, base hydrolysis and the dimerization of adjacent bases. The most common form of the latter type of damage is the dimerization of adjacent thymines on the same DNA strand (Friedberg, 1985). In the presence of UV light, the two pyrimidines can form either a cyclobutane dimer (CBD), or a (6–4) dimer (Cadet, Anselmino, Douki & Voituriez, 1992). The CBD is the more prevalent of the two photoproducts, and therefore has been studied extensively (Wulff & Fraenkel, 1961; Ragini, 1965; Gangamani, Cheravakkattu & Ganesh, 1994). In organisms such as *E. coli*, *D. melanogaster*, and *X. laevis* this damage is repaired, in the presence of light, by CBD photolyase (Sancar, 1994). On the other hand, the (6–4) dimer is relatively poorly understood. This photoproduct is postulated to form after an initial Paterno–Büchi reaction between the 5,6-double bond of the 5′-thymine, and the C-4 carbonyl of the 3′-thymine, followed by a ring opening of the subsequent oxetane (Varghese & Wang, 1968).

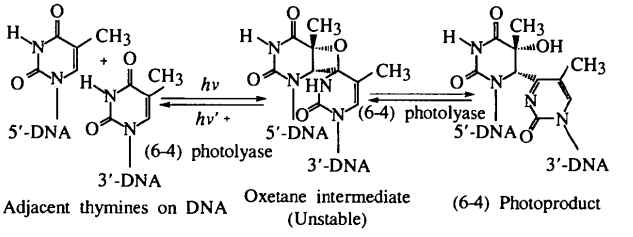

Fig. 1. Formation of the (6–4) photoproduct between two thymines in DNA.

The (6–4) dimer is repaired by the enzyme (6–4) photoproduct photolyase (Todo *et al.*, 1993). A mechanism has been proposed for this enzyme, which is as follows: the enzyme binds to the damaged part and first converts the (6–4) dimer to the oxetane, then, in the presence of light, and certain electron-rich enzyme cofactors, (6–4) photolyase breaks the oxetane ring to yield the two parent thymines (Kim, Malhotra, Smith, Taylor & Sancar, 1994). Unfortunately, the postulated oxetane intermediate between two thymines is unstable above 193 K (Rahn & Hosszu, 1969), and is unhelpful in the support of this mechanism. On the other hand, various stable thietanes between adjacent thymidines have been synthesized and characterized (Clivio, Fourrey, Gasche & Farve, 1992; Liu & Taylor, 1996).

In order to test this proposed mechanism, we have prepared an oxetane of 1,3-dimethylthymine (DMT) with benzaldehyde, and have shown that this oxetane, (I), can be split into its constituent parts in the presence of light, and a variety of electron-donating and electron-accepting sensitizers (Prakash & Falvey, 1995). Unlike the 'natural' oxetane, this compound is stable at room temperature. Although the actual mechanism of (6–4) photoproduct photolyase is still under investigation, our results are consistent with the proposed mechanism (Kim, Malhotra, Smith, Taylor & Sancar, 1994). In

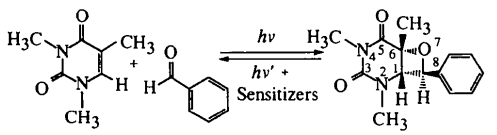

Fig. 2. Formation of the stable oxetane, (I), from DMT and benzaldehyde.

this paper we present the crystal structure of this DMT/benzophenone oxetane.

The X-ray structure of the oxetane ring shows a slight puckering about the O atom and therefore the oxetane ring is not planar. This effect is similar to that observed in other oxetanes (Morris, Smith & Walsh, 1987; Khan, Morris, Smith & Walsh, 1991). The bulky phenyl ring is found to be *exo*, or away from the thymine ring, and this causes the two oxetane ring H atoms to be *trans*, with a dihedral angle of 143.5°. This *trans* geometry of the H atoms has been confirmed by ^{1}H NMR (200 MHz), which provides a coupling constant of 6.2 Hz (Prakash & Falvey, 1995). The compound crystallizes in discrete molecular units. There are no short intermolecular contacts.

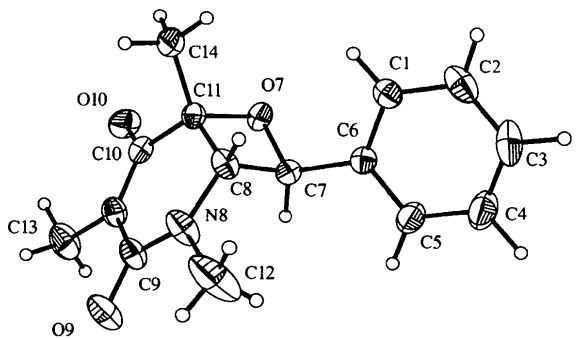

Fig. 3. *ORTEP*II (Johnson, 1976) diagram of the title oxetane with 30% probability ellipsoids.

Experimental

The oxetane was prepared by first dissolving 0.16 g of benzaldehyde and 0.15 g of DMT in 15 ml of CH_3CN. The resulting solution was placed in a quartz tube, equipped with a septum and a stir-bar, purged with nitrogen for 30 min, and irradiated with the unfiltered output of a 150 W Hg–Xe lamp for 8 h. The solvent was then rotary evaporated and the oxetane was purified by silica gel chromatography using a 4:1 hexane/ethyl acetate solvent mixture. The fractions containing the oxetane were combined, and the solvent removed by rotary evaporation. The purified oxetane was subsequently crystallized by dissolving the residue in 10 ml of toluene and adding heptane to the solution until it turned cloudy. Upon standing at room temperature, long colorless needles appeared, which were separated from the solvent by decantation.

Crystal data

$C_{14}H_{16}N_2O_3$
M_r = 260.29
Monoclinic
$P2_1/c$
a = 8.9803 (8) Å
b = 16.3083 (10) Å
c = 9.2752 (7) Å
β = 93.541 (7)°
V = 1355.8 (2) Å^3
Z = 4
D_x = 1.275 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 17.6–18.9°
μ = 0.091 mm^{-1}
T = 153 (2) K
Block
0.50 × 0.30 × 0.25 mm
Clear, colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: by integration
T_{min} = 0.974, T_{max} = 0.979
2540 measured reflections
2381 independent reflections
1856 reflections with $I > 2\sigma(I)$
R_{int} = 0.0138
θ_{max} = 24.97°
h = −10 → 10
k = −19 → 0
l = −11 → 0
6 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.108
S = 1.038
2381 reflections
237 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0423P)^2 + 0.5644P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.179 e Å^{-3}
$\Delta\rho_{min}$ = −0.149 e Å^{-3}
Extinction correction: *SHELXL* (Sheldrick, 1993)
Extinction coefficient: 0.0044 (12)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

C6—C7	1.489 (2)	O9—C9	1.214 (2)
O7—C11	1.454 (2)	N9—C10	1.370 (2)
O7—C7	1.461 (2)	N9—C9	1.409 (2)
C7—C8	1.534 (3)	N9—C13	1.477 (3)
N8—C9	1.340 (2)	C10—O10	1.217 (2)
N8—C8	1.435 (2)	C10—C11	1.518 (3)
N8—C12	1.467 (4)	C11—C14	1.503 (3)
C8—C11	1.522 (3)		
C1—C6—C7	121.5 (2)	C9—N9—C13	115.6 (2)
C5—C6—C7	119.2 (2)	O9—C9—N8	123.2 (2)
C11—O7—C7	91.69 (12)	O9—C9—N9	119.3 (2)
O7—C7—C6	114.26 (15)	N8—C9—N9	117.5 (2)
O7—C7—C8	89.57 (13)	O10—C10—N9	121.4 (2)
C6—C7—C8	118.62 (15)	O10—C10—C11	120.8 (2)
C9—N8—C8	123.7 (2)	N9—C10—C11	117.8 (2)
C9—N8—C12	117.8 (2)	O7—C11—C14	111.3 (2)
C8—N8—C12	115.9 (2)	O7—C11—C10	108.76 (14)
N8—C8—C11	117.1 (2)	C14—C11—C10	111.2 (2)
N8—C8—C7	118.8 (2)	O7—C11—C8	90.29 (13)
C11—C8—C7	86.36 (13)	C14—C11—C8	119.0 (2)
C10—N9—C9	126.3 (2)	C10—C11—C8	114.2 (2)
C10—N9—C13	118.1 (2)		

Data were corrected for Lorentz and polarization factors and reduced to F_o^2 and $\sigma(F_o^2)$ using *XCAD*4 (Harms, 1993). The structure was determined by direct methods. After several cycles of refinement, all of the non-H atoms were refined anisotropically. An additional difference Fourier map revealed nearly all of the H-atom positions. Since a few were missing, all H atoms bonded to C atoms were initially placed in calculated positions. The H atoms during the final stages of refinement were allowed to refine freely. A final difference Fourier map was essentially featureless with the largest peaks, $|\Delta\rho| < 0.18$ e Å^{-3}.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994). Cell refinement: *CAD*-4 *EXPRESS*. Data reduction: *XCAD*4 (Harms, 1993), *SHELXTL-Plus* (Sheldrick, 1991). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976) in *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXTL-Plus*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1020). Services for accessing these data are described at the back of the journal.

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(20*S*)-6β-Methoxy-20-(*p*-toluenesulfonyloxymethyl)-3α,5-cyclo-5α-pregnane

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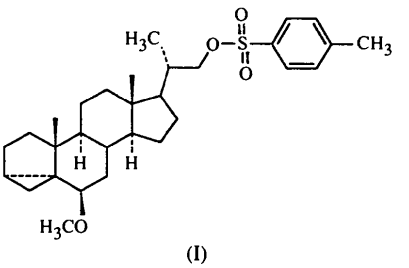
Abstract

The crystal and molecular structure of the title compound, $C_{30}H_{44}O_4S$, has been determined to confirm the molecular conformation. The fused cyclopropane moiety corresponding to part of ring *A* has a β-configuration and the associated cyclopentane ring has an envelope conformation.

Comment

(20*S*)-20-Hydroxymethyl-6β-methoxy-3α,5-cyclo-5α-pregnane is a key intermediate in the synthesis of sterol side chains from simple pregnane-type compounds. The crystal structure analysis of its *p*-toluenesulfonate derivative, (I) (Fig. 1), established the 20*S* configuration previously assigned on the basis of chemical and spectroscopic data (Partridge, Faber & Uskokovic, 1974; Dasgupta, Crump & Gut, 1974; Vanderah & Djerassi, 1978). The cyclopentane ring, fused to the cyclopropane moiety, adopts an envelope conformation, with C1 0.512 Å out of the plane defined by atoms C2, C3, C5 and C10.



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