C(16)—C(17)—F(2)	111.1 (6)	F(8)—C(20)—F(9)	112.3 (9)
C(16)—C(17)—F(1)	112.4 (6)	F(7)—C(20)—F(9)	109.5 (10)
F(2)—C(17)—C(18)	106.3 (6)	F(7)—C(20)—F(8)	102.8 (10)

C(3)—N(1)—C(4)—O(2)	154.5 (7)
C(1)—N(1)—C(4)—O(2)	−10.4 (10)
C(1)—N(1)—C(3)—C(2)	9.3 (7)
C(3)—N(1)—C(1)—N(2)	−14.9 (7)
C(1)—N(2)—C(2)—O(1)	172.9 (7)
C(2)—N(2)—C(1)—N(1)	15.9 (8)
C(1)—N(2)—C(2)—C(3)	−10.8 (8)
O(1)—C(2)—C(3)—N(1)	177.2 (7)
N(2)—C(2)—C(3)—N(1)	0.7 (7)
O(1)—C(2)—C(3)—C(16)	52.9 (9)
C(2)—C(3)—C(16)—C(17)	62.5 (8)
N(1)—C(3)—C(16)—C(17)	−52.4 (9)
N(1)—C(4)—C(5)—C(10)	−43.8 (10)
C(3)—C(16)—C(17)—F(1)	−39.6 (9)
C(3)—C(16)—C(17)—F(2)	77.1 (8)
C(3)—C(16)—C(17)—C(18)	−162.8 (6)
C(16)—C(17)—C(18)—C(19)	−174.8 (7)
F(2)—C(17)—C(18)—F(3)	75.2 (7)
C(17)—C(18)—C(19)—C(20)	−171.6 (8)

The positional parameters of all H atoms were refined with a common isotropic displacement factor. Refinement was by full-matrix least squares.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *SDP* (Frenz, 1984). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *PEANUT* (Hummel, Hauser & Bürgi, 1990). Software used to prepare tables for publication: *PARST* (Nardelli, 1983).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and intermolecular contacts less than 3.5 Å have been deposited with the IUCr (Reference: SH1082). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Beckwith, A. L. J. & Chai, C. L. L. (1990). *J. Chem. Soc. Chem. Commun.* pp. 1087–1088.
Büchel, R. (1994). PhD thesis, Univ. of Berne.
Chakrabarti, P. & Dunitz, J. D. (1982). *Helv. Chim. Acta*, **65**, 1555–1562.
Duax, W. L., Weeks, C. M. & Rohrer, D. C. (1976). *Top. Stereochem.* **9**, 271–383.
Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Frenz, B. A. (1984). *Enraf–Nonius Structure Determination Package*. College Station, Texas, USA, and Enraf–Nonius, Delft, The Netherlands.
Hummel, W., Hauser, J. & Bürgi, H.-B. (1990). *J. Mol. Graphics*, **8**, 214–220.
Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.
Sereda, S. V., Antipin, M. Yu., Timofeeva, T. V. & Struchkov, Yu. T. (1988). *Sov. Phys. Crystallogr.* **33**, 223–225.
Sereda, S. V., Antipin, M. Yu., Timofeeva, T. V., Struchkov, Yu. T. & Shelyazhenko, S. V. (1987a). *Sov. Phys. Crystallogr.* **32**, 204–208.
Sereda, S. V., Antipin, M. Yu., Timofeeva, T. V., Struchkov, Yu. T. & Shelyazhenko, S. V. (1987b). *Sov. Phys. Crystallogr.* **32**, 685–691.
Sheldrick, G. M. (1976). *SHELX*76. *Program for Crystal Structure Determination*. Univ. of Cambridge, England.
Sheldrick, G. M. (1985). *SHELXS*86. *Program for the Solution of Crystal Structures*. Univ. of Göttingen, Germany.

Product of a Paterno–Büchi Reaction of Pentafluorobenzaldehyde and 1-Acetoxycyclododecene

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Abstract

The stereochemistry of 14-pentafluorophenyl-13-oxa-bicyclo[10.2.0]tetradecan-1-yl acetate, $C_{21}H_{25}F_5O_3$, the photoaddition product of pentafluorobenzaldehyde to 1-acetoxycyclododecene, has been established. The aryl and acetoxy substituents are *cis*, and the ring fusion is *trans*.

Comment

In the course of the development of a synthesis of the 3-acetoxyoxetane subunit in the antineoplastic agent taxol (Wani, Taylor, Wall, Coggan & McPhail, 1971), we examined the prospects for using a Paterno–Büchi reaction of enol acetates and benzaldehydes to introduce this particular moiety. The stereoselectivity of the photoaddition of various benzaldehydes was investigated in several acyclic and cyclic enol acetates. As expected (Paterno & Chietti, 1909; Büchi, Imman & Lipinsky, 1954; Jones, 1981), the aryl and acetoxy groups have a *cis* relationship in the products, a finding supported by chemical-shift data in the ^1H NMR spectra. In the case of 1-acetoxycyclododecene, the enol acetate (1) was a mixture of *E*/*Z* isomers and the photoaddition with pentafluorobenzaldehyde, (2), could lead to a product in which the acetoxy group and the bridgehead methine

possessed either a cis, (3), or trans, (4), relationship. The structure determination established that the principal product of the reaction was the oxetane (4) arising from (1E)-1-acetoxycyclododecene, (1E).
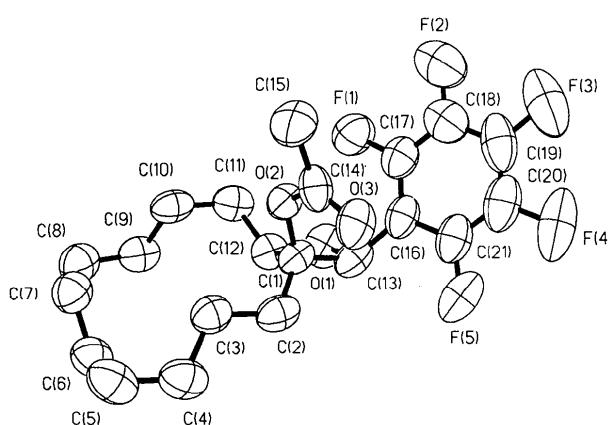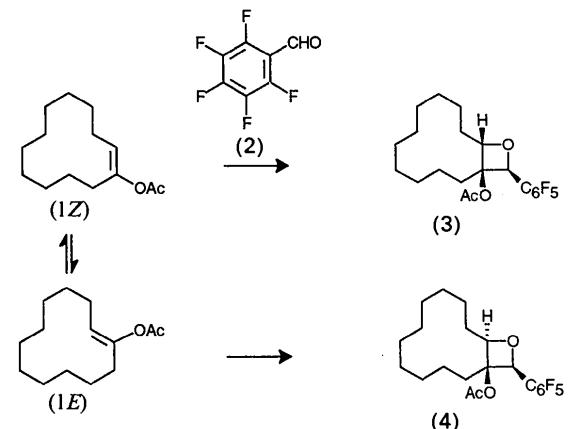

Fig. 1. Perspective drawing of the molecule showing the atom-numbering scheme. The ellipsoids have been drawn at the 50% probability level. H atoms have been omitted for clarity.


Fig. 2. Stereoscopic drawing of the unit cell. The b axis runs from right to left, the c axis runs downwards and the a axis points out of the plane of the paper.

Experimental

The compound was obtained by the procedure described by Vasuderan, Brock, Watt & Morita (1994). Crystals were grown by slow evaporation of EtOH solutions.

Crystal data

$C_{21}H_{25}F_5O_3$	Mo $K\alpha$ radiation
$M_r = 420.42$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 22
$P2_1/n$	reflections
$a = 8.6548$ (4) Å	$\theta = 12.2-13.1°$
$b = 15.8640$ (7) Å	$\mu = 0.114$ mm^{-1}
$c = 14.9305$ (12) Å	$T = 296$ (1) K
$\beta = 94.338$ (5)°	Rhomboidal tablet; major
$V = 2044.1$ (2) Å^3	faces {010}
$Z = 4$	$0.5 \times 0.4 \times 0.3$ mm
$D_x = 1.366$ Mg m^{-3}	Colorless

Data collection

Enraf–Nonius CAD-4-VAX	$\theta_{max} = 27.5°$
diffractometer	$h = 0 \rightarrow 11$
$\omega/2\theta$ scans	$k = 0 \rightarrow 20$
Absorption correction:	$l = -19 \rightarrow 19$
none	3 standard reflections
4682 measured reflections	frequency: 60 min
4682 independent reflections	intensity variation: <0.1%
1823 observed reflections	
$[I > 2\sigma(I)]$	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.048$
$R[F^2 > 2\sigma(F^2)] = 0.043$	$\Delta\rho_{max} = 0.13$ e Å^{-3}
$wR(F^2) = 0.132$	$\Delta\rho_{min} = -0.18$ e Å^{-3}
$S = 1.130$	Extinction correction: none
4681 reflections	Atomic scattering factors
262 parameters	from International Tables
H-atom parameters not	for Crystallography (1992,
refined	Vol. C, Tables 4.2.6.8 and
$w = 1/[\sigma^2(F_o^2) + (0.1000P)^2]$	6.1.1.4)
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
F1	0.3749 (2)	0.41062 (10)	0.47800 (10)	0.1111 (5)
F2	0.2851 (2)	0.54301 (12)	0.5671 (2)	0.1435 (7)
F3	0.2577 (2)	0.53413 (15)	0.7466 (2)	0.1662 (9)
F4	0.3245 (2)	0.3881 (2)	0.83472 (12)	0.1620 (9)
F5	0.4161 (2)	0.25315 (14)	0.74559 (10)	0.1264 (6)
O1	0.5524 (2)	0.26332 (12)	0.49334 (12)	0.0958 (6)
O2	0.20181 (15)	0.24463 (8)	0.46420 (9)	0.0665 (4)
O3	0.0956 (2)	0.23770 (11)	0.59673 (11)	0.0866 (5)
C1	0.3368 (2)	0.19814 (14)	0.49725 (13)	0.0665 (6)
C2	0.2980 (3)	0.10833 (14)	0.5226 (2)	0.0780 (7)
C3	0.2229 (3)	0.05893 (14)	0.4446 (2)	0.0774 (6)
C4	0.2251 (3)	−0.0363 (2)	0.4552 (2)	0.0947 (8)
C5	0.1878 (3)	−0.0850 (2)	0.3691 (2)	0.1022 (9)
C6	0.2920 (3)	−0.0620 (2)	0.2941 (2)	0.0904 (7)
C7	0.2221 (3)	0.0029 (2)	0.2296 (2)	0.0911 (8)
C8	0.3366 (3)	0.0543 (2)	0.1801 (2)	0.0961 (8)
C9	0.4315 (3)	0.1169 (2)	0.2381 (2)	0.0829 (7)
C10	0.3417 (3)	0.1928 (2)	0.2690 (2)	0.0807 (7)
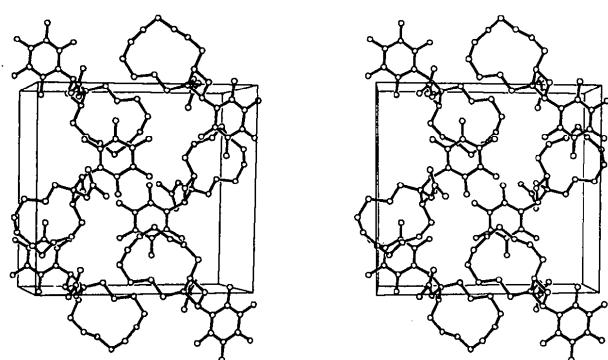
C11	0.4309 (3)	0.2477 (2)	0.3398 (2)	0.0823 (7)
C12	0.4619 (2)	0.2084 (2)	0.4302 (2)	0.0744 (6)
C13	0.4502 (3)	0.2483 (2)	0.5626 (2)	0.0810 (7)
C14	0.0881 (2)	0.25864 (15)	0.5201 (2)	0.0717 (6)
C15	−0.0429 (3)	0.3047 (2)	0.4712 (2)	0.1093 (9)
C16	0.4012 (2)	0.3267 (2)	0.6089 (2)	0.0787 (6)
C17	0.3660 (3)	0.4026 (2)	0.5664 (2)	0.0851 (7)
C18	0.3191 (3)	0.4710 (2)	0.6125 (3)	0.1016 (8)
C19	0.3048 (3)	0.4666 (3)	0.7033 (3)	0.1107 (10)
C20	0.3393 (3)	0.3934 (3)	0.7464 (2)	0.1087 (10)
C21	0.3864 (3)	0.3250 (2)	0.6996 (2)	0.0951 (8)

Table 2. *Selected geometric parameters* (Å, °)

F1—C17	1.334 (3)	C5—C6	1.534 (4)
F2—C18	1.349 (3)	C6—C7	1.504 (3)
F3—C19	1.331 (4)	C7—C8	1.518 (3)
F4—C20	1.337 (3)	C8—C9	1.518 (4)
F5—C21	1.345 (3)	C9—C10	1.523 (3)
O1—C13	1.431 (3)	C10—C11	1.533 (3)
O1—C12	1.466 (3)	C11—C12	1.492 (3)
O2—C14	1.356 (2)	C13—C16	1.501 (3)
O2—C1	1.437 (2)	C14—C15	1.492 (3)
O3—C14	1.188 (3)	C16—C21	1.370 (3)
C1—C2	1.518 (3)	C16—C17	1.384 (3)
C1—C12	1.538 (3)	C17—C18	1.363 (4)
C1—C13	1.550 (3)	C18—C19	1.372 (4)
C2—C3	1.509 (3)	C19—C20	1.350 (5)
C3—C4	1.519 (3)	C20—C21	1.369 (4)
C4—C5	1.513 (4)		
C13—O1—C12	92.1 (2)	C16—C13—C1	121.9 (2)
C14—O2—C1	118.8 (2)	O3—C14—O2	123.9 (2)
O2—C1—C2	112.2 (2)	O3—C14—C15	126.3 (2)
O2—C1—C12	108.4 (2)	O2—C14—C15	109.8 (2)
C2—C1—C12	116.2 (2)	C21—C16—C17	115.9 (3)
O2—C1—C13	114.4 (2)	C21—C16—C13	119.3 (3)
C2—C1—C13	117.8 (2)	C17—C16—C13	124.7 (2)
C12—C1—C13	84.9 (2)	F1—C17—C18	117.7 (3)
C3—C2—C1	112.7 (2)	F1—C17—C16	120.6 (2)
C2—C3—C4	115.8 (2)	C18—C17—C16	121.6 (3)
C5—C4—C3	114.8 (2)	F2—C18—C17	118.9 (3)
C4—C5—C6	113.5 (2)	F2—C18—C19	120.5 (3)
C7—C6—C5	113.6 (2)	C17—C18—C19	120.7 (3)
C6—C7—C8	115.7 (2)	F3—C19—C20	121.7 (4)
C9—C8—C7	114.8 (2)	F3—C19—C18	119.5 (4)
C8—C9—C10	115.1 (2)	C20—C19—C18	118.8 (3)
C9—C10—C11	114.6 (2)	F4—C20—C19	119.3 (4)
C12—C11—C10	115.7 (2)	F4—C20—C21	120.6 (4)
O1—C12—C11	112.6 (2)	C19—C20—C21	120.1 (3)
O1—C12—C1	90.7 (2)	F5—C21—C20	117.6 (3)
C11—C12—C1	123.1 (2)	F5—C21—C16	119.5 (3)
O1—C13—C16	114.0 (2)	C20—C21—C16	122.8 (3)
O1—C13—C1	91.6 (2)		

Data collection and cell refinement; CAD-4-VAX diffractometer software (Enraf–Nonius, 1988). Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993).

References

Büchi, G., Imman, C. G. & Lipinsky, E. S. (1954). *J. Am. Chem. Soc.* **76**, 4327–4331.

Enraf–Nonius (1988). *CAD-4 Manual*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Jones, G. II (1981). *Organic Photochemistry*, Vol. 5, edited by A. Padwa, pp. 1–122. New York: Marcel Dekker.

Paterno, E. & Chietti, G. (1909). *Gazz. Chim. Ital.* **39**, 341–361.

Sheldrick, G. M. (1990). *SHELXTL/PC Users Manual*. Siemens Analytical Instruments, Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1993). *SHELXL93. Program for Crystal Structure Refinement*. Univ. of Göttingen, Germany.

Vasuderan, S., Brock, C. P., Watt, D. S. & Morita, H. (1994). *J. Org. Chem.* In the press.

Wani, M. C., Taylor, H. L., Wall, M. E., Coggan, P. & McPhail, A. T. (1971). *J. Am. Chem. Soc.* **93**, 2325–2327.

Bis(pyridiniopropionate) Hydrogen Bromide

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Abstract

A novel anhydrous 2:1 acid adduct of a betaine derivative, pyridiniopropionate (ppbet), has been prepared, $C_{16}H_{19}N_2O_4^+ \cdot Br^-$ (I). X-ray crystallography revealed that the carboxylate groups of a pair of ppbet molecules are bridged by a proton in an unusual non-coplanar configuration to form a U-shaped dimeric cation [(ppbet)$_2$H]$^+$, featuring a very strong hydrogen bond of length 2.450 (6) Å.

Comment

As zwitterions with terminal quaternary ammonium and carboxylate groups, betaine and its derivatives are good proton acceptors, and very strong hydrogen bonds are found in crystalline acid adducts such as [(bet)$_2$H]Cl.H$_2$O (bet = Me$_3$N$^+$CH$_2$CO$_2^-$) (Chen & Mak, 1990a) and [(pybet)$_2$H]Cl.H$_2$O (pybet = C$_5$H$_5$N$^+$CH$_2$CO$_2^-$) (Chen & Mak, 1990b). In the strongly hydrogen-bonded dimeric cations of these two betaine–acid adducts, the pair of carboxylate groups are centrosymmetrically related with an O···O distance of ca 2.45 Å. It is found that the carboxylate group of betaines is significantly affected by