As part of the modelling of the disorder in one thiophene ring, both components were restrained to have bond lengths and valence angles similar to those in the ordered ring. A common isotropic thermal displacement parameter for the C atoms of the minor component refined to 0.040 (8) Å^2.

Data collection: *DIF*4 (Stoe & Cie, 1992). Cell refinement: *DIF*4. Data reduction: *X-RED* (Stoe & Cie, 1995). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1994). Software used to prepare material for publication: *SHELXL*93.

We thank EPSRC for provision of a four-circle diffractometer and for postdoctoral support (to JPD).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HA1177). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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An Unusual 3*H*-Pyrrole at 150 K

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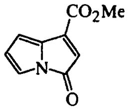
Abstract

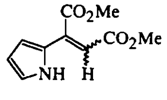
Most pyrroles are observed to form the 1*H*-tautomer; here we report the structure of a rare example of a 3*H*-pyrrole, trimethyl 6-oxo-5,5a,10b,10c-tetrahydro-3*H*-pyrrolizino[1,2-*e*]indole-4,5,10b-tricarboxylate, $C_{19}H_{18}N_2O_7$. The molecules pack as dimers linked *via* bifurcated hydrogen bonds.

Comment

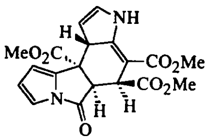
As part of our studies of the unusual properties of 1-methoxycarbonylpyrrolizin-3-one, (1), obtained by flash vacuum pyrolysis of the vinylpyrroles, (2) (Comer, Despinoy, Gould, McNab & Parsons, 1996), we adventitiously obtained a single crystal of (3), which is formally a [4 + 2] cycloadduct of (1) and (2). Here we report details of the structure of (3) which is of interest in view of the unusual tautomeric form of the pyrrole unit, and because of the boat conformation of the central cyclohexene ring.



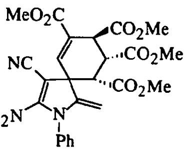
(1)



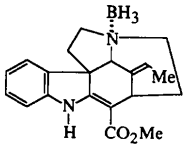
(2*a*) *E* isomer
(2*b*) *Z* isomer



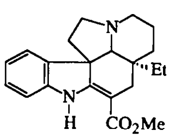
(3)



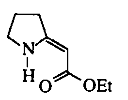
(4)



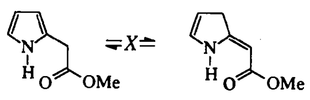
(5)



(6)



(7)



(8)

Compound (3) is composed of a 3*H*-pyrrole unit and a dihydropyrrolizinone unit linked *via* a cyclohexene ring in the boat conformation (Cremer–Pople puckering parameters θ = 88.3°, φ = 305.5°; Spek, 1995); ester substituents are located on C1, C13 and C14 (Fig. 1). The formulation of the 3*H*-pyrrole substructure was based on H-atom positions derived from electron density difference maps and supported by examination of the bond lengths. Thus the bond length C8—C12 [1.515 (7) Å] is much longer than anticipated for a typical pyrrole α–β double bond [1.375 (18) Å; Allen *et al.*, 1987], and the sum of the angles at C8 (331.0°) is clearly inconsistent with the normal 1*H*-pyrrole tautomer. There is little structural precedent for a pyrrole of this type in the literature; the spiro compound (4) is 3,3-disubstituted and encumbered by polar substituents (Kildea, Hiller, Frey & Eger, 1990). Other 3*H*-pyrrole structures have endocyclic N1=C2 double bonds (van Meersche, Gilson, Germain & Declercq, 1981; Chiu, Lai & Sammes, 1990). A range of indole alkaloid skeletons, exemplified by (5) and (6), have been structurally investigated and are tautomerically similar to (3) (Wang & Paul, 1977; Palmisano & Pilati, 1993), though again they are disubstituted in the β position.

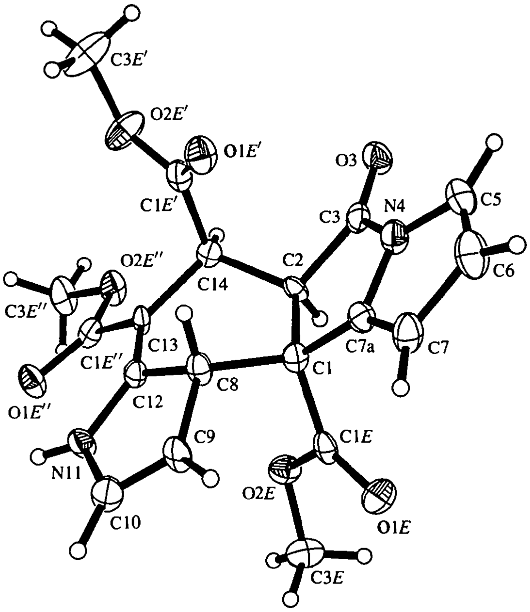


Fig. 1. A view of (3) with atom-numbering scheme. Displacement ellipsoids enclose 50% probability surfaces.

Compounds (3), (5) and (6) contain an electronically modified enaminoester sub-unit, exemplified by N11—C12—C13—C1*E*″—O1*E*″ in (3), which is also found in the pyrrolidine derivative (7) (Philoche-Levisalles, Bois, Célérier & Lhommet, 1982). The effect of strong delocalization of the N11 lone pair in (3) through to the ester at C13 is reflected in the much shorter bond length of N11—C12 [1.349 (6) Å] compared with C10—N11 [1.408 (6) Å]. This trend is found to a greater extent in (7), in which the corresponding distances are 1.313 (4) and 1.466 (5) Å, which implies that in (3) some delocalization of the N11 lone pair into the enamine N11—C10—C9 system can also take place. In the indole derivatives (5) and (6), the effect of competition for the nitrogen lone pair between the enaminoester and the aromatic ring sub-structures causes the C—N bond within the former to be lengthened to 1.376 (5) and 1.385 (3) Å in (5) and (6), respectively. The carbonyl group C1*E*″—O1*E*″ in (3) obtains electron density from the N11 atom and, in consequence, the adjacent C1*E*″—O2*E*″ bond length of 1.360 (6) Å is slightly longer than corresponding values for C1*E*′—O2*E*′ and C1*E*—O2*E* [1.336 (6) and 1.335 (6) Å, respectively] within the other electronically isolated ester units. Other bond lengths in the enaminoester moieties of (3) and (5)–(7) are relatively unaffected by the electronic environment of the N atom.

The pyrrole N—H in (3) forms a bifurcated hydrogen bond (Fig. 2) to O1*E*″ and a centrosymmetrically related O1*E*″ atom in a neighbouring molecule (at $-x, 2-y, -z$); the N···O distances are 2.800 (5) and 2.964 (5) Å, respectively. This intermolecular interaction is predictably the dominant feature in the packing of (3), while the intramolecular hydrogen bond closes a six-membered ring, with the entire C9—C10—N11—C12—C13—C1*E*″—O1*E*″ unit planar to within 0.098 Å. A similar hydrogen-bonded motif is observed in (5)–(7). The stability of this substructure is presumably partly responsible for the observation of the unusual tautomer in (3), though it is noteworthy that there is no evidence for the 3*H* tautomer in the proton NMR spectrum of the pyrrole-2-acetic acid esters (8) (Falling & Rapoport, 1980).

The *trans* disposition of the ester functions in (3) at C1 and C14 is consistent with the compound having been formed by a concerted cycloaddition of the *E* ester (2*a*) (the 4π component) and the pyrrolizinone (1) (as the 2π component).

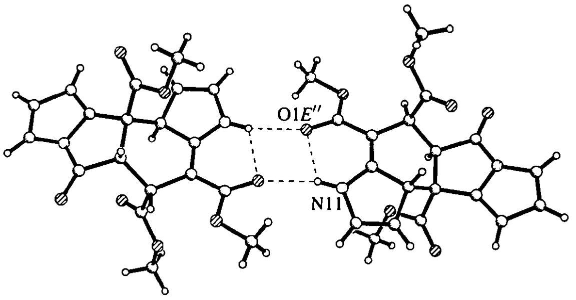


Fig. 2. Bifurcating hydrogen-bond formation in (3).

Experimental

Compound (3) was obtained by flash vacuum pyrolysis of (2) at 973 K (10^{-3} Torr) followed by dry flash chromatography on silica after the expected dimerization was complete (Comer *et al.*, 1996). The crystal of (3) was selected from the fraction which was predominantly the *cis* [2 + 2] dimer of (1) after slow recrystallization from isopropyl alcohol.

Crystal data

$C_{19}H_{18}N_2O_7$
$M_r = 386.35$
Triclinic
$P\bar{1}$
$a = 9.027\ (5)$ Å
$b = 10.945\ (5)$ Å
$c = 10.913\ (5)$ Å
$\alpha = 112.790\ (5)°$
$\beta = 99.240\ (5)°$
$\gamma = 109.720\ (5)°$
$V = 881.5\ (8)$ Å^3
$Z = 2$
$D_x = 1.456$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 12.5–15°$
$\mu = 0.113$ mm^{-1}
$T = 150.0\ (2)$ K
Column
0.78 × 0.31 × 0.23 mm
Colourless

Data collection

Stoe Stadi-4 four-circle diffractometer
ω–2θ scans
Absorption correction: none
2304 measured reflections
2304 independent reflections
1500 observed reflections $[I > 2\sigma(I)]$
$\theta_{\max} = 22.52°$
$h = -9 \rightarrow 9$
$k = -11 \rightarrow 10$
$l = 0 \rightarrow 11$
3 standard reflections frequency: 60 min intensity decay: 3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0698$
$wR(F^2) = 0.1979$
$S = 1.024$
2292 reflections
254 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.1280P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.001$
$\Delta\rho_{\max} = 0.37$ e Å^{-3}
$\Delta\rho_{\min} = -0.39$ e Å^{-3}
Extinction correction: *SHELXTL/PC* (Sheldrick, 1995)
Extinction coefficient: 0.007 (5)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

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

	x	y	z	$U_{\rm eq}$
C1	0.1883 (6)	0.7429 (5)	0.3142 (5)	0.0181 (12)
C2	0.2000 (6)	0.6344 (5)	0.1749 (5)	0.0158 (12)
C3	0.3194 (6)	0.5782 (6)	0.2199 (5)	0.0201 (12)
O3	0.3592 (5)	0.4891 (4)	0.1452 (4)	0.0276 (10)
N4	0.3712 (5)	0.6435 (5)	0.3660 (4)	0.0230 (11)
C5	0.4731 (7)	0.6359 (6)	0.4691 (6)	0.0285 (14)
C6	0.4680 (7)	0.7255 (6)	0.5932 (6)	0.0330 (15)
C7	0.3600 (7)	0.7895 (6)	0.5680 (5)	0.0256 (13)
C7a	0.3033 (6)	0.7391 (5)	0.4272 (5)	0.0187 (12)
C8	0.2436 (7)	0.9006 (5)	0.3286 (5)	0.0190 (12)
C9	0.1918 (7)	1.0033 (5)	0.4273 (5)	0.0222 (13)
C10	0.1149 (7)	1.0533 (6)	0.3594 (5)	0.0264 (13)
N11	0.1022 (5)	0.9896 (5)	0.2163 (4)	0.0219 (11)
C12	0.1686 (6)	0.8925 (5)	0.1895 (5)	0.0160 (12)
C13	0.1653 (6)	0.7934 (5)	0.0654 (5)	0.0152 (12)
C14	0.2467 (6)	0.6951 (5)	0.0727 (5)	0.0173 (12)
C1*E*	0.0132 (7)	0.6931 (5)	0.3214 (5)	0.0192 (12)
O1*E*	−0.0222 (5)	0.6900 (4)	0.4229 (4)	0.0285 (10)
O2*E*	−0.0996 (4)	0.6577 (4)	0.2028 (3)	0.0227 (9)
C3*E*	−0.2695 (7)	0.6165 (6)	0.2029 (6)	0.0298 (14)
C1*E*′	0.4328 (7)	0.7792 (6)	0.1120 (5)	0.0213 (13)
O1*E*′	0.5343 (5)	0.8372 (4)	0.2285 (4)	0.0274 (10)
O2*E*′	0.4739 (5)	0.7862 (4)	0.0018 (4)	0.0356 (11)
C3*E*′	0.6474 (8)	0.8701 (8)	0.0279 (7)	0.050 (2)
C1*E*″	0.0791 (6)	0.7785 (5)	−0.0665 (5)	0.0188 (12)
O1*E*″	0.0210 (5)	0.8616 (4)	−0.0772 (3)	0.0245 (9)
O2*E*″	0.0625 (5)	0.6590 (4)	−0.1818 (3)	0.0251 (9)
C3*E*″	−0.0149 (8)	0.6455 (6)	−0.3165 (5)	0.032 (2)

Table 2. *Geometric parameters (Å, °)*

C1—C7a	1.503 (7)	C10—N11	1.408 (6)
C1—C1*E*	1.515 (7)	N11—C12	1.349 (6)
C1—C8	1.561 (7)	C12—C13	1.355 (7)
C1—C2	1.572 (6)	C13—C1*E*″	1.442 (7)
C2—C3	1.515 (7)	C13—C14	1.511 (7)
C2—C14	1.549 (7)	C14—C1*E*′	1.508 (7)
C3—O3	1.208 (6)	C1*E*—O1*E*	1.211 (6)
C3—N4	1.387 (7)	C1*E*—O2*E*	1.335 (6)
N4—C5	1.383 (7)	O2*E*—C3*E*	1.445 (6)
N4—C7a	1.393 (6)	C1*E*′—O1*E*′	1.211 (6)
C5—C6	1.349 (8)	C1*E*′—O2*E*′	1.336 (6)
C6—C7	1.429 (8)	O2*E*′—C3*E*′	1.436 (7)
C7—C7a	1.352 (7)	C1*E*″—O1*E*″	1.225 (6)
C8—C9	1.490 (7)	C1*E*″—O2*E*″	1.360 (6)
C8—C12	1.515 (7)	O2*E*″—C3*E*″	1.450 (6)
C9—C10	1.318 (7)		
C7a—C1—C1*E*	110.3 (4)	C10—C9—C8	109.3 (4)
C7a—C1—C8	112.7 (4)	C9—C10—N11	110.7 (5)
C1*E*—C1—C8	107.0 (4)	C12—N11—C10	110.1 (4)
C7a—C1—C2	102.8 (4)	N11—C12—C13	130.5 (5)
C1*E*—C1—C2	112.9 (4)	N11—C12—C8	107.4 (4)
C8—C1—C2	111.3 (4)	C13—C12—C8	121.9 (4)
C3—C2—C14	112.3 (4)	C12—C13—C1*E*″	120.7 (4)
C3—C2—C1	106.3 (4)	C12—C13—C14	116.8 (4)
C14—C2—C1	116.8 (4)	C1*E*″—C13—C14	122.4 (4)
O3—C3—N4	125.1 (5)	C1*E*′—C14—C13	108.9 (4)
O3—C3—C2	127.8 (5)	C1*E*′—C14—C2	112.5 (4)
N4—C3—C2	107.1 (4)	C13—C14—C2	111.7 (4)
C5—N4—C3	135.9 (5)	O1*E*—C1*E*—O2*E*	123.2 (5)
C5—N4—C7a	110.2 (4)	O1*E*—C1*E*—C1	125.1 (5)
C3—N4—C7a	113.9 (4)	O2*E*—C1*E*—C1	111.7 (4)
C6—C5—N4	106.1 (5)	C1*E*—O2*E*—C3*E*	115.6 (4)
C5—C6—C7	109.4 (5)	O1*E*′—C1*E*′—O2*E*′	123.1 (5)
C7a—C7—C6	107.2 (5)	O1*E*′—C1*E*′—C14	125.4 (4)
C7—C7a—N4	107.1 (4)	O2*E*′—C1*E*′—C14	111.4 (4)
C7—C7a—C1	142.9 (5)	C1*E*′—O2*E*′—C3*E*′	116.6 (4)
N4—C7a—C1	109.9 (4)	O1*E*″—C1*E*″—O2*E*″	121.7 (4)
C9—C8—C12	102.2 (4)	O1*E*″—C1*E*″—C13	124.6 (4)
C9—C8—C1	118.1 (4)	O2*E*″—C1*E*″—C13	113.7 (4)
C12—C8—C1	110.7 (4)	C1*E*″—O2*E*″—C3*E*″	115.1 (4)

Data collection: *DIF*4 (Stoe & Cie, 1990). Cell refinement: *DIF*4. Data reduction: *XRED* (Stoe & Cie, 1995). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXTL/PC* (Sheldrick, 1995). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXTL/PC*.

We thank the EPSRC for provision of a four-circle diffractometer, and Glaxo-Wellcome for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1270). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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The Major Isoxazoline Cycloadduct from Reaction of a Xylopyranosylnitrile Oxide with a Hex-5-enopyranoside

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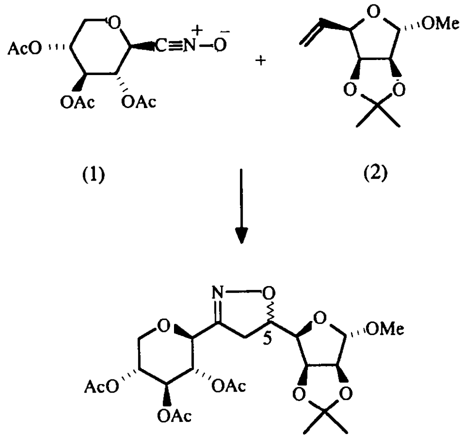
Abstract

The present structure determination of (5*R*)-5-(2,3-*O*-isopropylidene-1-*O*-methyl-α-D-*lyxo*-tetrafuranos-4-yl)-3-(2,3,4-tri-*O*-acetyl-β-D-xylopyranos-2-yl)-4,5-dihydroisoxazole, $C_{22}H_{31}NO_{12}$, at 150 K, taken with the known absolute configurations of the starting alkene and the nitrile oxide precursor, establishes the configuration (*R*) of the new stereogenic centre C(5) in the title compound, the major cycloadduct. The five-membered 4,5-dihydroisoxazole ring adopts a mainly envelope conformation folded between O(5) and O(6), whereas the furanoside and dioxolane rings lie between twist and envelope. The xylopyranosyl ring adopts a near ideal chair conformation.

Comment

As part of a programme aimed at developing a synthetic route to carbon-linked disaccharides (*C*-disaccharides) (Levy & Tang, 1995) based on nitrile oxide/isoxazoline chemistry (Kanemasa & Tsuge, 1990, and references therein), we have investigated the reaction of D-xylose-derived nitrile oxide, (1), with D-mannose-derived alkene, (2) (see Scheme). Two diastereomeric 4,5-dihydroisoxazole cycloadducts, (3) and (4), were formed in the ratio 82:18 in a combined yield of 67%. The major product provided crystals suitable for X-ray crystallography. Taken with the known absolute configurations of the starting alkene (Bock & Petersen, 1977) and the nitrile oxide precursor (Förtsch, Kogelberg & Köll, 1987), the present structure determination firmly establishes that this compound has structure (3) in which the new stereogenic centre C(5) has the *R*-configuration, and that the minor isomer has the 5*S* structure (4).



(3) 5*R*
(4) 5*S*

The Cremer–Pople puckering parameters (Cremer & Pople, 1975; Gould, Taylor & Thorpe, 1995) for the four rings are given in Table 2. The five-membered dihydroisoxazole ring adopts a mainly envelope conformation (E_5, corresponding to an ideal value of $\varphi = 324°$) with the fold between O(5) and C(6); the torsion angle for the O(5)—N(7)=C(7)—C(6) unit is 0.8 (5)° with C(5) lying 0.19 Å out of the best plane through these atoms. For the furanoside ring, $\varphi = 6.6°$ indicating that it is intermediate between envelope ($\varphi = 0°$) and twist ($\varphi = 18°$). Likewise, the conformation of the dioxolane lies between twist ($\varphi = 18°$), and envelope ($\varphi = 36°$). The θ value for the pyranoid ring (3.4°) indicates that it is very close to the ideal chair $^4C_1$ with $\theta = 0°$. No anomalies are found in the bond lengths and angles. The crystal structure consists of layers of molecules of (3); there appear to be no significant interactions between the layers, and only rather weak intermolecular C—H···O interactions [minimum and maximum C···O distances 3.261 (6) and 3.467 (6) Å, respectively] within the layers.

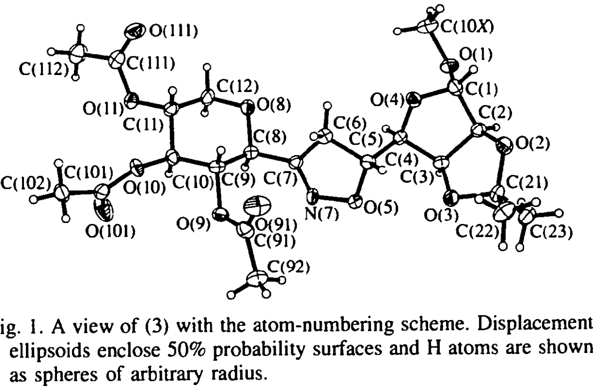


Fig. 1. A view of (3) with the atom-numbering scheme. Displacement ellipsoids enclose 50% probability surfaces and H atoms are shown as spheres of arbitrary radius.