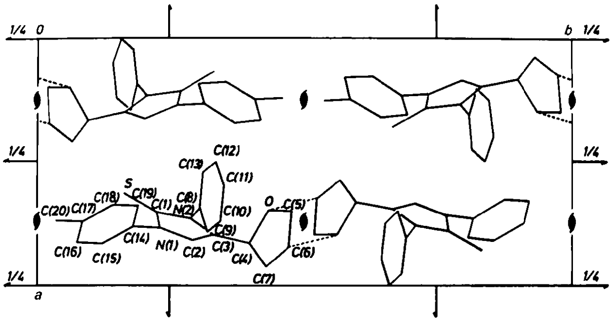

Fig. 1. The unit cell viewed along **c**. Broken lines are hydrogen bonds.

molecule is linked by a hydrogen bond to another molecule related by a twofold screw axis parallel to **c**, giving rise to infinite helical chains parallel to [001]: C(6)—H(6) 0·94 (6), C(6)···O 3·454 (8), H(6)···O 2·66 (6) Å and C(6)—H(6)···O 143 (5)°. No other intermolecular contacts shorter than the sum of the van der Waals radii have been detected. This type of hydrogen bond linking a C—H group with an O atom, both from the sugar ring, is not usual for the imidazole *C*-nucleosides studied. It is known that the ring-O atom is also excluded from the hydrogen-bonding schemes in pyranose crystal structures (Jeffrey & Lewis, 1978).

The authors thank Professor Fernández-Bolaños for supplying the crystals and Professor López-Castro for valuable help in the data-collection process. The present work forms part of a wide program supported by the Government through the 'Comisión Asesora de Investigación Científica y Técnica'.

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Structures of Four Derivatives of 5,7-Dichloro-2,3-dihydro-4-(*p*-nitrobenzoyl)-4*H*-1,4-benzoxazine

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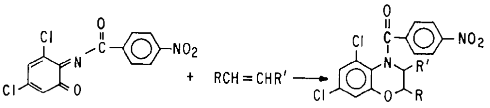
(*Received* 26 *September* 1984; *accepted* 10 *April* 1985)

Abstract. Compound (II): 5,7-dichloro-2-ethoxy-2,3-dihydro-4-(*p*-nitrobenzoyl)-4*H*-1,4-benzoxazine, $C_{17}H_{14}Cl_2N_2O_5$, $M_r = 397$, triclinic, $P\bar{1}$, $a = 7{\cdot}174$ (3), $b = 7{\cdot}859$ (4), $c = 16{\cdot}965$ (9) Å, $\alpha = 85{\cdot}50$ (4), $\beta = 79{\cdot}27$ (4), $\gamma = 71{\cdot}62$ (3)°, $V = 891{\cdot}7$ Å^3, $Z = 2$, $D_x = 1{\cdot}48$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 4{\cdot}0$ cm^{-1},

0108-2701/85/081217-06$01.50

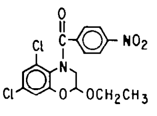
$F(000) = 405\cdot95$, room temperature, $R = 0\cdot0681$ for 1404 unique observed reflections. Compound (III): 5,7-dichloro-2,3-dihydro-2-(*p*-methoxyphenyl)-4-(*p*-nitrobenzoyl)-4*H*-1,4-benzoxazine, $C_{22}H_{16}Cl_2N_2O_5$, $M_r = 459$, monoclinic, $P2_1/a$, $a = 11\cdot696\,(9)$, $b = 9\cdot151\,(4)$, $c = 19\cdot72\,(3)$ Å, $\beta = 93\cdot33\,(9)^\circ$, $V = 2107$ Å^3, $Z = 4$, $D_x = 1\cdot45$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0\cdot71069$ Å, $\mu = 3\cdot5$ cm^{-1}, $F(000) = 943\cdot87$, room temperature, $R = 0\cdot0948$ for 1289 unique observed reflections. Compound (IV): 5,7-dichloro-2,3-dihydro-2-methoxy-4-(*p*-nitrobenzoyl)-3-phenyl-4*H*-1,4-benzoxazine, $C_{22}H_{16}Cl_2N_2O_5$, $M_r = 459$, monoclinic, $P2_1/n$, $a = 11\cdot269\,(3)$, $b = 13\cdot585\,(4)$, $c = 13\cdot965\,(3)$ Å, $\beta = 90\cdot98\,(2)^\circ$, $V = 2137\cdot5$ Å^3, $Z = 4$, $D_x = 1\cdot43$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0\cdot71069$ Å, $\mu = 3\cdot5$ cm^{-1}, $F(000) = 943\cdot87$, room temperature, $R = 0\cdot0368$ for 2043 unique observed reflections. Compound (V): 6,8-dichloro-3a,9a-dihydro-9-(*p*-nitrobenzoyl)-9*H*-furo[3,2-*b*][1,4]benzoxazine, $C_{17}H_{10}Cl_2N_2O_5$, $M_r = 393$, monoclinic, $P2_1/n$, $a = 11\cdot967\,(3)$, $b = 8\cdot663\,(3)$, $c = 15\cdot996\,(5)$ Å, $\beta = 91\cdot19\,(2)^\circ$, $V = 1658$ Å^3, $Z = 4$, $D_x = 1\cdot58$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0\cdot71069$ Å, $\mu = 4\cdot3$ cm^{-1}, $F(000) = 799\cdot89$, room temperature, $R = 0\cdot0507$ for 1555 unique observed reflections. All four compounds exhibit slight shortening of the N—carbonyl bond (1·378–1·397 Å), indicative of partial double-bond character. Compounds (II), (III) and (IV) have a half-chair conformation with bulky substituents axial. Compound (V) contains a *cis*-fused dihydrofuran ring and is constrained to a boat conformation.

Introduction. Several derivatives of 5,7-dichloro-2,3-dihydro-4-(*p*-nitrobenzoyl)-4*H*-1,4-benzoxazine and related compounds were recently prepared by the novel 1,4-cycloaddition reaction of electron-rich alkenes with *N*-(2,4-dichloro-6-oxo-2,4-cyclohexadien-1-ylidene)-4-nitrobenzamide (I) (Heine, Barchiesi & Williams, 1984):

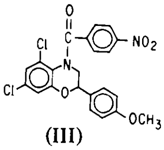


(I)

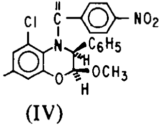
These cycloadditions were found to proceed regiospecifically with the more electron-rich C of the dienophile adding to the N atom of the heterodiene system of (I). Thus, reaction of (I) with ethyl vinyl ether (R=OCH_2CH_3, R'=H) gave compound (II), with *p*-methoxystyrene gave compound (III), with *cis*-*β*-methoxystyrene gave compound (IV), and with furan gave compound (V).



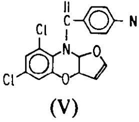
(II)



(III)

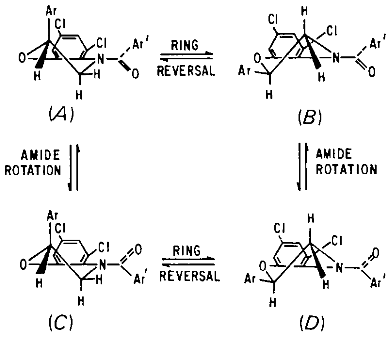


(IV)



(V)

The direction of the addition was deduced from the ^{13}C NMR data for the aliphatic C atoms adjacent to N and O in the benzoxazine ring. The NMR data also showed dynamic processes occurring at room temperature for these compounds. In addition to slow rotation about the N—carbonyl bond of the amide which was observed for (II)–(V), another slow process was observed for (III) at 243 K. This has been tentatively assigned to slow ring reversal in the benzoxazine ring as opposed to inversion about pyramidal N. A similar ring flipping has been observed for the 2,3-dihydro-1,4-dioxins in solution (Pfundt & Farid, 1966). Thus, for (III) at 243 K four species were observed in the ^{13}C NMR spectrum. The four isomers in solution have been assigned structures (*A*)–(*D*) (Heine, Barchiesi & & Williams, 1984):



In order to confirm the direction of addition in the synthesis, and to understand better dynamic processes observed by both ^1H and ^{13}C NMR for (II)–(V) in solution, the single-crystal structure determinations were undertaken.

Experimental. All data were collected on a Nicolet P3F automated single-crystal diffractometer using monochromated Mo $K\alpha$ radiation. Data collection was performed at room temperature in air. Values for D_m were not determined. Details of the data collection are included in Table 1. Each of the structures was solved using the *SHELXTL* program package (Sheldrick, 1981). All H positions were located by a difference Fourier synthesis, and in the final stages of refinement (on F) were constrained to have bond lengths of 0·96 Å, appropriate bond angles, and thermal parameters of 0·06 Å^2. All non-hydrogen atoms were treated as anisotropic. No absorption or extinction corrections were applied for any of the structures.

Discussion. Atomic coordinates, bond lengths and bond angles are presented in Table 2–9.* Thermal-ellipsoid plots (50% probability) showing the numbering schemes are in Figs. 1–4. The high thermal motion of the O atoms of the NO_2 group in each of the structures may be an indication of disorder. However, since individual sites could not be located in the difference Fourier map and since this functional group is not important to the discussion, no attempt was made to model this motion.

Table 1. *Experimental details*

Compound	(II)	(III)	(IV)	(V)
Crystal				
habit	Prismatic	Plate	Prismatic	Plate
size (mm)	0·3×0·2×0·1	0·2×0·4×0·005	0·2×0·2×0·4	0·3×0·3×0·1
Lattice parameters				
No. reflections	13	12	15	18
2θ range (°)	5·4–12·6	7·1–12·7	6·6–17·4	5·3–13·6
Reflection range				
h	0 to 8	0 to 13	0 to 13	0 to 13
k	−9 to 9	0 to 10	0 to 15	0 to 13
l	−19 to 19	−20 to 20	−16 to 16	−18 to 18
Max. $\sin\theta/\lambda$(Å^{-1})	0·538	0·538	0·538	0·538
Check				
reflections	122, 210	212, 214	021, 210	103, 022
variation (%)	1 1	1 1	1 1	1 1
Reflections				
collected	2451	3111	2276	2478
unique observed	1404	1289	2043	1555
Observed criterion	$F>3\sigma(F)$	$F>3\sigma(F)$	$F>3\sigma(F)$	$F>3\sigma(F)$
No. parameters	235	280	280	235
R	0·0681	0·0948	0·0368	0·0507
wR	0·0503	0·0515	0·0428	0·0342
Weighting factor (*g*)	0·00014	0·0001	0·00025	0·00001
$w^{-1} = \sigma^2(F) + gF^2$				
Fourier difference peaks				
min. (e Å^{-3})	−0·39	−0·43	−0·22	−0·28
max. (e Å^{-3})	0·35	0·43	0·17	0·27
Max. shift/error	−0·052	0·009	0·019	−0·506

Table 2. *Atom coordinates* (×10^4) *and temperature factors* (Å^2 ×10^3) *for* (II)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	*y*	*z*	U_{eq}
Cl(1)	7831 (2)	−363 (2)	1186 (1)	50 (1)
Cl(2)	5603 (3)	3874 (2)	−1331 (1)	60 (1)
N(1)	3469 (7)	965 (6)	1925 (3)	34 (2)
N(2)	2418 (11)	−2058 (14)	5596 (5)	89 (4)
O(1)	376 (6)	3835 (5)	2421 (2)	44 (2)
O(2)	557 (6)	3302 (5)	1076 (2)	48 (2)
O(3)	5269 (6)	2331 (6)	2513 (2)	57 (2)
O(4)	2771 (12)	−3609 (11)	5633 (5)	157 (5)
O(5)	1640 (9)	−1053 (10)	6174 (4)	108 (4)
C(1)	4028 (9)	1680 (8)	1150 (3)	36 (3)
C(2)	2569 (9)	2807 (8)	752 (4)	37 (3)
C(3)	3022 (9)	3468 (8)	−15 (3)	39 (3)
C(4)	4990 (11)	3007 (8)	−374 (4)	41 (3)
C(5)	6501 (9)	1880 (8)	−6 (4)	41 (3)
C(6)	5974 (9)	1200 (8)	746 (4)	38 (3)
C(7)	60 (9)	2721 (8)	1898 (4)	40 (3)
C(8)	1423 (8)	863 (8)	2046 (4)	39 (3)
C(9)	4200 (10)	1396 (9)	2566 (4)	40 (3)
C(10)	3632 (8)	499 (9)	3351 (3)	42 (3)
C(11)	2960 (10)	1505 (9)	4057 (3)	55 (3)
C(12)	2555 (10)	688 (12)	4782 (4)	65 (4)
C(13)	2839 (11)	−1113 (12)	4805 (4)	57 (4)
C(14)	3528 (11)	−2167 (11)	4146 (5)	70 (4)
C(15)	3912 (9)	−1318 (9)	3401 (4)	52 (3)
C(16)	−1043 (11)	5553 (9)	2501 (5)	75 (4)
C(17)	−516 (11)	6621 (10)	3057 (5)	86 (4)

Table 3. *Bond lengths* (Å) *and angles* (°) *for* (II)

Cl(1)–C(6)	1·742 (6)	Cl(2)–C(4)	1·746 (6)
N(1)–C(1)	1·427 (7)	N(1)–C(8)	1·471 (8)
N(1)–C(9)	1·398 (9)	N(2)–O(4)	1·163 (13)
N(2)–O(5)	1·240 (11)	N(2)–C(13)	1·508 (11)
O(1)–C(7)	1·389 (8)	O(1)–C(16)	1·410 (7)
O(2)–C(2)	1·386 (7)	O(2)–C(7)	1·448 (7)
O(3)–C(9)	1·207 (9)	C(1)–C(2)	1·386 (8)
C(1)–C(6)	1·383 (8)	C(2)–C(3)	1·382 (8)
C(3)–C(4)	1·373 (9)	C(4)–C(5)	1·382 (9)
C(5)–C(6)	1·377 (9)	C(7)–C(8)	1·511 (8)
C(9)–C(10)	1·506 (9)	C(10)–C(11)	1·409 (9)
C(10)–C(15)	1·376 (10)	C(11)–C(12)	1·368 (9)
C(12)–C(13)	1·363 (13)	C(13)–C(14)	1·365 (11)
C(14)–C(15)	1·404 (10)	C(16)–C(17)	1·481 (13)

C(1)–N(1)–C(8)	111·8 (5)	C(1)–N(1)–C(9)	117·7 (6)
C(8)–N(1)–C(9)	119·9 (5)	O(4)–N(2)–O(5)	124·4 (9)
O(4)–N(2)–C(13)	120·8 (8)	O(5)–N(2)–C(13)	114·8 (9)
C(7)–O(1)–C(16)	115·0 (5)	C(2)–O(2)–C(7)	116·0 (4)
N(1)–C(1)–C(2)	119·6 (5)	N(1)–C(1)–C(6)	122·6 (5)
C(2)–C(1)–C(6)	117·6 (5)	O(2)–C(2)–C(1)	122·9 (5)
O(2)–C(2)–C(3)	115·1 (5)	C(1)–C(2)–C(3)	121·9 (5)
C(2)–C(3)–C(4)	117·9 (5)	Cl(2)–C(4)–C(3)	118·8 (5)
Cl(2)–C(4)–C(5)	118·8 (5)	C(3)–C(4)–C(5)	122·5 (6)
C(4)–C(5)–C(6)	117·6 (6)	Cl(1)–C(6)–C(1)	119·3 (5)
Cl(1)–C(6)–C(5)	118·3 (4)	C(1)–C(6)–C(5)	122·4 (5)
O(1)–C(7)–O(2)	110·0 (5)	O(1)–C(7)–C(8)	106·1 (5)
O(2)–C(7)–C(8)	110·3 (4)	N(1)–C(8)–C(7)	107·6 (5)
N(1)–C(9)–O(3)	124·8 (6)	N(1)–C(9)–C(10)	114·0 (6)
O(3)–C(9)–C(10)	121·1 (6)	C(9)–C(10)–C(11)	119·5 (6)
C(9)–C(10)–C(15)	121·0 (5)	C(11)–C(10)–C(15)	119·3 (6)
C(10)–C(11)–C(12)	120·3 (7)	C(11)–C(12)–C(13)	118·6 (7)
N(2)–C(13)–C(12)	120·0 (7)	N(2)–C(13)–C(14)	116·1 (8)
C(12)–C(13)–C(14)	123·9 (7)	C(13)–C(14)–C(15)	117·3 (7)
C(10)–C(15)–C(14)	120·6 (6)	O(1)–C(16)–C(17)	109·8 (6)

Table 4. *Atom coordinates* (×10^4) *and temperature factors* (Å^2 ×10^3) *for* (III)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	*y*	*z*	U_{eq}
Cl(1)	623 (2)	−1003 (3)	3450 (1)	68 (1)
Cl(2)	2125 (2)	1543 (3)	5778 (1)	82 (1)
N(1)	−634 (5)	1865 (8)	3164 (3)	44 (3)
N(2)	−3067 (6)	2030 (11)	154 (4)	102 (5)
O(1)	−665 (5)	4090 (7)	4159 (3)	71 (3)
O(2)	928 (5)	1648 (7)	2525 (3)	65 (3)
O(3)	1173 (6)	7549 (9)	1672 (4)	92 (3)
O(4)	−3827 (8)	1167 (12)	87 (5)	124 (5)
O(5)	−2911 (10)	2985 (17)	−250 (5)	184 (7)
C(1)	34 (8)	1741 (12)	3797 (5)	48 (4)
C(2)	−18 (7)	2867 (10)	4255 (4)	47 (4)
C(3)	617 (8)	2803 (11)	4879 (5)	61 (5)
C(4)	1276 (7)	1578 (10)	5018 (4)	57 (4)
C(5)	1283 (7)	403 (10)	4582 (4)	52 (4)
C(6)	650 (7)	507 (11)	3967 (4)	45 (4)
C(7)	−1324 (8)	4238 (13)	3524 (5)	60 (5)
C(8)	−1661 (7)	2740 (10)	3243 (4)	56 (4)
C(9)	−94 (7)	1821 (10)	2554 (4)	53 (4)
C(10)	−869 (8)	1872 (11)	1925 (4)	50 (4)
C(11)	−1744 (7)	877 (11)	1814 (4)	54 (4)
C(12)	−2462 (8)	877 (12)	1231 (5)	68 (5)
C(13)	−2276 (8)	1965 (12)	769 (5)	63 (5)
C(14)	−1383 (7)	2941 (12)	854 (5)	82 (5)
C(15)	−682 (7)	2863 (10)	1423 (4)	59 (4)
C(16)	−678 (10)	5121 (11)	3043 (5)	55 (5)
C(17)	501 (7)	5282 (10)	3088 (4)	58 (4)
C(18)	1097 (8)	6074 (12)	2641 (5)	66 (5)
C(19)	520 (9)	6773 (11)	2099 (5)	61 (4)
C(20)	−674 (10)	6659 (12)	2001 (5)	67 (5)
C(21)	−1216 (9)	5844 (11)	2480 (5)	68 (5)
C(22)	648 (9)	8435 (12)	1162 (5)	112 (6)

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42181 (100 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 5. *Bond lengths* (Å) *and angles* (°) *for* (III)

Cl(1)–C(6)	1·717 (10)	Cl(2)–C(4)	1·748 (9)
N(1)–C(1)	1·438 (11)	N(1)–C(8)	1·460 (11)
N(1)–C(9)	1·392 (11)	N(2)–O(4)	1·191 (13)
N(2)–O(5)	1·204 (16)	N(2)–C(13)	1·483 (12)
O(1)–C(2)	1·357 (11)	O(1)–C(7)	1·438 (11)
O(2)–C(9)	1·211 (10)	O(3)–C(19)	1·368 (13)
O(3)–C(22)	1·405 (12)	C(1)–C(2)	1·375 (14)
C(1)–C(6)	1·371 (14)	C(2)–C(3)	1·402 (12)
C(3)–C(4)	1·379 (13)	C(4)–C(5)	1·378 (13)
C(5)–C(6)	1·386 (12)	C(7)–C(8)	1·522 (15)
C(7)–C(16)	1·487 (15)	C(9)–C(10)	1·494 (12)
C(10)–C(11)	1·378 (13)	C(10)–C(15)	1·369 (13)
C(11)–C(12)	1·384 (12)	C(12)–C(13)	1·376 (15)
C(13)–C(14)	1·377 (14)	C(14)–C(15)	1·352 (12)
C(16)–C(17)	1·384 (14)	C(16)–C(21)	1·409 (14)
C(17)–C(18)	1·364 (13)	C(18)–C(19)	1·388 (14)
C(19)–C(20)	1·401 (16)	C(20)–C(21)	1·386 (15)

C(1)–N(1)–C(8)	111·1 (7)	C(1)–N(1)–C(9)	119·8 (7)
C(8)–N(1)–C(9)	121·7 (7)	O(4)–N(2)–O(5)	123·2 (9)
O(4)–N(2)–C(13)	119·4 (9)	O(5)–N(2)–C(13)	117·4 (9)
C(2)–O(1)–C(7)	117·7 (7)	C(19)–O(3)–C(22)	120·2 (8)
N(1)–C(1)–C(2)	118·0 (8)	N(1)–C(1)–C(6)	121·9 (9)
C(2)–C(1)–C(6)	119·9 (8)	O(1)–C(2)–C(1)	124·9 (8)
O(1)–C(2)–C(3)	114·8 (8)	C(1)–C(2)–C(3)	120·3 (9)
C(2)–C(3)–C(4)	118·1 (9)	Cl(2)–C(4)–C(3)	117·9 (7)
Cl(2)–C(4)–C(5)	119·8 (7)	C(3)–C(4)–C(5)	122·3 (8)
C(4)–C(5)–C(6)	118·1 (8)	Cl(1)–C(6)–C(1)	121·7 (7)
Cl(1)–C(6)–C(5)	117·1 (7)	C(1)–C(6)–C(5)	121·2 (9)
O(1)–C(7)–C(8)	110·3 (8)	O(1)–C(7)–C(16)	109·9 (8)
C(8)–C(7)–C(16)	112·8 (8)	N(1)–C(8)–C(7)	109·6 (7)
N(1)–C(9)–O(2)	123·0 (8)	N(1)–C(9)–C(10)	115·6 (7)
O(2)–C(9)–C(10)	121·2 (8)	C(9)–C(10)–C(11)	121·4 (8)
C(9)–C(10)–C(15)	120·4 (8)	C(11)–C(10)–C(15)	118·1 (8)
C(10)–C(11)–C(12)	122·8 (9)	C(11)–C(12)–C(13)	116·0 (9)
N(2)–C(13)–C(12)	117·1 (9)	N(2)–C(13)–C(14)	120·5 (9)
C(12)–C(13)–C(14)	122·4 (9)	C(13)–C(14)–C(15)	119·1 (9)
C(10)–C(15)–C(14)	121·4 (9)	C(7)–C(16)–C(17)	123·9 (9)
C(7)–C(16)–C(21)	122·6 (10)	C(17)–C(16)–C(21)	113·5 (9)
C(16)–C(17)–C(18)	124·0 (8)	C(17)–C(18)–C(19)	119·9 (9)
O(3)–C(19)–C(18)	116·7 (9)	O(3)–C(19)–C(20)	122·8 (9)
C(18)–C(19)–C(20)	120·6 (9)	C(19)–C(20)–C(21)	115·9 (9)
C(16)–C(21)–C(20)	126·0 (10)		

Table 6. *Atom coordinates* (×10^4) *and temperature factors* (Å^2 ×10^3) *for* (IV)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	*y*	*z*	U_{eq}
Cl(1)	−530 (1)	−1710 (1)	2494 (1)	61 (1)
Cl(2)	−4227 (1)	664 (1)	1825 (1)	68 (1)
O(1)	−332 (3)	2019 (2)	3058 (2)	47 (1)
O(2)	1425 (3)	2743 (2)	3432 (2)	44 (1)
O(3)	247 (3)	−910 (2)	4422 (2)	47 (1)
O(4)	6094 (4)	−1654 (4)	5653 (3)	99 (2)
O(5)	6443 (4)	−1800 (4)	4150 (4)	106 (2)
N(1)	758 (3)	141 (3)	3212 (2)	38 (1)
N(2)	5820 (4)	−1607 (3)	4810 (4)	71 (2)
C(1)	−479 (4)	246 (3)	2901 (3)	33 (2)
C(2)	−970 (4)	1186 (3)	2820 (3)	40 (2)
C(3)	−2109 (4)	1319 (3)	2468 (3)	40 (2)
C(4)	−2759 (4)	508 (3)	2224 (3)	42 (2)
C(5)	−2322 (5)	−438 (3)	2285 (3)	45 (2)
C(6)	−1163 (4)	−549 (3)	2590 (3)	39 (2)
C(7)	806 (4)	1871 (3)	3525 (3)	38 (2)
C(8)	1473 (4)	1017 (3)	3065 (3)	36 (2)
C(9)	1011 (4)	−490 (3)	3982 (3)	35 (1)
C(10)	2313 (4)	−679 (3)	4170 (3)	34 (1)
C(11)	2699 (4)	−699 (3)	5110 (3)	47 (2)
C(12)	3837 (5)	−978 (4)	5325 (3)	56 (2)
C(13)	4565 (4)	−1259 (3)	4592 (3)	46 (2)
C(14)	4201 (5)	−1246 (4)	3651 (3)	50 (2)
C(15)	3047 (4)	−940 (3)	3448 (3)	41 (2)
C(16)	1263 (6)	3418 (4)	4203 (4)	77 (2)
C(17)	1842 (4)	1167 (3)	2022 (3)	36 (2)
C(18)	1206 (5)	825 (5)	1237 (4)	78 (2)
C(19)	1619 (6)	997 (6)	326 (4)	106 (3)
C(20)	2653 (5)	1514 (5)	177 (4)	70 (2)
C(21)	3279 (5)	1841 (3)	937 (3)	50 (2)
C(22)	2886 (4)	1667 (3)	1844 (3)	43 (2)

Table 7. *Bond lengths* (Å) *and angles* (°) *for* (IV)

Cl(1)–C(6)	1·737 (4)	Cl(2)–C(4)	1·749 (5)
O(1)–C(2)	1·379 (5)	O(1)–C(7)	1·443 (5)
O(2)–C(7)	1·381 (5)	O(2)–C(16)	1·429 (6)
O(3)–C(9)	1·209 (5)	O(4)–N(2)	1·213 (7)
O(5)–N(2)	1·198 (7)	N(1)–C(1)	1·461 (6)
N(1)–C(8)	1·453 (5)	N(1)–C(9)	1·401 (5)
N(2)–C(13)	1·517 (7)	C(1)–C(2)	1·395 (6)
C(1)–C(6)	1·392 (6)	C(2)–C(3)	1·379 (6)
C(3)–C(4)	1·362 (6)	C(4)–C(5)	1·379 (7)
C(5)–C(6)	1·374 (7)	C(7)–C(8)	1·531 (6)
C(8)–C(17)	1·535 (6)	C(9)–C(10)	1·508 (6)
C(10)–C(11)	1·376 (6)	C(10)–C(15)	1·362 (6)
C(11)–C(12)	1·367 (7)	C(12)–C(13)	1·377 (7)
C(13)–C(14)	1·370 (7)	C(14)–C(15)	1·389 (7)
C(17)–C(18)	1·380 (7)	C(17)–C(22)	1·384 (6)
C(18)–C(19)	1·382 (8)	C(19)–C(20)	1·379 (9)
C(20)–C(21)	1·340 (7)	C(21)–C(22)	1·369 (7)

C(2)–O(1)–C(7)	116·8 (3)	C(7)–O(2)–C(16)	114·1 (4)
C(1)–N(1)–C(8)	114·0 (3)	C(1)–N(1)–C(9)	117·9 (3)
C(8)–N(1)–C(9)	120·3 (3)	O(4)–N(2)–O(5)	126·3 (5)
O(4)–N(2)–C(13)	115·6 (4)	O(5)–N(2)–C(13)	118·1 (5)
N(1)–C(1)–C(2)	119·3 (4)	N(1)–C(1)–C(6)	122·5 (4)
C(2)–C(1)–C(6)	117·9 (4)	O(1)–C(2)–C(1)	121·8 (4)
O(1)–C(2)–C(3)	117·2 (4)	C(1)–C(2)–C(3)	121·0 (4)
C(2)–C(3)–C(4)	118·4 (4)	Cl(2)–C(4)–C(3)	118·9 (3)
Cl(2)–C(4)–C(5)	117·8 (4)	C(3)–C(4)–C(5)	123·3 (4)
C(4)–C(5)–C(6)	117·2 (4)	Cl(1)–C(6)–C(1)	120·2 (4)
Cl(1)–C(6)–C(5)	117·6 (3)	C(1)–C(6)–C(5)	122·0 (4)
O(1)–C(7)–O(2)	106·5 (3)	O(1)–C(7)–C(8)	110·8 (3)
O(2)–C(7)–C(8)	111·0 (4)	N(1)–C(8)–C(7)	106·5 (3)
N(1)–C(8)–C(17)	113·8 (3)	C(7)–C(8)–C(17)	116·2 (3)
O(3)–C(9)–N(1)	122·8 (4)	O(3)–C(9)–C(10)	122·0 (4)
N(1)–C(9)–C(10)	115·0 (3)	C(9)–C(10)–C(11)	117·4 (4)
C(9)–C(10)–C(15)	121·1 (4)	C(11)–C(10)–C(15)	121·0 (4)
C(10)–C(11)–C(12)	119·7 (4)	C(11)–C(12)–C(13)	118·8 (4)
N(2)–C(13)–C(12)	120·1 (4)	N(2)–C(13)–C(14)	117·4 (4)
C(12)–C(13)–C(14)	122·5 (5)	C(13)–C(14)–C(15)	117·6 (4)
C(10)–C(15)–C(14)	120·4 (4)	C(8)–C(17)–C(18)	124·3 (4)
C(8)–C(17)–C(22)	118·7 (4)	C(18)–C(17)–C(22)	117·0 (4)
C(17)–C(18)–C(19)	119·7 (6)	C(18)–C(19)–C(20)	121·6 (6)
C(19)–C(20)–C(21)	118·9 (5)	C(20)–C(21)–C(22)	120·1 (5)
C(17)–C(22)–C(21)	122·6 (4)		

Table 8. *Atom coordinates* (×10^4) *and temperature factors* (Å^2 ×10^3) *for* (V)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	*y*	*z*	U_{eq}
Cl(1)	699 (1)	−1121 (2)	1787 (1)	54 (1)
Cl(2)	−3463 (1)	1133 (2)	2015 (1)	71 (1)
O(1)	−683 (2)	1363 (3)	4450 (1)	43 (1)
O(2)	898 (2)	−2671 (3)	3542 (2)	47 (1)
O(3)	1830 (2)	2386 (3)	3546 (2)	49 (1)
O(4)	6401 (2)	−3236 (4)	4867 (2)	69 (1)
O(5)	6702 (2)	−1009 (4)	4317 (2)	83 (1)
N(1)	960 (2)	−52 (4)	3620 (2)	30 (1)
N(2)	6086 (3)	−2072 (5)	4509 (2)	51 (1)
C(1)	−92 (3)	169 (4)	3197 (2)	30 (1)
C(2)	−912 (3)	940 (5)	3637 (2)	34 (1)
C(3)	−1950 (3)	1264 (5)	3282 (2)	41 (1)
C(4)	−2154 (3)	775 (5)	2471 (3)	43 (2)
C(5)	−1361 (3)	34 (5)	2016 (3)	42 (2)
C(6)	−315 (3)	−250 (5)	2374 (2)	36 (1)
C(7)	407 (3)	2094 (5)	4571 (2)	37 (1)
C(8)	1355 (3)	1257 (5)	4103 (2)	35 (1)
C(9)	1425 (3)	−1501 (4)	3695 (2)	31 (1)
C(10)	2652 (3)	−1583 (4)	3928 (2)	31 (1)
C(11)	3417 (3)	−574 (5)	3581 (2)	41 (2)
C(12)	4548 (3)	−732 (5)	3764 (3)	42 (2)
C(13)	4880 (3)	−1910 (5)	4300 (2)	37 (1)
C(14)	4143 (3)	−2920 (5)	4650 (2)	42 (2)
C(15)	3015 (3)	−2753 (5)	4452 (3)	41 (2)
C(16)	1250 (4)	3727 (6)	3659 (3)	50 (2)
C(17)	459 (4)	3664 (5)	4203 (3)	46 (2)

All four compounds exhibit a slight shortening of the carbonyl—N bond (1·378–1·397 Å), indicative of partial double-bond character. This corroborates the observation in the ^{13}C NMR spectra of (II)–(V) of two amide isomers which arise from restricted rotation about this bond. These isomers are evident to temperatures of up to 353–373 K when rotation becomes rapid and an averaged spectrum is observed. This behavior is typical of amides and the large barrier to rotation around the amide bond has been the subject of numerous NMR studies (Stewart & Siddall, 1970). The predominant isomer in the solid state for (II)–(V) has been found to be that with the carbonyl group *cis* to the bulky Cl atom on the chlorinated aromatic ring. This is consistent with the NMR data which suggest predominance of this isomer in solution as well (Williams, Heine, Donahue & Smith, 1985).

Compounds (II), (III) and (IV) exist in a half-chair conformation in which the bulky substituents are axial. Compound (V) contains a *cis*-fused dihydrofuran ring and is constrained to a boat conformation. The bond

Table 9. *Bond lengths* (Å) *and angles* (°) *for* (V)

Cl(1)–C(6)	1·723 (5)	Cl(2)–C(4)	1·741 (5)
O(1)–C(2)	1·372 (5)	O(1)–C(7)	1·459 (5)
O(2)–C(9)	1·216 (5)	O(3)–C(8)	1·449 (6)
O(3)–C(16)	1·368 (6)	O(4)–N(2)	1·216 (6)
O(5)–N(2)	1·222 (6)	N(1)–C(1)	1·429 (5)
N(1)–C(8)	1·446 (6)	N(1)–C(9)	1·378 (6)
N(2)–C(13)	1·482 (6)	C(1)–C(2)	1·391 (6)
C(1)–C(6)	1·386 (6)	C(2)–C(3)	1·383 (6)
C(3)–C(4)	1·383 (6)	C(4)–C(5)	1·368 (6)
C(5)–C(6)	1·387 (6)	C(7)–C(8)	1·552 (6)
C(7)–C(17)	1·483 (7)	C(9)–C(10)	1·509 (6)
C(10)–C(11)	1·390 (6)	C(10)–C(15)	1·380 (6)
C(11)–C(12)	1·386 (6)	C(12)–C(13)	1·386 (6)
C(13)–C(14)	1·370 (6)	C(14)–C(15)	1·388 (6)
C(16)–C(17)	1·300 (7)		
C(2)–O(1)–C(7)	113·7 (3)	C(8)–O(3)–C(16)	106·5 (3)
C(1)–N(1)–C(8)	115·0 (3)	C(1)–N(1)–C(9)	120·9 (3)
C(8)–N(1)–C(9)	122·8 (3)	O(4)–N(2)–O(5)	124·1 (4)
O(4)–N(2)–C(13)	118·4 (4)	O(5)–N(2)–C(13)	117·5 (4)
N(1)–C(1)–C(2)	116·6 (3)	N(1)–C(1)–C(6)	124·4 (3)
C(2)–C(1)–C(6)	118·8 (3)	O(1)–C(2)–C(1)	118·6 (3)
O(1)–C(2)–C(3)	119·6 (3)	C(1)–C(2)–C(3)	121·8 (4)
C(2)–C(3)–C(4)	117·6 (4)	Cl(2)–C(4)–C(3)	118·6 (3)
Cl(2)–C(4)–C(5)	119·3 (3)	C(3)–C(4)–C(5)	122·1 (4)
C(4)–C(5)–C(6)	119·6 (4)	Cl(1)–C(6)–C(1)	120·5 (3)
Cl(1)–C(6)–C(5)	119·5 (3)	C(1)–C(6)–C(5)	120·0 (4)
O(1)–C(7)–C(8)	113·2 (3)	O(1)–C(7)–C(17)	113·0 (3)
C(8)–C(7)–C(17)	101·5 (3)	O(3)–C(8)–N(1)	109·2 (3)
O(3)–C(8)–C(7)	106·4 (3)	N(1)–C(8)–C(7)	112·9 (3)
O(2)–C(9)–N(1)	122·4 (3)	O(2)–C(9)–C(10)	120·6 (4)
N(1)–C(9)–C(10)	117·0 (3)	C(9)–C(10)–C(11)	121·2 (3)
C(9)–C(10)–C(15)	118·5 (3)	C(11)–C(10)–C(15)	120·2 (4)
C(10)–C(11)–C(12)	120·2 (4)	C(11)–C(12)–C(13)	118·0 (4)
N(2)–C(13)–C(12)	118·3 (4)	N(2)–C(13)–C(14)	118·7 (4)
C(12)–C(13)–C(14)	123·0 (4)	C(13)–C(14)–C(15)	118·1 (4)
C(10)–C(15)–C(14)	120·5 (4)	O(3)–C(16)–C(17)	115·6 (4)
C(7)–C(17)–C(16)	110·0 (4)		

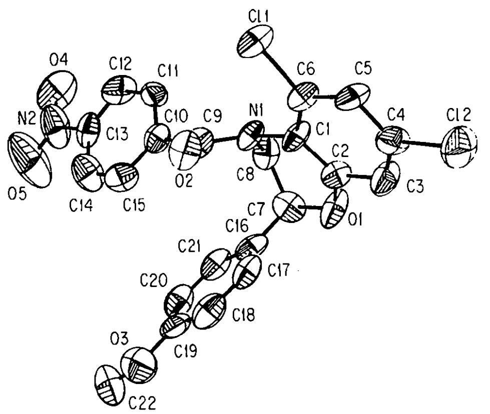

Fig. 2. Thermal-ellipsoid (50% probability) plot of (III) showing numbering scheme employed. Hydrogen atoms have been omitted for clarity.

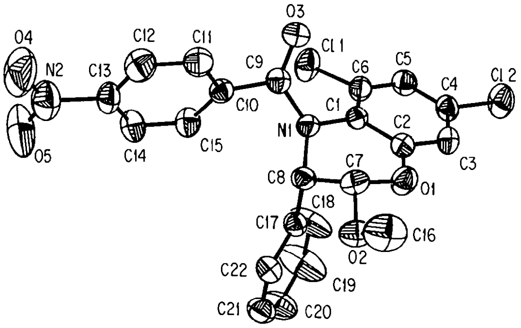

Fig. 3. Thermal-ellipsoid (50% probability) plot of (IV) showing numbering scheme employed. Hydrogen atoms have been omitted for clarity.

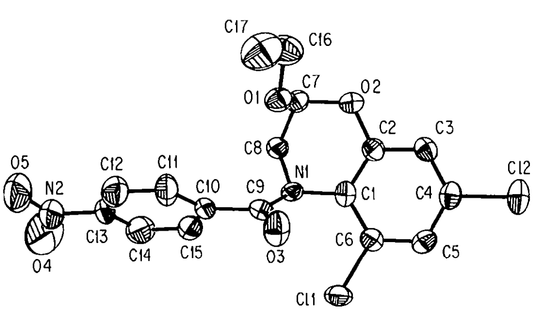

Fig. 1. Thermal-ellipsoid (50% probability) plot of (II) showing numbering scheme employed. Hydrogen atoms have been omitted for clarity.

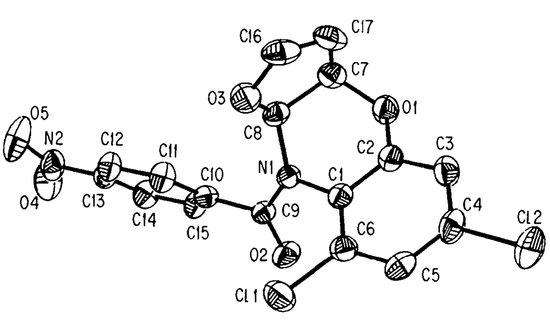

Fig. 4. Thermal-ellipsoid (50% probability) plot of (V) showing numbering scheme employed. Hydrogen atoms have been omitted for clarity.

angles around the amide N in (II)–(V) show this atom to be only slightly pyramidal. For this reason we believe it is highly unlikely that there would be slow inversion about the benzoxazine ring N atom. We conclude, therefore, that the second process which is slow on the NMR time scale for (III) at 243 K is ring reversal in the benzoxazine ring, and the structures (*A*)–(*D*) are indeed the four species observed by ^{13}C NMR. Structure (*C*) is the isomer for which the crystal structure has been obtained. It is also the only species in the solid as determined by powder diffraction data.

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A New 20,24-Dimethylscalarane Derivative Isolated from the Sponge *Carteriospongia foliascens*, $C_{30}H_{42}O_6$

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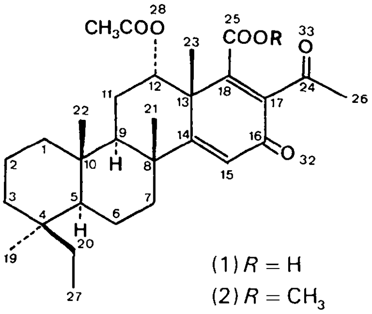
(*Received* 11 *February* 1985; *accepted* 9 *April* 1985)

Abstract. Methyl 12α-acetoxy-20,24-dimethyl-16,24-dioxoscalara-14,17-dien-25-oate, $M_r = 498{\cdot}66$, orthorhombic, $P2_12_12_1$, $a = 7{\cdot}943$ (2), $b = 14{\cdot}198$ (5), $c = 25{\cdot}232$ (6) Å, $V = 2845$ (1) Å^3, $Z = 4$, $D_x = 1{\cdot}16$ g cm^{-3}, Mo *Kα*, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}85$ cm^{-1}, $F(000) = 1080$, $T = 291$ K, $R = 0{\cdot}053$ for 1676 observed reflections. Particular features of this molecule are the high degree of unsaturation of ring *D* [it contains two double bonds of 1·327 (8) and 1·339 (8) Å] and the presence of an axial ethyl group at the C(4) position.

Introduction. In the course of our work on the chemical defense of sponges, six new 20,24-dimethylscalarane derivatives have been isolated from the ichthyotoxic fraction of the chloroform extract of the marine sponge *Carteriospongia foliascens* (Spongiidae–Dictyoceratida) collected around Laing Island (King Leopold III Biological Station, Laing Island, Papua–New Guinea; contribution No. 78). We describe here the determination of the molecular structure of one of these (1) (Fig. 1), isolated as its methyl ester (2).

Experimental. D_m not measured. Parallelepiped crystal 0·22 × 0·25 × 0·45 mm. Lattice parameters refined using 15 reflections in the range 3° ≤ 2θ ≤ 17°. Syntex $P2_1$ diffractometer, graphite-monochromatized Mo *Kα* radiation. 2418 independent *hkl* reflections with $\sin\theta/\lambda \leq 0{\cdot}561$ Å^{-1}, 1676 with $I \geq 2{\cdot}5\sigma(I)$. Standard reflection 201 checked every 50 reflections: no significant variation. No correction for absorption or extinction. Structure solved by *MULTAN*80 (Main, Fiske, Hull,



(1) $R = H$

(2) $R = CH_3$

Fig. 1. Scheme of the molecule and atom numbering; also: –O(28)–C(29)[O(31)]–C(30)H_3 and –C(25)[O(34)]–O(35)–C(36)H_3.

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* Senior Research Associate of the National Fund for Scientific Research (Belgium).