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Crystal Structure of 6-Nitro-cholest-5-ene

Abstract The crystal structure of the title compound ($C_{27}H_{45}NO_2$) has been determined by X-ray crystallographic techniques. The compound crystallizes in the monoclinic space group $P2_1$, with unit cell parameters $a = 12.143(2)$, $b = 10.835(2)$, $c = 19.747(4)$ Å, $\beta = 101.29(1)^\circ$. The structure has been solved by direct methods and refined to $R=0.064$. There are two crystallographically independent molecules, I and II, in the asymmetric unit. In both the molecules, rings A, B and C are conformationally very similar, however pronounced differences are observed in the D ring which assumes a distorted envelope conformation in molecule I and a distorted half-chair conformation in molecule II. The A/B ring junction is *quasi-trans* while ring systems B/C and C/D are *trans* fused in both the molecules I and II. Two bifurcated intramolecular hydrogen bonds have been observed. Molecules are held together by intermolecular C-H...O hydrogen bonds.

Keywords: X-ray crystallography, crystal structure, steroid, conformations

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1. Introduction

The structure analysis of 6-nitro-cholest-5-ene has been taken up as a part of our crystallographic investigations on steroids (GUPTA et al.1994a, 1994b, 1994c; SINGH et al.1994a,1994b,1996). The scheme of preparation for the title compound goes the following way: A suspension of finely powdered cholest-5-ene (12 mg) and acetic acid (100 ml) was vigorously stirred at room temperature with fuming HNO_3 (30 ml) followed by gradual addition of $NaNO_2$ (6 mg) over a period of 2 hours. After complete addition of $NaNO_2$, the mixture was further stirred for about 1 h. Icy-cold water was added and the yellowish solid obtained was extracted with ether. The ethereal solution was thus washed with water and sodium bicarbonate, dried over anhydrous sodium sulphate. Recrystallization from methanol gave 6-nitrocholest-5-ene (8.5 mg) as plates [m.p. 392-393 K].The chemical structure as shown in Figure 1 has been assigned on the basis of IR, UV, NMR and mass spectral data (FIROZ).

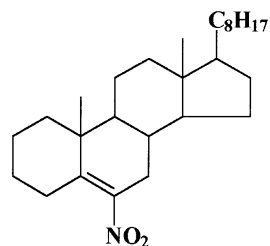


Fig. 1: Chemical structure of 6-nitro-cholest-5-ene

2. Experimental

Three-dimensional intensity data for the steroidal molecule were collected on an Enraf-Nonius CAD-4 diffractometer using $\text{CuK}\alpha$ radiation. $\omega/2\theta$ scan mode was employed. Two strong reflections monitored every 100 reflections showed no significant change in the intensity, confirming the stability of the crystal towards X-rays. The unit cell parameters were refined from measured 2θ values of 25 reflections in the range $9.4 < \theta < 18.2^\circ$. A total of 4023 reflections were recorded upto the θ -value of 60° . Out of these 3832 reflections were treated as observed with $F_o > 4\sigma(F_o)$. The data were corrected for Lorentz and polarization effects. Absorption and extinction corrections were not applied.

The structure has been solved by direct methods using SHELXS86 software (SHELDRICK, 1986). Isotropic refinement of the structure by least-squares methods has been carried out by using SHELXL93 (SHELDRICK, 1993) followed by anisotropic refinement on F^2 of all the non-hydrogen atoms. All H-atom positions were calculated geometrically with $U_{\text{iso}}(\text{H})=1.2 U_{\text{eq}}$ (parent atom). A riding model was used in their refinement ($\text{C-H} = 0.96\text{\AA}$). The final R-index converged to $R=0.064$ and $wR(F^2)=0.213$. Atomic scattering factors were taken from International Tables for Crystallography (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4.). The crystallographic data are summarized in Table 1.

Table 1: Crystal data and other experimental details

Crystal description	: Yellowish plate
Chemical formula	: $\text{C}_{27}\text{H}_{45}\text{NO}_2$
Molecular weight	: 415.7
Cell parameters	: $a = 12.143(2)$, $b = 10.835(2)$, $c = 19.747(4)$ \AA , $\beta = 101.29(1)^\circ$
Unit cell volume	: 2547.82\AA^3
Crystal system	: Monoclinic
Space group	: $P2_1$
Density (calculated)	: 1.084 Mg m^{-3}
No. of molecules per unit cell (Z)	: 4
Radiation	: $\text{CuK}\alpha$
Wavelength (λ)	: 1.5418\AA
Absorption coefficient (μ)	: 0.51 mm^{-1}
F(000)	: 920
Crystal size	: $0.35 \times 0.20 \times 0.10 \text{ mm}$
Refinement of unit cell	: 25 reflections, ($9.4 < \theta < 18.2^\circ$)
θ range for entire data collection	: $2 < \theta < 60^\circ$
No. of measured reflections	: 4023
No. of unique reflections	: 3832
No. of observed reflections	: 3364 [$F_o > 4\sigma(F_o)$]
No. of parameters refined	: 542
Final R-factor	: 0.064
wR	: 0.213
Weight	: $1/[\sigma^2(F_o^2) + (0.1616P)^2 + 0.71P]$; $P = [F_o^2 + 2F_c^2]/3$
Final residual electron density	: $-0.25 < \Delta\rho < 0.33 \text{ e}\text{\AA}^{-3}$
$(\Delta/\sigma)_{\text{max}}$ in the final cycle	: -0.758 (for $U_{13} O1'$)

3. Results and Discussion

The fractional coordinates and equivalent isotropic temperature factors for non-hydrogen atoms are given in Table 2. A general view of the molecule with atomic numbering scheme is shown in Figure 2 (JOHNSON).

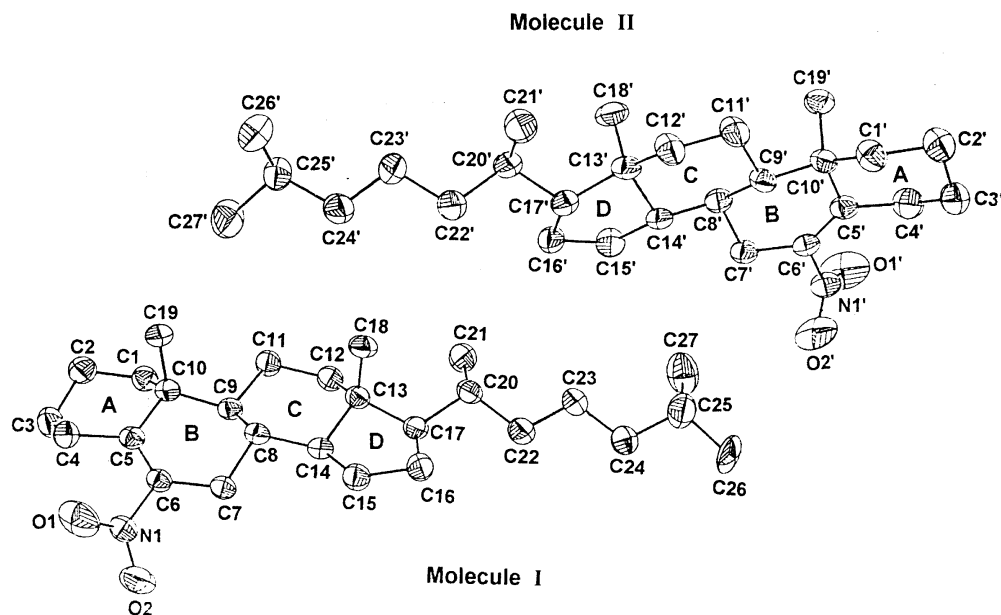


Fig. 2: General view of the molecule, with thermal ellipsoids at 50% probability.

Bond distances and bond angles show good agreement with equivalent parameters reported for 5-ene steroidal molecules (GRIFFIN et al). The agreement in bond lengths and angles of the two crystallographically independent molecules is well within experimental error but the differences become significant in the torsion angles leading to the conformational differences.

In molecule I, ring A has a chair conformation with asymmetry parameters $\Delta C_s(C2-C5) = 3.36$, $\Delta C_2(C2-C3) = 4.11$ (DUAX et al). The ring B adopts half-chair conformation with asymmetry parameter $\Delta C_s(C5-C6) = 7.55$. Ring C has a chair conformation with the best rotational axis bisecting C9-C11 and C13-C14 and asymmetry parameter $\Delta C_2(C9-C11) = 4.29$. The best mirror plane passes through C9 and C13, with $\Delta C_s(C9-C13) = 3.24$. Ring D is a distorted 13β -envelope with a phase angle of pseudo-rotation $\Delta = 18.65^\circ$ and maximum angle of torsion $\phi_m = 46.72^\circ$ (ALTONA et al). The asymmetry parameter $\Delta C_s(C13)$ which gives the distortion from ideal mirror symmetry bisecting the C15-C16 bond is 8.66. Atom C13 is disposed $0.700(4)\text{\AA}$ above the plane defined by the other four ring atoms.

In molecule II, ring A has a chair conformation with asymmetry parameters $\Delta C_s(C2'-C5') = 2.23$, $\Delta C_2(C2'-C3') = 4.14$. The ring B adopts half-chair conformation with asymmetry parameter $\Delta C_2(C5'-C6') = 5.51$. Ring C has a chair conformation with the best rotational axis bisecting C9'-C11' and C13'-C14' and asymmetry parameter $\Delta C_2(C9'-C11') = 3.42$. The best mirror plane passes through C11' and C14', with $\Delta C_s(C11'-C14') = 3.51$. Ring D is a distorted

13 β -14 α half chair with a phase angle of pseudorotation $\Delta = 11.71^\circ$ and maximum angle of torsion $\phi_m = 47.14^\circ$. The asymmetry parameter $\Delta C_2(C13'-C14') = 7.84$.

Table 2: Atomic coordinates and equivalent isotropic thermal parameters (\AA^2)

atom	x	y	z	U_{eq}^*
MOLECULE I				
C1	1.0540(4)	-0.1245(6)	-0.1342(3)	0.069(2)
C2	1.0616(5)	-0.1058(6)	-0.2089(3)	0.078(2)
C3	1.0042(5)	-0.2127(7)	-0.2524(3)	0.084(2)
C4	0.8834(4)	-0.2241(6)	-0.2447(3)	0.072(2)
C5	0.8675(4)	-0.2309(4)	-0.1708(2)	0.055(1)
C6	0.7989(3)	-0.3115(4)	-0.1476(2)	0.051(1)
N1	0.7342(3)	-0.3995(4)	-0.1956(2)	0.062(1)
O1	0.6754(4)	-0.3660(5)	-0.2491(3)	0.121(2)
O2	0.7389(5)	-0.5070(5)	-0.1791(3)	0.113(2)
C7	0.7787(4)	-0.3254(5)	-0.0764(2)	0.056(2)
C8	0.8244(3)	-0.2181(4)	-0.0294(2)	0.053(1)
C9	0.9397(3)	-0.1789(4)	-0.0448(2)	0.053(1)
C10	0.9331(4)	-0.1370(4)	-0.1202(2)	0.056(1)
C19	0.8710(5)	-0.0132(5)	-0.1361(3)	0.068(2)
C11	0.9982(5)	-0.0863(5)	0.0094(3)	0.069(2)
C12	1.0009(4)	-0.1226(5)	0.0843(2)	0.066(2)
C13	0.8845(4)	-0.1517(4)	0.0980(2)	0.057(1)
C18	0.8107(5)	-0.0361(5)	0.0911(3)	0.075(2)
C14	0.8358(3)	-0.2533(4)	0.0460(2)	0.053(1)
C15	0.7326(4)	-0.3003(5)	0.0708(2)	0.067(2)
C16	0.7643(4)	-0.2877(6)	0.1500(3)	0.072(2)
C17	0.8790(4)	-0.2198(5)	0.1665(2)	0.059(2)
C20	0.8969(5)	-0.1458(5)	0.2350(2)	0.069(2)
C21	1.0113(6)	-0.0818(7)	0.2506(3)	0.101(3)
C22	0.8843(5)	-0.2319(6)	0.2955(3)	0.079(2)
C23	0.8929(6)	-0.1695(7)	0.3643(3)	0.086(2)
C24	0.8715(6)	-0.2525(7)	0.4202(3)	0.093(3)
C25	0.8698(7)	-0.1880(9)	0.4898(3)	0.106(3)
C26	0.9695(7)	-0.1167(11)	0.5180(4)	0.114(3)
C27	0.8407(1)	-0.2818(12)	0.5405(4)	0.129(5)
MOLECULE II				
C1'	0.4642(5)	0.3630(7)	0.5943(3)	0.081(2)
C2'	0.4639(5)	0.3824(7)	0.6701(3)	0.090(2)
C3'	0.5264(6)	0.2763(7)	0.7117(3)	0.091(3)
C4'	0.6459(5)	0.2667(7)	0.6996(3)	0.088(2)
C5'	0.6512(4)	0.2588(5)	0.6239(3)	0.062(2)
C6'	0.7152(4)	0.1783(5)	0.5974(3)	0.059(2)
N1'	0.7831(4)	0.0894(5)	0.6433(3)	0.073(2)

O1'	0.8511(6)	0.1169(8)	0.6892(4)	0.161(3)
O2'	0.7740(7)	-0.0150(7)	0.6288(5)	0.128(3)
C7'	0.7269(4)	0.1640(5)	0.5246(2)	0.061(2)
C8'	0.6784(3)	0.2727(5)	0.4793(2)	0.057(2)
C9'	0.5673(4)	0.3145(5)	0.4991(2)	0.059(1)
C10'	0.5815(4)	0.3541(5)	0.5765(3)	0.062(2)
C19'	0.6422(6)	0.4778(5)	0.5900(3)	0.086(2)
C11'	0.5066(5)	0.4106(6)	0.4482(3)	0.083(2)
C12'	0.4951(4)	0.3750(6)	0.3722(3)	0.078(2)
C13'	0.6062(4)	0.3401(4)	0.3530(2)	0.060(1)
C18'	0.6850(5)	0.4513(5)	0.3568(3)	0.084(2)
C14'	0.6563(4)	0.2360(4)	0.4038(2)	0.052(1)
C15'	0.7529(4)	0.1847(6)	0.3728(3)	0.070(2)
C16'	0.7096(4)	0.1942(5)	0.2941(3)	0.067(2)
C17'	0.5986(4)	0.2708(5)	0.2828(2)	0.060(2)
C20'	0.5819(4)	0.3476(5)	0.2157(3)	0.067(2)
C21'	0.4697(5)	0.4198(7)	0.2041(3)	0.089(2)
C22'	0.5864(5)	0.2658(6)	0.1531(3)	0.076(2)
C23'	0.5951(6)	0.3365(6)	0.0876(3)	0.085(2)
C24'	0.6169(6)	0.2561(6)	0.0303(3)	0.086(2)
C25'	0.6456(5)	0.3244(6)	-0.0321(3)	0.079(2)
C26'	0.5498(5)	0.4019(8)	-0.0698(3)	0.096(3)
C27'	0.6855(9)	0.2351(9)	-0.0813(4)	0.120(3)

$$* U_{eq} = (1/3)\sum_i\sum_j U_{ij} a_i^* a_j^* a_i a_j$$

The conformation of ring D in both the crystallographically independent molecules is different to the extent of difference in the value for the phase angle of pseudorotation.

Unit cell packing of the molecules down b-axis is shown in Figure 3. The molecules depict the trueness of monoclinic symmetry with the steroid nucleus overlapping with each other. The intra- and intermolecular C-H...O hydrogen bonds as described in Table 3 contribute to the stabilization of the molecular and crystal structure.

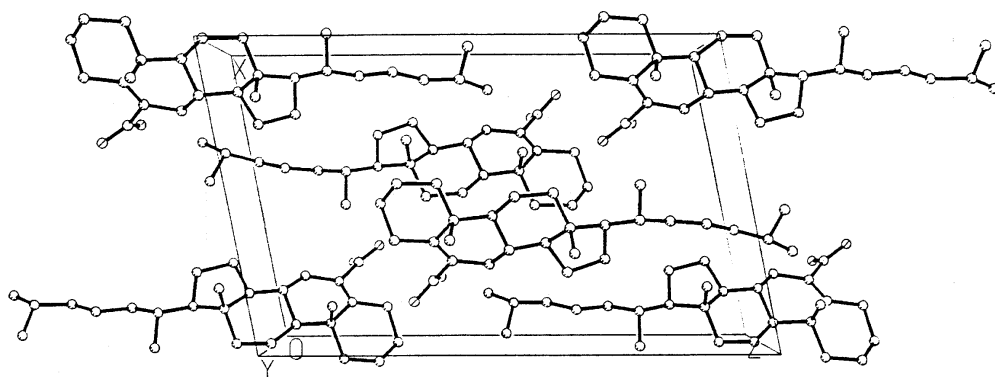


Fig. 3: Packing diagram viewed down the b-axis.

Table 3: Geometry of intra- and intermolecular hydrogen bonds with e.s.d.'s in parentheses

C-H...O	H...O(Å)	C...O(Å)	C-H...O(°)
C4-H42...N1	2.478(7)	2.919(7)	107.4(5)
C4-H42...O1	2.366(8)	2.944(7)	117.6(5)
C4'-H4'2...N1'	2.462(9)	2.903(9)	107.3(6)
C4'-H4'2...O1'	2.438(10)	3.014(10)	117.7(6)
C4-H41...O2 ⁽ⁱ⁾	2.554(11)	3.441(10)	152.0(6)
C4'-H4'1...O2 ⁽ⁱⁱ⁾	2.590(9)	3.459(9)	149.2(7)
C19'-H196...O1 ⁽ⁱⁱ⁾	2.631(8)	3.553(8)	160.8(6)
C27'-H275...O2 ⁽ⁱⁱⁱ⁾	2.660(11)	3.528(11)	150.6(9)

Symmetry Code: (i) X, Y, Z - 1 ;(ii) X, Y + 1, Z + 1 ; (iii) X, Y + 1, Z

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