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Solid-State Stereochemistry of Diels–Alder Adducts between a Bicyclic Cyclohexadienone Derivative and α-Acyloxyacrylonitrile

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Abstract. λ(Cu $K\overline{\alpha}$) = 1·54056 Å, T = 298 K. (4*a*): *rel*-(1*S*,7*S*,9*S*,11*R*)-11-Cyano-1-methyl-8-oxo-9,9-(oxoethylenedioxy)tricyclo[5.2.2.0^{2,6}]undec-2(6)-en-11-yl acetate, $C_{17}H_{17}NO_6$, M_r = 331·32, monoclinic, $P2_1/a$, a = 9·3791 (5), b = 14·8506 (15), c = 12·7209 (15) Å, β = 110·188 (7)°, V = 1663·0 (3) Å^3, Z = 4, D_x = 1·323 Mg m^{-3}, μ = 0·81 mm^{-1}, F(000) = 695·91, $R(F)$ = 0·079, wR = 0·045, S = 4·35 for 2127 significant reflections. (4*b*): *rel*-(1*S*,7*S*,9*S*,11*R*)-11-Cyano-1-methyl-8-oxo-9,9-(oxoethylenedioxy)tricyclo[5.2.2.0^{2,6}]undec-2(6)-en-11-yl 3,3-ethylenedioxybutanoate, $C_{21}H_{23}NO_8$, M_r = 417·41, orthorhombic, $P2_1nb$, a = 8·5159 (3), b = 10·3035 (3), c = 23·1263 (8) Å, V = 2029·18 (12) Å^3, Z = 4, D_x = 1·366 Mg m^{-3}, μ = 0·85 mm^{-1}, F(000) = 879·89, $R(F)$ = 0·038, wR = 0·027, S = 1·709 for 2039 significant reflections. (5*a*): *rel*-(1*S*,7*S*,9*R*,11*R*)-11-Cyano-1-methyl-8-oxo-9,9-(oxoethylenedioxy)tricyclo[5.2.2.0^{2,6}]undec-2(6)-en-11-yl acetate, $C_{17}H_{17}NO_6$, M_r = 331·32, triclinic, $P\overline{1}$, a = 8·3623 (8), b = 9·0673 (6), c = 11·4951 (10) Å, α = 102·982 (8), β = 95·983 (6), γ = 106·828 (5)°, V = 799·45 (6) Å^3, Z = 2, D_x = 1·376 Mg m^{-3}, μ = 0·84 mm^{-1}, F(000) = 347·95, $R(F)$ = 0·039, wR = 0·030, S = 3·75 for 2685 significant reflections. (5*b*): *rel*-(1*S*,7*S*,9*R*,11*R*)-11-Cyano-1-methyl-8-oxo-9,9-(oxoethylenedioxy)tricyclo[5.2.2.0^{2,6}]undec-2(6)-en-11-yl 3,3-ethylenedioxybutanoate, $C_{21}H_{23}NO_8$, M_r = 417·41, monoclinic, $A2/n$, a = 17·8531 (5), b = 11·2599 (3), c = 20·7317 (7) Å, β = 104·593 (3)°, V = 4033·13 (8) Å^3, Z = 8, D_x = 1·375 Mg m^{-3}, μ = 0·85 mm^{-1}, F(000) = 1759·77, $R(F)$ = 0·042, wR = 0·024, S = 1·27 for 2803 significant reflections. The crystal structures of the two pairs of Diels–Alder adducts reveal the stereochemistry of the spirolactonic ring and the cyanoester moiety. In the four molecules the cyano groups are *cis* to the cyclopentene bridge. The high values of $R(F)$ (0·079) and S (4·35) for (4*a*) reflect the poor quality of the crystals. This spatial arrangement is compatible with the classical *endo* approach of the reagents.

Introduction. In the course of the total synthesis of ryanodol (1) (Deslongchamps, Bélanger, Berney, Borschberg, Brousseau, Doutheau, Durand, Katayama, Lapalme, Leturc, Liao, Maclachlan, Maffrand, Marazza, Martino, Moreau, Ruest, St-Laurent, Saintonge & Soucy, 1990), the Diels–Alder reactions between spirolactone dienone (2) and dienophiles (3*a*) and (3*b*) were investigated. Fol-

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lowing this strategy, the use of 2-acyloxyacrylonitrile derivatives would have eased some subsequent chemical transformation in the synthesis. It was also hoped that an aldol condensation between C(17) and C(1) in Diels–Alder adducts (4) and (5) could be performed. This connection would have initiated a regio- and stereospecific formation of ring *A* of ryanodol (1). As this aldolization was not successful in our hands, this approach was abandoned for a better one. Classical spectroscopy (data included in the material for deposit) was unsuccessful in determining the stereochemistry of the compounds involved. Nevertheless, the spatial implications underlying these results needed to be clarified and required further structural studies.

(1)

(2)

(3a) R = H
(3b) R = CH₃C(OCH₂)₂

(4a) R = H
(4b) R = CH₃C(OCH₂)₂

(5a) R = H
(5b) R = CH₃C(OCH₂)₂
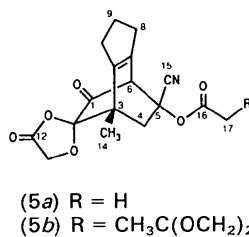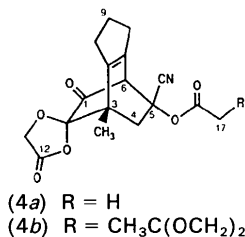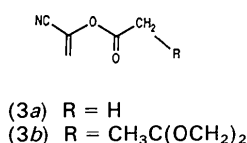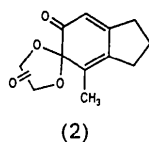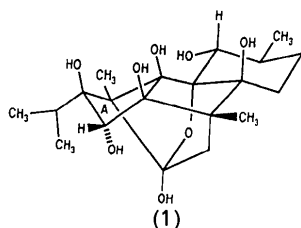
Experimental. Crystals of (4a), (4b), (5a) and (5b) were obtained by evaporation of a CH_2Cl_2–hexane solution (1:4). Intensities were collected on an Enraf–Nonius CAD-4 automatic diffractometer; graphite monochromator, Cu $K\bar{\alpha}$ radiation. The unit-cell dimensions were obtained by least-squares fit of 24 [(4a), (5a)], 31 [(4b), (5b)] well centered reflections in the range $60 \le 2\theta \le 100°$. Reflections were measured with a constant speed of 3° min⁻¹; $2\theta_{max} = 143.6°$; reflections satisfying $I \ge 3\sigma(I)$ were considered as observed. During data collection, the intensities of two standard reflections were monitored every 150 reflections, no significant variation observed.

Compound (4a): Crystal 0.30 × 0.30 × 0.25 mm; a total of 3238 reflections collected (3228 independent, 2127 observed) in the ranges $-11 \le h \le 10$, $0 \le k \le 17$, $0 \le l \le 15$; maximum Δ/σ (for non-H atoms) = 0.34; maximum and minimum density peaks = 0.30

Table 1. *Final coordinates and equivalent B values with e.s.d.'s in parentheses*

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{eq}(\text{Å}^2)$
Compound (4a)				
O(1)	0.5624 (4)	0.56353 (23)	0.1563 (3)	6.97 (23)
O(2)	0.6137 (3)	0.52016 (19)	0.38776 (25)	4.49 (17)
O(3)	0.8359 (4)	0.58699 (20)	0.4789 (3)	5.38 (18)
O(4)	0.6895 (4)	0.41007 (20)	0.2946 (3)	5.27 (19)
O(5)	0.2565 (4)	0.60593 (19)	0.2324 (3)	4.61 (19)
O(6)	0.1093 (4)	0.60153 (24)	0.3407 (3)	6.9 (3)
N	-0.0478 (4)	0.4698 (3)	0.1160 (3)	5.81 (25)
C(1)	0.4879 (6)	0.5124 (3)	0.1885 (4)	4.2 (3)
C(2)	0.5598 (5)	0.4558 (3)	0.2967 (4)	4.1 (3)
C(3)	0.4421 (5)	0.3927 (3)	0.3141 (4)	3.82 (23)
C(4)	0.3107 (6)	0.4524 (3)	0.3208 (4)	3.71 (25)
C(5)	0.2403 (5)	0.5081 (3)	0.2126 (4)	3.58 (23)
C(6)	0.3219 (5)	0.4903 (3)	0.1283 (4)	3.53 (24)
C(7)	0.3200 (5)	0.3887 (3)	0.1124 (4)	3.8 (3)
C(8)	0.2623 (9)	0.3342 (4)	0.0063 (5)	5.6 (4)
C(9)	0.2980 (9)	0.2364 (4)	0.0550 (6)	7.9 (5)
C(10)	0.3800 (10)	0.2413 (4)	0.1800 (6)	6.2 (4)
C(11)	0.3834 (5)	0.3417 (3)	0.2049 (4)	3.9 (3)
C(12)	0.7677 (6)	0.5306 (3)	0.4142 (4)	4.5 (3)
C(13)	0.8215 (7)	0.4645 (4)	0.3479 (6)	5.7 (3)
C(14)	0.5043 (6)	0.3327 (3)	0.4179 (4)	5.7 (3)
C(15)	-0.0753 (5)	0.4879 (3)	0.1588 (4)	4.04 (24)
C(16)	0.1814 (7)	0.6409 (4)	0.2964 (5)	5.4 (3)
C(17)	0.2069 (9)	0.7453 (4)	0.3028 (6)	8.5 (5)
Compound (4b)				
O(1)	0.5226 (5)	0.9976 (3)	0.08997 (11)	4.68 (14)
O(2)	0.5954 (4)	0.88132 (21)	0.19682 (10)	3.39 (10)
O(3)	0.3607 (4)	0.8981 (3)	0.24090 (13)	5.01 (15)
O(4)	0.67395	1.09267 (23)	0.19673 (11)	3.74 (12)
O(5)	0.7420 (5)	0.73710 (21)	0.05475 (10)	3.40 (10)
O(6)	0.8928 (5)	0.5621 (3)	0.07507 (12)	4.34 (13)
O(7)	0.3801 (5)	0.4576 (3)	0.07889 (12)	4.80 (13)
O(8)	0.5266 (4)	0.59346 (23)	0.13550 (11)	3.93 (11)
N	1.1240 (5)	0.8001 (3)	0.01770 (15)	4.90 (17)
C(1)	0.6557 (6)	0.9781 (3)	0.10439 (16)	3.19 (15)
C(2)	0.7006 (6)	0.9715 (3)	0.16982 (15)	3.08 (14)
C(3)	0.8738 (6)	0.9311 (3)	0.17649 (15)	3.14 (14)
C(4)	0.8923 (5)	0.8029 (3)	0.14281 (4)	3.19 (14)
C(5)	0.8633 (5)	0.8228 (3)	0.07684 (14)	2.98 (14)
C(6)	0.7975 (5)	0.9619 (3)	0.06580 (14)	3.05 (14)
C(7)	0.9193 (5)	1.0534 (3)	0.08910 (16)	3.52 (16)
C(8)	1.0026 (7)	1.1636 (4)	0.06070 (19)	4.92 (20)
C(9)	1.1155 (8)	1.2076 (5)	0.10831 (24)	9.1 (4)
C(10)	1.0857 (7)	1.1299 (4)	0.16255 (20)	5.34 (22)
C(11)	0.9600 (5)	1.0364 (3)	0.14377 (16)	3.46 (15)
C(12)	0.4746 (6)	0.9493 (4)	0.22137 (16)	3.71 (16)
C(13)	0.5193 (5)	1.0905 (4)	0.21936 (17)	4.19 (18)
C(14)	0.9211 (6)	0.9151 (4)	0.23973 (17)	4.54 (19)
C(15)	1.0107 (6)	0.8076 (3)	0.04322 (16)	3.55 (16)
C(16)	0.7716 (6)	0.6056 (3)	0.05855 (15)	3.37 (16)
C(17)	0.6258 (6)	0.5333 (3)	0.04151 (15)	3.67 (16)
C(18)	0.5378 (6)	0.4880 (3)	0.09581 (16)	3.62 (17)
C(19)	0.6144 (7)	0.3734 (4)	0.12469 (17)	5.06 (21)
C(20)	0.2767 (7)	0.5402 (5)	0.10943 (24)	6.8 (3)
C(21)	0.3756 (7)	0.6523 (4)	0.12708 (19)	5.15 (21)
Compound (5a)				
N	0.78397 (24)	0.65415 (20)	0.37036 (16)	5.84 (11)
O(1)	0.71231 (17)	0.09531 (15)	-0.00875 (10)	4.51 (7)
O(2)	0.65750 (14)	-0.10124 (13)	0.15693 (10)	3.43 (6)
O(3)	0.65527 (19)	-0.34872 (15)	0.07281 (13)	6.19 (8)
O(4)	0.93715 (14)	0.03914 (14)	0.17066 (10)	3.54 (6)
O(5)	0.98480 (15)	0.45512 (14)	0.18158 (10)	3.59 (6)
O(6)	1.16919 (17)	0.61558 (16)	0.34957 (12)	5.50 (7)
C(1)	0.72663 (20)	0.14686 (20)	0.09900 (15)	2.93 (8)
C(2)	0.77698 (19)	0.05605 (18)	0.18839 (14)	2.64 (7)
C(3)	0.78052 (19)	0.14613 (18)	0.31902 (14)	2.48 (7)
C(4)	0.91190 (22)	0.31396 (20)	0.34104 (15)	2.86 (8)
C(5)	0.85857 (21)	0.40656 (19)	0.25478 (14)	2.89 (8)
C(6)	0.69461 (23)	0.29880 (21)	0.16286 (15)	2.97 (8)
C(7)	0.56450 (21)	0.24286 (20)	0.23842 (14)	2.97 (8)
C(8)	0.3923 (3)	0.2618 (3)	0.24366 (21)	4.51 (12)
C(9)	0.3360 (4)	0.1811 (5)	0.3421 (3)	7.22 (21)
C(10)	0.4744 (3)	0.1201 (3)	0.39006 (20)	4.11 (11)
C(11)	0.60812 (20)	0.16785 (19)	0.31618 (14)	2.71 (7)
C(12)	0.7313 (3)	-0.20982 (22)	0.11007 (16)	3.91 (9)
C(13)	0.9131 (3)	-0.1232 (3)	0.1160 (3)	4.70 (11)
C(14)	0.8270 (3)	0.06205 (24)	0.41125 (18)	3.43 (10)
C(15)	0.82125 (24)	0.54924 (21)	0.32143 (16)	3.59 (9)

Table 1 (cont.)

	x	y	z	$B_{eq}(\text{Å}^2)$
C(16)	1·1380 (3)	0·56339 (21)	0·24152 (18)	4·05 (10)
C(17)	1·2515 (4)	0·6076 (4)	0·1542 (3)	6·07 (16)

Compound (5b)

	x	y	z	$B_{eq}(\text{Å}^2)$
O(1)	0·57472 (9)	0·45102 (17)	0·94926 (8)	4·97 (9)
O(2)	0·58446 (8)	0·55726 (13)	0·82684 (7)	3·20 (7)
O(3)	0·71265 (9)	0·58492 (16)	0·84983 (9)	5·40 (10)
O(4)	0·57648 (8)	0·35523 (13)	0·81974 (7)	2·95 (7)
O(5)	0·41493 (8)	0·25690 (13)	0·89644 (7)	3·02 (7)
O(6)	0·32797 (9)	0·15605 (14)	0·81890 (8)	4·01 (8)
O(7)	0·30992 (9)	0·13541 (18)	0·97447 (8)	5·11 (10)
O(8)	0·43676 (9)	0·12488 (15)	1·02909 (8)	4·29 (8)
N	0·24605 (11)	0·41288 (20)	0·85228 (11)	5·19 (13)
C(1)	0·52165 (13)	0·45541 (20)	0·90050 (11)	2·96 (10)
C(2)	0·53543 (12)	0·45760 (19)	0·82945 (10)	2·53 (9)
C(3)	0·45735 (12)	0·46925 (19)	0·77750 (10)	2·44 (9)
C(4)	0·40892 (14)	0·36095 (22)	0·78862 (11)	2·66 (11)
C(5)	0·39136 (12)	0·36426 (20)	0·85815 (10)	2·66 (10)
C(6)	0·43641 (13)	0·46759 (22)	0·89979 (11)	2·98 (11)
C(7)	0·41160 (12)	0·57886 (21)	0·85982 (11)	3·10 (10)
C(8)	0·37373 (20)	0·6901 (3)	0·87644 (17)	4·74 (16)
C(9)	0·3670 (3)	0·7653 (3)	0·81392 (21)	6·33 (21)
C(10)	0·39044 (19)	0·6883 (3)	0·76106 (16)	4·39 (15)
C(11)	0·42088 (12)	0·57854 (20)	0·79873 (11)	2·82 (10)
C(12)	0·65958 (13)	0·51742 (23)	0·84026 (12)	3·57 (12)
C(13)	0·65777 (14)	0·38403 (25)	0·83989 (14)	3·61 (13)
C(14)	0·46632 (16)	0·4714 (3)	0·70641 (13)	3·39 (12)
C(15)	0·30775 (14)	0·38734 (21)	0·85326 (11)	3·37 (11)
C(16)	0·37511 (13)	0·15638 (23)	0·87153 (11)	3·19 (11)
C(17)	0·39639 (16)	0·05095 (24)	0·91625 (13)	3·50 (12)
C(18)	0·37678 (13)	0·06325 (23)	0·98339 (11)	3·39 (11)
C(19)	0·3653 (3)	−0·0581 (3)	1·01115 (18)	5·71 (20)
C(20)	0·3209 (3)	0·2091 (6)	1·03249 (25)	8·7 (3)
C(21)	0·4056 (3)	0·2194 (3)	1·05758 (19)	6·41 (21)

Table 2. *Bond lengths (Å) and angles (°) with e.s.d.'s in parentheses*

Compound (4a)

O(1)—C(1)	1·196 (6)	C(3)—C(11)	1·509 (6)
O(2)—C(2)	1·451 (5)	C(3)—C(14)	1·531 (6)
O(2)—C(12)	1·374 (6)	C(4)—C(5)	1·546 (6)
O(3)—C(12)	1·193 (6)	C(5)—C(6)	1·540 (7)
O(4)—C(2)	1·402 (6)	C(5)—C(15)	1·491 (6)
O(4)—C(13)	1·437 (6)	C(6)—C(7)	1·521 (6)
O(5)—C(5)	1·474 (5)	C(7)—C(8)	1·505 (7)
O(5)—C(16)	1·351 (7)	C(7)—C(11)	1·320 (6)
O(6)—C(16)	1·175 (7)	C(8)—C(9)	1·568 (9)
N—C(15)	1·126 (6)	C(9)—C(10)	1·510 (10)
C(1)—C(2)	1·554 (7)	C(10)—C(11)	1·523 (7)
C(1)—C(6)	1·516 (7)	C(12)—C(13)	1·491 (8)
C(2)—C(3)	1·521 (7)	C(16)—C(17)	1·567 (8)
C(3)—C(4)	1·545 (7)		

C(2)—O(2)—C(12)	108·5 (4)	C(4)—C(5)—C(15)	111·0 (4)
C(2)—O(4)—C(13)	109·3 (4)	C(6)—C(5)—C(15)	109·4 (4)
C(5)—O(5)—C(16)	115·9 (4)	C(1)—C(6)—C(5)	106·3 (4)
O(1)—C(1)—C(2)	121·4 (4)	C(1)—C(6)—C(7)	104·2 (4)
O(1)—C(1)—C(6)	125·7 (4)	C(5)—C(6)—C(7)	106·1 (4)
C(2)—C(1)—C(6)	112·7 (4)	C(6)—C(7)—C(8)	129·6 (4)
O(2)—C(2)—O(4)	105·6 (3)	C(6)—C(7)—C(11)	115·1 (4)
O(2)—C(2)—C(1)	106·0 (4)	C(8)—C(7)—C(11)	115·2 (4)
O(2)—C(2)—C(3)	111·2 (4)	C(7)—C(8)—C(9)	100·5 (5)
O(4)—C(2)—C(1)	111·0 (4)	C(8)—C(9)—C(10)	109·5 (5)
O(4)—C(2)—C(3)	112·5 (4)	C(9)—C(10)—C(11)	103·4 (5)
C(1)—C(2)—C(3)	110·3 (4)	C(3)—C(11)—C(7)	117·7 (4)
C(2)—C(3)—C(4)	106·7 (4)	C(3)—C(11)—C(10)	131·1 (4)
C(2)—C(3)—C(11)	103·2 (4)	C(7)—C(11)—C(10)	111·2 (4)
C(2)—C(3)—C(14)	113·9 (4)	O(2)—C(12)—O(3)	121·1 (5)
C(4)—C(3)—C(11)	107·1 (4)	O(2)—C(12)—C(13)	108·6 (4)
C(4)—C(3)—C(14)	111·1 (4)	O(3)—C(12)—C(13)	130·3 (5)
C(11)—C(3)—C(14)	114·3 (4)	O(4)—C(13)—C(12)	103·5 (4)
C(3)—C(4)—C(5)	111·2 (4)	N—C(15)—C(5)	177·2 (5)
O(5)—C(5)—C(4)	112·8 (3)	O(5)—C(16)—O(6)	127·2 (5)
O(5)—C(5)—C(6)	104·0 (3)	O(5)—C(16)—C(17)	108·0 (5)
O(5)—C(5)—C(15)	107·9 (4)	O(6)—C(16)—C(17)	124·8 (6)
C(4)—C(5)—C(6)	111·5 (4)		

Compound (4b)

O(1)—C(1)	1·198 (6)	C(3)—C(4)	1·542 (5)
O(2)—C(2)	1·433 (5)	C(3)—C(11)	1·514 (5)
O(2)—C(12)	1·368 (5)	C(3)—C(14)	1·526 (5)
O(3)—C(12)	1·193 (6)	C(4)—C(5)	1·559 (5)

Table 2 (cont.)

O(4)—C(2)	1·413 (4)	C(5)—C(6)	1·560 (5)
O(4)—C(13)	1·418 (4)	C(5)—C(15)	1·484 (6)
O(5)—C(5)	1·452 (5)	C(6)—C(7)	1·501 (6)
O(5)—C(16)	1·381 (4)	C(7)—C(8)	1·491 (6)
O(6)—C(16)	1·188 (6)	C(7)—C(11)	1·323 (5)
O(7)—C(18)	1·434 (6)	C(8)—C(9)	1·530 (8)
O(7)—C(20)	1·414 (7)	C(9)—C(10)	1·510 (7)
O(8)—C(18)	1·426 (4)	C(10)—C(11)	1·504 (6)
O(8)—C(21)	1·435 (6)	C(12)—C(13)	1·505 (5)
N—C(15)	1·134 (6)	C(16)—C(17)	1·501 (6)
C(1)—C(2)	1·562 (5)	C(17)—C(18)	1·535 (6)
C(1)—C(6)	1·511 (6)	C(18)—C(19)	1·505 (6)
C(2)—C(3)	1·540 (7)	C(20)—C(21)	1·487 (7)

C(2)—O(2)—C(12)	108·6 (3)	C(1)—C(6)—C(7)	105·7 (3)
C(2)—O(4)—C(13)	107·3 (3)	C(5)—C(6)—C(7)	105·7 (3)
C(5)—O(5)—C(16)	116·4 (3)	C(6)—C(7)—C(8)	130·4 (3)
C(18)—O(7)—C(20)	108·4 (3)	C(6)—C(7)—C(11)	116·2 (3)
C(18)—O(8)—C(21)	107·2 (3)	C(8)—C(7)—C(11)	113·4 (4)
O(1)—C(1)—C(2)	120·5 (4)	C(7)—C(8)—C(9)	102·0 (4)
O(1)—C(1)—C(6)	127·6 (3)	C(8)—C(9)—C(10)	109·6 (4)
C(2)—C(1)—C(6)	111·8 (4)	C(9)—C(10)—C(11)	102·7 (4)
O(2)—C(2)—O(4)	106·3 (3)	C(3)—C(11)—C(7)	116·4 (4)
O(2)—C(2)—C(1)	107·3 (3)	C(3)—C(11)—C(10)	131·3 (3)
O(2)—C(2)—C(3)	112·3 (3)	C(7)—C(11)—C(10)	112·2 (4)
O(4)—C(2)—C(1)	110·4 (3)	O(2)—C(12)—O(3)	122·8 (3)
O(4)—C(2)—C(3)	110·4 (3)	O(2)—C(12)—C(13)	107·0 (3)
C(1)—C(2)—C(3)	110·0 (3)	O(3)—C(12)—C(13)	130·2 (4)
C(2)—C(3)—C(4)	106·2 (3)	O(4)—C(13)—C(12)	105·1 (3)
C(2)—C(3)—C(11)	102·8 (3)	N—C(15)—C(5)	177·8 (4)
C(2)—C(3)—C(14)	112·2 (3)	O(5)—C(16)—O(6)	123·3 (4)
C(4)—C(3)—C(11)	108·2 (3)	O(5)—C(16)—C(17)	108·6 (4)
C(4)—C(3)—C(14)	111·4 (3)	O(6)—C(16)—C(17)	128·0 (3)
C(11)—C(3)—C(14)	115·4 (3)	C(16)—C(17)—C(18)	109·9 (3)
C(3)—C(4)—C(5)	111·4 (3)	O(7)—C(18)—O(8)	106·2 (4)
O(5)—C(5)—C(4)	112·1 (3)	O(7)—C(18)—C(17)	107·5 (3)
O(5)—C(5)—C(6)	104·2 (3)	O(7)—C(18)—C(19)	110·8 (3)
O(5)—C(5)—C(15)	110·7 (3)	O(8)—C(18)—C(17)	109·1 (3)
C(4)—C(5)—C(6)	109·8 (3)	O(8)—C(18)—C(19)	110·0 (3)
C(4)—C(5)—C(15)	111·4 (3)	C(17)—C(18)—C(19)	113·0 (4)
C(6)—C(5)—C(15)	108·4 (3)	O(7)—C(20)—C(21)	104·6 (5)
C(1)—C(6)—C(5)	107·0 (3)	O(8)—C(21)—C(20)	102·5 (5)

Compound (5a)

N—C(15)	1·1341 (23)	C(3)—C(11)	1·5085 (22)
O(1)—C(1)	1·2015 (19)	C(3)—C(14)	1·518 (3)
O(2)—C(2)	1·4252 (19)	C(4)—C(5)	1·545 (3)
O(2)—C(12)	1·3504 (20)	C(5)—C(6)	1·5522 (24)
O(3)—C(12)	1·1880 (22)	C(5)—C(15)	1·4820 (22)
O(4)—C(2)	1·4215 (18)	C(6)—C(7)	1·5069 (25)
O(4)—C(13)	1·4099 (23)	C(7)—C(8)	1·504 (3)
O(5)—C(5)	1·4487 (20)	C(7)—C(11)	1·320 (3)
O(5)—C(16)	1·3653 (23)	C(8)—C(9)	1·523 (4)
O(6)—C(16)	1·1965 (24)	C(9)—C(10)	1·525 (4)
C(1)—C(2)	1·550 (3)	C(10)—C(11)	1·4974 (25)
C(1)—C(6)	1·5195 (23)	C(12)—C(13)	1·482 (3)
C(2)—C(3)	1·5326 (20)	C(16)—C(17)	1·493 (3)
C(3)—C(4)	1·5453 (23)		

C(2)—O(2)—C(12)	110·27 (13)	C(4)—C(5)—C(15)	111·95 (14)
C(2)—O(4)—C(13)	108·64 (13)	C(6)—C(5)—C(15)	106·94 (14)
C(5)—O(5)—C(16)	116·93 (13)	C(1)—C(6)—C(5)	107·78 (14)
O(1)—C(1)—C(2)	121·17 (15)	C(1)—C(6)—C(7)	103·82 (14)
O(1)—C(1)—C(6)	126·06 (17)	C(5)—C(6)—C(7)	105·75 (13)
C(2)—C(1)—C(6)	112·74 (13)	C(6)—C(7)—C(8)	130·93 (18)
O(2)—C(2)—O(4)	106·81 (12)	C(6)—C(7)—C(11)	115·82 (15)
O(2)—C(2)—C(1)	108·56 (12)	C(8)—C(7)—C(11)	113·23 (17)
O(2)—C(2)—C(3)	111·03 (13)	C(7)—C(8)—C(9)	102·04 (18)
O(4)—C(2)—C(1)	108·03 (13)	C(8)—C(9)—C(10)	109·51 (19)
O(4)—C(2)—C(3)	112·31 (13)	C(9)—C(10)—C(11)	102·61 (19)
C(1)—C(2)—C(3)	109·95 (13)	C(3)—C(11)—C(7)	116·95 (15)
C(2)—C(3)—C(4)	105·93 (13)	C(3)—C(11)—C(10)	130·43 (17)
C(2)—C(3)—C(11)	104·37 (12)	C(7)—C(11)—C(10)	112·61 (16)
C(2)—C(3)—C(14)	112·59 (14)	O(2)—C(12)—O(3)	122·69 (18)
C(4)—C(3)—C(11)	106·92 (13)	O(2)—C(12)—C(13)	107·82 (15)
C(4)—C(3)—C(14)	111·09 (14)	O(3)—C(12)—C(13)	129·49 (17)
C(11)—C(3)—C(14)	115·27 (14)	O(4)—C(13)—C(12)	106·03 (15)
C(3)—C(4)—C(5)	111·71 (13)	N—C(15)—C(5)	176·43 (20)
O(5)—C(5)—C(4)	112·61 (14)	O(5)—C(16)—O(6)	122·30 (17)
O(5)—C(5)—C(6)	105·45 (12)	O(5)—C(16)—C(17)	110·82 (20)
O(5)—C(5)—C(15)	109·11 (14)	O(6)—C(16)—C(17)	126·85 (21)
C(4)—C(5)—C(6)	110·42 (14)		

Compound (5b)

O(1)—C(1)	1·200 (3)	C(3)—C(4)	1·545 (3)
O(2)—C(2)	1·433 (3)	C(3)—C(11)	1·508 (3)

Table 2 (*cont.*)

O(2)—C(12)	1·374 (3)	C(3)—C(14)	1·524 (3)
O(3)—C(12)	1·192 (3)	C(4)—C(5)	1·551 (3)
O(4)—C(2)	1·407 (2)	C(5)—C(6)	1·548 (3)
O(4)—C(13)	1·442 (3)	C(5)—C(15)	1·493 (3)
O(5)—C(5)	1·449 (3)	C(6)—C(7)	1·506 (3)
O(5)—C(16)	1·367 (3)	C(7)—C(8)	1·504 (4)
O(6)—C(16)	1·198 (3)	C(7)—C(11)	1·318 (3)
O(7)—C(18)	1·417 (3)	C(8)—C(9)	1·528 (5)
O(7)—C(20)	1·433 (4)	C(9)—C(10)	1·535 (5)
O(8)—C(18)	1·419 (3)	C(10)—C(11)	1·490 (4)
O(8)—C(21)	1·399 (4)	C(12)—C(13)	1·502 (4)
N—C(15)	1·134 (3)	C(16)—C(17)	1·495 (4)
C(1)—C(2)	1·553 (3)	C(17)—C(18)	1·525 (3)
C(1)—C(6)	1·524 (3)	C(18)—C(19)	1·516 (4)
C(2)—C(3)	1·537 (3)	C(20)—C(21)	1·475 (7)

C(2)—O(2)—C(12)	108·12 (17)	C(1)—C(6)—C(7)	103·57 (19)
C(2)—O(4)—C(13)	107·25 (16)	C(5)—C(6)—C(7)	106·21 (18)
C(5)—O(5)—C(16)	115·62 (16)	C(6)—C(7)—C(8)	130·82 (22)
C(18)—O(7)—C(20)	106·83 (24)	C(6)—C(7)—C(11)	115·83 (20)
C(18)—O(8)—C(21)	109·91 (23)	C(8)—C(7)—C(11)	113·27 (23)
O(1)—C(1)—C(2)	121·30 (19)	C(7)—C(8)—C(9)	102·17 (24)
O(1)—C(1)—C(6)	125·89 (20)	C(8)—C(9)—C(10)	108·4 (3)
C(2)—C(1)—C(6)	112·68 (18)	C(9)—C(10)—C(11)	102·9 (3)
O(2)—C(2)—O(4)	106·93 (15)	C(3)—C(11)—C(7)	116·71 (20)
O(2)—C(2)—C(1)	107·01 (16)	C(3)—C(11)—C(10)	130·69 (21)
O(2)—C(2)—C(3)	111·22 (17)	C(7)—C(11)—C(10)	112·58 (21)
O(4)—C(2)—C(1)	109·58 (17)	O(2)—C(12)—O(3)	121·32 (22)
O(4)—C(2)—C(3)	112·52 (16)	O(2)—C(12)—C(13)	107·86 (19)
C(1)—C(2)—C(3)	109·41 (16)	O(3)—C(12)—C(13)	130·82 (22)
C(2)—C(3)—C(4)	105·78 (17)	O(4)—C(13)—C(12)	104·19 (19)
C(2)—C(3)—C(11)	104·37 (16)	N—C(15)—C(5)	174·6 (3)
C(2)—C(3)—C(14)	112·37 (18)	O(5)—C(16)—O(6)	121·71 (22)
C(4)—C(3)—C(11)	107·61 (17)	O(5)—C(16)—C(17)	113·36 (20)
C(4)—C(3)—C(14)	110·80 (19)	O(6)—C(16)—C(17)	124·93 (23)
C(11)—C(3)—C(14)	115·26 (19)	C(16)—C(17)—C(18)	114·40 (21)
C(3)—C(4)—C(5)	111·73 (18)	O(7)—C(18)—O(8)	106·01 (19)
O(5)—C(5)—C(4)	112·97 (18)	O(7)—C(18)—C(17)	108·22 (19)
O(5)—C(5)—C(6)	106·45 (17)	O(7)—C(18)—C(19)	112·07 (24)
O(5)—C(5)—C(15)	109·25 (17)	O(8)—C(18)—C(17)	110·22 (20)
C(4)—C(5)—C(6)	109·76 (18)	O(8)—C(18)—C(19)	109·80 (22)
C(4)—C(5)—C(15)	111·95 (18)	C(17)—C(18)—C(19)	110·43 (24)
C(6)—C(5)—C(15)	106·09 (18)	O(7)—C(20)—C(21)	104·7 (3)
C(1)—C(6)—C(5)	108·36 (18)	O(8)—C(21)—C(20)	105·8 (3)

and -0.32 e Å^{-3}; the secondary-extinction coefficient $= 0.56$ (4) (Larson, 1967; Zachariasen, 1963).

Compound (4b): Crystal $0.20 \times 0.36 \times 0.30$ mm; a total of 2139 reflections collected (2139 independent, 2039 observed) in the ranges $0 \le h \le 10$, $0 \le k \le 12$, $0 \le l \le 28$; maximum Δ/σ (for non-H atoms) $= 0.054$; maximum and minimum density peaks $= 0.23$ and -0.17 e Å^{-3}; the secondary-extinction coefficient $= 0.41$ (1).

Compound (5a): Crystal $0.12 \times 0.15 \times 0.15$ mm; a total of 4522 reflections collected (3089 independent, 2685 observed) in the ranges $-9 \le h \le 9$, $0 \le k \le 10$, $-14 \le l \le 13$; maximum Δ/σ (for non-H atoms) $= 0.036$; maximum and minimum density peaks $= 0.21$ and -0.18 e Å^{-3}; the secondary-extinction coefficient $= 0.78$ (2).

Compound (5b): Crystal $0.10 \times 0.15 \times 0.15$ mm; 4226 reflections collected (3969 independent, 2803 observed) in the ranges $-21 \le h \le 21$, $0 \le k \le 13$, $0 \le l \le 25$; maximum Δ/σ (for non-H atoms) $= 0.03$; maximum and minimum density peaks $= 0.27$ and -0.01 e Å^{-3}; the secondary-extinction coefficient $= 0.75$ (3).

The structures were solved by direct methods and refined by full-matrix least squares using the *NRCVAX* system (Gabe, Lee & Le Page, 1985). No absorption correction was applied. Hydrogen positions were located in difference Fourier maps. The final refinement included anisotropic thermal parameters for non-H atoms. The H atoms were isotropi-
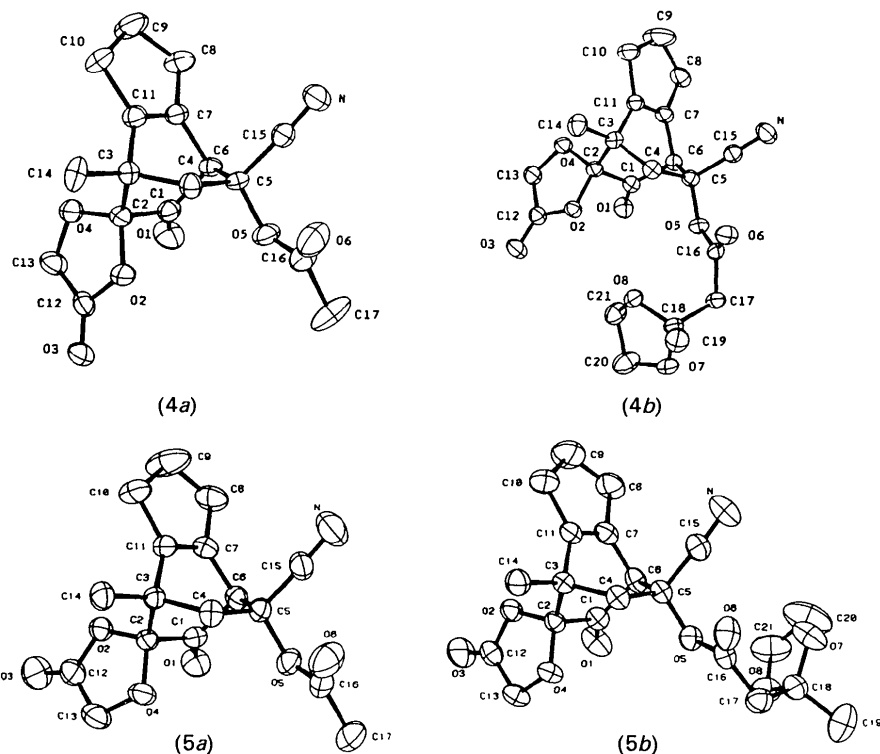
(4a)

(4b)

(5a)

(5b)

Fig. 1. *ORTEP* view of the crystal structures (Johnson, 1976).

cally refined. Atomic scattering factors as stored in the *NRCVAX* program were those of Cromer & Waber (1974). Function minimized: $\sum w(|F_o| - |F_c|)^2$, $w = 1/\sigma^2(F)$.

Discussion. The atomic parameters x, y, z and B_{eq} are listed in Table 1.* Intramolecular distances and angles are given in Table 2. The numbering scheme is shown along with an *ORTEP* view of the molecules in Fig. 1.

The tricyclic carbon backbone is identical in the four compounds. The crystal structure determinations of the two pairs of Diels–Alder adducts show that the compounds have the convenient stereochemistry at C(5) to permit a possible connection between C(17) and C(1) (Fig. 1). The reasons for the failure of the cyclization reaction *via* aldol condensation are still to be clarified.

Interestingly, the separations of pairs of diastereomers (4*a*)/(5*a*) and (4*b*)/(5*b*) by thin-layer chromatography was made possible by the differences in polarities generated by different orientations of the lactone moiety, as revealed by the present study.

No abnormal intermolecular contacts were observed.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, torsion angles and spectroscopic data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53595 (84 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of Two Pyrethroid Insecticides: Acrynathryn (RU 38702) and a Derivative (RU 38181)*

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Abstract. The crystal structures of two crystalline pyrethroid insecticides have been determined at 293 K from three-dimensional X-ray diffraction data. (I), α-cyano-3-phenoxybenzyl 2-(*tert*-butoxycarbonylvinyl)-3,3-dimethylcyclopropanecarboxylate (RU 38181), $C_{27}H_{29}NO_5$, monoclinic, $P2_1$, $M_r = 447.5$, $a = 17.740$ (9), $b = 6.133$ (3), $c = 11.064$ (7) Å, $\beta = 98.96$ (0.5)°, $Z = 2$, $V = 1189.1$ Å^3, $D_x = 1.25$ Mg m^{-3}, Mo $K\bar{\alpha}$, $\lambda = 0.7107$ Å, $\mu = 0.50$ mm^{-1}, $F(000) = 476$. (II), α-cyano-3-phenoxybenzyl 2-(1,1,1,3,3,3-hexafluoro-2-propoxy-carbonylvinyl)-3,3-dimethylcyclopropanecarboxylate (RU 38702), $C_{26}H_{21}F_6NO_5$, orthorhombic, $P2_12_12_1$, $M_r = 541.4$, $a = 9.400$ (7), $b = 37.323$ (13), $c = 7.535$ (4) Å, $Z = 4$, $V = 2643.6$ Å^3, $D_x = 1.36$ Mg m^{-3}, Mo $K\bar{\alpha}$, $\lambda = 0.7107$ Å, $\mu = 0.81$ mm^{-1}, $F(000) = 1112$. The residual R factors are 0.054 and 0.084 respectively for the observed structure factors with $I > 3\sigma(I)$. The most significant

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* The insecticides have been patented by Roussel UCLAF, European Patent Number 48186 (26 June 1981).