twist conformation ($C_2$ symmetry) is characterized by $\varphi = 18{,}54, \ldots°$, and the envelope ($C_s$ symmetry) by $\varphi = 0{,}36, \ldots°$. A typical $Q$ value is 0·35 Å in the furanoid ring of sucrose (Brown & Levy, 1973). In the same way, it can be shown that the conformation of the rings in BN52022 are nearly the same as in BN52021, except that the ring $C$ of BN52022 $B$ is almost an envelope, ring $E$ is intermediate between twist and envelope in BN52022 $A$, and envelope in BN52022 $B$; ring $F$ has an intermediate conformation in BN52022 $B$.

The crystal of BN52020 contains van der Waals interactions and four hydrogen bonds: O2H···O100 ($-x$, 0·5+$y$, $-1{\cdot}5-z$), 2·712 (6) Å, O3H···O100 (1$-x$, 0·5+$y$, $-1{\cdot}5-z$), 2·774 (6) Å, O8···HO100 [$x$, 1+$y$, $z$], 2·865 (6) Å and O9···HO100 ($-0{\cdot}5-x$, $-1-y$, 0·5+$z$), 2·726 Å. The distance O4···O10 ($-0{\cdot}5+x$, $-0{\cdot}5-y$, 1$-z$), 2·859 (6) Å is also significantly shorter than the sum of two oxygen van der Waals radii, currently about 3·0 Å. According to Nyburg & Faerman (1985), O4 linked to a single carbon atom by a double bond should have a spherical shape with a radius of 1·54 Å. So the possibility of a non-spherical shape for O(10) in this lactone can be inferred. In the crystal of BN52022, there is a rather complex network of hydrogen bonds involving ethanol and water molecules. Only some C–OH···O angles and OH···O distances are consistent with linear hydrogen bonds: the H included in O22H···O28 and O2H···O202. O23H···O21 and O3H···O1 are intramolecular hydrogen bonds. The other –OH groups participate in bifurcated hydrogen bonds, but it was not possible to identify their hydrogen positions.

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# Crystallographic Studies and Physicochemical Properties of π-Electron Systems. XVI. The Structure of *N,N*-Diethyl-3,4-dinitroaniline: Non-Additivity of Substituent Effect on the Geometry of the Benzene Ring


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**Abstract.** $C_{10}H_{13}N_3O_4$, $M_r = 239{\cdot}23$, monoclinic, $P2_1/c$, $a = 14{\cdot}379$ (2), $b = 9{\cdot}814$ (1), $c = 17{\cdot}793$ (2) Å, $\beta = 109{\cdot}71$ (1)°, $V = 2363{\cdot}9$ (5) Å$^3$, $Z = 8$, $D_m = 1{\cdot}330$, $D_x = 1{\cdot}344$ (10) g cm$^{-3}$; $\lambda$(Cu $K\alpha$) = 1·54178 Å, $\mu = 9{\cdot}63$ cm$^{-1}$, $F(000) = 1008$, room temperature. Final $R = 0{\cdot}0479$, $wR = 0{\cdot}048$ for 2443 counter intensities. The mean e.s.d.'s for bond lengths between heavy atoms are 0·004–0·009 Å and 0·25° for valence angles. Non-additivity of valence angles has been studied by the use of the substituent angular parameters of Domenicano & Murray-Rust [*Tetrahedron Lett.* (1979), **24**, 2283–2286] and Norrestam &

0108-2701/87/122381-04$01.50

Table 1. *Fractional coordinates* ($\times 10^4$), $U_{eq}$($\times 10^4$) *for non-hydrogen atoms*

$U_{eq} = (U_{11}U_{22}U_{33})^{1/3}$.

| | $x$ | $y$ | $z$ | $U_{eq}$(Å$^2$) |
|---|---|---|---|---|
| *CA*1 | −392 (2) | 1079 (3) | 1352 (2) | 460 (16) |
| *CA*2 | 640 (2) | 1074 (3) | 1496 (2) | 486 (18) |
| *CA*3 | 1076 (2) | 1 (3) | 1262 (1) | 459 (17) |
| *CA*4 | 546 (2) | −1130 (3) | 880 (2) | 479 (17) |
| *CA*5 | −461 (2) | −1144 (3) | 735 (2) | 521 (19) |
| *CA*6 | −914 (2) | −75 (3) | 966 (2) | 517 (19) |
| *NA*1 | −831 (2) | 2129 (2) | 1589 (1) | 560 (15) |
| *NA*2 | 2160 (2) | 91 (3) | 1475 (2) | 648 (19) |
| *NA*3 | 988 (2) | −2248 (3) | 601 (2) | 658 (18) |
| *CA*7 | −1911 (2) | 2188 (4) | 1396 (2) | 703 (25) |
| *CA*8 | −119 (3) | 4422 (4) | 1551 (3) | 880 (33) |
| *CA*9 | −274 (3) | 3276 (4) | 2053 (2) | 695 (24) |
| *CA*10 | −2223 (3) | 1516 (6) | 2038 (3) | 926 (34) |
| *OA*1 | 2473 (2) | 790 (3) | 1058 (2) | 1100 (22) |
| *OA*2 | 2656 (2) | −500 (3) | 2067 (2) | 974 (21) |
| *OA*3 | 1842 (2) | −2130 (2) | 631 (2) | 1004 (20) |
| *OA*4 | 499 (2) | −3257 (2) | 338 (2) | 973 (20) |
| *CB*1 | 5495 (2) | 400 (3) | 4046 (2) | 539 (19) |
| *CB*2 | 4452 (2) | 477 (3) | 3811 (2) | 491 (18) |
| *CB*3 | 4001 (2) | 1686 (3) | 3844 (2) | 450 (17) |
| *CB*4 | 4526 (2) | 2877 (3) | 4092 (2) | 482 (17) |
| *CB*5 | 5545 (2) | 2837 (3) | 4297 (2) | 577 (20) |
| *CB*6 | 6016 (2) | 1632 (3) | 4271 (2) | 597 (21) |
| *NB*1 | 5960 (2) | −790 (2) | 4032 (2) | 676 (17) |
| *NB*2 | 2913 (2) | 1709 (3) | 3490 (2) | 593 (17) |
| *NB*3 | 4062 (2) | 4129 (3) | 4212 (1) | 570 (16) |
| *CB*7 | 5426 (2) | −2079 (3) | 3798 (2) | 663 (24) |
| *CB*8 | 5034 (3) | −2335 (5) | 2910 (2) | 925 (31) |
| *CB*9 | 7055 (3) | −893 (6) | 4333 (3) | 804 (43) |
| *CB*10 | 7369 (5) | −485 (6) | 3642 (3) | 1263 (51) |
| *CB*11 | 6886 (6) | −708 (16) | 3835 (7) | 621 (53) |
| *CB*12 | 7744 (11) | −905 (17) | 4597 (7) | 715 (50) |
| *OB*1 | 2458 (2) | 811 (2) | 3683 (2) | 917 (19) |
| *OB*2 | 2542 (1) | 2590 (3) | 2999 (1) | 770 (16) |
| *OB*3 | 3328 (1) | 4061 (2) | 4408 (1) | 749 (16) |
| *OB*4 | 4453 (2) | 5215 (2) | 4131 (1) | 756 (17) |

Table 2. *Bond lengths* (Å) *and valence angles* (°); *distances corrected for libration are in square brackets*

The second column for angles contains values of angles calculated by use of angular parameters (Domenicano & Murray-Rust, 1979). Parameters for nitro group twisted by more than 30° are taken from Norrestam & Schepper (1981). All C—H distances are in the range 0·91–1·08 Å. Assignments: C*A*1 to C*A*6 and C*B*1 to C*B*6 refer to carbon atoms in *A* and *B* molecules, respectively; N*A*1 and C*A*7–C*A*10 and N*B*1 and C*B*7–C*B*12 refer to atoms of the *N,N*-diethylamino group; N*A*2, O*A*1, O*A*2 and N*A*3, O*A*3, O*A*4 and N*B*2, O*B*1, O*B*2 and N*B*3, O*B*3, O*B*4 are atoms belonging to nitro groups.

| | | | | | |
|---|---|---|---|---|---|
| *CA*1–*CA*22 | 1·419 (4) | [1·425] | *CB*1–*CB*2 | 1·416 (4) | [1·423] |
| *CA*2–*CA*3 | 1·361 (4) | 1·367 | *CB*2–*CB*3 | 1·364 (4) | 1·367 |
| *CA*3–*CA*4 | 1·387 (4) | 1·395 | *CB*3–*CB*4 | 1·381 (4) | 1·387 |
| *CA*4–*CA*5 | 1·383 (4) | 1·388 | *CB*4–*CB*5 | 1·387 (4) | 1·392 |
| *CA*5–*CA*6 | 1·369 (5) | 1·375 | *CB*5–*CB*6 | 1·372 (5) | 1·375 |
| *CA*6–*CA*1 | 1·403 (4) | 1·412 | *CB*6–*CB*1 | 1·407 (4) | 1·414 |
| *CA*3–*NA*2 | 1·477 (4) | 1·484 | *CB*3–*NB*2 | 1·477 (3) | 1·483 |
| *CA*4–*NA*3 | 1·438 (4) | 1·446 | *CB*4–*NB*3 | 1·448 (4) | 1·450 |
| *NA*2–*OA*1 | 1·205 (5) | 1·211 | *NB*2–*OB*1 | 1·214 (4) | 1·221 |
| *NA*2–*OA*2 | 1·202 (4) | 1·209 | *NB*2–*OB*2 | 1·216 (3) | 1·222 |
| *NA*3–*OA*3 | 1·217 (4) | 1·223 | *NB*3–*OB*3 | 1·220 (4) | 1·226 |
| *NA*3–*OA*4 | 1·213 (4) | 1·220 | *NB*3–*OB*4 | 1·236 (3) | 1·244 |
| *CA*1–*NA*1 | 1·349 (4) | 1·354 | *CB*1–*NB*1 | 1·349 (4) | 1·354 |
| *NA*1–*CA*7 | 1·473 (4) | 1·481 | *NB*1–*CB*7 | 1·465 (4) | 1·472 |
| *CA*7–*CA*10 | 1·513 (7) | 1·521 | *CB*7–*CB*8 | 1·509 (5) | 1·517 |
| *NA*1–*CA*9 | 1·464 (4) | 1·473 | *NB*1–*CB*9 | 1·486 (4) | 1·492 |
| *CA*9–*CA*8 | 1·499 (6) | 1·507 | *CB*9–*CB*10 | 1·501 (9) | 1·509 |
| | | | *NB*1–*CB*11 | 1·490 (11) | |
| | | | *CB*11–*CB*12 | 1·506 (15) | |
| *CA*1–*CA*2–*CA*3 | 120·6 (3) | 117·92 | *CB*1–*CB*2–*CB*3 | 120·4 (3) | 118·40 |
| *CA*2–*CA*3–*CA*4 | 122·3 (3) | 123·81 | *CB*2–*CB*3–*CB*4 | 122·2 (2) | 122·73 |
| *CA*3–*CA*4–*CA*5 | 117·9 (3) | 118·22 | *CB*3–*CB*4–*CB*5 | 118·4 (3) | 119·63 |
| *CA*4–*CA*5–*CA*6 | 120·7 (3) | 119·56 | *CB*4–*CB*5–*CB*6 | 120·4 (3) | 118·48 |
| *CA*5–*CA*6–*CA*1 | 122·4 (3) | 122·43 | *CB*5–*CB*6–*CB*1 | 121·9 (3) | 122·19 |
| *CA*6–*CA*1–*CA*2 | 116·1 (3) | 118·06 | *CB*6–*CB*1–*CB*2 | 116·6 (3) | 119·19 |
| *CA*2–*CA*3–*NA*2 | 115·5 (2) | | *CB*2–*CB*3–*NB*2 | 116·5 (2) | |
| *NA*2–*CA*3–*CA*4 | 122·1 (3) | | *NB*2–*CB*3–*CB*4 | 120·7 (2) | |
| *CA*3–*NA*2–*OA*1 | 117·2 (2) | | *CB*3–*NB*2–*OB*1 | 117·5 (2) | |
| *CA*3–*NA*2–*OA*2 | 117·4 (3) | | *CB*3–*NB*2–*OB*2 | 117·5 (3) | |
| *OA*1–*NA*2–*OA*2 | 125·4 (3) | | *OB*1–*NB*2–*OB*2 | 124·9 (2) | |
| *CA*3–*CA*4–*NA*3 | 123·0 (3) | | *CB*3–*CB*4–*NB*3 | 122·4 (2) | |
| *NA*3–*CA*4–*CA*5 | 119·0 (2) | | *NB*3–*CB*4–*CB*5 | 119·0 (2) | |
| *CA*4–*NA*3–*OA*3 | 118·0 (3) | | *CB*4–*NB*3–*OB*3 | 118·8 (2) | |
| *CA*4–*NA*3–*OA*4 | 119·3 (3) | | *CB*4–*NB*3–*OB*4 | 117·7 (3) | |
| *OA*3–*NA*3–*OA*4 | 122·7 (3) | | *OB*3–*NB*3–*OB*4 | 123·5 (3) | |
| *CA*2–*CA*1–*NA*1 | 121·2 (2) | | *CB*2–*CB*1–*NB*1 | 121·5 (3) | |
| *NA*1–*CA*1–*CA*6 | 122·7 (3) | | *NB*1–*CB*1–*CB*6 | 121·9 (3) | |
| *CA*1–*NA*1–*CA*7 | 121·6 (2) | | *CB*1–*NB*1–*CB*7 | 122·5 (2) | |
| *CA*1–*NA*1–*CA*9 | 122·6 (2) | | *CB*1–*NB*1–*CB*9 | 121·6 (3) | |
| *CA*7–*NA*1–*CA*9 | 115·8 (3) | | *CB*7–*NB*1–*CB*9 | 115·7 (3) | |
| *NA*1–*CA*7–*CA*10 | 111·3 (3) | | *NB*1–*CB*7–*CB*9 | 114·6 (3) | |
| *NA*1–*CA*9–*CA*8 | 113·8 (3) | | *NB*1–*CB*9–*CB*10 | 105·2 (4) | |
| | | | *NB*1–*CB*11–*CB*12 | 107·9 (11) | |
| | | | *CB*1–*NB*1–*CB*11 | 116·4 (7) | |

Schepper [*Acta Chem. Scand. Ser. A* (1981), **35**, 91–103]. The percentage of quinoid structure contribution has been estimated by the HOSE model [Krygowski, Anulewicz & Kruszewski (1983). *Acta Cryst.* B**39**, 732–739].

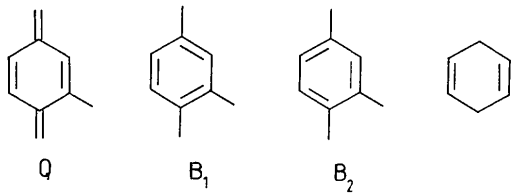
**Introduction.** As a continuation of our studies on derivatives of *p*-nitroaniline (Maurin & Krygowski, 1987*a*,*b*), the title compound, hereafter abbreviated DDA, was chosen to analyse the role of overcrowding of substituents on the geometry of the benzene ring.

**Experimental.** Orange prismatic crystals were grown from ethanol solution. Monoclinic symmetry was estimated from oscillation and Weissenberg photographs. A crystal *ca* 0·3 × 0·3 × 0·3 mm was mounted on a Syntex $P2_1$ single-crystal diffractometer. $D_m$ measured by flotation at 293 K in aqueous solution of KI. Systematic absences: *h*0*l*, *l* odd, 0*k*0 *k* odd, space group $P2_1/c$. Cell constants determined by the least-squares treatment of 15 reflections with $2\theta$ values between 22·6 and 28·1°. Intensities collected at room temperature using Cu $K\alpha$ radiation monochromated by graphite up to $2\theta = 115{\cdot}0°$, $-15 \le h \le 14$, $0 \le k \le 10$ and $0 \le l \le 19$, $\omega$–$2\theta$ scan mode. Profile analysis according to Lehmann & Larsen (1974), no significant variation for 2 standard reflections, 3206 unique intensities collected, 155 of them systematically absent, 2443 classified as observed [$F_o > 3{\cdot}92\sigma(F)$]. Corrections for Lorentz–polarization effects and for secondary extinction but not for absorption. The structure was solved using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and refined using *SHELX*76 (Sheldrick, 1976). Atomic structure factors supplied by the program. *E* map gave position of 22 non-hydrogen atoms. Other heavy atoms were located from $\Delta\rho$ map ($R = 0{\cdot}314$). Isotropic refinement gave an *R* value of 0·166, anisotropic refinement gave 0·099. Location of hydrogen atoms and refinement of their positions led to final $R = 0{\cdot}061$ and $wR = 0{\cdot}062$ with $(\Delta/\sigma)_{max} = 0{\cdot}18$ and mean value 0·05. Weights were based on $w_i(F) = G/\sigma^2(F_i)$. The final difference density map showed two maxima of heights 0·66 and 0·5 e Å$^{-3}$ in the ethyl-group region in

one molecule. Application of the partial-disorder model for this group led to final $R = 0.0479$ and $wR = 0.0483$. Differenece Fourier peaks $-0.193$ and $0.208$ e Å$^{-3}$. $\Delta/\sigma$ values in final cycle of the refinement were in the same range as before. The s.o.f. factors for the disordered ethyl group were 0·7624 and 0·2376, respectively.

**Discussion.** The final atomic parameters are given in Table 1,* and Table 2 presents bond lengths and valence angles, measured (first column) and calculated by the use of angular parameters (Domenicano & Murray-Rust, 1979; Norrestam & Schepper, 1981). Fig. 1 presents a projection of the cell contents along the $x$ axis, and the assignment of atoms. No significant short contacts are observed for DDA. Bond lengths and angles of the substituted ring are significantly deformed from $C_6$ symmetry.

The changes in bond lengths due to the substituent have been studied by the HOSE model (Krygowski, Anulewicz & Kruszewski, 1983). This model utilizes the geometry of the molecule to calculate its stabilization energy, and then to estimate the weights of the contributions of the canonical structures taken into account. The following results are obtained.




* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44169 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

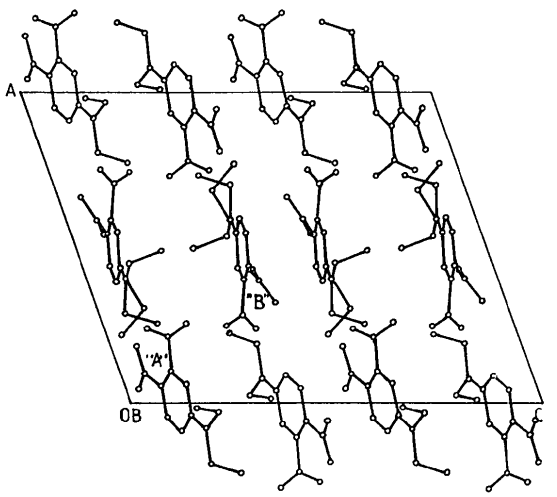



Fig. 1. Projection of the cell contents along **b**.

For molecule $A$ $\%B_1 = 25.2$, $\%B_2 = 33.2$ and $\%Q = 41.6$, whereas for molecule $B$ $\%B_1 = 27.7$, $\%B_2 = 31.1$ and $\%Q = 41.2$. As a rule the C5–C6 bond length is longer by *ca* 0·008 Å than the C2–C3 one, most probably owing to the electronegativity effect of the nitro group at C3 as required by the Walsh rule (Domenicano, Vaciago & Coulson, 1975). As a result $\%B_2 > \%B_1$ for both molecules of DDA. The C1–N1 bond length, 1·354 Å [corrected for libration by *THMB*6 (Trueblood, 1984)], is significantly shorter than the same bond in aniline [1·402 Å (Lister, Tyler & Hog, 1974)] and almost of the same length as in *p*-nitroaniline (Colapietro, Domenicano, Marciante & Portalone, 1982) for which $\%Q = 40.4$.

The changes in valence angles are analysed by using angular substituent parameters (Domenicano & Murray-Rust, 1979; Norrestam & Schepper, 1981) for the $NO_2$ group non-coplanar with the ring plane.

The angles deviating most from additivity are those at C1, C2 and C5. This result cannot be easily rationalized. The sum of the exocyclic valence angles N3–C4–C3 and C4–C3–N2 is 245·2° for the $A$ molecule and 243·1° for the $B$ molecule. These values are in line with the angles between the $NO_2$ planes and the benzene ring: 9·27 and 80·07° for the $A$ molecule and 32·28 and 47·61° for the $B$ molecule.

Evidently, in the first case steric hindrance between both nitro groups may lead to larger values of the above-mentioned sum of angles. Another consequence is a lengthening of the C4–C3 bond [1·395 (4) Å] in comparison with molecule $B$ where no such interactions were observed and hence the bond length is 1·387 (4) Å. Similar effects were observed in *o*-nitro-substituted benzoic acids (Więckowski & Krygowski, 1985; Grabowski & Krygowski, 1985).

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# Structure of a New Deoxygenated Etorphine Analogue

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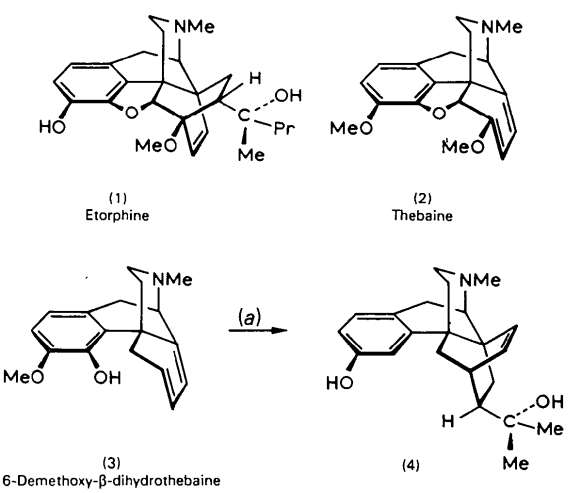
**Abstract.** (+)-3-Hydroxy-α,α,17-trimethyl-6β,14β-ethenomorphinan-7β-methanol, $C_{22}H_{29}NO_2$, $M_r$ = 339·5, orthorhombic, $P2_12_12_1$, $a$ = 7·810 (2), $b$ = 14·152 (2), $c$ = 16·705 (4) Å, $V$ = 1846·4 Å$^3$, $Z$ = 4, $D_x$ = 1·23 Mg m$^{-3}$, Mo $K\alpha$, $\lambda$ = 0·71069 Å, $\mu$ = 0·083 mm$^{-1}$, $F(000)$ = 736, $T$ = 293 K, $R$ = 0·040 for 2387 observed [$I > \sigma(I)$] reflections. The etheno bridge is in the 6β,14β position and the dimethylmethanol substituent is in the 7β position of the morphinan skeleton, confirming that the title compound is a novel deoxygenated etorphine analogue.

**Introduction.** Etorphine, (−)-(*R*)-4,5α-epoxy-3-hydroxy-6-methoxy-α,17-dimethyl-α-propyl-6α,14α-ethenomorphinan-7α-methanol (1) is a semisynthetic analgesic which is approximately 1000 times more potent than morphine; however, it has undesirable side effects. It is prepared from the opium alkaloid thebaine (2) (Lewis, Bentley & Cowan, 1971). In our search for the synthesis of etorphine analogues with fewer oxygen-containing substituents we started from 6-demethoxy-β-dihydrothebaine [6,7,8,14-tetradehydro-3-methoxy-17-methylmorphinan-4-ol, (3)]. Diels–Alder reaction with methyl vinyl ketone afforded 7β-acetyl-3-methoxy-17-methyl-6β,14β-ethenomorphinan-4-ol (van Koningsveld, Lie & Maat, 1984). In order to remove the hydroxyl group in position 4, it was converted into the phenyl ether through an Ullmann reaction with bromobenzene, followed by treatment with sodium in liquid ammonia. The methanol substituent on position 7β was obtained from the acetyl substituent by means of a Grignard reaction with methyl magnesium bromide. Finally, the methyl ether in position 3 was hydrolyzed with potassium hydroxide in boiling 1,2-ethanediol. It is plausible that during the Ullmann reaction or the treatment in liquid ammonia epimerization of the acetyl substituent in position 7β could occur. The single-crystal X-ray analysis of the end product (4), reported here, proved that the methanol substituent was still in the 7β position.




(*a*) (i) $CH_2=CHCOCH_3$, (ii) PhBr, (iii) MeMgBr, (iv) KOH/$CH_2OHCH_2OH$

**Experimental.** Title compound was prepared in the Laboratory of Organic Chemistry (Linders, Kokje, Overhand, Lie & Maat, 1987). Crystals grown from hexane/diethyl ether, m.p. 457–459 K, $[\alpha]_D^{25°C}$ + 55° [chloroform/ethanol 9:1, 0·7 g dm$^{-3}$]. $D_m$ not

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