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N^6,N^6-Dimethyladenine–tetraiodoethene (2/1)

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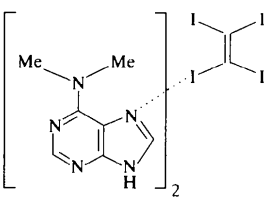
Abstract

The partner molecules of the title complex, $C_7H_9N_5 \cdot 0.5C_2I_4$, form chains held together by hydrogen bonds and weak N···I bonds. Two I atoms of a tetraiodoethene molecule are bonded to the N7 atoms of two N^6,N^6-dimethyladenine molecules, not to N1 where I is bonded in a complex investigated earlier between 9-cyclohexyladenine and iodine.

Comment

Crystal structures of many molecular complexes of amines with halogens or organic halides have been reported (Hassel & Rømming, 1962; Prout & Kamenar, 1973). Apart from the much longer N···halogen distance in complexes with halides, the geometry of all these complexes is quite similar. The complexes with halogens are classified as charge-transfer complexes, whereas the nature of the intermolecular interactions in those with halides has been discussed. It has been shown, however, that charge transfer plays a role also in the latter complexes (Lommerse *et al.*, 1996).

The present work is part of a study of the protonation and intermolecular interactions of N6-substituted adenine derivatives (Dahl, 1987; Dahl *et al.*, 1996). Many attempts have been made to crystallize molecular complexes of such molecules with halogens or organic halides, but so far only the title complex, (I), has been obtained. The crystal structure of the iodine complex with 9-cyclohexyladenine has, however, been reported earlier (van der Helm, 1973).



(I)

The partner molecules of the title complex form chains running along the *a* axis. In these chains the molecules are held together by N9—H9···N3 hydrogen bonds between two N^6,N^6-dimethyladenine molecules situated around a centre of symmetry, and by N···I interactions, where two I atoms of a tetraiodoethene molecule are bonded to the N7 atoms of two N^6,N^6-dimethyladenine molecules. The N···I distance is 3.173 (4) Å, which is 0.194 Å longer than in a similar complex between pyrazine and tetraiodoethene (Dahl & Hassel, 1968), and the angle N···I—C is 172.6 (1)°. In the complex between 9-cyclohexyladenine and iodine there are monomeric units, and I is bonded to N1 with a nearly linear N···I—I arrangement and an N···I distance of 2.520 Å. This distance is 0.21 Å longer than in a similar complex between 4-picoline and iodine (Hassel *et al.*, 1961).

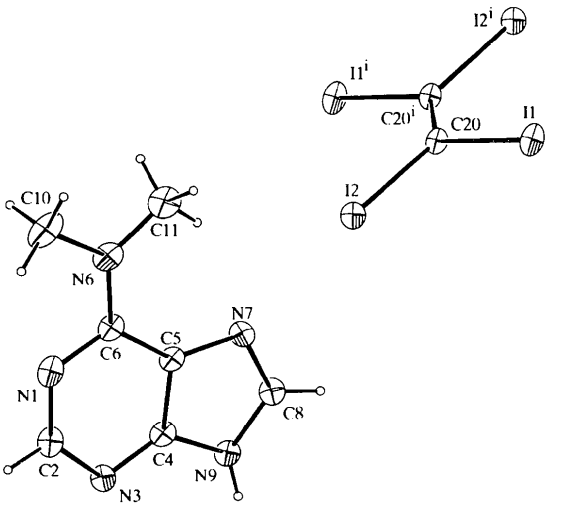


Fig. 1. The title complex with the atom-labelling scheme showing 50% probability displacement ellipsoids. [Symmetry code: (i) $1-x$, $1-y$, $-z$.]

Steric hindrance was suggested to be the reason for the long N···I distance in the 9-cyclohexyladenine–iodine complex. A similar explanation seems reasonable for the present complex. The angle C5—N7···I2 is 57.8 (4)° larger than C8—N7···I2. This difference has the effect of increasing the distance from I2 to the methyl group at C11, which is larger than the van der Waals distance, and reducing the distance to C8. The latter distance, 3.56 (1) Å, is shorter than the van der Waals distance. The N···I bond makes an angle of 15.9 (1)° with the least-squares plane through to the ring system of the N^6,N^6-dimethyladenine molecule. The dimethylamino group is twisted 5.3 (4)° out of this plane around the C6—N6 bond in such a direction that C11 and I2 are on the same side of the plane.

The complex formation results in a slight deformation of the tetraiodoethene molecule, as the distance between the two I atoms involved in N···I bonds are 0.045 (1) Å longer than that between the two other I atoms. A similar but smaller deformation was observed in the pyrazine–tetraiodoethene complex.

The finding that I is bonded to N1 in the 9-cyclohexyladenine–iodine complex was as expected since N1 has a larger negative charge than N3 and N7, and protonation of this kind of adenine derivative usually occurs at N1 (van der Helm, 1973). It may therefore seem surprising that I is bonded to N7 in the present complex. It has, however, been observed that many N6-mono- and disubstituted adenine derivatives are protonated in an unusual way with H atoms bonded to N3 and N7 rather than to N1 and N9 (Dahl *et al.*, 1996). There may be a connection between these observations, but no obvious explanation has been found. *AM*1 calculations (Dewar *et al.*, 1985), using the computer program *GAUSSIAN*86 (Frisch *et al.*, 1984), indicate that the charges on N1, N3 and N7 change by less than 0.01 e by methyl substitution on N6. This substitution may cause steric hindrance and make N1 less accessible for hydrogen bonding and N···I interactions. One should, however, expect the steric conditions at N1 and N7 in N6 dimethylated adenines to be approximately the same. The finding that it seems unimportant for the protonation whether the molecule is mono- or dimethylated (Dahl *et al.*, 1996) also makes such steric arguments less reasonable.

In conclusion, the observation that I is bonded to N7 in this complex is difficult to explain, but seems to fit well into the picture obtained earlier concerning the protonation of N6-substituted adenine derivatives.

Experimental

N^6,N^6-Dimethyladenine, obtained from Sigma Chemical Company, and tetraiodoethene, from Merck KGaA, were dissolved in dichloromethane in the molar ratio 2:1. The complex was crystallized by evaporating the solvent at 263 K.

Crystal data

$C_7H_9N_5{\cdot}0.5C_2I_4$
M_r = 429.00
Monoclinic
$P2_1/c$
a = 18.093 (3) Å
b = 5.093 (2) Å
c = 13.358 (2) Å
β = 105.48 (2)°
V = 1186.3 (5) Å^3
Z = 4
D_x = 2.402 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71070 Å
Cell parameters from 25 reflections
θ = 6.33–15.31°
μ = 5.279 mm^{-1}
T = 293 (2) K
Plate
0.30 × 0.18 × 0.12 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: Gaussian (*PLATON*; Spek, 1998)
T_{min} = 0.384, T_{max} = 0.569
2959 measured reflections
2853 independent reflections
2137 reflections with $I > 2\sigma(I)$
R_{int} = 0.065
θ_{max} = 27.98°
$h = -23 \rightarrow 23$
$k = 0 \rightarrow 6$
$l = 0 \rightarrow 17$
3 standard reflections
frequency: 60 min
intensity decay: 5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.083
S = 1.041
2853 reflections
138 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0526P)^2 + 0.2377P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.011
$\Delta\rho_{max}$ = 1.019 e Å^{-3}
$\Delta\rho_{min}$ = −1.048 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

I1—C20	2.097 (4)	C20—C20^i	1.332 (8)
I2—C20	2.098 (4)		
C20^i—C20—I2	125.1 (4)	I2—C20—I1	112.53 (19)
C20^i—C20—I1	122.3 (4)		

Symmetry code: (i) $1-x, 1-y, -z$.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *XCAD*-4 (Harms, 1996). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*a*). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*b*). Molecular graphics: *PLATON* (Spek, 1998).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1064). Services for accessing these data are described at the back of the journal.

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Cholest-5-ene-3β,4β-diyl diacetate

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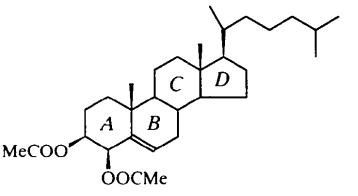
Abstract

The title steroid, $C_{31}H_{50}O_4$, is shown to pack in a highly anisotropic manner. Only α-face-to-β-face contacts are found in the stacks formed along the *b* direction, there are only head-to-tail contacts in the *c* direction and the acetate groups lie in layers normal to **c**.

Comment

Although the basic biological functions of cholesterol have been known for many years, little is known in detail of its molecular interactions with enzymes, cholesterol-binding proteins and related effectors of gene transcription. As part of our continuing programme studying fluoro-cholesterols for this purpose, we attempted to generate oxygenated steroids for subsequent fluorination. A rearrangement of 4,5-epoxycholestanyl-3β-acetate was attempted using acetic and sulfuric acids. 5α-Hydroxycholestan-3β,4β-diacetate was formed and subsequently treated with diethylaminosulfur trifluoride. The expected fluorination did not occur, with the dehydrated steroid cholest-5-ene-3β,4β-diyl diacetate, (I), being the only isolated product. The crystal structure of (I) was determined, both to confirm its composition and to determine its stereochemistry.



(I)

The molecular structure of (I) (Fig. 1) shows that the acetate groups are positioned at the 3- and 4-sites and that both are substituents of the β-face of the steroid. Their methyl groups project out from the β-face and the CO groups are *syn* to the C_{ring}—O bonds [C5—O2—C2—O1 −7.8 (4), C10—O4—C4—O3 0.9 (4)°]. A similar arrangement is found for the monoacetate cholest-5-en-3β-yl acetate (II; Sawzik & Craven, 1979; Weber *et al.*, 1991). No previous structures of 3,4-substituted cholest-5-en species were found in the Cambridge Structural Database (Allen & Kennard, 1993) and only the β-ketone cholest-5-en-4-one (Wawrzak *et al.*, 1991) had a substituent at the 4-position. However, the C9=C15 bond length of 1.330 (4) Å is in good agreement with the average distance of 1.324 (3) Å found for the 123 cholest-5-en-based fragments with substituents at the 3-position.

The aliphatic chain adopts a fully extended geometry with −*gauche*, *trans* conformation as defined by Duax *et al.* (1980). The C18—C21—C24—C25 torsion angle of 158.7 (3)° is, however, twisted further from 180° than any of the 69 examples given therein (the closest is 166°; see Gilliland *et al.*, 1977). As in (II), the steroid rings *A* and *C* adopt chair conformations, with ring *A* being the more distorted. Ring *B* is a half-chair, with

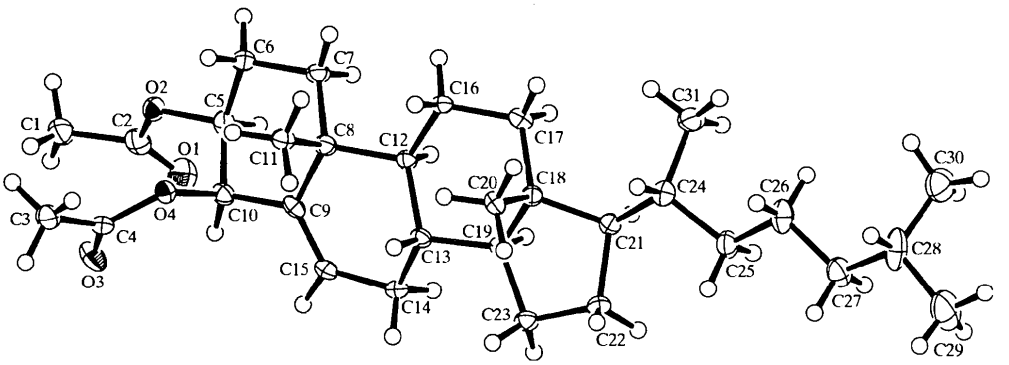


Fig. 1. The molecular structure of (I) showing the atom-numbering scheme. Non-H atoms are drawn as 40% probability displacement ellipsoids and H atoms as spheres of an arbitrary size.