

O4—C6—C7	122.0 (3)	C1—C14—C13	122.9 (3)
O4—C6—C5	120.0 (3)	C5—C14—C13	119.8 (3)
C7—C6—C5	118.0 (3)	O2—C16—C2	122.7 (4)

Part of the cost of this study was met by a Scientific Research Grant from the Ministry of Education, Science and Culture of Japan.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71375 (5 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: OH1034]

References

- Hiramatsu, T., Imoto, M., Koyano, T. & Umezawa, K. (1993). *Cancer Lett.* In the press.
- Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
- Konoshima, T., Kozuka, M., Koyama, J., Okatani, T., Tagahara, K. & Tokuda, H. (1989). *J. Nat. Prod.* **52**, 987–995.
- MAC Science (1992). *CRYSTAN-GM. Program System for X-ray Crystal Structure Analysis*. MAC Science, Tokyo, Japan.
- Maniukiewicz, W. & Bukowska-Strzyżewska, M. (1992). *Acta Cryst.* **C48**, 1324–1326.

Acta Cryst. (1993). **C49**, 2151–2153

Two Diastereoisomers of 1-(10-Tri-fluoromethyl-11,12-dioxatetracyclo-[6.2.1.1^{3,6}.0^{2,7}]-dodeca-4,9-dien-9-yl)ethyl Phenylacetate, C₂₁H₁₉F₃O₄: Members of a Series of Adducts Generated by Repeated Diels–Alder Cycloaddition of Furan to 5,5,5-Trifluoropent-3-yn-2-yl Phenylacetate

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(Received 28 September 1992; accepted 6 July 1993)

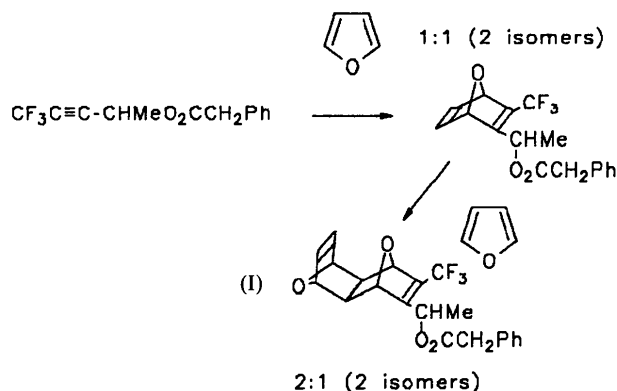
Abstract

Both the title bis adducts are *anti* joined, differing only in the enantiomeric form of the (phenylacetoxyl)ethyl substituent relative to the main ring system. In each case, a CF₃ fluorine nearly eclipses the double bond [F—C=C; isomer (1), 5.9 (7); isomer (2), 10 (2)°], thereby

permitting the adjacent substituent to stagger and the bulky phenylacetoxyl group to project away [C=C—C—O; isomer (1), –161.6 (4); isomer (2), 157 (1)°]. Changes in steric congestion introduced by the structural differences are relatively minor, allowing similar quantities of both compounds to be produced [isomer (1), 10; isomer (2), 8%].

Comment

This structural determination was undertaken to identify the two title diastereoisomers (I) and relate their stereochemistry to the 1:1 adducts (see reaction scheme below), which had been separated (Barlow, Tajammal & Tipping, 1993; Tajammal, 1991) but for which X-ray structure determination was not possible because they were liquids.



The exclusive production of *anti*-joined products indicates that the reaction pathway from 1:1 to 1:2 adducts is stereoselective. The absence of *syn*-joined bis adducts was also noted by Hall, Harkema, den Hertog, van Hummel & Reinhoudt (1981) when they reacted 2-butyndinitrile with 2,3,4,5-tetramethylfuran. They con-

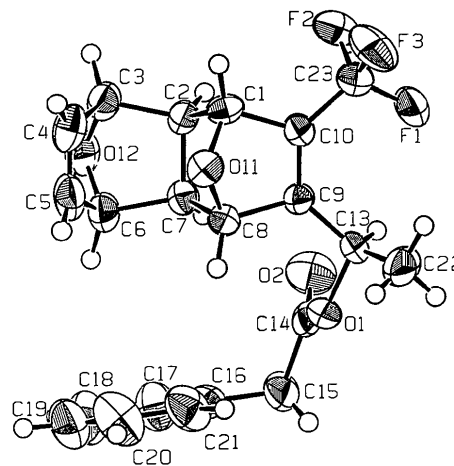


Fig. 1. Isomer (1) (1*R*,2*S*,3*R*,6*S*,7*R*,8*S*,13*R*) including atomic numbering scheme, drawn using *ORTEPII* (Johnson, 1976).

cluded that a secondary orbital effect involving the cyano groups along with low steric hindrance and O...O repulsion governed the shape of their transition state and hence their final product. Clearly the latter two factors are sufficient restriction in the present case.

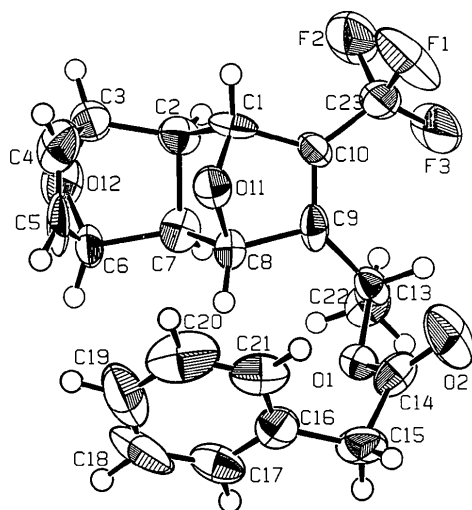


Fig. 2. Isomer (2) (1*R*,2*S*,3*R*,6*S*,7*R*,8*S*,13*S*).

Experimental

Isomer (1)

Crystal data

$C_{21}H_{19}F_3O_4$

$M_r = 392.37$

Triclinic

$P\bar{1}$

$a = 5.707$ (1) Å

$b = 10.227$ (2) Å

$c = 16.625$ (2) Å

$\alpha = 80.48$ (1)°

$\beta = 87.25$ (1)°

$\gamma = 74.50$ (1)°

$V = 922.3$ (5) Å³

$Z = 2$

$D_x = 1.413$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.7107$ Å

Cell parameters from 25 reflections

$\theta = 10.15$ – 24.27°

$\mu = 0.1101$ mm⁻¹

$T = 296$ K

Plate

$0.35 \times 0.20 \times 0.20$ mm

Colourless

Crystal source: Diels–Alder addition reaction

Data collection

CAD-4 diffractometer

$\omega/2$ - θ scans

Absorption correction: not applied

2975 measured reflections

2894 independent reflections

1544 observed reflections

[$F > 3\sigma(F)$]

$R_{int} = 0.019$

Refinement

Refinement on F

$R = 0.0522$

$wR = 0.0298$

$\theta_{max} = 23.97^\circ$

$h = 0 \rightarrow 6$

$k = -11 \rightarrow 11$

$l = -18 \rightarrow 18$

3 standard reflections

monitored every 150

reflections

intensity variation: none

$(\Delta/\sigma)_{max} = 0.0003$

$\Delta\rho_{max} = 0.23758$ e Å⁻³

$\Delta\rho_{min} = -0.20708$ e Å⁻³

$S = 1.734$

1544 reflections

329 parameters

All H-atom parameters refined

Weighting scheme based on measured e.s.d.'s

Extinction correction: not applied

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å²) for isomer (1)

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
F1	0.7097 (5)	0.1057 (3)	0.0338 (2)	0.0860
F2	0.9911 (5)	-0.0040 (2)	0.1187 (2)	0.0722
F3	0.6890 (5)	-0.0847 (3)	0.1056 (2)	0.0864
O1	0.2379 (5)	0.4622 (3)	0.1221 (2)	0.0490
O2	0.5943 (7)	0.5172 (3)	0.1059 (2)	0.0770
O11	0.4323 (5)	0.1049 (3)	0.2962 (2)	0.0430
O12	0.8963 (5)	0.2594 (3)	0.3887 (2)	0.0589
C1	0.6692 (8)	0.0519 (4)	0.2636 (3)	0.0419
C2	0.8211 (8)	0.1412 (4)	0.2911 (2)	0.0393
C3	0.9076 (9)	0.1178 (5)	0.3814 (3)	0.0514
C4	0.707 (1)	0.0927 (6)	0.4378 (3)	0.0597
C5	0.540 (1)	0.2105 (6)	0.4337 (3)	0.0621
C6	0.6378 (9)	0.3111 (5)	0.3743 (3)	0.0519
C7	0.6273 (8)	0.2805 (4)	0.2859 (2)	0.0396
C8	0.4004 (8)	0.2445 (4)	0.2575 (2)	0.0382
C9	0.4564 (7)	0.2260 (4)	0.1684 (2)	0.0364
C10	0.6198 (7)	0.1056 (4)	0.1728 (2)	0.0392
C13	0.3467 (9)	0.3285 (4)	0.0964 (3)	0.0434
C14	0.383 (1)	0.5472 (4)	0.1211 (3)	0.0518
C15	0.238 (1)	0.6841 (5)	0.1430 (3)	0.0720
C16	0.1955 (9)	0.6777 (4)	0.2348 (3)	0.0542
C17	0.322 (1)	0.7418 (5)	0.2774 (4)	0.0760
C18	0.282 (1)	0.7405 (7)	0.3599 (4)	0.0923
C19	0.125 (1)	0.6760 (7)	0.4001 (4)	0.0930
C20	-0.001 (1)	0.6104 (7)	0.3597 (5)	0.0976
C21	0.035 (1)	0.6130 (6)	0.2760 (4)	0.0760
C22	0.140 (1)	0.2935 (6)	0.0592 (4)	0.0661
C23	0.7513 (9)	0.0324 (5)	0.1076 (3)	0.0567

Table 2. Geometric parameters (Å, °) for isomer (1)

C1–C2	1.548 (5)	C5–C6	1.506 (6)
C1–C10	1.530 (5)	C6–C7	1.561 (5)
C2–C3	1.563 (5)	C7–C8	1.551 (5)
C2–C7	1.545 (5)	C8–C9	1.533 (5)
C3–C4	1.493 (6)	C9–C10	1.325 (4)
C4–C5	1.317 (6)		
C1–C2–C3	120.9 (4)	C2–C7–C6	100.6 (3)
C1–C2–C7	100.4 (3)	C2–C7–C8	101.8 (3)
C3–C2–C7	101.6 (3)	C6–C7–C8	119.9 (4)

Isomer (2)

Crystal data

$C_{21}H_{19}F_3O_4$

$M_r = 392.37$

Orthorhombic

$P2_12_12_1$

$a = 5.870$ (1) Å

$b = 13.845$ (2) Å

$c = 22.664$ (2) Å

$V = 1841.9$ (7) Å³

$Z = 4$

$D_x = 1.415$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.7107$ Å

Cell parameters from 25 reflections

$\theta = 11.36$ – 17.36°

$\mu = 0.1102$ mm⁻¹

$T = 296$ K

Plate

$0.40 \times 0.40 \times 0.05$ mm

Colourless

Crystal source: Diels–Alder addition reaction

Data collection

CAD-4 diffractometer	$\theta_{\max} = 23.93^\circ$
$\omega/2-\theta$ scans	$h = 0 \rightarrow 6$
Absorption correction:	$k = 0 \rightarrow 15$
not applied	$l = 0 \rightarrow 25$
1776 measured reflections	3 standard reflections
1719 independent reflections	monitored every 150 reflections
866 observed reflections	intensity variation: none
$[F > 3\sigma(F)]$	
$R_{\text{int}} = 0.024$	

Refinement

Refinement on F	$(\Delta/\sigma)_{\max} = 0.0016$
$R = 0.0689$	$\Delta\rho_{\max} = 0.26681 \text{ e } \text{\AA}^{-3}$
$wR = 0.0349$	$\Delta\rho_{\min} = -0.29936 \text{ e } \text{\AA}^{-3}$
$S = 1.954$	Extinction correction: not applied
866 reflections	Atomic scattering factors from <i>International Tables for X-ray Crystallography</i> (1974, Vol. IV)
253 parameters	
H-atom parameters not refined	
Weighting scheme based on measured e.s.d.'s	

Table 3. Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2) for isomer (2)
$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
F1	0.548 (2)	0.5572 (6)	0.8244 (3)	0.1138
F2	0.798 (1)	0.6551 (4)	0.8249 (2)	0.0950
F3	0.878 (2)	0.5067 (6)	0.8250 (3)	0.1440
O1	0.940 (1)	0.3594 (4)	0.6565 (3)	0.0466
O2	0.678 (2)	0.2748 (6)	0.7006 (3)	0.0907
O11	0.575 (1)	0.6058 (4)	0.6487 (3)	0.0449
O12	1.029 (2)	0.7960 (6)	0.6035 (4)	0.0749
C1	0.651 (2)	0.6558 (8)	0.7003 (4)	0.0468
C2	0.853 (2)	0.7173 (7)	0.6796 (4)	0.0473
C3	0.826 (3)	0.8041 (8)	0.6379 (4)	0.0632
C4	0.643 (3)	0.7844 (9)	0.5933 (6)	0.0720
C5	0.736 (3)	0.7230 (9)	0.5561 (5)	0.0715
C6	0.968 (3)	0.7045 (8)	0.5778 (5)	0.0660
C7	0.960 (2)	0.6406 (8)	0.6352 (4)	0.0449
C8	0.794 (2)	0.5587 (7)	0.6395 (4)	0.0415
C9	0.831 (2)	0.5115 (7)	0.7002 (4)	0.0423
C10	0.745 (2)	0.5742 (7)	0.7376 (4)	0.0367
C13	0.967 (2)	0.4233 (8)	0.7083 (4)	0.0396
C14	0.770 (2)	0.2958 (8)	0.6571 (5)	0.0506
C15	0.741 (2)	0.2534 (8)	0.5964 (4)	0.0620
C16	0.658 (3)	0.3327 (9)	0.5550 (5)	0.0544
C17	0.797 (3)	0.367 (1)	0.5123 (7)	0.0623
C18	0.742 (4)	0.438 (1)	0.4748 (7)	0.1071
C19	0.546 (4)	0.480 (1)	0.4825 (7)	0.0989
C20	0.393 (2)	0.449 (1)	0.5244 (8)	0.0937
C21	0.451 (3)	0.373 (1)	0.5605 (6)	0.0630
C22	1.226 (2)	0.4413 (8)	0.7146 (4)	0.0572
C23	0.757 (3)	0.5673 (9)	0.8022 (5)	0.0673

Table 4. Geometric parameters (\AA , $^\circ$) for isomer (2)

C1—C2	1.53 (1)	C5—C6	1.47 (2)
C1—C10	1.51 (1)	C6—C7	1.57 (1)
C2—C3	1.54 (1)	C7—C8	1.50 (1)
C2—C7	1.59 (1)	C8—C9	1.54 (1)
C3—C4	1.50 (2)	C9—C10	1.31 (1)
C4—C5	1.32 (1)		
C1—C2—C3	123 (1)	C2—C7—C6	99.2 (8)
C1—C2—C7	97.3 (8)	C2—C7—C8	102.0 (8)
C3—C2—C7	100.0 (8)	C6—C7—C8	120 (1)

A solution of 5,5,5-trifluoropent-3-yn-2-yl phenylacetate (4.03 g, 15.7 mmol) in dichloromethane (10 cm³) and furan (1.16 g, 17.1 mmol), heated *in vacuo* in a Rotaflo tube (ca 30 cm³) at 373 K (9 d), gave, after removal of the solvent, a mixture (5.2 g) which was separated by repeated DCFC (silica Merck Kieselgel 60H) into (i) a monohydrate of 1-(3-trifluoromethyl-7-oxabicyclo[2.2.1]hepta-2,5-dien-2-yl)ethyl phenylacetate (0.92 g, 2.7 mmol, 17%) [eluant petroleum ether (b.p. 313–333 K) and CH₂Cl₂ 1:2 v/v], (ii) a monohydrate of 1-(3-trifluoromethyl-7-oxabicyclo[2.2.1]hepta-2,5-dien-2-yl)ethyl phenylacetate (0.53 g, 1.55 mmol, 10%) (same eluant), (iii) a mixture of two isomers of the title 2:1 adduct (1.20 g, 3.1 mmol, 20%) (same eluant), and (iv) a mixture of two isomers of the 3:1 adduct 1-(12-trifluoromethyl-15,16,17-trioxahexacyclo[6.6.1.1^{3,6}.1^{10,13}.0^{2,7}.0^{9,14}]heptadeca-4,11-dien-11-yl)ethyl phenylacetate (0.38 g, 0.8 mmol, 5%) (same eluant).

The two isomers of the title 2:1 adduct were separated by repeated DCFC (eluant CH₂Cl₂) to give (i) isomer (1) (0.60 g, 1.5 mmol, 10%), m.p. 391 K (found: C 64.3, H 5.0, F 14.2%, M^+ 392; C₂₁H₁₉F₃O₄ requires C 64.3, H 4.8, F 14.5%, M^+ 392), and isomer (2) (0.50 g, 1.3 mmol, 8%), m.p. 366 K (found: C 64.1, H 4.9, F 14.3%, M^+ 392). Crystals for the X-ray study were obtained by recrystallization from a mixture of CH₂Cl₂ and petroleum ether (b.p. 313–333 K) in the ratio 1:3 v/v.

The anomalous component of Mo was too low for absolute-configuration determinations.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *TEXSAN*; *MITHRIL* (Gilmore, 1984). Program(s) used to refine structure: *TEXSAN LS*. Molecular graphics: *TEXSAN*; *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *TEXSAN FINISH*.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71421 (40 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HU1033]

References

- Barlow, M. G., Tajammal, S. & Tipping, A. E. (1993). *J. Fluorine Chem.* **62**, 51–61.
- CSSR (1984). *Crystal Structure Search and Retrieval Instruction Manual*. SERC Daresbury Laboratory, Warrington, England.
- Gilmore, C. J. (1984). *J. Appl. Cryst.* **17**, 42–46.
- Hall, R. H., Harkema, S., den Hertog, H. J., van Hummel, C. J. & Reinholdt, D. N. (1981). *Recl. Trav. Chim. Pays-Bas*, **100**, 312–314.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Tajammal, S. (1991). PhD thesis, Univ. of Manchester, England.