C9	0.25369 (11)	−0.0045 (4)	0.9099 (2)	0.0445 (8)
O10	0.05879 (6)	0.1848 (2)	0.48419 (9)	0.0384 (5)
C11	0.05805 (11)	0.0067 (4)	0.4126 (2)	0.0407 (8)

Table 2. *Selected geometric parameters* (Å, °)

O2—C1	1.362 (3)	O8—C4	1.373 (2)
C7a—C1	1.358 (3)	C6—C5	1.445 (3)
C3—O2	1.364 (2)	C7—C6	1.350 (3)
C3a—C3	1.360 (3)	C7a—C7	1.431 (3)
C4—C3a	1.432 (3)	O10—C7	1.374 (2)
C7a—C3a	1.441 (2)	C9—O8	1.431 (3)
C5—C4	1.349 (3)	C11—O10	1.428 (3)
O2—C1—C7a	109.9 (2)	C7—C6—C5	121.4 (2)
C3—O2—C1	107.8 (2)	C7a—C7—O10	114.3 (2)
C3a—C3—O2	109.6 (2)	C7a—C7—C6	118.8 (2)
C4—C3a—C7a	119.7 (2)	O10—C7—C6	126.9 (2)
C4—C3a—C3	133.9 (2)	C1—C7a—C3a	106.2 (2)
C7a—C3a—C3	106.4 (2)	C1—C7a—C7	134.1 (2)
C5—C4—O8	127.0 (2)	C3a—C7a—C7	119.7 (2)
C5—C4—C3a	118.7 (2)	C9—O8—C4	116.3 (2)
O8—C4—C3a	114.2 (2)	C11—O10—C7	116.59 (15)
C6—C5—C4	121.7 (2)		

Data collection: Siemens *P3* data collection software. Cell refinement: Siemens *P3* data collection software. Data reduction: *SHELXTL-Plus* (Sheldrick, 1991). Program(s) used to solve structure: *SHELXTL-Plus*. Program(s) used to refine structure: *SHELXTL-Plus*. Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *FUER* (Larson, 1982).
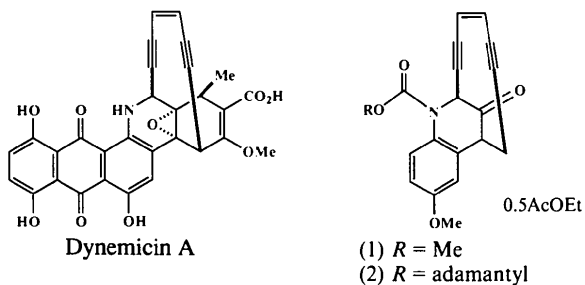
Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, including bond distances and angles involving H atoms, have been deposited with the IUCr (Reference: BK1080). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Two [7.3.1]Azabicyclo-z-3-ene-1,5-diyne Analogues of Dynemicin A

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Abstract

The crystal structures of methyl 6-methoxy-17-oxo-2-azatricyclo[7.7.1.0³,⁸]heptadeca-3(8),4,6,13-tetraene-11,15-diyne-2-carboxylate ethyl acetate solvate, (1), $2C_{19}H_{15}NO_4.0.5C_4H_8O_2$, and tricyclo[3.3.1.1³,⁷]decyl 6-methoxy-17-oxo-2-azatricyclo[7.7.1.0³,⁸]heptadeca-3(8),4,6,13-tetraene-11,15-diyne-2-carboxylate ethyl acetate solvate, (2), $C_{28}H_{27}NO_4.0.5C_4H_8O_2$, are reported. For compound (1), two crystallographically independent molecules are observed. Interestingly, for both compounds (1) and (2), a molecule of ethyl acetate is found in the crystal lattice disordered about an inversion center. The azabicyclo[7.3.1]enediyne core appears to be fairly rigid. Only minor differences are observed in the ring conformation between the two independent molecules in (1) and between compounds (1) and (2) themselves. The conformation is also similar to that found in deoxydynemicin A [Shiomi, Iinuma, Naganawa, Hamada, Hattori, Nakamura, Takeuchi & Iitaka (1990). *J. Antibiot.* 43, 1000–1005] and triacetyldynemicin A [Konishi, Ohkuma, Tsuno, Oki, Van Duyne & Clardy (1990). *J. Am. Chem. Soc.* 112, 3715–3716]. The transannular diyne distance (C3···C8) averages 3.428 (2) Å for compound (1) and is 3.403 (3) Å for compound (2).

Comment

Dynemicin, a member of the recently discovered z-3-ene-1,5-diyne-containing family of natural products, has been shown to possess exceptional antitumor activity (Konishi, Ohkuma, Tsuno, Kamei, Miyaki, Oki, Kawaguchi, Van Duyne & Clardy, 1989). A novel mode of action involving cycloaromatization of the z-3-ene-1,5-diyne functionality to generate a 1,4-benzenoid biradical is believed to be responsible for this activity (Semmelhack, Gallagher & Cohen, 1990). As a result, this family of natural products has become the focus of significant attention (Nicolau, Smith & Yue, 1993). Our synthetic and mechanistic interests led to the preparation of the two analogues N-(methoxycarbonyl)-15-keto-13-methoxy-10-aza-14a,10a-benzobicyclo[7.3.1]trideca-

3,7-diyn-5-ene ethyl acetate solvate, (1), and N-(adam-antyloxycarbonyl)-15-keto-13-methoxy-10-aza-14a,10a-benzobicyclo[7.3.1]trideca-3,7-diyn-5-ene ethyl acetate solvate, (2), i.e. the title compounds, which possess the [7.3.1]azabicyclic z-3-ene-1,5-diyne core structure.

Dynemicin A

(1) R = Me
(2) R = adamantyl

0.5AcOEt

The enediyne moiety is nearly perpendicular to the aromatic ring of the dihydroquinoline fragment, the dihedral angle averaging 77.4 (1)° for compound (1) and being 74.0 (1)° for compound (2). For deoxydynemicin A (Shiomi, Iinuma, Naganawa, Hamada, Hattori, Nakamura, Takeuchi & Iitaka, 1990) and triacetyldynemicin A (Konishi, Ohkuma, Tsuno, Oki, Van Duyne & Clardy, 1990), both with two molecules per asymmetric unit, the dihedral angles average 75.4 and 84.4°, respectively. For monocyclic systems, the 1,6-transannular distance

Fig. 2. Displacement ellipsoid plot of compound (2) showing the atom-labelling scheme. Ellipsoids are scaled to the 30% probability level. H atoms are represented as spheres of arbitrary size. The geometry of the adamantyl group is normal with C—C bond lengths averaging 1.529 (1) Å and C—C—C bond angles averaging 109.48 (5)°.
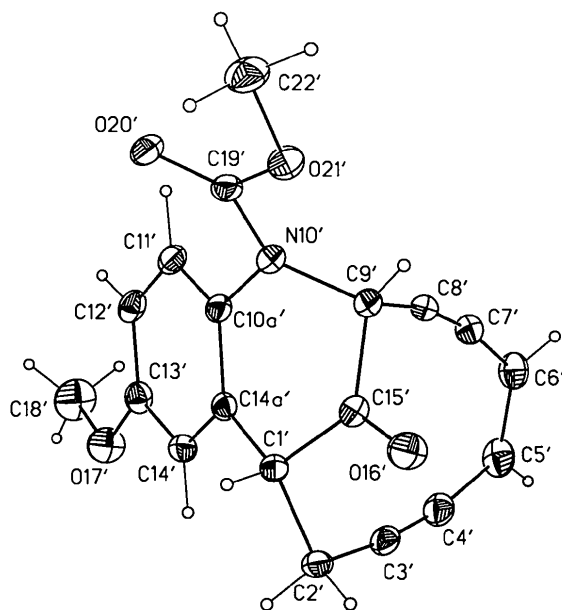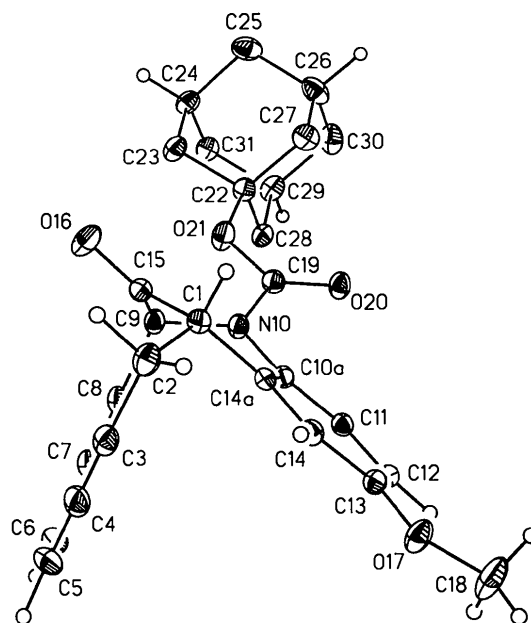
Fig. 1. Displacement ellipsoid plot of compound (1) showing the atom-labelling scheme for molecule A. Ellipsoids are scaled to the 30% probability level. The only significant difference between the two independent molecules of (1) is in the orientation of the ester group. The C9—N10—C19—O20 torsion angle is 11.7 (2)° for molecule A and 179.3 (3)° for molecule B. H atoms are represented as spheres of arbitrary size.
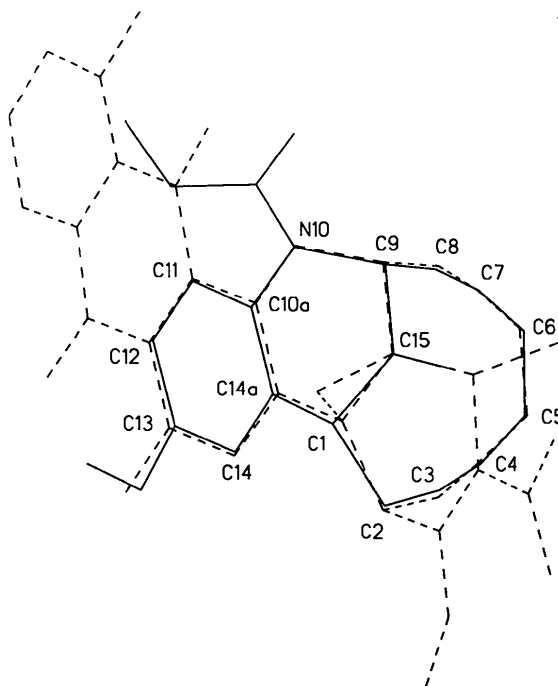
Fig. 3. View showing the least-squares fit of the atoms of the [7.3.1]enediyne fragment of molecule A of compound (1) (solid lines) to the equivalent atoms of deoxydynemicin A (dashed lines). The fit is remarkably close even though in (1) there is a carbonyl O atom bound to atom C15 while in deoxydynemicin A an epoxide O atom bridges atoms C1 and C15. Atoms used in the fit are labelled.

(C3$\cdots$C8) is related to the ease of cycloaromatization (Nicolau & Dai, 1991). For compound (1), the C3$\cdots$C8 distance is 3.416 (3) and 3.440 (3) Å for molecules A and B, respectively. For compound (2), the distance is 3.403 (3) Å. These values are close to those reported for deoxydynemicin A (3.603 Å) and triacetyldynemicin A (3.542 Å). In more complex systems, reduction of strain in the transition state is also an important consideration (Magnus, Fortt, Pitterna & Snyder, 1990). The internal angle at the one-carbon bridge, C15, is believed to be an important feature in controlling the rate of cycloaromatization (Magnus & Fairhurst, 1994). The ease with which this angle can approach that expected for an sp^3-hybridized C atom, the faster is the rate of cycloaromatization. The internal angle at atom C15 averages 117.04 (9)° for compounds (1) and (2). Ring strain is apparent in the bond angles at the acetylenic C atoms, which average 168.5 (1) for molecule A and 168.4 (1)° for molecule B of (1), and 168.7 (1)° for compound (2). The angles at the olefinic C atoms are less affected and have near normal values, averaging 118.9 (1) for (1) and 118.8 (2)° for (2). The bond lengths of the enediyne fragment, however, are near normal.
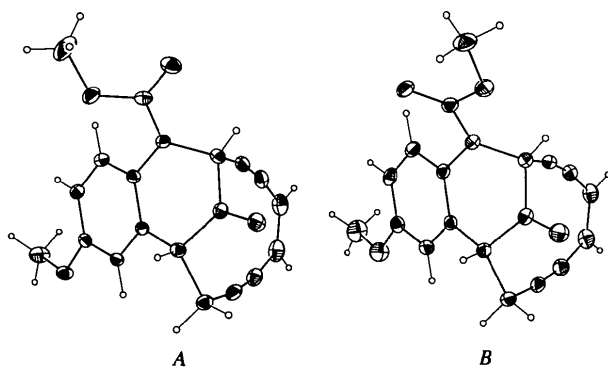

Fig. 4. A side-by-side displacement ellipsoid plot of the two independent enediyne molecules of compound (1). The orientations are not as they are found in the unit cell but are arranged so as to illustrate the differing orientations of the ester groups.

Experimental

The synthesis of both compounds (1) and (2) was achieved utilizing an adaptation of the previously described procedure of Magnus & Fortt (1991) starting from 6-methoxy-3-*tert*-butyldimethylsiloxyquinoline, z-hept-4-ene-2,6-diyn-1-ol, tetrahydropyranyl ether and the appropriate chloroformate. Crystals were grown by slow evaporation from ethyl acetate.

Compound (1)

Crystal data

2C$_{19}$H$_{15}$NO$_4$.0.5C$_4$H$_8$O$_2$
M_r = 686.72

Mo $K\alpha$ radiation
λ = 0.71073 Å

Triclinic
$P\bar{1}$
a = 10.734 (3) Å
b = 13.096 (4) Å
c = 13.712 (4) Å
α = 72.34 (2)°
β = 72.07 (2)°
γ = 71.82 (2)°
V = 1695.9 (9) Å^3
Z = 2
D_x = 1.34 Mg m^{-3}

Cell parameters from 28 reflections
θ = 8.2–12.0°
μ = 0.0895 mm^{-1}
T = 188 (1) K
Block
0.6 × 0.5 × 0.4 mm
Colorless

Data collection

Nicolet $P3$ diffractometer
ω scans
Absorption correction: none
7283 measured reflections
6880 independent reflections
5393 observed reflections
[$F > 4.0\sigma(F)$]
R_{int} = 0.024

θ_{max} = 26.25°
$h = 0 \rightarrow 13$
$k = -15 \rightarrow 16$
$l = -17 \rightarrow 17$
4 standard reflections monitored every 96 reflections
intensity decay: 1.6%

Refinement

Refinement on F
R = 0.0437
wR = 0.0543
S = 1.830
5393 reflections
572 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F) + 0.0004F^2]$
$(\Delta/\sigma)_{max}$ = 0.013
$\Delta\rho_{max}$ = 0.40 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

Extinction correction: modified Larson (1970) (*SHELXTL-Plus*; Sheldrick, 1991)
Extinction coefficient: 1.3 (4) × 10^{-6}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Compound (2)

Crystal data

C$_{28}$H$_{27}$NO$_4$.0.5C$_4$H$_8$O$_2$
M_r = 485.58
Triclinic
$P\bar{1}$
a = 10.747 (3) Å
b = 11.529 (3) Å
c = 11.661 (2) Å
α = 89.82 (2)°
β = 70.51 (2)°
γ = 67.43 (2)°
V = 1244.7 (6) Å^3
Z = 2
D_x = 1.30 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 41 reflections
θ = 7.55–10.9°
μ = 0.0820 mm^{-1}
T = 173 (1) K
Plate
0.5 × 0.4 × 0.3 mm
Colorless

Data collection

Nicolet $P3$ diffractometer
ω scans
Absorption correction: none

θ_{max} = 27.5°
$h = 0 \rightarrow 13$
$k = -14 \rightarrow 14$
$l = -15 \rightarrow 15$

6040 measured reflections
5736 independent reflections
4452 observed reflections
[F > 4.0σ(F)]
R_{int} = 0.015

4 standard reflections
monitored every 96
reflections
intensity decay: 1.3%

Refinement

Refinement on F
R = 0.0530
wR = 0.0692
S = 2.297
4452 reflections
434 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F) + 0.0004F^2]$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.49$ e Å^{-3}
$\Delta\rho_{min} = -0.31$ e Å^{-3}

Extinction correction:
modified Larson (1970)
(*SHELXTL-Plus*;
Sheldrick, 1991)
Extinction coefficient:
1.4 (2) × 10^{-6}
Atomic scattering factors
from *International Tables
for X-ray Crystallography*
(1974, Vol. IV)

	x	y	z	U_{eq}
O17′	−0.3677 (2)	0.58508 (12)	0.38183 (12)	0.0493 (7)
C18′	−0.4096 (3)	0.6542 (2)	0.2905 (2)	0.0642 (12)
C1A	−0.0442 (3)	−0.1626 (2)	0.1254 (2)	0.0689 (14)
C2A	0.0052 (4)	−0.0730 (3)	0.1070 (3)	0.037 (2)
O3A	0.0390 (3)	−0.0458 (3)	0.1695 (3)	0.0505 (14)
O4A	0	0	0	0.0553 (11)
C5A	0.0642 (5)	0.0867 (4)	−0.0192 (4)	0.053 (2)

† Primed atoms belong to molecule B.

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å²) *for* (2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
C1	0.4156 (2)	−0.1028 (2)	−0.1035 (2)	0.0273 (8)
C2	0.4859 (2)	−0.2250 (2)	−0.1972 (2)	0.0336 (9)
C3	0.4722 (2)	−0.1942 (2)	−0.3156 (2)	0.0334 (8)
C4	0.4467 (2)	−0.1518 (2)	−0.4029 (2)	0.0388 (9)
C5	0.3928 (3)	−0.0788 (3)	−0.4880 (2)	0.0446 (11)
C6	0.2821 (3)	0.0343 (3)	−0.4465 (2)	0.0423 (11)
C7	0.2208 (2)	0.0780 (2)	−0.3173 (2)	0.0339 (9)
C8	0.1891 (2)	0.0938 (2)	−0.2088 (2)	0.0296 (8)
C9	0.1736 (2)	0.0896 (2)	−0.0783 (2)	0.0280 (8)
N10	0.2423 (2)	0.1636 (2)	−0.04115 (14)	0.0266 (6)
C10a	0.3934 (2)	0.1240 (2)	−0.1094 (2)	0.0236 (7)
C11	0.4548 (2)	0.2113 (2)	−0.1438 (2)	0.0253 (7)
C12	0.6015 (2)	0.1713 (2)	−0.2099 (2)	0.0272 (8)
C13	0.6872 (2)	0.0417 (2)	−0.2434 (2)	0.0272 (7)
C14	0.6252 (2)	−0.0451 (2)	−0.2114 (2)	0.0269 (8)
C14a	0.4793 (2)	−0.0062 (2)	−0.1442 (2)	0.0233 (7)
C15	0.2517 (2)	−0.0500 (2)	−0.0662 (2)	0.0289 (8)
O16	0.1853 (2)	−0.1146 (2)	−0.0273 (2)	0.0444 (7)
O17	0.83253 (14)	−0.00977 (14)	−0.30981 (14)	0.0394 (6)
C18	0.9058 (3)	0.0721 (3)	−0.3299 (3)	0.0622 (12)
C19	0.1725 (2)	0.2556 (2)	0.0606 (2)	0.0276 (7)
O20	0.22829 (14)	0.31668 (13)	0.09188 (12)	0.0328 (6)
O21	0.0379 (2)	0.26417 (14)	0.11771 (13)	0.0386 (6)
C22	−0.0640 (2)	0.3605 (2)	0.2261 (2)	0.0288 (7)
C23	−0.1956 (2)	0.3278 (2)	0.2628 (2)	0.0341 (8)
C24	−0.3159 (2)	0.4224 (2)	0.3743 (2)	0.0322 (8)
C25	−0.2612 (3)	0.4136 (3)	0.4811 (2)	0.0435 (10)
C26	−0.1280 (2)	0.4457 (2)	0.4423 (2)	0.0424 (10)
C27	−0.0077 (2)	0.3501 (2)	0.3305 (2)	0.0369 (9)
C28	−0.1039 (2)	0.4932 (2)	0.1906 (2)	0.0324 (8)
C29	−0.2238 (2)	0.5878 (2)	0.3016 (2)	0.0351 (8)
C30	−0.1683 (3)	0.5800 (2)	0.4072 (2)	0.0439 (10)
C31	−0.3564 (2)	0.5559 (2)	0.3404 (2)	0.0337 (8)
C1A	0.2352 (6)	0.5804 (5)	0.2108 (5)	0.059 (3)
C2A	0.2996 (5)	0.5780 (3)	0.0702 (3)	0.090 (3)
C3A	0.4623 (4)	0.5154 (3)	0.0525 (2)	0.061 (2)
O4A	0.4660 (5)	0.5169 (4)	0.1514 (4)	0.075 (3)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å²) *for* (1)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
C1	0.5859 (2)	0.66606 (14)	−0.08305 (14)	0.0238 (6)
C2	0.7178 (2)	0.6823 (2)	−0.0730 (2)	0.0293 (7)
C3	0.6865 (2)	0.7681 (2)	−0.0154 (2)	0.0317 (8)
C4	0.6406 (2)	0.8370 (2)	0.0349 (2)	0.0368 (9)
C5	0.5606 (3)	0.9124 (2)	0.1002 (2)	0.0438 (11)
C6	0.4320 (3)	0.9110 (2)	0.1455 (2)	0.0415 (10)
C7	0.3779 (2)	0.8346 (2)	0.1259 (2)	0.0350 (8)
C8	0.3535 (2)	0.7656 (2)	0.09913 (14)	0.0296 (7)
C9	0.3570 (2)	0.6732 (2)	0.05849 (14)	0.0268 (7)
N10	0.29985 (14)	0.70876 (12)	−0.03403 (11)	0.0256 (6)
C10a	0.3617 (2)	0.78345 (14)	−0.12160 (13)	0.0238 (7)
C11	0.2856 (2)	0.8731 (2)	−0.17996 (14)	0.0271 (7)
C12	0.3462 (2)	0.9470 (2)	−0.26255 (14)	0.0272 (7)
C13	0.4853 (2)	0.93257 (14)	−0.28373 (13)	0.0250 (7)
C14	0.5611 (2)	0.84494 (14)	−0.22334 (13)	0.0240 (7)
C14a	0.5014 (2)	0.76829 (13)	−0.14303 (13)	0.0219 (6)
C15	0.5074 (2)	0.61638 (14)	0.02566 (13)	0.0243 (7)
O16	0.56016 (13)	0.53616 (10)	0.08362 (10)	0.0350 (5)
C19	0.2093 (2)	0.65582 (14)	−0.03619 (14)	0.0268 (7)
O20	0.15793 (13)	0.59347 (11)	0.03936 (10)	0.0367 (6)
O21	0.18473 (13)	0.68333 (11)	−0.13155 (11)	0.0360 (6)
C22	0.0881 (3)	0.6342 (2)	−0.1407 (2)	0.0670 (14)
O17	0.55611 (12)	1.00131 (10)	−0.36188 (10)	0.0350 (5)
C18	0.4793 (2)	1.0999 (2)	−0.4168 (2)	0.0457 (9)
C1′ †	−0.0328 (2)	0.32076 (14)	0.56189 (14)	0.0259 (7)
C2′	−0.1448 (2)	0.2621 (2)	0.6339 (2)	0.0310 (7)
C3′	−0.1756 (2)	0.1980 (2)	0.5774 (2)	0.0344 (7)
C4′	−0.1822 (2)	0.1459 (2)	0.5217 (2)	0.0390 (8)
C5′	−0.1611 (2)	0.0868 (2)	0.4442 (2)	0.0436 (9)
C6′	−0.0485 (2)	0.0836 (2)	0.3663 (2)	0.0405 (9)
C7′	0.0475 (2)	0.1388 (2)	0.3661 (2)	0.0328 (8)
C8′	0.1128 (2)	0.1883 (2)	0.38140 (14)	0.0291 (7)
C9′	0.1772 (2)	0.24197 (14)	0.42564 (14)	0.0280 (7)
N10′	0.1683 (2)	0.35851 (12)	0.37182 (12)	0.0294 (6)
C10a′	0.0331 (2)	0.42370 (14)	0.37165 (14)	0.0265 (7)
C11′	0.0011 (2)	0.5013 (2)	0.2830 (2)	0.0324 (8)
C12′	−0.1320 (2)	0.5592 (2)	0.2835 (2)	0.0342 (8)
C13′	−0.2323 (2)	0.5358 (2)	0.3725 (2)	0.0337 (8)
C14′	−0.2004 (2)	0.4580 (2)	0.4607 (2)	0.0308 (8)
C14a′	−0.0675 (2)	0.40135 (14)	0.46250 (13)	0.0253 (7)
C15′	0.0999 (2)	0.23482 (14)	0.54087 (14)	0.0278 (7)
O16′	0.14276 (14)	0.16436 (12)	0.61052 (11)	0.0430 (6)
C19′	0.2755 (2)	0.4058 (2)	0.34415 (14)	0.0298 (8)
O20′	0.27145 (14)	0.50119 (11)	0.29901 (10)	0.0374 (6)
O21′	0.38404 (13)	0.33232 (11)	0.37235 (11)	0.0377 (6)
C22′	0.5061 (2)	0.3713 (2)	0.3429 (2)	0.0456 (10)

Table 3. *Comparison of bond lengths* (Å) *and angles* (°) *for compounds* (1) *and* (2)

	Compound (1)		Compound (2)
	Molecule A	Molecule B	
C2—C1	1.547 (3)	1.547 (3)	1.546 (3)
C14a—C1	1.525 (2)	1.518 (2)	1.516 (3)
C15—C1	1.528 (2)	1.524 (2)	1.526 (3)
C3—C2	1.463 (3)	1.462 (4)	1.466 (3)
C4—C3	1.193 (3)	1.198 (4)	1.195 (3)
C5—C4	1.431 (3)	1.421 (4)	1.427 (4)
C6—C5	1.331 (4)	1.343 (4)	1.334 (3)
C7—C6	1.425 (4)	1.430 (4)	1.431 (3)
C8—C7	1.195 (4)	1.188 (3)	1.190 (3)
C9—C8	1.465 (3)	1.470 (3)	1.477 (3)
N10—C9	1.465 (3)	1.467 (2)	1.470 (3)
C15—C9	1.539 (2)	1.531 (2)	1.534 (3)
C10a—N10	1.429 (2)	1.436 (2)	1.432 (2)
C19—N10	1.370 (3)	1.373 (3)	1.378 (2)
C11—C10a	1.386 (2)	1.385 (2)	1.393 (3)
C14a—C10a	1.397 (2)	1.397 (2)	1.401 (2)
C12—C11	1.384 (2)	1.392 (3)	1.387 (3)

C13—C12	1.393 (3)	1.383 (3)	1.393 (3)
C14—C13	1.386 (2)	1.381 (3)	1.390 (3)
O17—C13	1.370 (2)	1.377 (2)	1.369 (2)
C14a—C14	1.388 (2)	1.392 (3)	1.384 (3)
O16—C15	1.206 (2)	1.203 (2)	1.209 (3)
O20—C19	1.208 (2)	1.208 (2)	1.209 (3)
O21—C19	1.333 (3)	1.336 (2)	1.339 (3)
C22—O21	1.432 (4)	1.452 (3)	1.477 (2)
C18—O17	1.429 (2)	1.413 (3)	1.418 (4)
C2—C1—C14a	114.5 (2)	115.0 (2)	113.9 (2)
C14a—C1—C15	113.67 (13)	113.34 (14)	114.2 (2)
C15—C1—C2	109.4 (2)	109.35 (14)	109.5 (2)
C3—C2—C1	110.01 (14)	110.4 (2)	110.4 (2)
C4—C3—C2	169.7 (2)	170.3 (2)	170.3 (2)
C5—C4—C3	168.2 (3)	167.5 (2)	167.8 (2)
C6—C5—C4	119.5 (3)	119.5 (3)	119.2 (2)
C7—C6—C5	118.5 (2)	118.1 (2)	118.6 (2)
C8—C7—C6	169.1 (2)	168.9 (2)	167.9 (2)
C9—C8—C7	167.0 (2)	166.8 (2)	168.9 (2)
N10—C9—C15	108.41 (14)	108.89 (15)	108.6 (2)
N10—C9—C8	112.88 (14)	112.2 (2)	111.1 (2)
C15—C9—C8	105.5 (2)	105.9 (2)	106.7 (2)
C10a—N10—C19	125.3 (2)	121.99 (15)	121.0 (2)
C10a—N10—C9	115.6 (2)	114.23 (15)	115.46 (15)
C19—N10—C9	118.26 (14)	122.41 (15)	123.2 (2)
C11—C10a—C14a	120.21 (15)	120.7 (2)	120.0 (2)
C11—C10a—N10	121.53 (15)	121.69 (15)	121.8 (2)
C14a—C10a—N10	118.12 (14)	117.49 (14)	118.2 (2)
C12—C11—C10a	121.1 (2)	120.4 (2)	121.0 (2)
C13—C12—C11	118.9 (2)	119.1 (2)	119.0 (2)
C14—C13—O17	115.6 (2)	114.8 (2)	115.4 (2)
C14—C13—C12	120.2 (2)	120.4 (2)	119.9 (2)
O17—C13—C12	124.21 (14)	124.7 (2)	124.7 (2)
C14a—C14—C13	121.1 (2)	121.2 (2)	121.5 (2)
C1—C14a—C10a	120.13 (14)	121.1 (2)	120.7 (2)
C1—C14a—C14	121.3 (2)	120.70 (14)	120.6 (2)
C10a—C14a—C14	118.51 (14)	118.1 (2)	118.6 (2)
O16—C15—C1	121.90 (14)	122.3 (2)	121.6 (2)
O16—C15—C9	121.05 (14)	121.03 (15)	121.0 (2)
C1—C15—C9	117.05 (13)	116.66 (14)	117.4 (2)
O20—C19—O21	125.0 (2)	124.9 (2)	126.6 (2)
O20—C19—N10	123.9 (2)	123.9 (2)	123.6 (2)
O21—C19—N10	111.12 (14)	111.2 (2)	109.8 (2)
C22—O21—C19	115.1 (2)	116.4 (2)	121.3 (2)
C18—O17—C13	116.96 (14)	117.8 (2)	117.9 (2)

The structure of (1) was refined in blocks of 308 parameters. Independent molecules were refined in separate blocks. The overall scale factor, the secondary-extinction correction factor and the atoms of the disordered solvent molecule were refined in each block. A molecule of ethyl acetate was found to be disordered about an inversion center at 0,0,0. It was disordered in such a way that the ester O atom O4A was situated on the inversion center. The position of O4A was fixed at 0,0,0 while the remaining atoms were allowed to refine without constraints. Site-occupancy factors were set to 0.5. No solvent H atoms were included. For compound (2), a molecule of ethyl acetate was also found to be disordered about an inversion center at $\frac{1}{2},\frac{1}{2},0$. The inversion center lies halfway between the ester O atom and the carbonyl C atom of the solvent. No H atoms were included in the refinement for the solvent molecule.

For both compounds, the scan range was 1.2° in ω with backgrounds measured at the limits of the scan range. For (1), methyl H atoms on C22 and C18' were calculated in idealized positions with $U_{iso}(H)$ set to $1.2U_{eq}(C)$. For (2), methyl H

atoms on C18 were calculated in idealized positions with $U_{iso}(H)$ set to $1.2U_{eq}(C18)$. The refined C—H bond lengths ranged from 0.93 (3) for H5 and H22E to 1.05 (2) Å for H18C in compound (1), and from 0.92 (3) for H28B to 1.12 (3) Å for H30A in compound (2).

For both compounds, data collection: *P3/V Data Collection Software* (Siemens, 1989); cell refinement: *P3/V Data Collection Software*; data reduction: *SHELXTL-Plus* (Sheldrick, 1991); program(s) used to solve structures: *SHELXTL-Plus*; program(s) used to refine structures: *SHELXTL-Plus*; molecular graphics: *SHELXTL-Plus*; software used to prepare material for publication: *MPLN* (Cordes, 1983) and *FUER* (Larson, 1982).

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