

The X-Ray Molecular Structures of Methyl 4,5,7,8,9,10,11,12,13,14-Decahydro-7,9-dioxo-8,15-methenopyrrolo[3,2,1-*op*][1]benzazacyclododecine-16-carboxylate, Methyl (*Z*)-1',2',4',5'-Tetrahydro-2,4'-dioxospiro(cycloheptane-1,6'-[6*H*]pyrrolo[3,2,1-*ij*]quinolin)-5'-ylideneacetate, and Methyl (*Z*)-1,1a,2,3,4,8,9,9a-Octahydro-1-methoxycarbonylmethyl-11-methoxycarbonylmethylene-12-oxo-1b,4a-epoxyethanoindolizino[2,3,4,5,6-*jk/m*]carbazole-1-carboxylate

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The structures of three adducts obtained from substituted indoles and dimethyl acetylenedicarboxylate have been determined by X-ray crystallography. One of these reveals that its formation is *via* an unusual 1,3-shift of an acyl group.

Dimethyl acetylenedicarboxylate (DMAD) has been found¹ to add to the substituted indole (1) (IND) in moist acetic acid to give, among other products, two (1 IND + 1 DMAD - CH₂) adducts referred to as compounds (D) and (E).¹ These isomers are both amides, but differ in that (D) exhibits no olefinic hydrogen signal and (E) has one olefinic hydrogen, as seen from their n.m.r. spectra. From a consideration of likely structures for (D), it would seem most likely that the amide function is derived from the familiar amino ketone intermediate (3), and that a skeletal rearrangement follows, leading to several possible structures for (D), which include (4), (5), and (6). As spectroscopy could not readily distinguish between the various possible structures, single-crystal X-ray analysis was carried out. The resulting structure was shown to be (4) (see Figure 1), thus suggesting that the product is formed from compound (3) *via* a benz[*b*]azepinone together with an unusual 1,3-shift of an acyl group, which we have discussed.¹

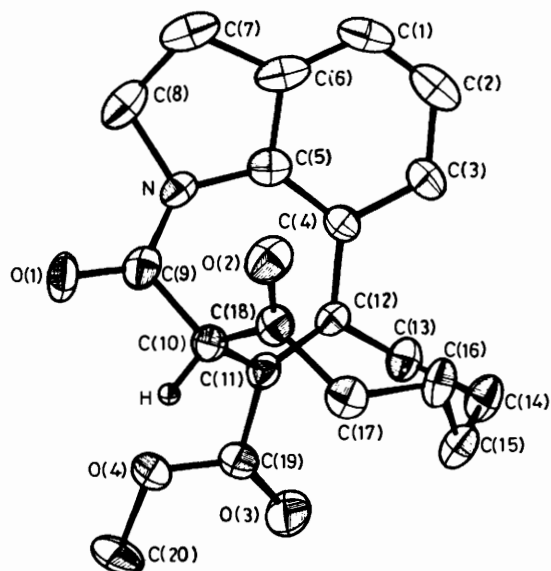
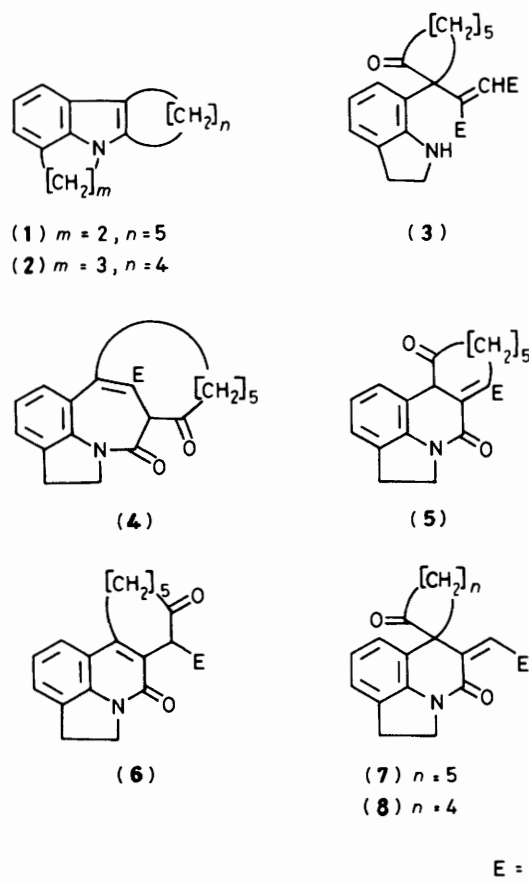


Figure 1. Perspective view of the X-ray molecular structure of methyl 4,5,7,8,9,10,11,12,13,14-decahydro-7,9-dioxo-8,15-methenopyrrolo[3,2,1-*op*][1]benzazacyclododecine-16-carboxylate (4)

In the light of this rearrangement and others which we have observed^{2,3} for IND-DMAD adducts, the isomeric compound



(E), previously reported¹ as having the unrearranged structure (7), could now conceivably have an alternative structure. We now confirm its structure as (7) (see Figure 2) by X-ray analysis, and this in turn confirms the structure of its analogue (8).^{4,5}

We have previously shown⁶ that DMAD adds to the substituted indole (2) to give, among other products, three isomeric (1 IND + 2 DMAD - CH₂) adducts referred to as compounds (C), (D), and (E), and from X-ray crystallography we have shown⁶ (E) to be compound (9).¹³C N.m.r. spectroscopy revealed that compound (9) differed from (C) and (D) only in the geometry about the double bond [(9) and (C) have the *Z*- and (D) has the *E*-configuration], and in the

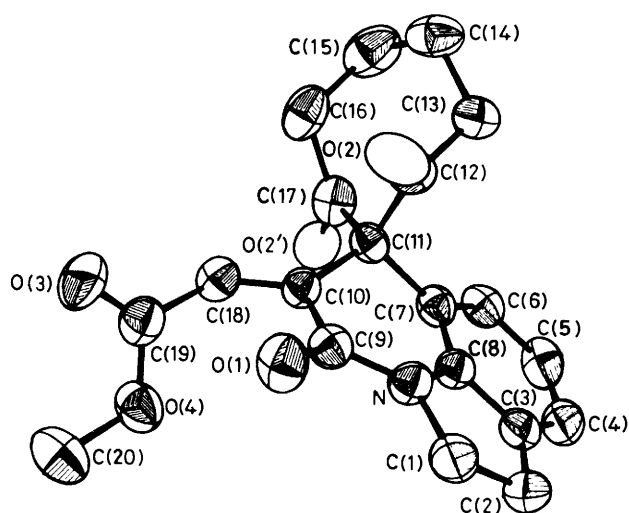


Figure 2. Perspective view of the X-ray molecular structure of methyl (Z)-1',2',4',5'-tetrahydro-2,4'-dioxospiro(cycloheptane-1,6'-[6H]pyrrolo[3,2,1-ij]quinolin)-5'-ylideneacetate (7)

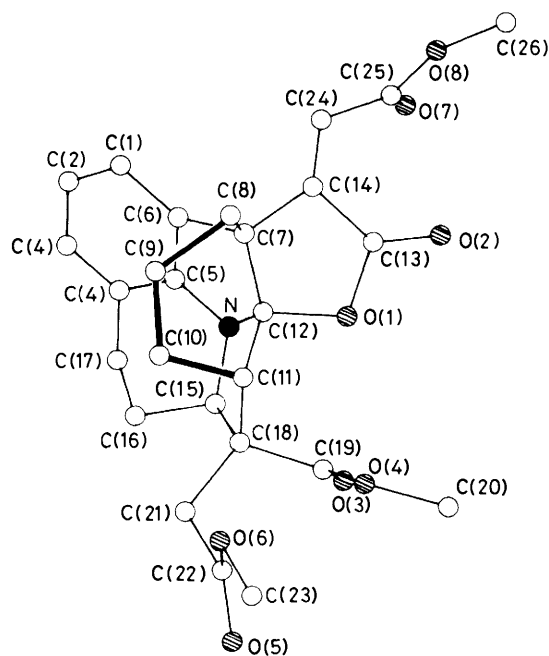
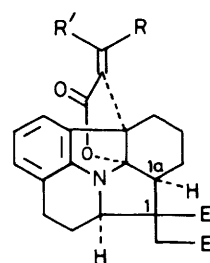


Figure 3. Perspective view of the X-ray molecular structure of one of the two independent molecules of methyl (Z)-1,1a,2,3,4,8,9,9a-octa-hydro-1-methoxycarbonylmethyl-11-methoxycarbonylmethylene-12-oxo-1b,4a-epoxyethanoindolizino[2,3,4,5,6-jklm]carbazole-1-carboxylate (11)

stereochemistry at either C-1 or C-1a. As spectroscopy could not determine the latter feature, a single-crystal X-ray analysis of compound (C) was carried out to establish the correct structure. The resulting structure (11) (see Figure 3) reveals that compounds (9) and (C) are identical except for the stereochemistry at C-1. Since compounds (C) and (D) have identical spectra except for signals directly attributable to the geometry of the olefinic double bond,⁶ it follows that (D) is compound (10).

The confirmation of these three structures, together with our four previously determined X-ray structures,^{2,6} show that in all cases our structural assignments based on the relatively new



- (9) R = H, R' = E (CH₂E *exo*)
 (10) R = E, R' = H (CH₂E *endo*)
 (11) R = H, R' = E (CH₂E *endo*)

method of assigning alkene stereochemistry from ¹H-¹³C coupling constants⁵ have been correct.

Experimental

X-Ray Crystal Structure Analysis of Compounds (4), (7), and (11).—Intensity data for compounds (4) and (11) were measured on a Nicolet R3m diffractometer and those for (7) on a Syntex P2₁ diffractometer using, in all cases, the θ - 2θ scanning technique in the bisecting mode, with variable scan speeds and a scan range from 1° below the $K_{\alpha 1}$ peak to 1° above the $K_{\alpha 2}$ peak. Background counts were taken for one-half of the scan time at each end of the scan range. The intensities of three check reflections, monitored every 125 data measurements, fluctuated within $\pm 1\%$ and showed no systematic decline. The radiation used was graphite-monochromatized Mo- K_{α} (λ 0.710 69 Å). No absorption corrections were made. Further details of the collection of intensity data are given in Table 1.

Reflections with $|F_o| > 3\sigma(|F_o|)$ were considered to be observed and were used in subsequent calculations. Unit-cell dimensions were obtained from a least-squares fit to 20 high-angle reflections.

Compound (4).—Crystal data. C₂₀H₂₁NO₄, $M = 339.39$, orthorhombic, $a = 8.587(1)$, $b = 11.131(2)$, $c = 17.118(3)$ Å, $V = 1636.2(4)$ Å³, $P2_12_12_1$, $Z = 4$, $D_x = 1.377$ g cm⁻³, $\mu(\text{Mo-}K_{\alpha}) = 0.90$ cm⁻¹.

The structure was solved by direct methods with MULTAN 78⁷ and refined by full matrix least-squares. The resulting difference map revealed peaks for the corresponding hydrogen atoms. Four strong reflections (020, 101, 031, and 002) with large residuals ($|F_o^2 - F_c^2|$) were given zero weight. During the last cycles the atomic co-ordinates of all non-hydrogen atoms were kept in one matrix while the anisotropic temperature factors and the scale factor were kept in another. The hydrogen-atom parameters were not refined. The final R index was 0.040 for 1712 reflections and the 'goodness of fit' $[\sum w(F_o^2 - F_c^2)^2 / (m - s)]^{1/2} = 3.9$, where m is the number of reflections and s is the number of parameters.

Compound (7).—Crystal data. C₂₀H₂₁NO₄, $M = 339.39$, monoclinic, $a = 7.239(2)$, $b = 16.486(5)$, $c = 14.679(8)$ Å, $\beta = 109.37(3)^\circ$, $V = 1652.6(9)$, $P2_1/c$, $Z = 4$, $D_x = 1.364$ g cm⁻³, $\mu(\text{Mo-}K_{\alpha}) = 0.89$ cm⁻¹.

The structure was solved by direct methods with MULTAN 78.⁷ After several cycles of least-squares adjustment of atomic co-ordinates and isotropic temperature factors for the non-hydrogen atoms, refinement converged but the temperature factor of O(2) became abnormally large. A difference Fourier synthesis was calculated with the contribution of all non-hydrogen atoms except O(2), and the resulting map showed two peaks with density much above background. One peak (*ca.* 4.5 e

Table 1.

Compd.	Crystal size (mm)	$2\theta_{\max}$ (°)	Scan speeds (° min ⁻¹)	No. of unique reflections	No. of reflections with $ F_o > 3\sigma(F_o)$
(4)	0.5 × 0.4 × 0.4	52	2.55—8.37	1 821	1 716
(7)	0.20 × 0.26 × 0.26	45	2	1 913	1 126
(11)	0.24 × 0.20 × 0.12	45	0.99—7.32	2 830	1 651

Table 2. Fractional atomic co-ordinates ($\times 10^4$) for non-hydrogen atoms in compound (4) with estimated standard deviations in parentheses

Atom	x	y	z
C(1)	2 101(5)	9 368(3)	4 964(2)
C(2)	3 347(4)	9 396(3)	4 458(2)
C(3)	3 182(3)	9 072(3)	3 689(2)
C(4)	1 738(3)	8 670(2)	3 380(1)
C(5)	506(3)	8 630(2)	3 913(2)
C(6)	676(4)	9 011(2)	4 688(2)
C(7)	-858(4)	8 930(3)	5 105(2)
C(8)	-2 031(4)	8 771(3)	4 446(2)
C(9)	-1 636(3)	7 457(3)	3 294(2)
C(10)	-448(3)	6 860(2)	2 763(1)
C(11)	431(3)	7 732(2)	2 248(1)
C(12)	1 575(3)	8 433(2)	2 535(1)
C(13)	2 795(3)	8 976(2)	2 002(2)
C(14)	4 215(3)	8 134(3)	1 888(2)
C(15)	3 863(3)	6 793(3)	1 836(2)
C(16)	3 540(3)	6 161(3)	2 631(2)
C(17)	1 971(3)	5 460(2)	2 691(2)
C(18)	720(3)	6 040(2)	3 191(3)
C(19)	-5(3)	7 708(3)	1 398(2)
C(20)	-2 124(4)	7 606(4)	527(2)
N	-1 063(3)	8 318(2)	3 783(1)
O(1)	-3 012(2)	7 191(2)	3 275(1)
O(2)	608(3)	5 837(2)	3 880(1)
O(3)	837(3)	7 834(3)	852(1)
O(4)	-1 521(2)	7 587(2)	1 321(1)

Å^{-3}) was found at the position originally chosen for O(2) and the other ($ca. 2.5 e \text{Å}^{-3}$) was found at a distance 1.1 Å from C(17) and in a position which could be an alternative site for O(2) and which was subsequently labelled as O(2'). During the last cycles of anisotropic least-squares refinement the disordered oxygen atom was represented by O(2) and O(2') with initial occupancy factors of 0.65 and 0.35 respectively. The hydrogen atoms were inserted in their calculated positions with assigned isotropic temperature factors. The final *R* factor was 0.090 for 1 913 non-zero reflections and 0.046 for 1 126 reflections with $I > 3\sigma(I)$. The 'goodness of fit' was 1.31.

Compound (11).—*Crystal data.* $\text{C}_{26}\text{H}_{27}\text{NO}_8$, $M = 481.51$, orthorhombic, $a = 13.080(4)$, $b = 12.710(5)$, $c = 27.34(1)$ Å, $V = 4 545(2)$ Å³, $D_m = 1.40(1)$ g cm⁻³, $Z = 8$, $D_x = 1.407$ g cm⁻³, systematic absences: $0kl$ with l odd and $h0l$ with h odd, space group $Pca2_1$ (confirmed by structure analysis), $\mu(\text{Mo-K}\alpha) = 0.98$ cm⁻¹.

Normalized structure factors were generated from the $|F_o|$ data, and the statistical distributions of the $|E|$ values were consistent with those expected for a non-centrosymmetric crystal. Structure solution in space group $Pca2_1$ by the direct method based on negative quartets⁸ revealed the positions of fifty non-hydrogen atoms, belonging to the two crystallographically distinct molecules in the asymmetric unit. The remaining twenty non-hydrogen atoms were located from subsequent difference Fourier maps. These atoms were varied isotropically, and anisotropic refinement was not attempted in view of the unfavourable data-to-parameter ratio. In the last

Table 3. Fractional atomic co-ordinates ($\times 10^4$) for non-hydrogen atoms in compound (7) with estimated standard deviations in parentheses

Atom	x	y	z
C(1)	-2 254(6)	1 434(2)	5 324(3)
C(2)	-3 056(6)	835(3)	4 488(3)
C(3)	-2 559(5)	13(5)	4 944(3)
C(4)	-2 933(6)	-765(3)	4 585(3)
C(5)	-2 325(6)	-1 411(3)	5 202(3)
C(6)	-1 378(6)	-1 308(2)	6 186(3)
C(7)	-985(5)	-522(2)	6 572(2)
C(8)	-1 583(5)	99(2)	5 921(3)
C(9)	-46(6)	1 185(2)	7 011(3)
C(10)	979(5)	516(2)	7 691(2)
C(11)	-117(5)	-285(2)	7 631(2)
C(12)	-1 892(6)	-110(3)	7 975(3)
C(13)	-3 091(6)	-830(3)	8 077(3)
C(14)	-2 464(7)	-1 120(2)	9 112(3)
C(15)	-468(8)	-1 503(3)	9 452(3)
C(16)	1 203(7)	-1 009(2)	9 311(3)
C(17)	1 151(7)	-957(2)	8 264(3)
C(18)	2 747(6)	659(2)	8 311(3)
C(19)	3 868(6)	1 433(2)	8 427(3)
C(20)	5 806(6)	2 235(2)	7 764(3)
N	-1 309(4)	923(2)	6 172(2)
O(1)	303(4)	1 905(2)	7 204(2)
O(2)*	-2 219(6)	515(2)	8 208(3)
O(2')*	2 288(13)	-1 244(5)	7 957(5)
O(3)	4 338(4)	1 841(2)	9 132(2)
O(4)	4 505(4)	1 564(2)	7 681(2)

* Occupancies for O(2) and O(2') are respectively 0.673(5) and 0.327(5).

Table 4. Fractional atomic co-ordinates ($\times 10^4$) for non-hydrogen atoms in compound (11) with estimated standard deviations in parentheses

Atom	x	y	z
Molecule I			
C(1)	8 444(16)	1 084(16)	2 626(7)
C(2)	8 221(17)	992(17)	3 106(8)
C(3)	7 500(15)	191(14)	3 291(7)
C(4)	7 015(15)	-402(14)	2 937(7)
C(5)	7 219(16)	-243(14)	2 467(8)
C(6)	7 953(15)	455(15)	2 290(7)
C(7)	8 024(15)	209(14)	1 754(6)
C(8)	9 190(19)	56(16)	1 564(11)
C(9)	9 713(16)	-903(16)	1 829(7)
C(10)	8 931(15)	-1 801(16)	1 979(7)
C(11)	7 979(14)	-1 847(15)	1 630(7)
C(12)	7 454(14)	-788(14)	1 682(7)
C(13)	6 900(18)	436(19)	1 095(10)
C(14)	7 540(18)	1 068(15)	1 423(8)
C(15)	6 530(16)	-1 971(14)	2 180(7)
C(16)	6 695(14)	-2 264(14)	2 748(7)
C(17)	6 365(15)	-1 316(14)	3 071(7)
C(18)	7 162(17)	-2 606(17)	1 794(7)
C(19)	6 389(18)	-2 807(17)	1 355(8)
C(20)	6 302(16)	-3 158(18)	497(8)
C(21)	7 542(18)	-3 677(15)	1 999(7)
C(22)	7 871(12)	-4 448(13)	1 617(6)
C(23)	9 304(17)	-4 727(17)	1 048(8)

Table 4. (continued)

Atom	x	y	z
Molecule I			
C(24)	7 590(15)	2 057(14)	1 417(7)
C(25)	6 927(15)	2 690(15)	1 086(7)
C(26)	6 853(17)	3 736(17)	360(8)
N	6 782(11)	-851(11)	2 102(5)
O(1)	6 857(9)	-656(10)	1 218(4)
O(2)	6 409(11)	-696(11)	722(5)
O(3)	5 487(12)	-2 831(11)	1 398(6)
O(4)	6 917(10)	-3 004(11)	948(5)
O(5)	7 580(13)	-5 331(12)	1 559(6)
O(6)	8 753(11)	-4 090(11)	1 417(5)
O(7)	6 076(12)	2 887(12)	1 158(6)
O(8)	7 458(11)	3 065(10)	703(5)
Molecule II			
C(1')	4 171(17)	6 004(16)	3 014(7)
C(2')	4 404(17)	5 898(18)	2 503(8)
C(3')	5 045(16)	5 219(15)	2 358(8)
C(4')	5 584(15)	4 502(16)	2 625(7)
C(5')	5 357(19)	4 641(18)	3 166(9)
C(6')	4 661(17)	5 390(17)	3 340(7)
C(7')	4 487(15)	5 192(14)	3 878(7)
C(8')	3 409(18)	4 998(15)	4 030(10)
C(9')	2 918(15)	4 064(14)	3 771(7)
C(10')	3 629(13)	3 153(15)	3 642(7)
C(11')	4 590(16)	3 104(16)	3 974(8)
C(12')	5 133(14)	4 172(15)	3 958(7)
C(13')	5 792(15)	5 279(15)	4 507(8)
C(14')	5 105(15)	5 879(15)	4 184(8)
C(15')	6 071(14)	2 896(14)	3 413(6)
C(16')	5 846(16)	2 640(17)	2 864(8)
C(17')	6 221(15)	3 505(14)	2 528(7)
C(18')	5 426(13)	2 319(13)	3 814(6)
C(19')	6 166(14)	2 058(14)	4 271(7)
C(20')	6 204(20)	1 404(20)	5 090(8)
C(21')	5 037(17)	1 231(16)	3 632(8)
C(22')	4 616(21)	449(20)	4 019(10)
C(23')	3 426(16)	188(17)	4 652(7)
C(24')	5 060(15)	6 955(15)	4 230(7)
C(25')	5 733(18)	7 646(18)	4 566(8)
C(26')	5 786(21)	8 330(20)	5 337(10)
N'	5 828(11)	4 021(11)	3 525(5)
O(1')	5 751(10)	4 299(10)	4 383(5)
O(2')	6 339(11)	5 572(11)	4 848(5)
O(3')	7 035(12)	2 033(12)	4 217(5)
O(4')	5 590(11)	1 817(12)	4 660(5)
O(5')	5 075(12)	-273(12)	4 139(6)
O(6')	3 764(10)	838(11)	4 225(5)
O(7')	6 577(12)	7 918(12)	4 459(6)
O(8')	5 209(11)	7 748(11)	4 973(5)

stage of refinement, all hydrogen atoms except those belonging to methyl groups were generated geometrically and allowed to ride on their respective parent carbon atoms with the same assigned isotropic thermal parameter. Convergence was reached at $R_f = 0.108$, and the final difference map was essentially flat, with residual extrema lying between 0.55 and $-0.46 e \text{ \AA}^{-3}$.

Description of structure. The fractional atomic co-ordinates of molecules I (x, y, z) and II (x', y', z') are approximately related by $x' = 1.26 - x$, $y' = 0.49 + y$, and $z' = 0.56 - z$ (Table 4). The two molecules thus have virtually the same conformation (Figure 3), including the dispositions of the ester groups. Their central molecular skeletons (torsion angles in Table 7) also closely resemble that of the (*Z*)-isomer as described in ref. 6.

Calculations for compounds (4) and (7) were carried out on an IBM 3031 computer using the CRYM system.⁹ The quantity minimized in full matrix least-squares refinement was $\Sigma w(F_o^2 -$

Table 5. Bond lengths (Å), bond angles (°), and torsion angles (°) for compound (4)

Bond length			
C(1)-C(2)	1.376(5)	C(11)-C(12)	1.348(3)
C(2)-C(3)	1.372(4)	C(12)-C(4)	1.477(3)
C(3)-C(4)	1.420(4)	C(12)-C(13)	1.515(4)
C(4)-C(5)	1.397(4)	C(13)-C(14)	1.551(4)
C(5)-C(6)	1.402(4)	C(14)-C(15)	1.526(4)
C(6)-C(1)	1.371(4)	C(15)-C(16)	1.557(4)
C(6)-C(7)	1.500(4)	C(16)-C(17)	1.560(4)
C(7)-C(8)	1.522(4)	C(17)-C(18)	1.519(4)
C(8)-N	1.495(4)	C(18)-C(10)	1.541(4)
N-C(5)	1.409(3)	C(18)-O(2)	1.204(3)
N-C(9)	1.364(3)	C(11)-C(19)	1.503(4)
C(9)-O(1)	1.219(3)	C(19)-O(3)	1.190(4)
C(9)-C(10)	1.519(4)	C(19)-O(4)	1.316(3)
C(10)-C(11)	1.512(3)	O(4)-C(20)	1.453(4)
Bond angle			
C(6)-C(1)-C(2)	118.9(3)	C(10)-C(11)-C(19)	115.4(2)
C(1)-C(2)-C(3)	121.2(3)	C(19)-C(11)-C(12)	123.0(2)
C(2)-C(3)-C(4)	122.0(3)	C(11)-C(12)-C(13)	121.1(2)
C(3)-C(4)-C(5)	115.4(2)	C(11)-C(12)-C(4)	122.0(2)
C(3)-C(4)-C(12)	120.3(2)	C(4)-C(12)-C(13)	116.9(2)
C(5)-C(4)-C(12)	124.1(2)	C(12)-C(13)-C(14)	112.3(2)
C(4)-C(5)-C(6)	122.0(2)	C(13)-C(14)-C(15)	116.3(2)
C(4)-C(5)-N	129.0(2)	C(14)-C(15)-C(16)	115.3(2)
C(6)-C(5)-N	108.9(2)	C(15)-C(16)-C(17)	115.9(2)
C(5)-C(6)-C(1)	120.5(3)	C(16)-C(17)-C(18)	115.8(2)
C(5)-C(6)-C(7)	109.9(2)	C(17)-C(18)-C(10)	116.4(2)
C(1)-C(6)-C(7)	129.6(3)	C(17)-C(18)-O(2)	121.9(2)
C(6)-C(7)-C(8)	103.6(3)	C(10)-C(18)-O(2)	121.7(2)
C(7)-C(8)-N	103.5(3)	C(11)-C(19)-O(3)	127.5(3)
N-C(9)-C(10)	115.6(2)	C(11)-C(19)-O(4)	110.2(2)
N-C(9)-O(1)	122.5(2)	O(3)-C(19)-O(4)	122.2(3)
O(1)-C(9)-C(10)	121.9(2)	C(19)-O(4)-C(20)	116.3(2)
C(9)-C(10)-C(11)	113.8(2)	C(5)-N-C(8)	109.2(2)
C(9)-C(10)-C(18)	114.3(2)	C(5)-N-C(9)	128.0(2)
C(18)-C(10)-C(11)	109.4(2)	C(8)-N-C(9)	120.2(2)
C(10)-C(11)-C(12)	121.6(2)		
Torsion angle (°)			
N-C(5)-C(6)-C(7)			1.1(3)
C(5)-C(6)-C(7)-C(8)			-14.2(3)
C(6)-C(7)-C(8)-N			20.7(3)
C(7)-C(8)-N-C(5)			-21.4(3)
C(8)-N-C(5)-C(6)			13.1(3)
N-C(5)-C(4)-C(12)			3.2(4)
C(5)-C(4)-C(12)-C(11)			-26.2(4)
C(4)-C(12)-C(11)-C(10)			-18.4(4)
C(12)-C(11)-C(10)-C(9)			75.7(3)
C(11)-C(10)-C(9)-N			-57.2(3)
C(10)-C(9)-N-C(5)			-7.2(4)
C(9)-N-C(5)-C(4)			36.7(4)
C(9)-C(10)-C(11)-C(12)			75.7(3)
C(10)-C(11)-C(12)-C(13)			159.1(2)
C(11)-C(12)-C(13)-C(14)			-88.7(3)
C(12)-C(13)-C(14)-C(15)			37.3(3)
C(13)-C(14)-C(15)-C(16)			-78.1(3)
C(14)-C(15)-C(16)-C(17)			125.3(3)
C(15)-C(16)-C(17)-C(18)			-107.0(3)
C(16)-C(17)-C(18)-C(10)			92.9(3)
C(17)-C(18)-C(10)-C(11)			-48.8(3)
C(18)-C(10)-C(11)-C(12)			-53.5(3)

$F_o^2)^2$, with $w = 1/\sigma^2(F_o^2)$. Atomic scattering factors were obtained from ref. 10. All computations for compound (11) were performed on a Data General Nova 3/12 minicomputer with the SHELXTL program package.¹¹ Analytic expressions¹² of atomic scattering factors¹³ were employed, and anomalous

Table 6. Bond lengths (Å), bond angles (°), and torsion angles (°) for compound (7)

Bond length		Bond angle					
C(1)–C(2)	1.532(6)	C(11)–C(12)	1.555(5)	N–C(1)–C(2)	104.7(3)	C(11)–C(10)–C(18)	124.0(3)
C(2)–C(3)	1.502(6)	C(12)–O(2)	1.135(6)	C(1)–C(2)–C(3)	104.7(3)	C(7)–C(11)–C(10)	108.2(3)
C(3)–C(4)	1.378(6)	C(12)–C(13)	1.507(6)	C(2)–C(3)–C(4)	132.9(4)	C(7)–C(11)–C(12)	105.9(3)
C(4)–C(5)	1.372(6)	C(13)–C(14)	1.513(6)	C(2)–C(3)–C(8)	109.6(3)	C(7)–C(11)–C(17)	113.1(3)
C(5)–C(6)	1.389(6)	C(14)–C(15)	1.502(7)	C(4)–C(3)–C(8)	117.5(4)	C(10)–C(11)–C(12)	106.9(3)
C(6)–C(7)	1.404(5)	C(15)–C(16)	1.529(6)	C(3)–C(4)–C(5)	119.3(4)	C(10)–C(11)–C(17)	113.1(3)
C(7)–C(8)	1.370(5)	C(16)–C(17)	1.526(6)	C(4)–C(5)–C(6)	122.1(4)	C(12)–C(11)–C(17)	109.2(3)
C(8)–C(3)	1.380(5)	C(17)–O(2')	1.162(10)	C(5)–C(6)–C(7)	119.8(4)	C(11)–C(12)–C(13)	116.8(3)
C(1)–N	1.471(5)	C(17)–C(11)	1.539(6)	C(6)–C(7)–C(8)	115.6(3)	O(2)–C(12)–C(11)	123.0(4)
C(8)–N	1.405(5)	C(10)–C(18)	1.322(5)	C(6)–C(7)–C(11)	127.6(3)	O(2)–C(12)–C(13)	120.0(4)
C(9)–N	1.338(5)	C(18)–C(19)	1.491(6)	C(11)–C(7)–C(8)	116.6(3)	C(12)–C(13)–C(14)	111.0(3)
C(9)–O(1)	1.227(5)	C(19)–O(3)	1.186(5)	C(7)–C(8)–C(3)	125.7(4)	C(13)–C(14)–C(15)	113.7(4)
C(9)–C(10)	1.508(5)	C(19)–O(4)	1.339(5)	C(7)–C(8)–N	123.8(3)	C(14)–C(15)–C(16)	116.6(4)
C(10)–C(11)	1.528(5)	O(4)–C(20)	1.431(5)	C(3)–C(8)–N	110.6(3)	C(15)–C(16)–C(17)	114.2(4)
C(11)–C(7)	1.522(5)			C(1)–N–C(8)	110.3(3)	C(16)–C(17)–C(11)	117.3(3)
				C(1)–N–C(9)	125.3(3)	O(2')–C(17)–C(16)	125.7(6)
				C(8)–N–C(9)	123.2(3)	O(2')–C(17)–C(11)	114.6(5)
				N–C(9)–O(1)	123.4(4)	C(10)–C(18)–C(19)	126.6(4)
				N–C(9)–C(10)	114.2(3)	C(18)–C(19)–O(3)	124.9(4)
				O(1)–C(9)–C(10)	122.4(3)	C(18)–C(19)–O(4)	111.6(4)
				C(9)–C(10)–C(11)	117.5(3)	O(3)–C(19)–O(4)	123.0(4)
				C(9)–C(10)–C(18)	118.5(3)	C(19)–O(4)–C(20)	116.8(3)
Torsion angle							
C(7)–C(11)–C(12)–C(13)		70.9(3)		C(10)–C(11)–C(17)–O(2')		–75.2(6)	
C(7)–C(11)–C(12)–O(2)		–114.6(4)		C(11)–C(12)–C(13)–C(14)		97.2(4)	
C(7)–C(11)–C(17)–C(16)		–148.7(4)		C(12)–C(13)–C(14)–C(15)		–69.6(3)	
C(7)–C(11)–C(17)–O(2')		48.2(5)		C(13)–C(14)–C(15)–C(16)		53.4	
C(10)–C(11)–C(12)–C(13)		–173.9(3)		C(14)–C(15)–C(16)–C(17)		–73.4(4)	
C(10)–C(11)–C(12)–O(2)		0.5(4)		C(15)–C(16)–C(17)–C(11)		85.7(4)	
C(10)–C(11)–C(17)–C(16)		87.9(4)					

Table 7. Bond lengths (Å), bond angles (°), and torsion angles (°) for compound (11)

Bond lengths	Molecule			Molecule	
	I	II		I	II
C(1)–C(2)	1.35(3)	1.43(3)	C(1)–C(6)	1.38(3)	1.35(3)
C(2)–C(3)	1.48(3)	1.27(3)	C(3)–C(4)	1.38(3)	1.36(3)
C(4)–C(5)	1.33(3)	1.52(3)	C(4)–C(17)	1.49(3)	1.54(3)
C(5)–C(6)	1.40(3)	1.40(3)	C(5)–N	1.39(3)	1.40(3)
C(6)–C(7)	1.50(3)	1.51(3)	C(7)–C(8)	1.62(3)	1.49(3)
C(7)–C(12)	1.48(3)	1.56(3)	C(7)–C(14)	1.55(3)	1.45(3)
C(8)–C(9)	1.57(3)	1.53(3)	C(9)–C(10)	1.59(3)	1.53(3)
C(10)–C(11)	1.57(3)	1.55(3)	C(11)–C(12)	1.52(3)	1.53(3)
C(11)–C(18)	1.51(3)	1.54(3)	C(12)–N	1.45(2)	1.51(2)
C(12)–O(1)	1.50(2)	1.42(2)	C(13)–C(14)	1.47(3)	1.47(3)
C(13)–O(1)	1.43(3)	1.29(2)	C(13)–O(2)	1.25(3)	1.23(3)
C(14)–C(24)	1.26(3)	1.38(3)	C(15)–C(16)	1.61(3)	1.56(3)
C(15)–C(18)	1.57(3)	1.57(3)	C(15)–N	1.48(2)	1.50(2)
C(16)–C(17)	1.56(3)	1.51(2)	C(18)–C(19)	1.59(3)	1.62(3)
C(18)–C(21)	1.56(3)	1.56(2)	C(19)–O(3)	1.19(3)	1.15(2)
C(19)–O(4)	1.34(3)	1.34(3)	C(20)–O(4)	1.49(3)	1.52(3)
C(21)–C(22)	1.50(3)	1.56(3)	C(22)–O(5)	1.20(2)	1.15(3)
C(22)–O(6)	1.36(2)	1.34(3)	C(23)–O(6)	1.48(3)	1.50(2)
C(24)–C(25)	1.49(3)	1.55(3)	C(25)–O(7)	1.16(3)	1.19(3)
C(25)–O(8)	1.34(2)	1.32(3)	C(26)–O(8)	1.49(3)	1.45(3)
Bond angles					
C(1)–C(2)–C(3)	122(2)	121(2)	C(2)–C(1)–C(6)	120(2)	119(2)
C(3)–C(4)–C(5)	120(2)	110(2)	C(2)–C(3)–C(4)	115(2)	129(2)
C(5)–C(4)–C(17)	118(2)	112(2)	C(3)–C(4)–C(17)	121(2)	137(2)
C(4)–C(5)–N	122(2)	122(2)	C(4)–C(5)–C(6)	125(2)	122(2)
C(1)–C(6)–C(5)	117(2)	119(2)	C(6)–C(5)–N	113(2)	115(2)
C(5)–C(6)–C(7)	104(2)	108(2)	C(1)–C(6)–C(7)	138(2)	132(2)
C(6)–C(7)–C(12)	106(2)	101(2)	C(6)–C(7)–C(8)	113(2)	116(2)
C(6)–C(7)–C(14)	113(2)	112(2)	C(8)–C(7)–C(12)	109(2)	110(2)
C(12)–C(7)–C(14)	108(2)	97(2)	C(8)–C(7)–C(14)	106(2)	118(2)
C(8)–C(9)–C(10)	113(2)	116(2)	C(7)–C(8)–C(9)	111(2)	113(2)

Table 7 (continued)

Bond angle	Molecule			Molecule	
	I	II		I	II
C(10)-C(11)-C(12)	106(2)	109(2)	C(9)-C(10)-C(11)	112(2)	113(2)
C(12)-C(11)-C(18)	103(2)	104(2)	C(10)-C(11)-C(18)	114(2)	116(2)
C(7)-C(12)-N	104(1)	109(1)	C(7)-C(12)-C(11)	123(2)	119(2)
C(7)-C(12)-O(1)	106(1)	109(2)	C(11)-C(12)-N	107(1)	101(2)
N-C(12)-O(1)	111(1)	108(1)	C(11)-C(12)-O(1)	105(1)	110(2)
C(14)-C(13)-O(2)	130(2)	131(2)	C(14)-C(13)-O(1)	114(2)	108(2)
C(7)-C(14)-C(13)	102(2)	112(2)	O(1)-C(13)-O(2)	115(2)	121(2)
C(13)-C(14)-C(24)	125(2)	119(2)	C(7)-C(14)-C(24)	133(2)	129(2)
C(16)-C(15)-N	109(1)	111(1)	C(16)-C(15)-C(18)	117(2)	118(2)
C(15)-C(16)-C(17)	109(1)	112(2)	C(18)-C(15)-N	106(2)	101(1)
C(11)-C(18)-C(15)	104(2)	106(1)	C(4)-C(17)-C(16)	108(2)	109(2)
C(15)-C(18)-C(19)	105(2)	108(1)	C(11)-C(18)-C(19)	109(2)	110(1)
C(15)-C(18)-C(21)	112(2)	112(1)	C(11)-C(18)-C(21)	116(2)	116(2)
C(18)-C(19)-O(3)	124(2)	120(2)	C(19)-C(18)-C(21)	109(2)	105(1)
O(3)-C(19)-O(4)	126(2)	131(2)	C(18)-C(19)-O(4)	109(2)	109(1)
C(21)-C(22)-O(5)	128(2)	121(2)	C(18)-C(21)-C(22)	114(2)	118(2)
O(5)-C(22)-O(6)	122(2)	128(2)	C(21)-C(22)-O(6)	108(2)	110(2)
C(24)-C(25)-O(7)	125(2)	123(2)	C(14)-C(24)-C(25)	121(2)	127(2)
O(7)-C(25)-O(8)	124(2)	131(2)	C(24)-C(25)-O(8)	111(2)	105(2)
C(5)-N-C(15)	122(2)	119(2)	C(5)-N-C(12)	107(2)	102(2)
C(12)-O(1)-C(13)	107(1)	110(2)	C(12)-N-C(15)	108(1)	114(1)
C(22)-O(6)-C(23)	120(2)	112(2)	C(19)-O(4)-C(20)	116(2)	113(2)
C(25)-O(8)-C(26)	115(2)	111(2)			

Torsion angle	Molecule			Molecule	
	I	II		I	II
C(5)-C(6)-C(7)-C(12)	-11(2)	-4(2)	C(7)-C(12)-O(1)-C(13)	-13(2)	-16(2)
C(6)-C(7)-C(12)-N	21(2)	15(2)	C(12)-O(1)-C(13)-C(14)	4(2)	5(2)
C(7)-C(12)-N-C(5)	-23(2)	-20(2)	O(1)-C(13)-C(14)-C(7)	6(2)	9(2)
C(12)-N-C(5)-C(6)	17(2)	18(2)	C(13)-C(14)-C(7)-C(12)	-14(2)	-16(2)
N-C(5)-C(6)-C(7)	-4(2)	-9(3)	C(14)-C(7)-C(12)-O(1)	17(2)	18(2)
C(5)-N-C(15)-C(16)	8(2)	6(2)	C(7)-C(8)-C(9)-C(10)	30(3)	33(3)
N-C(15)-C(16)-C(17)	37(2)	43(2)	C(8)-C(9)-C(10)-C(11)	29(2)	24(2)
C(15)-C(16)-C(17)-C(4)	-60(2)	-67(2)	C(9)-C(10)-C(11)-C(12)	-62(2)	-54(2)
C(16)-C(17)-C(4)-C(5)	41(2)	39(2)	C(10)-C(11)-C(12)-C(7)	36(2)	31(2)
C(17)-C(4)-C(5)-N	5(3)	10(3)	C(11)-C(12)-C(7)-C(8)	21(2)	23(2)
C(4)-C(5)-N-C(15)	-32(3)	-34(3)	C(12)-C(7)-C(8)-C(9)	-56(2)	-56(2)

* The relationship between atomic co-ordinates in molecules I and II is given in the text.

dispersion corrections¹⁴ were incorporated. The weighting scheme employed for the blocked-cascade least-squares refinement and analysis of variance was $w = [\sigma^2(|F_o|) + 0.0005|F_o|^2]^{-1}$.

The final atomic co-ordinates for compounds (4), (7), and (11) are, respectively, given in Tables 2, 3, and 4. Bond distances and angles, and selected torsion angles, are listed in Tables 5, 6, and 7, respectively. The anisotropic [compounds (4) and (7)] and isotropic [compound (11)] thermal parameters for the non-hydrogen atoms, and the positional and thermal parameters for the hydrogen atoms, are in Supplementary Publication No. SUP 56280 (8 pp).*

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* For details of the Supplementary Publications Scheme, see Instructions for Authors (1985), *J. Chem. Soc., Perkin Trans. I*, 1985, Issue 1. Structure factors are available from the editorial office on request.

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