

The Crystal Structures of (Z)-Dimethyl 3-Methoxycarbonylmethyl-11-methyl-2-oxo-1,4,5,6,6a,11-hexahydrofuro[2',3':2,3]cyclohexa[1,2-b]-indol-6a-ylfumarate, (E)-Dimethyl-3-methoxycarbonylmethyl-12-methyl-2-oxo-4,5,6,7,7a,12-hexahydro-1H-furo[2',3':2,3]cyclohepta[1,2-b]indol-7a-ylmaleate, and Trimethyl 6-Bromo-9-methyl-2-oxo-1,2,3,9a-tetrahydro-3,9a-ethenocarbazole-1-spirocyclopentane-4,10,11-tricarboxylate

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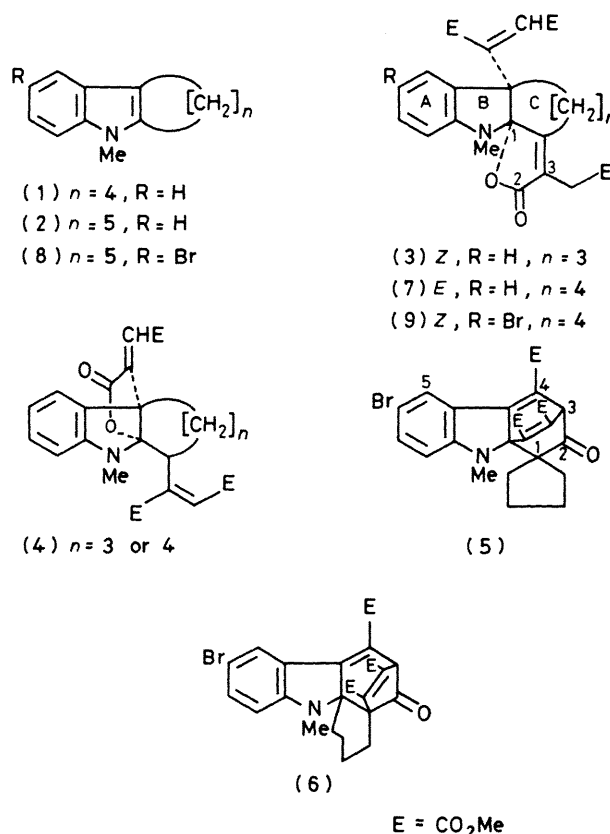
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The structures of two (1 IND + 2 DMAD - CH₂) adducts, and a (1 IND + 2 DMAD - CH₄O) adduct, obtained from the addition of dimethyl acetylenedicarboxylate (DMAD) to *N*-methylindoles (IND) having a polymethylene chain linking positions 2 and 3, have been determined by X-ray crystallography.

Dimethyl acetylenedicarboxylate (DMAD) has been found¹ to add to the *N*-methylindoles (IND) (1) and (2) to give, among other products, one (1 IND + 2 DMAD - CH₂) adduct in each case and referred to as compounds D and F respectively.¹ These adducts have remarkably similar spectra and were considered to have very closely analogous structures. Spectroscopy however was unable to establish the size of the lactone ring or the relative stereochemistry of the two sp³ carbon atoms which, though unlikely, could in the case of F, have a *trans*-fused b/c ring. Therefore, in order to establish their correct structures, single crystal X-ray analyses were carried out. The resultant structures are, (3) for D (see Figure 1) and (7) for F (see Figure 2), showing that they do in fact have analogous structures including *cis*-fused b/c rings, and that the ¹H n.m.r. spectral differences of the diastereotopic methylene protons are not diagnostic. We have recently reported three further examples of (1 IND + 2 DMAD - CH₂) adducts² analogous to D and F. It is interesting that no (1 IND + 2 DMAD - CH₂) adducts, such as (4) have been isolated, in which the γ -lactone is formed by the other side-chain [as in the case of the (1 IND + 1 DMAD - CH₂) adducts¹].

We have recently found that DMAD adds to indoles which possess either a penta- or hexa- methylene chain joining positions 2 and 3, to give orange coloured (1 IND + 2 DMAD - CH₄O) adducts, all of which exhibit very similar spectral characteristics,^{2,3} and which indicate that they are formed through processes not previously observed in DMAD additions to indoles.^{1,4} Proton coupled ¹³C n.m.r. spectra is also largely uninformative,⁵ revealing only that all four carbonyl carbon atoms are weakly coupled to the sp³ C-H proton; further clues did however come from their thermolysis,² but still no single structure could be established with confidence [for example both structures (5) and (6) fit the data]. We therefore carried out an X-ray analysis of the (1 IND + 2 DMAD - CH₄O) adduct obtained from the addition of DMAD to the bromo(pentamethylene)indole (8). The resulting structure proved to be (5) and is shown in Figure 3. The probable mechanism of formation and reactions of (5) and other (1 IND + 2 DMAD - CH₄O) adducts have been discussed.²

Addition of DMAD to the indole (8) yielded (5) together with a colourless (1 IND + 2 DMAD - CH₂) adduct with spectral characteristics reminiscent of (7) and consequently deduced as (9).



Experimental

The instruments and procedures are given in refs. 4 and 5.

Preparation of the Indole (8).—Reduction of *p*-bromo-*N*-methyl-*N*-nitrosoaniline, m.p. 74 °C (lit.,⁶ 74 °C) with lithium aluminium hydride in ether gave *N*-*p*-bromophenyl-*N*-methylhydrazine (b.p. 96 °C at 0.2 mmHg) which formed a hydrochloride, m.p. 166–167 °C (ethanol-diethyl ether) (Found: C, 35.5; H, 4.2; N, 11.8. C₇H₁₀N₂BrCl requires C, 35.8; H, 4.3; N, 11.7%). The hydrazine with cycloheptanone, by the method of Perkin,⁴ gave 2-bromo-5-methyl-5,6,7,8,9,10-hexahydrocyclohept[b]indole (8) (from ethanol), m.p.

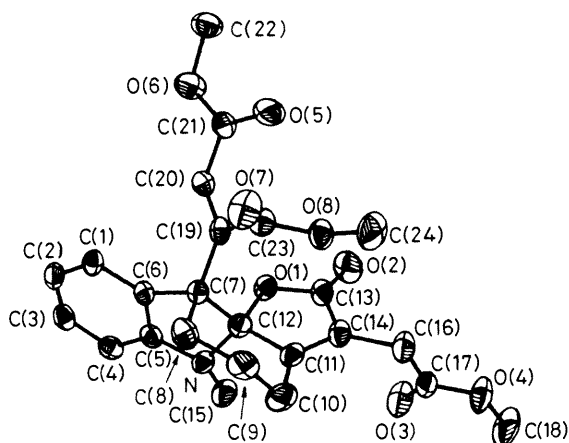


Figure 1. Perspective view of the (*Z*)-dimethyl 3-methoxycarbonylmethyl-11-methyl-2-oxo-1,4,5,6,6a,11-hexahydrofuro[2',3':2,3]-cyclohexa[1,2-*b*]indol-6a-ylfumurate (3)

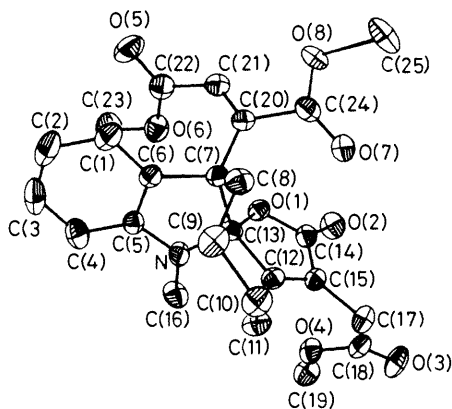


Figure 2. Perspective view of the (*E*)-dimethyl 3-methoxycarbonylmethyl-12-methyl-2-oxo-4,5,6,7,7a,12-hexahydro-1*H*-furo[2',3':2,3]-cyclohepta[1,2-*b*]indol-7a-ylmaleate (7)

62–63 °C (Found: C, 60.8; H, 5.8; N, 4.8. $C_{14}H_{16}BrN$ requires C, 60.5; H, 5.8; N, 5.0%); δ 7.56 (1 H, d, J 1.8 Hz), 7.17 (1 H, dd, J 1.8 and 8.3 Hz), 6.99 (1 H, d, J 8.3 Hz), 3.58 (3 H, s, NMe), and 3.0–2.0 (10 H, m, aliphatic H).

The Indole (8) with Dimethyl Acetylenedicarboxylate.—The indole (8) (1.0 g) and DMAD (2.0 g) were heated at 80 °C in moist 98% acetic acid for 3 days. Evaporation and p.l.c. (chloroform) gave numerous bands when viewed under u.v. light (254 nm). Apart from the indole (8) (0.25 g), crystalline material was obtained from two bands.

(i) The pale yellow band (R_f 0.2) gave colourless rods (from ethanol) (0.25 g, 16%) of (*Z*)-dimethyl 9-bromo-3-methoxycarbonylmethyl-12-methyl-2-oxo-4,5,6,7,7a,12-hexahydro-1*H*-furo[2',3':2,3]cyclohepta[1,2-*b*]indol-7a-ylmaleate (9), m.p. 174–175 °C (Found: C, 55.0; H, 5.0; N, 2.4. $C_{25}H_{26}BrNO_4$ requires C, 54.8; H, 4.8; N, 2.55%); ν_{max} . 1770(s), 1740(s), and 1728 cm^{-1} (s); λ_{max} . 256 (ϵ 18 000) and 321 nm (4 010) unchanged on the addition of 1 drop of 70% perchloric acid; m/z 549/547 (M^+ , 100%), 518/516 (25), 490/488 (100), and 431/429 (100); δ 7.33 (1 H, dd, J 2 and 8.3 Hz, 10-H), 7.02 (1 H, d, J 2 Hz, 8-H), 6.43 (1 H, d, J 8.3 Hz, 11-H), 5.67 (1 H, s, olefinic H), 3.74 (6 H, s, 2 \times OMe), 3.67 (3 H, s, OMe), 3.42 (2 H, s, CH_2), 2.63 (3 H, s, NMe), 3.0–0.8 (8 H, m, aliphatic H), unchanged on shaking with D_2O ; ^{13}C n.m.r.

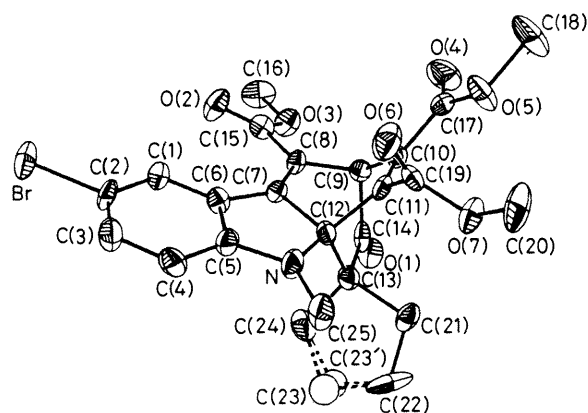


Figure 3. Perspective view of the trimethyl 6-bromo-9-methyl-2-oxo-1,2,3,9a-tetrahydro-3,9a-ethenocarbazole-1-spirocyclopentane-4,10,11-tricarboxylate (5)

Table 1. Fractional atomic co-ordinates ($\times 10^4$) for non-hydrogen atoms in compound (3) with standard deviations in parentheses

Atom	x	y	z
C(1)	3 545(3)	4 623(5)	2 508(2)
C(2)	3 277(3)	5 821(6)	2 922(2)
C(3)	2 418(3)	6 187(6)	2 764(2)
C(4)	1 775(3)	5 411(6)	2 188(2)
C(5)	2 044(3)	4 223(5)	1 774(2)
C(6)	2 922(3)	3 829(5)	1 927(2)
C(7)	2 988(3)	2 375(5)	1 402(2)
C(8)	2 984(3)	381(6)	1 719(2)
C(9)	2 643(3)	−1 254(6)	1 214(2)
C(10)	1 752(3)	−861(6)	677(3)
C(11)	1 763(3)	988(6)	341(2)
C(12)	2 082(3)	2 664(5)	811(2)
C(13)	1 850(3)	3 503(7)	−316(2)
C(14)	1 632(3)	1 501(7)	−303(2)
C(15)	637(3)	3 747(7)	808(2)
C(16)	1 363(3)	283(7)	−946(2)
C(17)	430(3)	572(7)	−1 401(2)
C(18)	−675(3)	−316(10)	−2 457(3)
C(19)	3 751(3)	2 657(5)	1 168(2)
C(20)	4 206(3)	4 296(6)	1 247(2)
C(21)	4 961(3)	4 449(6)	1 034(2)
C(22)	6 244(4)	6 142(8)	1 172(3)
C(23)	4 052(3)	981(6)	880(2)
C(24)	3 798(4)	−907(8)	−114(3)
N	1 535(2)	3 212(5)	1 183(2)
O(1)	2 117(2)	4 213(4)	343(1)
O(2)	1 826(2)	4 489(5)	−790(2)
O(3)	−64(2)	1 627(6)	−1 282(2)
O(4)	221(2)	−470(5)	−1 958(2)
O(5)	5 118(2)	3 400(5)	640(2)
O(6)	5 478(2)	5 855(4)	1 348(2)
O(7)	4 600(2)	−106(5)	1 223(2)
O(8)	3 587(2)	752(4)	207(1)

carbon resonances 169.9 (s^a , lactone CO), 169.5 (s^b , ester CO), 167.4 (s^c , ester CO), 165.1 (s^d , ester CO), 162.1(s), 150.0(s), 148.4(s), 132.4(d), 130.7(s), 127.6(d), 125.6(s), 124.4(d), 110.2(s), 108.8(s), 107.5(d), 59.5(s), 52.4(q, OMe)₂, 51.9(q, OMe), 36.1(t), 28.7(t), 26.9(q, NMe), 26.5 (t \times 2), 23.4(t).

(ii) The orange band (R_f 0.5) gave orange prisms (from

* With coupling constants (Hz) from proton-coupled spectra: ^a t, J_{CO,CH_2} 5.3; ^b m; ^c dq, $J_{CO,H}$ 11.7, J_{CO,CH_3} 4.0; ^d dq, $J_{CO,H}$ 1.5, J_{CO,CH_3} 4.0.

ethanol) (0.35 g, 24%) of *trimethyl 6-bromo-9-methyl-2-oxo-1,2,3,9a-tetrahydro-3,9a-ethenocarbazole-1-spirocyclopentane-4,10,11-tricarboxylate* (5), m.p. 221–222 °C (Found: C, 56.5; H, 4.65; Br, 14.9; N, 2.65. $C_{25}H_{24}BrNO_7$ requires C, 56.6; H, 4.55; N, 2.65; Br, 15.05%), v_{max} . 1738w, 1721s, and 1718w cm^{-1} ; λ_{max} . 204 (ϵ 17 110), 246 (22 400), and 461 nm (6 200), unchanged on the addition of 1 drop of 70% perchloric acid; m/z 531/529 (M^+ , 8%), 435/433 (100), 389 (10), and 317 (28); δ 8.74 (1 H, d, J 2.2 Hz, 5-H), 7.44 (1 H, dd, J 2.2 and 8.8 Hz, 7-H), 6.50 (1 H, d, J 8.8 Hz, 8-H), 5.39 (1 H,

Table 2. Fractional atomic co-ordinates ($\times 10^4$) for non-hydrogen atoms in compound (7) with standard deviations in parentheses

Atom	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	2 905(3)	-1 644(1)	3 322(1)
C(2)	3 045(4)	-2 343(1)	3 474(1)
C(3)	3 940(4)	-2 484(1)	3 839(1)
C(4)	4 704(3)	-1 946(1)	4 081(1)
C(5)	4 537(3)	-1 253(1)	3 926(1)
C(6)	3 667(3)	-1 103(1)	3 553(1)
C(7)	3 635(3)	-304(1)	3 472(1)
C(8)	1 742(3)	-49(1)	3 464(1)
C(9)	650(3)	-226(1)	3 856(1)
C(10)	699(3)	350(1)	4 195(1)
C(11)	2 422(3)	434(1)	4 421(1)
C(12)	3 934(3)	581(1)	4 144(1)
C(13)	4 711(3)	-6(1)	3 866(1)
C(14)	6 404(3)	1 006(1)	3 852(1)
C(15)	4 947(3)	1 151(1)	4 133(1)
C(16)	6 236(4)	-603(1)	4 480(1)
C(17)	4 875(3)	1 845(1)	4 371(1)
C(18)	6 409(3)	1 980(1)	4 653(1)
C(19)	8 599(4)	1 452(2)	5 062(1)
C(20)	4 494(3)	-98(1)	3 049(1)
C(21)	5 537(4)	-494(1)	2 813(1)
C(22)	6 266(3)	-1 223(1)	2 889(1)
C(23)	8 164(4)	-1 926(2)	3 290(1)
C(24)	4 191(3)	657(1)	2 895(1)
C(25)	3 977(5)	1 414(2)	2 293(1)
N	5 105(3)	-628(1)	4 118(1)
O(1)	6 301(2)	319(1)	3 710(1)
O(2)	7 576(2)	1 393(1)	3 756(1)
O(3)	6 914(2)	2 563(1)	4 752(1)
O(4)	7 107(2)	1 372(1)	4 792(1)
O(5)	5 974(3)	-1 714(1)	2 650(1)
O(6)	7 343(2)	-1 240(1)	3 213(1)
O(7)	4 031(3)	1 159(1)	3 126(1)
O(8)	4 164(3)	703(1)	2 474(1)

Table 3. Fractional atomic co-ordinates ($\times 10^4$) for non-hydrogen atoms in compound (5) with standard deviations in parentheses

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Br	6 737(1)	506(1)	6 423(1)
N	8 315(7)	-745(4)	3 014(4)
O(1)	4 328(6)	-410(4)	770(3)
O(2)	4 839(6)	1 996(4)	3 465(4)
O(3)	3 724(6)	1 643(4)	2 087(4)
O(4)	6 700(7)	2 162(4)	441(4)
O(5)	8 784(7)	1 638(4)	603(4)
O(6)	10 326(6)	729(4)	2 382(3)
O(7)	9 989(5)	-85(4)	1 146(3)
C(1)	6 624(8)	421(6)	4 573(5)
C(2)	7 305(9)	73(6)	5 353(5)
C(3)	8 333(9)	-498(6)	5 410(5)
C(4)	8 763(9)	-815(5)	4 666(5)
C(5)	8 061(8)	-502(6)	3 847(5)
C(6)	7 051(8)	100(5)	3 800(5)
C(7)	6 598(7)	309(5)	2 874(4)
C(8)	5 711(8)	829(5)	2 393(5)
C(9)	5 773(8)	758(5)	1 410(5)

Table 3 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>
C(10)	7 195(8)	860(5)	1 264(5)
C(11)	8 082(7)	342(5)	1 749(4)
C(12)	7 432(8)	-278(5)	2 337(5)
C(13)	6 388(9)	-851(5)	1 696(5)
C(14)	5 391(8)	-209(6)	1 230(5)
C(15)	4 733(8)	1 426(6)	2 724(6)
C(16)	2 703(9)	2 199(6)	2 356(7)
C(17)	7 526(9)	1 616(5)	727(5)
C(18)	9 224(11)	2 383(7)	114(7)
C(19)	9 561(8)	372(5)	1 792(5)
C(20)	11 425(8)	-53(7)	1 107(5)
C(21)	7 004(8)	-1 373(6)	981(5)
C(22)	6 584(11)	-2 312(6)	1 088(8)
C(23) *	6 312(19)	-2 453(14)	1 986(12)
C(23) *	5 466(20)	-2 406(13)	1 618(12)
C(24)	5 718(9)	-1 563(6)	2 182(5)
C(25)	9 356(9)	-1 345(6)	2 874(5)

* Assumed half populated site.

Table 4. Bond lengths, angles, and torsion angles for compound (3)

Bond length (Å)			
C(1)–C(2)	1.386(7)	C(1)–C(6)	1.386(5)
C(2)–C(3)	1.360(7)	C(3)–C(4)	1.390(5)
C(4)–C(5)	1.381(6)	C(5)–C(6)	1.396(6)
C(5)–N	1.404(4)	C(6)–C(7)	1.529(6)
C(7)–C(8)	1.554(6)	C(7)–C(12)	1.565(5)
C(7)–C(19)	1.517(7)	C(8)–C(9)	1.522(6)
C(9)–C(10)	1.513(6)	C(10)–C(11)	1.483(6)
C(11)–C(12)	1.502(5)	C(11)–C(14)	1.322(6)
C(12)–N	1.437(6)	C(12)–O(1)	1.476(5)
C(13)–C(14)	1.461(7)	C(13)–O(1)	1.368(5)
C(13)–O(2)	1.192(6)	C(14)–C(16)	1.509(6)
C(15)–N	1.452(5)	C(16)–C(17)	1.500(6)
C(17)–O(3)	1.195(6)	C(17)–O(4)	1.305(5)
C(18)–O(4)	1.470(5)	C(19)–C(20)	1.357(6)
C(19)–C(23)	1.489(6)	C(20)–C(21)	1.470(7)
C(21)–O(5)	1.198(6)	C(21)–O(6)	1.317(5)
C(22)–O(6)	1.452(8)	C(23)–O(7)	1.202(5)
C(23)–O(8)	1.335(4)	C(24)–O(8)	1.449(7)
Bond angle (°)			
C(2)–C(1)–C(6)	118.7(4)	C(1)–C(2)–C(3)	120.5(4)
C(2)–C(3)–C(4)	122.5(5)	C(3)–C(4)–C(5)	117.0(4)
C(4)–C(5)–C(6)	121.4(3)	C(4)–C(5)–N	128.6(4)
C(6)–C(5)–N	109.9(4)	C(1)–C(6)–C(5)	120.0(4)
C(1)–C(6)–C(7)	131.8(4)	C(5)–C(6)–C(7)	108.0(3)
C(6)–C(7)–C(8)	107.2(3)	C(6)–C(7)–C(12)	100.0(3)
C(8)–C(7)–C(12)	107.4(3)	C(6)–C(7)–C(19)	114.9(3)
C(8)–C(7)–C(19)	112.7(3)	C(12)–C(7)–C(19)	113.7(3)
C(7)–C(8)–C(9)	117.0(3)	C(8)–C(9)–C(10)	112.6(4)
C(9)–C(10)–C(11)	109.4(4)	C(10)–C(11)–C(12)	116.7(4)
C(10)–C(11)–C(14)	133.6(4)	C(12)–C(11)–C(14)	109.2(4)
C(7)–C(12)–C(11)	114.5(3)	C(7)–C(12)–N	103.1(3)
C(11)–C(12)–N	114.7(4)	C(7)–C(12)–O(1)	110.9(3)
C(11)–C(12)–O(1)	104.2(3)	N–C(12)–O(1)	109.5(3)
C(14)–C(13)–O(1)	109.2(4)	C(14)–C(13)–O(2)	130.2(4)
O(1)–C(13)–O(2)	120.6(4)	C(11)–C(14)–C(13)	109.4(4)
C(11)–C(14)–C(16)	128.4(4)	C(13)–C(14)–C(16)	122.1(4)
C(14)–C(16)–C(17)	112.5(4)	C(16)–C(17)–O(3)	125.4(4)
C(16)–C(17)–O(4)	111.1(4)	O(3)–C(17)–O(4)	123.5(4)
C(7)–C(19)–C(20)	124.1(4)	C(7)–C(19)–C(23)	117.4(3)
C(20)–C(19)–C(23)	118.3(4)	C(19)–C(20)–C(21)	121.3(4)
C(20)–C(21)–O(6)	125.2(4)	C(20)–C(21)–O(6)	112.0(4)
O(5)–C(21)–O(6)	122.8(5)	C(19)–C(23)–O(7)	124.0(4)
C(19)–C(23)–O(8)	111.4(3)	O(7)–C(23)–O(8)	124.3(4)
C(5)–N–C(12)	108.1(3)	C(5)–N–C(15)	120.4(4)
C(12)–N–C(15)	120.2(3)	C(12)–O(1)–C(13)	108.0(3)
C(17)–O(4)–C(18)	117.1(4)	C(21)–O(6)–C(22)	116.7(4)
C(23)–O(8)–C(24)	115.7(3)		

Table 4 (continued)

Torsion angle (°)	
C(5)-C(6)-C(7)-C(12)	20.5(4)
C(6)-C(7)-C(12)-N	-31.0(4)
C(7)-C(12)-N-C(5)	32.0(4)
C(12)-N-C(5)-C(6)	-19.6(4)
N-C(5)-C(6)-C(7)	-2.1(4)
C(7)-C(8)-C(9)-C(10)	-52.7(6)
C(8)-C(9)-C(10)-C(11)	51.9(6)
C(9)-C(10)-C(11)-C(12)	-53.6(6)
C(10)-C(11)-C(12)-C(7)	52.2(6)
C(11)-C(12)-C(7)-C(8)	-44.6(5)
C(12)-C(7)-C(8)-C(9)	46.6(6)
C(12)-O(1)-C(13)-C(14)	0.2(5)
O(1)-C(13)-C(14)-C(11)	-0.3(5)
C(13)-C(14)-C(11)-C(12)	0.2(5)
C(14)-C(11)-C(12)-O(1)	-0.1(5)
C(11)-C(12)-O(1)-C(13)	0.0(4)
C(19)-C(7)-C(12)-C(11)	80.8(4)
C(19)-C(7)-C(12)-O(1)	-36.8(4)
C(19)-C(7)-C(12)-N	-153.9(3)
C(6)-C(7)-C(12)-C(11)	-156.3(4)
C(8)-C(7)-C(12)-O(1)	-162.2(3)

Table 5. Bond lengths, angles, and torsion angles for compound (7)

Bond length (Å)			
C(1)-C(2)	1.392(4)	O(1)-C(14)	1.362(3)
C(2)-C(3)	1.366(4)	C(14)-C(15)	1.461(3)
C(3)-C(4)	1.392(4)	C(15)-C(12)	1.326(3)
C(4)-C(5)	1.389(4)	C(14)-O(2)	1.204(3)
C(5)-C(6)	1.381(3)	C(15)-C(17)	1.499(3)
C(6)-C(1)	1.378(4)	C(17)-C(18)	1.508(4)
C(6)-C(7)	1.514(3)	C(18)-O(3)	1.200(3)
C(7)-C(13)	1.593(3)	C(18)-O(4)	1.333(3)
C(13)-N	1.437(3)	O(4)-C(19)	1.445(3)
N-C(5)	1.386(3)	C(7)-C(20)	1.533(3)
N-C(16)	1.438(3)	C(20)-C(21)	1.325(4)
C(7)-C(8)	1.551(3)	C(21)-C(22)	1.494(4)
C(8)-C(9)	1.532(4)	C(22)-O(5)	1.206(3)
C(9)-C(10)	1.513(4)	C(22)-O(6)	1.318(3)
C(10)-C(11)	1.527(4)	O(6)-C(23)	1.452(4)
C(11)-C(12)	1.490(3)	C(20)-C(24)	1.510(4)
C(12)-C(13)	1.526(3)	C(24)-O(7)	1.191(3)
C(13)-C(7)	1.593(3)	C(24)-O(8)	1.323(3)
C(13)-O(1)	1.464(3)	O(8)-C(25)	1.452(4)

Bond angle (°)			
C(6)-C(1)-C(2)	118.4(2)	O(1)-C(13)-C(12)	103.2(2)
C(1)-C(2)-C(3)	120.5(3)	O(1)-C(14)-O(2)	121.9(2)
C(2)-C(3)-C(4)	122.4(3)	O(1)-C(14)-C(15)	109.0(2)
C(3)-C(4)-C(5)	116.3(2)	O(2)-C(14)-C(15)	129.0(2)
C(4)-C(5)-C(6)	122.1(2)	C(12)-C(15)-C(14)	109.2(2)
C(4)-C(5)-N	127.2(2)	C(12)-C(15)-C(17)	131.3(2)
C(6)-C(5)-N	110.9(2)	C(14)-C(15)-C(17)	119.3(2)
C(5)-C(6)-C(1)	120.5(2)	C(15)-C(17)-C(18)	114.0(2)
C(5)-C(6)-C(7)	110.5(2)	C(17)-C(18)-O(3)	124.3(2)
C(7)-C(6)-C(1)	129.0(2)	C(17)-C(18)-O(4)	112.0(2)
C(6)-C(7)-C(8)	108.8(2)	O(3)-C(18)-O(4)	123.7(2)
C(6)-C(7)-C(13)	101.9(2)	C(18)-O(4)-C(19)	115.6(2)
C(8)-C(7)-C(13)	113.9(2)	C(7)-C(20)-C(21)	127.6(2)
C(6)-C(7)-C(20)	112.6(2)	C(7)-C(20)-C(24)	116.3(2)
C(8)-C(7)-C(20)	108.9(2)	C(21)-C(20)-C(24)	116.0(2)
C(13)-C(7)-C(20)	110.6(2)	C(20)-C(21)-C(22)	130.8(2)
C(7)-C(8)-C(9)	116.7(2)	C(21)-C(22)-O(5)	121.5(2)
C(8)-C(9)-C(10)	113.4(2)	C(21)-C(22)-O(6)	112.8(2)
C(9)-C(10)-C(11)	114.9(2)	O(5)-C(22)-O(6)	125.5(2)
C(10)-C(11)-C(12)	116.4(2)	C(22)-O(6)-C(23)	115.5(2)
C(11)-C(12)-C(13)	121.0(2)	C(20)-C(24)-O(7)	123.8(2)
C(11)-C(12)-C(15)	129.4(2)	C(20)-C(24)-O(8)	112.6(2)
C(13)-C(12)-C(15)	109.0(2)	O(7)-C(24)-O(8)	123.6(2)
C(7)-C(13)-N	104.9(2)	C(24)-O(8)-C(25)	116.8(2)
C(7)-C(13)-O(1)	109.3(2)	C(13)-O(1)-C(14)	109.4(2)

Table 5 (continued)

C(7)-C(13)-C(12)	119.0(2)	C(5)-N-C(13)	112.0(2)
N-C(13)-O(1)	109.7(2)	C(5)-N-C(16)	124.4(2)
N-C(13)-C(12)	110.6(2)	C(13)-N-C(16)	122.6(2)

Torsion angle (°)	
C(5)-C(6)-C(7)-C(13)	-1.6(2)
C(6)-C(7)-C(13)-N	3.1(2)
C(7)-C(13)-N-C(5)	-3.8(2)
C(13)-N-C(5)-C(6)	2.9(3)
N-C(5)-C(6)-C(7)	-0.6(3)
C(12)-C(13)-O(1)-C(14)	3.1(2)
C(13)-O(1)-C(14)-C(15)	-3.8(2)
O(1)-C(14)-C(15)-C(12)	3.1(3)
C(14)-C(15)-C(12)-C(13)	-1.1(3)
C(15)-C(12)-C(13)-O(1)	-1.1(2)
C(7)-C(8)-C(9)-C(10)	-90.4(3)
C(8)-C(9)-C(10)-C(11)	68.5(3)
C(9)-C(10)-C(11)-C(12)	-56.7(3)
C(10)-C(11)-C(12)-C(13)	73.5(3)
C(11)-C(12)-C(13)-C(7)	-68.3(3)
C(12)-C(13)-C(7)-C(8)	10.5(3)
C(13)-C(7)-C(8)-C(9)	57.7(3)
C(6)-C(7)-C(13)-O(1)	-114.5(2)
C(6)-C(7)-C(13)-C(12)	127.4(2)
C(6)-C(7)-C(13)-N	3.1(2)
C(8)-C(7)-C(13)-N	-113.8(2)
C(20)-C(7)-C(13)-N	123.1(2)

s, 3-H), 3.88 (3 H, s, OMe), 3.85 (3 H, s, OMe), 3.82 (3 H, s, OMe), 3.17 (3 H, s, NMe), and 2.2—0.8 (8 H, aliphatic H), unchanged on shaking with D₂O.

X-Ray Crystal Structure Analysis of Compounds (3), (7), and (5).—Intensity data for all three compounds were measured on a Nicolet R3m diffractometer using the θ — 2θ scanning technique in the bisecting mode, with variable scan speeds from 1.50 to 8.37° min⁻¹ 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 $\pm 1.5\%$ and showed no systematic decline. The radiation used was graphite monochromatized Mo- K_{α} ($\lambda = 0.71069$ Å). No absorption correction was made. Further details of the collection of intensity data are given below.

Compd.	Crystal size	$2\theta_{\max}$	No. of unique reflections	No. of reflections with $ F_o > 3\sigma(F_o)$
(3)	0.7 × 0.5 × 0.2 mm	50°	3 441	2 622
(7)	0.8 × 0.6 × 0.5 mm	54°	4 994	3 371
(5)	0.6 × 0.5 × 0.3 mm	54°	5 109	2 564

Reflections with $|F_o| > 3\sigma(|F_o|)$ were considered to be observed and used in subsequent calculations. The large number of weak reflections for compound (5) was mainly due to the poor quality of the crystal. Unit-cell dimensions were obtained from a least-squares fit to 20 high-angle reflections.

*Compound (3).*¹—Crystal data. C₂₄H₂₅NO₈, $M = 455.46$, monoclinic, $P2_1/c$, $a = 16.516(3)$, $b = 7.060(1)$, $c = 20.706(5)$ Å, $\beta = 111.27(2)^\circ$, $U = 2 250$ Å³, $D_m = 1.33$ g cm⁻³, $Z = 4$, $D_c = 1.345$ g cm⁻³, $F(000) = 960$, $\mu(\text{Mo-}K_{\alpha}) = 0.95$ cm⁻¹.

The structure was solved by the direct method based on negative quartets,⁷ and all non-hydrogen atoms appeared on

Table 6. Bond lengths, angles, and torsion angles for compound (5)

Bond length (Å)	
C(2)-Br	1.938(8)
C(1)-C(2)	1.386(11)
C(2)-C(3)	1.344(12)
C(3)-C(4)	1.371(12)
C(4)-C(5)	1.423(11)
C(5)-C(6)	1.362(11)
C(6)-C(1)	1.411(11)
C(6)-C(7)	1.457(10)
C(7)-C(12)	1.551(10)
C(12)-N	1.442(12)
N-C(5)	1.393(10)
N-C(25)	1.433(11)
C(7)-C(8)	1.327(10)
C(8)-C(9)	1.523(11)
C(9)-C(10)	1.487(11)
C(10)-C(11)	1.329(10)
C(11)-C(12)	1.526(11)
C(9)-C(14)	1.542(11)
C(14)-C(13)	1.501(11)
C(13)-C(12)	1.583(11)
C(8)-C(15)	1.488(11)
C(15)-O(2)	1.199(10)
C(15)-O(3)	1.332(10)
O(3)-C(16)	1.441(11)
C(10)-C(17)	1.488(11)
C(17)-O(4)	1.209(11)
C(17)-O(5)	1.306(10)
O(5)-C(18)	1.472(12)
C(11)-C(19)	1.476(11)
C(19)-O(6)	1.219(10)
C(19)-O(7)	1.339(9)
O(7)-C(20)	1.452(10)
C(14)-O(1)	1.221(10)
C(13)-C(21)	1.561(11)
C(21)-C(22)	1.514(13)
C(22)-C(23)	1.461(22)
C(22)-C(23')	1.493(22)
C(23)-C(24)	1.536(22)
C(23')-C(24)	1.553(21)
C(24)-C(13)	1.534(12)
Bond angle (°)	
C(2)-C(1)-C(6)	114.6(7)
Br-C(2)-C(1)	115.4(6)
Br-C(2)-C(3)	119.5(6)
C(1)-C(2)-C(3)	125.0(8)
C(2)-C(3)-C(4)	121.1(8)
C(3)-C(4)-C(5)	116.0(7)
C(4)-C(5)-C(6)	122.3(7)
N-C(5)-C(6)	112.1(7)
C(4)-C(5)-N	125.6(7)
C(5)-C(6)-C(1)	121.0(7)
C(5)-C(6)-C(7)	108.3(7)
C(1)-C(6)-C(7)	130.7(7)
C(5)-N-C(12)	110.3(6)
C(5)-N-C(25)	123.6(7)
C(12)-N-C(25)	126.1(6)
C(6)-C(7)-C(8)	138.9(7)
C(6)-C(7)-C(12)	106.2(6)
C(8)-C(7)-C(12)	115.0(6)
C(7)-C(8)-C(9)	112.2(6)
C(7)-C(8)-C(15)	126.8(7)
C(9)-C(8)-C(15)	121.0(6)
C(8)-C(9)-C(10)	109.4(6)
C(8)-C(9)-C(14)	101.4(6)
C(10)-C(9)-C(14)	106.9(6)
C(9)-C(10)-C(11)	115.2(7)
C(9)-C(10)-C(17)	117.9(7)
C(11)-C(10)-C(17)	125.9(7)
C(10)-C(11)-C(12)	113.0(7)
C(10)-C(11)-C(19)	125.9(7)
C(12)-C(11)-C(19)	121.0(6)
N-C(12)-C(7)	103.1(6)
N-C(12)-C(11)	117.5(6)
N-C(12)-C(13)	116.3(6)
C(7)-C(12)-C(11)	105.7(6)
C(7)-C(12)-C(13)	107.0(6)
C(11)-C(12)-C(13)	106.3(6)
C(12)-C(13)-C(14)	104.9(6)
C(12)-C(13)-C(21)	115.0(6)
C(12)-C(13)-C(24)	112.9(6)
C(14)-C(13)-C(21)	108.1(6)
C(14)-C(13)-C(24)	112.8(7)
C(21)-C(13)-C(24)	103.3(6)
O(1)-C(14)-C(13)	124.3(7)
O(1)-C(14)-C(9)	121.0(7)
C(13)-C(14)-C(9)	114.6(7)
C(8)-C(15)-O(2)	125.0(8)
C(8)-C(15)-O(3)	111.6(7)
O(2)-C(15)-O(3)	123.4(8)
C(15)-O(3)-C(16)	115.4(7)
C(10)-C(17)-O(4)	122.6(8)
C(10)-C(17)-O(5)	114.0(7)
O(4)-C(17)-O(5)	123.4(8)
C(17)-O(5)-C(18)	118.0(7)
C(11)-C(19)-O(6)	123.8(7)
C(11)-C(19)-O(7)	112.9(6)
O(6)-C(19)-O(7)	123.1(7)
C(19)-O(7)-C(20)	116.7(6)
C(13)-C(21)-C(22)	105.2(7)
C(21)-C(22)-C(23)	109.8(11)
C(21)-C(22)-C(23')	113.4(10)
C(22)-C(23)-C(24)	101.0(13)
C(22)-C(23')-C(24)	98.8(12)
C(23)-C(24)-C(13)	108.8(10)
C(23')-C(24)-C(13)	111.4(9)
Torsion angle (°)	
C(5)-C(6)-C(7)-C(12)	2.2(8)
C(6)-C(7)-C(12)-N	-1.9(7)
C(7)-C(12)-N-C(5)	0.9(8)
C(12)-N-C(5)-C(6)	0.5(9)
N-C(5)-C(6)-C(7)	-1.7(9)
C(7)-C(8)-C(9)-C(10)	-50.7(8)
C(8)-C(9)-C(10)-C(11)	52.0(9)
C(9)-C(10)-C(11)-C(12)	2.1(10)
C(10)-C(11)-C(12)-C(7)	-53.8(8)
C(11)-C(12)-C(7)-C(8)	54.6(8)
C(12)-C(7)-C(8)-C(9)	-2.9(9)
C(10)-C(11)-C(12)-C(13)	59.7(8)
C(11)-C(12)-C(13)-C(14)	-61.2(7)
C(12)-C(13)-C(14)-C(9)	7.6(9)

Table 6 (continued)

C(13)-C(14)-C(9)-C(10)	49.7(8)
C(14)-C(9)-C(10)-C(11)	-57.1(9)
C(13)-C(21)-C(22)-C(23)	-24.2(12)
C(21)-C(22)-C(23)-C(24)	34.4(14)
C(22)-C(23)-C(24)-C(13)	-32.3(14)
C(23)-C(24)-C(13)-C(21)	18.2(11)
C(24)-C(13)-C(21)-C(22)	2.7(8)
C(13)-C(21)-C(22)-C(23')	15.8(12)
C(21)-C(22)-C(23')-C(24)	-26.2(14)
C(22)-C(23')-C(24)-C(13)	27.8(13)
C(23')-C(24)-C(13)-C(21)	-19.7(11)

the best *E*-map. These were refined anisotropically by several least-squares cycles, and the resulting difference map revealed peaks corresponding to all hydrogen atoms. In the last stage of refinement, the hydrogen atoms were generated and allowed to ride on their respective parent carbon atoms with assigned isotropic thermal parameters. The final R ($\Sigma|\Delta F|/\Sigma|F_o|$) index for 2 622 observed reflections was 0.063, the 'goodness of fit' (defined as $[\Sigma(w|\Delta F|^2)/(m-n)]^{1/2}$, where m = number of measurements and n = number of parameters) with $n = 298$ was 2.80.

All computations were performed with the SHELXTL⁸ package of crystallographic programs on a Nova 3/12 mini-computer. Analytic expressions⁹ of complex atomic scattering factors¹⁰ were used. The weighting scheme employed for the blocked-cascade least-squares refinement and analysis of variance was $w = [\sigma^2(|F_o|) + 0.0005|F_o|^2]^{-1}$.

Compound (7).¹—*Crystal data*. $C_{25}H_{27}NO_8$, $M = 469.69$, orthorhombic, *Pbca*, $a = 7.794(1)$, $b = 18.681(3)$, $c = 31.350(5)$ Å, $U = 4\ 565$ Å³, $D_m = 1.34$ g cm⁻³, $Z = 8$, $D_c = 1.366$ g cm⁻³, $F(000) = 1\ 984$, $\mu(\text{Mo-K}\alpha) = 1.08$ cm⁻¹.

The structure was solved by direct methods with MULTAN 78¹¹ and all non-hydrogen atoms appeared on the best *E*-map. The R index was 0.19. After several cycles of least-squares adjustment of the co-ordinates and anisotropic thermal parameters of the non-hydrogen atoms the R index was reduced to 0.10. For subsequent refinement the hydrogen atoms were inserted in their calculated positions and those belonging to the methyl groups were located from a difference map at a later stage. During the last cycles four very strong reflections (004, 020, 111, and 206) with residuals $|F_o^2 - F_c^2|$ over 30 times as large as the standard deviations $\sigma(F_o^2)$ were given zero weight. The final R index for 3 367 observed reflections was 0.060.

Compound (5).—*Crystal data*. $C_{25}H_{24}BrNO_7$, $M = 530.37$, monoclinic, $P2_1/n$, $a = 10.032(2)$, $b = 15.313(3)$, $c = 15.335(3)$ Å, $\beta = 99.15(1)^\circ$, $U = 2\ 326$ Å³, $D_m = 1.50$ g cm⁻³, $Z = 4$, $D_c = 1.515$ g cm⁻³, $F(000) = 1\ 088$, $\mu(\text{Mo-K}\alpha) = 19.04$ cm⁻¹.

The structure was partially solved by direct methods with MULTAN 78.¹¹ The bromine atom and 19 other non-hydrogen atoms appeared on the best *E*-map and the rest of the non-hydrogen atoms were recovered from subsequent Fourier syntheses. Some of the hydrogen atoms were kept at their calculated positions and the rest, which belong to the methyl groups, were located from a difference map at a later stage. One methylene carbon atom showed abnormally large anisotropic thermal motion and inspection of the difference map indicated that it was disordered and could best be represented by C(23) and C(23'), each with an occupancy factor of 0.5. These two half-atoms were treated isotropically along with anisotropic refinement of all other non-hydrogen atoms. Convergence was reached at $R = 0.104$ for 2 564

observed reflections and a 'goodness of fit' of 1.97 for 306 parameters.

Calculations for compounds (7) and (5) were carried out on an IBM 3031 computer using the CRYM system.¹² The quantity minimized in full-matrix least-squares refinement was $\sum w(F_o^2 - F_c^2)^2$ with $w = 1/\sigma^2(F_o^2)$. Atomic scattering factors were obtained from ref. 13 and the real part of anomalous dispersion was applied to that for bromine.

The final atomic co-ordinates for (3), (7), and (5) are, respectively, given in Tables 1, 2, and 3. Bond distances and angles, and selected torsion angles are listed in Tables 4, 5, and 6. The anisotropic thermal parameters for the non-hydrogen atoms, the positional and thermal parameters for the hydrogen atoms, and observed and calculated structure factors are in Supplementary publication No. SUP 23660 (55 pp.). *

* For details of the Supplementary publications scheme, see Instructions for Authors (1983), *J. Chem. Soc., Perkin Trans. 1*, 1983, Issue 1.

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