Fig. 2. Packing diagram of the crystal structure of acetamidine viewed along the c axis. Hydrogen bonds are indicated by thin lines.

The molecular packing in the crystal structure of acetamidine is shown in Fig. 2. Each molecule is hydrogen bonded to four adjacent molecules in such a way that a three-dimensional network of hydrogen bonds is formed. The amino N(2) atoms are donors in the hydrogen bonds while the imino N(1) are acceptors. The N···N distances in the two symmetry-independent hydrogen bonds, N(2)–H(6)···N(1;$y-\frac{1}{2},\bar{x},\frac{1}{2}+z$) and N(2)–H(5)···N(1;$-y,x,\frac{1}{2}-z$), are 2·960 (1) and 3·143 (1) Å respectively. The corresponding H···N distances are 2·05 (2) and 2·25 (2) Å. The rather short 3·277 (1) Å non-bonded contact N(2)···N(2;$\bar{x},\bar{y},1-z$) observed is probably due to the hydrogen-bond scheme.

The hydrogen H(4) of the imino group does not participate in hydrogen bonding but is directed into what can be considered as channels [passing through $\pm(\frac{1}{4}, \frac{3}{4}, 0)$] along the c direction (cf. Fig. 2). Similarly the methyl group at C(2) is pointing into hydrophobic channels along c [through $\pm(\frac{1}{4}, \frac{1}{4}, 0)$].

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Structures of Two Synthetic Homotaxanes, C21H30O

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Abstract. rel-(1S, 3S, 8R, 13R, 16S)-4,8,12,16-Tetra-methyltetracyclo[11.3.1.0^{3,8}.0^{11,16}]heptadeca-4,11-diene-9-one and its C(8) epimer [called (8t), (8c) respectively] are both monoclinic, $P2_1/c$, $M_r = 298\cdot4$. For (8t) (m.p. 419·5 − 420·0 K), $a = 9\cdot489$ (5), $b = 10\cdot692$ (4), $c = 16\cdot876$ (11) Å, $\beta = 95\cdot23$ (4)°, $Z = 4$, $F(000) = 656$, $D_m = 1\cdot14$, $D_x = 1\cdot17$ g cm^{-3}; and for (8c) (m.p. 384·0 − 384·5 K), $a = 12\cdot417$ (3), $b = 11\cdot762$ (3), $c = 25\cdot267$ (6) Å, $\beta = 110\cdot34$ (2)°, $Z = 8$, $F(000) = 1312$, $D_m = 1\cdot10$, $D_x = 1\cdot15$ g cm^{-3}. Diffractometer data (Mo $K\alpha$, Nb-filtered, $\lambda = 0\cdot7107$ Å, $\mu = 0\cdot62$ cm^{-1}) were collected at 292 K at low resolution ($\sin\theta/\lambda < 0\cdot5$ Å^{-1}) giving $R = 0\cdot08$ (2962 reflections) for (8t); $R = 0\cdot11$ (2633 reflections) for (8c). These structure determinations prove the utility of an intramolecular Diels–Alder reaction for direct construction of the homotaxane ring systems [(8t) and (8c)]. The synthetic (8t) has the same relative configuration as naturally occurring taxane diterpenes.

Introduction. The taxane diterpenes isolated from various species of Taxus have an unusual tricyclic

framework† (Fig. 1), with a sterically congested eight-membered B ring and a bridgehead double bond (Miller, 1980). Some of these diterpenes have highly promising antileukemic and antitumor activity (Wani, Taylor, Wall, Coggon & McPhail, 1971). Because of their structural, pharmacological and biogenetic properties, they have attracted considerable interest among synthetic chemists (for references, see Sakan & Craven, 1983). The major difficulty in achieving stereocontrolled closure of the B ring has recently been overcome by using an intramolecular Diels–Alder reaction (Sakan & Craven, 1983). X-ray crystal structure determinations have shown that in the presence of Me_2AlCl as catalyst, the product is $(8c)$‡ (Fig. 2), while $(8t)$ (Fig. 3) is the major product of the uncatalyzed reaction.

Experimental. Crystals were nearly opaque plates with many small inclusions which may explain $D_x > D_m$ (measurements by flotation in aqueous potassium sodium tartrate). After exploratory precession photography, crystals $0.2 \times 0.3 \times 0.5$ mm $(8c)$ and $0.2 \times 0.6 \times 0.8$ mm $(8t)$ were mounted with c^* close to the diffractometer φ axis (Enraf–Nonius CAD-4). Lattice parameters from least-squares fitting of $\sin^2\theta$ for 39 $(8c)$ and 104 $(8t)$ reflections with $\theta < 20°$ measured at $\pm\theta$. Integrated intensities obtained by $\theta/2\theta$ scans in one quadrant of reciprocal space with $\theta_{max} = 22°$ $(8c)$ and $25°$ $(8t)$. Beyond these limits reflections were very weak. Three monitor intensities constant within 5%. Variances in intensities assumed to be $\sigma^2(I) = \sigma^2 + (0.03I)^2$. No extinction or absorption corrections. For $(8c)$ the structure was based on 2633 reflections $(|F_o| > 3\sigma)$ out of 5257 total. For $(8t)$ all 2962 reflections included. In both structures, the phase problem was solved readily by symbolic addition and tangent refinement (Karle & Karle, 1966) giving well defined E maps with all C and O atoms. Structure refinement by block-diagonal least-squares methods minimizing $\sum w\Delta^2$ where $w = \sigma^2(F_o)$ and $\Delta = |F_o| - |F_c|$. All H atoms in $(8t)$ and all but nine in $(8c)$ [belonging to methyl groups $C(16)A$, $C(16)B$ and $C(18)B$] from difference Fourier map. The 51 observed H atoms were included with fixed parameters including B_{iso} derived from the appropriate bonded C atom. Atomic scattering factors from Cromer & Waber (1965) for C, O, and from Stewart, Davidson & Simpson (1965) for H. Refinement with anisotropic

temperature factors for $(8t)$ [isotropic for $(8c)$] gave convergence with $R_w = 0.07$, goodness-of-fit 1.16 for $(8t)$ and 0.10, 2.28 for $(8c)$. For $(8t)$, a difference Fourier map showed no significant residual electron density. For $(8c)$, the most significant residual features $[0.27, 0.23 (5) e Å^{-3}]$ appear to be H atoms bonded to $C(16)A$ and $C(18)B$. However, the $(8c)$ structure determination was terminated, it having been shown conclusively that both molecules A and B lack the desired $(8t)$ stereochemistry. No correction for secondary extinction.
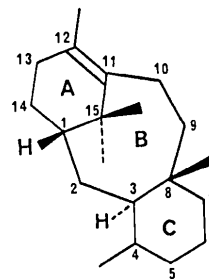

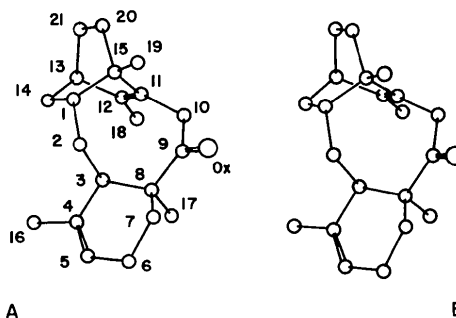Fig. 1. The taxane skeleton numbered according to Lythgoe et al. (1964).

Fig. 2. The two independent molecules A, B in the crystal structure $(8c)$ are viewed in orientations which simulate a stereopair.
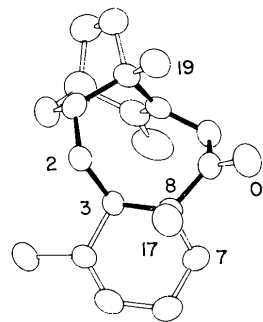
Fig. 3. The molecular framework as observed in the crystal structure of $(8t)$. Atoms are represented as 50% probability thermal ellipsoids. Bonds of the eight-membered B ring are emphasized.

† Except in the IUPAC name (*Abstract*), we used the atom numbering system proposed by Lythgoe, Nakanishi & Uyeo (1964). The two systems differ in the A ring.

‡ The synthetic products and their crystal structures are enantiomeric. For convenience we denote $(8t)$ as the product having the same relative configuration as the naturally occurring taxane skeleton (Fig. 1) and $(8c)$ as the product which differs only in the configuration at C(8). Here t or c refers to a B/C ring junction which is either *trans*, or *cis*.

Discussion. Final values for C- and O-atom parameters are in Tables 1 and 2.* In (8c), the two independent molecules A and B have very similar structures and orientations in the crystal. They are related by a pseudo-glide plane which accounts for the weakness of reflections h0l with h odd.

There are no unusual features in the bond lengths and angles. Thus, C—C distances between tetrahedral C atoms range from 1·52 to 1·58 (1) Å and C=C distances from 1·31 to 1·34 (1) Å. In (8c), the most significant differences between molecules A and B occur near C(10). Bond lengths C(9)—C(10) are 1·50, 1·53 (1) Å, bond angles C(9)—C(10)—C(11) are 116·0, 113·4 (7)° and torsion angles C(9)—C(10)—C(11)—C(15) are 59, 63 (1)° in A and B respectively. As expected, the most significant differences between (8t) and (8c) are in the torsion angles at the B/C ring junction and in the C ring (Table 3). The cyclohexene C ring has a half-chair conformation in both (8t) and (8c). However, the C-ring conformations in (8t) and (8c) are related by inversion as can be seen from the corresponding internal torsion angles which are similar in magnitude, but opposite in sign (Table 3). The eight-membered B ring in both (8t) and (8c) is folded at C(3)···C(11) to give the boat–chair conformation which appears to be preferred in cyclooctane rings (Dunitz & Mugnoli, 1966). The B ring has very similar conformations in the crystal structures of other taxane derivatives which are of natural origin (Shiro &

* Lists of structure factors, anisotropic thermal parameters for (8t), H-atom parameters, bond lengths and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38722 (50 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Koyama, 1971; Castellano & Hodder, 1973; Chauvière, Guénard, Pascard, Picot, Potier & Prangé, 1982).* In (8t) and (8c), the average internal bond angle in the B ring is 116° in each molecule. The shortest 1:5 transannular distance† C(3)···C(11) is 2·99 Å in (8t) and 3·01, 3·03 Å in (8c). The ring substituents give rise to non-bonding distances C(9)···C(19) which are 3·01 Å in (8t) and 3·17, 3·15 Å (8c), and also

* Detailed results are not available for two other taxane structure determinations (Chan, Halsall, Hornsby, Oxford, Sabel, Bjamer, Ferguson & Monteath Robertson, 1966; Wani et al., 1971). Structures have also been determined for natural products with ring systems similar to the taxanes (Turner & McEwen, 1974; Burke, Chan, Honkan, Blount & Marchand, 1980).

† E.s.d.'s in intramolecular distances are 0·01 Å.

Table 1. Atomic parameters for (8t)

For C and O atoms fractional atomic positional parameters ($\times 10^4$) are listed with their e.s.d.'s in parentheses. Values of B_{eq} were obtained according to Hamilton (1959).

	x	y	z	$B_{eq}(\text{Å}^2)$
C(1)	8051 (6)	1350 (5)	1823 (3)	4·3 (4)
C(2)	8671 (5)	2643 (5)	2047 (3)	3·5 (3)
C(3)	8771 (5)	3607 (5)	1359 (3)	3·0 (3)
C(4)	10252 (5)	4210 (5)	1369 (3)	3·2 (3)
C(5)	10448 (5)	5368 (5)	1141 (3)	4·1 (3)
C(6)	9308 (6)	6265 (5)	841 (3)	4·6 (4)
C(7)	7916 (6)	5591 (5)	661 (3)	3·9 (3)
C(8)	7607 (5)	4654 (5)	1320 (3)	3·2 (3)
C(9)	6083 (5)	4240 (5)	1064 (3)	3·7 (3)
C(10)	5749 (5)	3177 (5)	478 (3)	4·1 (3)
C(11)	6454 (5)	1946 (5)	652 (3)	3·5 (3)
C(12)	7201 (6)	1312 (5)	150 (3)	4·3 (4)
C(13)	7935 (7)	161 (6)	520 (4)	5·6 (4)
C(14)	8903 (6)	615 (6)	1238 (5)	5·4 (4)
C(15)	6477 (5)	1368 (5)	1486 (3)	4·2 (4)
C(16)	11531 (6)	3401 (6)	1581 (4)	5·2 (4)
C(17)	7627 (6)	5364 (6)	2117 (3)	4·7 (4)
C(18)	7453 (7)	1646 (7)	−696 (4)	6·4 (5)
C(19)	5513 (6)	1982 (6)	2050 (4)	5·5 (5)
C(20)	5970 (7)	−6 (6)	1378 (4)	6·4 (5)
C(21)	6832 (7)	−727 (6)	810 (5)	6·9 (6)
O	5110 (4)	4879 (4)	1257 (3)	5·9 (5)

Table 2. Atomic parameters for (8c)

Fractional atomic positional parameters ($\times 10^4$) and isotropic thermal parameters (Å^2) are listed with e.s.d.'s in parentheses. Tabulated coordinates give the opposite chirality for molecules A and B. Note the approximate glide-plane symmetry: $x_B \simeq 0.5 + x_A$; $y_B \simeq 0.6 - y_A$; $z_B \simeq z_A$.

	Molecule A				Molecule B			
	x	y	z	B	x	y	z	B
C(1)	2883 (6)	5809 (6)	773 (3)	3·4 (2)	7932 (7)	259 (7)	639 (3)	4·3 (2)
C(2)	2762 (6)	4488 (7)	767 (3)	3·8 (2)	7969 (6)	1564 (6)	645 (3)	3·4 (2)
C(3)	3844 (6)	3767 (6)	1096 (3)	3·2 (2)	9083 (6)	2188 (6)	1034 (3)	3·1 (1)
C(4)	3987 (6)	2831 (7)	718 (3)	4·1 (2)	9401 (6)	3097 (7)	682 (3)	3·8 (2)
C(5)	3713 (7)	1757 (7)	757 (4)	5·0 (2)	9259 (7)	4216 (8)	739 (4)	5·2 (2)
C(6)	3279 (8)	1290 (8)	1199 (4)	5·9 (2)	8735 (8)	4696 (8)	1138 (4)	6·2 (2)
C(7)	2994 (7)	2251 (7)	1538 (3)	4·5 (2)	8236 (7)	3800 (7)	1425 (3)	5·0 (2)
C(8)	3848 (6)	3256 (6)	1660 (3)	3·2 (2)	8977 (6)	2730 (6)	1574 (3)	3·1 (2)
C(9)	3583 (6)	4072 (6)	2065 (3)	3·5 (2)	8502 (7)	1942 (7)	1920 (3)	4·2 (2)
C(10)	4175 (6)	5193 (6)	2231 (3)	3·7 (2)	8951 (7)	742 (7)	2107 (3)	4·3 (2)
C(11)	4137 (6)	5971 (6)	1756 (3)	3·1 (1)	8971 (6)	5 (6)	1635 (3)	3·4 (2)
C(12)	5025 (6)	6263 (6)	1606 (3)	3·4 (2)	9891 (6)	−397 (7)	1558 (3)	3·6 (2)
C(13)	4725 (6)	6937 (7)	1071 (3)	3·4 (2)	9667 (7)	−1053 (7)	1022 (3)	5·0 (2)
C(14)	3888 (6)	6231 (7)	600 (3)	4·1 (2)	8982 (7)	−278 (7)	527 (3)	4·5 (2)
C(15)	2998 (6)	6362 (7)	1342 (3)	3·6 (2)	7862 (7)	−285 (7)	1178 (3)	4·1 (2)
C(16)	4479 (7)	3184 (8)	259 (4)	5·3 (2)	9943 (7)	2652 (8)	264 (3)	5·0 (2)
C(17)	5073 (7)	2838 (7)	1997 (3)	4·3 (2)	10192 (7)	3030 (7)	1976 (3)	4·9 (2)
C(18)	6296 (7)	5975 (7)	1905 (3)	4·6 (2)	11156 (7)	−239 (7)	1937 (3)	5·1 (2)
C(19)	1946 (7)	6145 (7)	1509 (3)	4·7 (2)	6738 (8)	54 (8)	1276 (4)	6·2 (2)
C(20)	3049 (7)	7675 (7)	1270 (3)	5·0 (2)	7794 (8)	−1612 (8)	1087 (4)	6·5 (2)
C(21)	4116 (7)	8027 (8)	1131 (4)	5·2 (2)	8902 (8)	−2086 (9)	1021 (4)	6·9 (2)
O	2893 (5)	3771 (5)	2300 (2)	5·5 (1)	7742 (5)	2325 (5)	2096 (3)	6·6 (1)

Table 3. *Torsion angles* (°) *in* (8t) *and* (8c)

Since the atomic coordinates listed for molecule B (8c) correspond to the opposite chirality from A, the signs of all the calculated torsion angles for molecule B have been changed. This enables a direct comparison with molecule A, and (8t).

	(8t)	(8c), A	(8c), B
C(15)–C(1)–C(2)–C(3)	−64·4 (6)	−72·3 (9)	−71·1 (9)
C(1)–C(2)–C(3)–C(8)	103·6 (5)	105·0 (8)	104·9 (8)
C(2)–C(3)–C(8)–C(9)	−69·6 (6)	−49·9 (9)	−49·8 (8)
C(3)–C(8)–C(9)–C(10)	−32·3 (7)	−50·1 (10)	−50·3 (10)
C(8)–C(9)–C(10)–C(11)	53·6 (7)	54·4 (10)	53·7 (10)
C(9)–C(10)–C(11)–C(15)	47·6 (7)	59·2 (9)	63·4 (9)
C(10)–C(11)–C(15)–C(1)	−114·6 (5)	−112·4 (7)	−115·5 (8)
C(11)–C(15)–C(1)–C(2)	71·5 (5)	66·7 (8)	65·4 (8)
C(2)–C(3)–C(4)=C(5)	−147·0 (5)	−103·2 (9)	−107·1 (9)
C(3)–C(4)=C(5)–C(6)	−0·1 (8)	−3·5 (14)	2·3 (13)
C(4)=C(5)–C(6)–C(7)	−12·6 (8)	10·0 (13)	7·2 (13)
C(5)–C(6)–C(7)–C(8)	44·6 (6)	−38·2 (10)	−38·2 (10)
C(6)–C(7)–C(8)–C(3)	−63·8 (5)	59·9 (9)	59·6 (9)
C(7)–C(8)–C(3)–C(4)	47·7 (5)	−49·9 (8)	−48·4 (8)
C(8)–C(3)–C(4)=C(5)	−18·5 (7)	24·1 (10)	18·8 (10)
C(1)–C(15)–C(11)=C(12)	60·2 (6)	59·4 (8)	61·7 (9)
C(15)–C(11)=C(12)–C(13)	−0·9 (7)	1·4 (10)	−1·2 (10)
C(11)=C(12)–C(13)–C(14)	−58·2 (6)	−58·2 (9)	−55·7 (9)
C(12)–C(13)–C(14)–C(1)	56·2 (6)	50·9 (8)	49·7 (9)
C(13)–C(14)–C(1)–C(15)	0·6 (6)	6·3 (8)	6·6 (9)
C(14)–C(1)–C(15)–C(11)	−56·6 (5)	−60·7 (7)	−60·5 (8)
C(14)–C(1)–C(15)–C(20)	57·9 (6)	55·3 (8)	55·7 (8)
C(1)–C(15)–C(20)–C(21)	−59·6 (6)	−63·0 (8)	−64·4 (9)
C(15)–C(20)–C(21)–C(13)	−0·5 (7)	3·8 (8)	4·3 (10)
C(20)–C(21)–C(13)–C(14)	60·7 (7)	59·2 (8)	59·0 (9)
C(20)–C(21)–C(13)–C(12)	−55·5 (7)	−57·8 (8)	−57·6 (9)
C(17)–C(8)–C(9)=O	30·4 (7)	−106·5 (8)	−107·2 (8)
C(7)–C(8)–C(9)=O	−84·7 (6)	10·5 (9)	10·2 (9)

O···C(19), 3·38 Å in (8t) and 3·40, 3·34 Å in (8c). Short intramolecular distances which are equivalent because of the different configuration at C(8) are O···C(17), 2·73 Å in (8t) and O···C(7), 2·66, 2·64 Å in (8c). Thus in both the C(8) epimers there is steric crowding of three B ring substituents, namely the O atom, the C(19) methyl group and either the C(17) methyl group in (8t) or the C(7) methylene group in

(8c). There are no unusually short intermolecular distances.

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The Structure of the Complex Between Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) and *N,N*-Dimethylformamide (DMF), C₄H₈N₈O₈.C₃H₇NO. A Second Polymorph

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Abstract. The structure of a previously unknown polymorph, α-HMX–DMF, is reported. $M_r = 369 \cdot 3$, monoclinic, $C2/c$, $a = 22 \cdot 627$ (10), $b = 16 \cdot 000$ (4), $c = 13 \cdot 849$ (6) Å, $\beta = 114 \cdot 09$ (3)°, $V = 4577 \cdot 0$ (30) Å³, $Z = 12$, $D_x = 1 \cdot 607$ g cm⁻³, Mo $K\alpha$, $\lambda = 0 \cdot 71073$ Å, $\mu = 1 \cdot 38$ cm⁻¹, $F(000) = 2304$, $T = 297$ K, $R = 0 \cdot 0618$ for 1858 observed reflections. The DMF molecule exhibits twofold disorder. Overall, this polymorph and a previously reported polymorph of HMX–DMF are very similar. The most important non-hydrogen-atom intermolecular interactions between HMX molecules are O···CNC and O···CNNO contacts. These are the same types of heavy-atom associations that dominate the pure HMX polymorphs, which suggests that

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