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1-Tosyl-1*H*-pyrrolo[2,3-*c*]pyridine-5carboxylic Acid Ethyl Ester

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Abstract

The title compound, $C_{17}H_{16}N_2O_4S$, was synthesized starting from 1*H*-pyrrole-2-carboxaldehyde under acidic conditions. The X-ray structure determination has proved that the compound was the expected pyrrolo[2,3-*c*]pyridine derivative and not the pyrrolo[3,2-*c*]pyridine isomer. The molecules are packed such that the azaindole rings are stacked in one set of parallel planes and the phenyl rings are stacked in another, with interplanar distances of 3.50 (1) and 3.83 (1) Å, respectively, giving the molecule a 'V' shape.

Comment

In connection with studies aimed at the development of new central nervous system agents, we recently prepared the title compound, (1), starting from 1*H*-pyrrole-2carboxaldehyde (Dekhane, Potier & Dodd, 1993). As the acidic conditions used to synthesize (1) have been shown to cause substituents at the C2 position of the pyrrole ring to migrate to the C3 position (Carson & Davis, 1981; Desales, Greenhouse & Muchowski, 1982), there was some doubt as to whether the compound isolated was actually an isomer of (1), that is, 1-tosyl-1*H*-pyrrolo[3,2-*c*]pyridine-6-carboxylic acid ethyl ester, (2). Such an isomer could not, however, be differentiated from (1) using conventional spectroscopic methods. Therefore, it was necessary to confirm the structure of (1) by an X-ray crystallographic study.



The molecular structure of (1) is shown in Fig. 1. It consists of two planar moieties bridged at the S atom, with a dihedral angle of 95° between the respective

© 1994 International Union of Crystallography Printed in Great Britain – all rights reserved mean planes of the azaindole ring (N1, C2, C3, C3a, C4, C5, N6, C7, C7a) and the phenyl ring. The azaindole ring is perfectly planar [maximum atomic deviation from the mean plane: 0.016(3)Å] and short distances at C2--C3 [1.335(5)Å] and N6--C7 [1.325(4)Å] have been found. Interestingly, the molecules are packed (Fig. 2) such that the azaindole rings on one hand and the phenyl rings on the other are stacked in parallel planes with distances of 3.50(1) and 3.83(1)Å, respectively, between the mean planes, giving the molecules a 'V' shape. This specific stacking is also depicted in Fig. 1 where the molecule is shown projected down the crystallographic *a* axis. Consequently, all the molecules obtained by translation along this axis are superimposable.



Fig. 1. Perspective view of the molecule projected along the *a* axis.



Fig. 2. Packing of the molecules. For clarity the molecules obtained by the centre of symmetry have been omitted.

$C_{17}H_{16}N_{2}O_{4}S \\$

Crystal data C11 0.6522 (6) 0.6591 (3) 0.4750 (2) 0.051 (4) Cy7H16NyO4S Cu K α radiation $\lambda = 1.5418$ Å Table 2. Selected geometric parameters (Å, °) Triclinic Cell parameters from 25 reflections NI—C2 1.406 (4) CS—010 1.330 (4) $a = 5.088$ (3) Å $\theta = 9.6 - 19.4^{\circ}$ C2—C3 1.335 (5) S13—014 1.424 (2) $c = 14.909$ (12) Å $T = 293$ K C3—C4 1.396 (4) S13—015 1.421 (2) $c = 14.909$ (12) Å $T = 293$ K C3—C4 1.396 (4) S13—015 1.421 (2) $a = 110.32$ (3)° Prism C3—C4 1.396 (4) S13—015 1.421 (2) $a = 110.32$ (3)° Colourless C5—C8 1.497 (4) C18—C19 1.338 (4) $\gamma = 815.3$ (9) Å ³ Colourless C5—C8 1.497 (4) C18—C19 1.338 (4) $D_{Z} = 1.40$ Mg m ⁻³ $L = -5 \rightarrow 5$ C3—C14 100 (3) NI—S13—015 102 (2) 1.488 (2) $D_{Z} = 3$ $L = 0 \rightarrow 17$ C3—C4 1338 (2) C3—C4=C13 1338 (2) C2—C1 1.338 (2) C3—C4=C13 1	Experimental		C20	0.8242 (6)	0.9074 (3) 0.5496 (2)	0.053 (3)
$ \begin{array}{c} C_{17}H_{16}N_{2}O_{4}S & Cu \ K\alpha \ radiation \ \lambda = 1.5418 \ \AA & Table 2. Selected geometric parameters (Å, °) \\ Triclinic & Cell parameters from 25 \\ PI & reflections & NI-C2 & 1406 (4) & C8-O10 & 1.330 (4) \\ NI-C7a & 1.397 (4) & O10-C11 & 1.453 (4) \\ a = 5.088 (3) \ \AA & \theta = 9, 6-19.4^{\circ} & NI-S13 & 1.674 (2) & C11-C12 & 1.498 (5) \\ b = 11.566 (8) \ \AA & \mu = 1.93 \ mm^{-1} & C2-C3 & 1.335 (5) \ S13-O15 & 1.421 (2) \\ c = 14.909 (12) \ \AA & T = 293 \ K & C3a-C4 & 1.396 (4) & S13-O15 & 1.421 (2) \\ a = 110.32 (3)^{\circ} & Prism & C3a-C7a & 1.406 (4) & C6-C17 & 1.376 (4) \\ \beta = 96.62 (3)^{\circ} & 0.40 \times 0.15 \times 0.03 \ mm & C3-C6 & 1.476 (4) & C16-C21 & 1.388 (4) \\ \beta = 96.62 (3)^{\circ} & 0.40 \times 0.15 \times 0.03 \ mm & C5-C8 & 1.477 (4) & C18-C19 & 1.388 (5) \\ V = 815.3 (9) \ \AA^{3} & Colourles & C-7 & 1.232 (4) & C19-C22 & 1.496 (5) \\ P_x = 1.40 \ Mg \ m^{-3} & Colourles & N6-C7 & 1.232 (4) & C19-C22 & 1.496 (5) \\ D_x = 1.40 \ Mg \ m^{-3} & Colourles & N6-C7 & 1.232 (4) & C19-C22 & 1.496 (5) \\ D_x = 1.40 \ Mg \ m^{-3} & Colourles & N6-C7 & 1.232 (4) & C19-C22 & 1.496 (5) \\ D_x = 1.40 \ Mg \ m^{-3} & Colourles & N6-C7 & 1.232 (4) & C19-C22 & 1.496 (5) \\ D_x = 1.40 \ Mg \ m^{-3} & Colourles & N6-C7 & 1.232 (4) & C19-C22 & 1.496 (5) \\ D_x = 1.40 \ Mg \ m^{-3} & Colourles & N6-C7 & 1.232 (4) & C19-C22 & 1.496 (5) \\ D_x = 1.40 \ Mg \ m^{-3} & Colourles & N6-C7 & 1.232 (4) & N1-S13-O16 & 1056 (1) \\ D_x = 0.43 \ M_1 = 0.021 \ M_2 = 0.04 \ M_2 = 0.04 \ M_1 = 0.021 \ M_2 = 0.04 \ M_2 = 0.04 \ M_2 = 0.04 \ M_2 = 0.021 \ M_2 = 0.04 \ M_2 = 0.021 \ M_2 = 0.04 \ M_2 = 0.04 \ M_2 = 0.021 \ M_2 = 0.04 \ M_2 = 0.04 \ M_2 = 0.021 \ M_2 = 0.04 \ M_2 = 0.021 \ M_2 = 0.021 \ M_2 = 0.021 \ M_2 = 0.04 \ M_2 = 0.04 \ M_2 =$	Crystal data		C21 C22	0.6232 (6) 1.1853 (7)	0.8507() 0.9051()	3) 0.4750(2) 4) 0.6782(2)	0.051 (3)
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	$C_{17}H_{16}N_2O_4S$	Cu $K\alpha$ radiation			•		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$M_r = 344.39$	$\lambda = 1.5418 \text{ Å}$	Tabl	le 2. Selec	ted geome	tric parameters (A	Λ, °)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Triclinic	Cell parameters from 25	N1—C2	1	1.406 (4)	C8010	1.330 (4)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	PĪ	reflections	N1—C7a	1	1.397 (4)	O10-C11	1.453 (4)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	a = 5.088 (3) Å	$\theta = 0.6 - 10.4^{\circ}$	N1	1	1.674 (2)	C11—C12	1.498 (5)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	a = 5.000 (5) R b = 11.566 (9) Å	$v = 1.02 \text{ mm}^{-1}$	C2—C3	1	1.335 (5)	\$13014	1.424 (2)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	D = 11.500 (8) A	$\mu = 1.93 \text{ mm}$	C3—C3a	1	1.436 (5)	\$13-015	1.421 (2)
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	c = 14.909 (12) A	T = 293 K	C3a—C4	1	1.396 (4)	S13-C16	1.758 (3)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$\alpha = 110.32 (3)^{\circ}$	Prism	C3a—C7a		1.406 (4)	C16C17	1.376 (4)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\beta = 96.62 (3)^{\circ}$	$0.40 \times 0.15 \times 0.03$ mm	C4C5		1.3/6(4)	C16C21	1.389 (4)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\gamma = 91.42 (3)^{\circ}$	Colourless	C_{5}	:	1.347 (3)	C1/-C18	1.378(3)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	V = 815.3 (9) Å ³		N6 C7		1.497 (4)	$C_{10} - C_{20}$	1.300(3) 1.387(4)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	7 = 315.5(9) A		$C7 - C7_{2}$		1 389 (4)	C19 - C20 C19 - C22	1.387 (4)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Z = 2		C8-09		1.206 (4)	C20-C21	1.382 (4)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$D_x = 1.40 \text{ Mg m}^{-3}$		C2_N1_C2	7a	107 8 (2)	09	123 4 (3)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			$C_{2} = N_{1} = S_{1}$	3	123.8 (2)	C8-010-C11	115.3 (2)
Nonius CAD-4 diffractome- ter $R_{int} = 0.028$ $N1-C2-C3$ $110.0(3)$ $N1-S13-O14$ $105.6(1)$ $d/2\theta$ scans $h = -5 \rightarrow 5$ $C2-C3-C3a$ $107.8(3)$ $N1-S13-O15$ $104.4(1)$ $d/2\theta$ scans $h = -5 \rightarrow 5$ $C3-C3a-C7a$ $107.3(3)$ $014-S13-O15$ $102.1(4)$ Absorption correction: $k = -13 \rightarrow 12$ $C3-C3a-C7a$ $107.3(3)$ $014-S13-O15$ $102.1(4)$ none $l = 0 \rightarrow 17$ $C3a-C4-C5$ $117.4(3)$ $014-S13-O16$ $109.6(1)$ 2864 measured reflections3 standard reflections $C4-C5-N6$ $124.8(3)$ $S13-C16-C17$ $120.0(2)$ 2749 independent reflectionsfrequency: 166 min intensity variation: none $C4-C5-C8$ $117.8(2)$ $S13-C16-C21$ $118.8(2)$ 1988 observed reflectionsfrequency: 166 min intensity variation: none $N1-C7a-C7a$ $120.9(3)$ $C17-C18-C19$ $120.9(3)$ $N1-C7a-C7a$ $120.9(3)$ $C17-C18-C19$ $120.9(3)$ $N1-C7a-C7a$ $120.9(3)$ $C17-C18-C19$ $120.9(3)$ $Refinement$ F $(\Delta/\sigma)_{max} = 0.04$ $\Delta\rho_{max} = 0.22$ e Å^{-3} $C5-C8-O9$ $123.1(3)$ $C19-C20-C21$ $118.2(3)$ $wR = 0.065$ $\Delta\rho_{min} = -0.38$ e Å^{-3} $C2-N1-S13-C16$ $-88.3(2)$ $N1-S13-C16-C21$ $85.3(2)$ $S = 1.35$ Extinction correction: none $133.5-C16-C21$ $85.3(2)$ $N1-S13-C16-C21$ $85.3(2)$ $N1-S13-C16$ $Atomic scattering factors$ $Atomic scattering factors$ $C2-N1-S13-C16$ $-88.3(2)$ $N1-S13-C16-C21$ $85.3(2)$ </td <td>Data collection</td> <td></td> <td>C7a—N1—S</td> <td>13</td> <td>126.9 (2)</td> <td>010-C11-C12</td> <td>107.7 (3)</td>	Data collection		C7a—N1—S	13	126.9 (2)	010-C11-C12	107.7 (3)
ter $\theta_{max}^{max} = 64.94^{\circ}$ $C_2-C_3-C_3a$ $107.8(3)$ $N1-S13-O15$ $104.4(1)$ $\theta/2\theta$ scans $h = -5 \rightarrow 5$ C_3-C_3a-C4 $135.2(3)$ $N1-S13-C16$ $105.6(1)$ Absorption correction: $k = -13 \rightarrow 12$ C_4-C_3a-C7a $107.3(3)$ $O14-S13-O15$ $122.1(1)$ none $l = 0 \rightarrow 17$ $C_3a-C4-C5$ $117.4(3)$ $O14-S13-C16$ $109.6(1)$ 2864 measured reflections3 standard reflections $C_4-C5-N6$ $124.8(3)$ $S13-C16-C17$ $120.0(2)$ 2749 independent reflectionsfrequency: 166 min $N6-C5-C8$ $117.8(2)$ $S13-C16-C21$ $118.8(2)$ 1988 observed reflectionsintensity variation: none $N6-C7-C7a$ $120.9(3)$ $C17-C16-C21$ $121.2(3)$ $I > 3.0\sigma(I)$]intensity variation: none $N6-C7-C7a$ $120.9(3)$ $C17-C18-C19-C22$ $121.0(3)$ $Refinement$ $R = 0.043$ $\Delta \rho_{max} = 0.22$ e Å ⁻³ $C5-C8-O9$ $123.1(3)$ $C19-C20-C21$ $121.8(3)$ $wR = 0.065$ $\Delta \rho_{min} = -0.38$ e Å ⁻³ $C5-C8-O10$ $113.5(2)$ $C16-C17-C17$ $120.9(2)$ $S = 1.35$ Extinction correction: none 108.3^{-3} $C2-N1-S13-C16$ $75.8(2)$ $N1-S13-C16-C21$ $85.3(2)$ 1983 reflectionsAtomic scattering factors $C4-C5-R8-O10$ $113.5(2)$ $N1-S13-C16-C17$ $-95.0(2)$ $Refinement$ $R = 0.043$ $\Delta \rho_{max} = 0.22$ e Å^{-3} $C5-C8-O10$ $113.5(2)$ $N1-S13-C16-C17$ $-95.0(2)$ $R = 0.065$ $\Delta \rho_{min} = -0.38$ e Å^{-3} $C2-N1-S13-C1$	Nonius CAD-4 diffractome-	$R_{\rm int} = 0.028$	N1-C2-C3	3	110.0 (3)	N1-S13-014	105.6(1)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	ter	$\theta_{\rm max} = 64.94^{\circ}$	C2-C3-C3	Ba	107.8 (3)	N1-S13-015	104.4 (1)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	A/2A scans	$h = -5 \implies 5$	C3—C3a—C	24	135.2 (3)	N1-S13-C16	105.6(1)
Absorption correction: $k = -15 \rightarrow 12$ $C4-C3a-C7a$ 117.4 (3) $O14-S13-C16$ 108.8 (1)none $l = 0 \rightarrow 17$ $C3a-C4-C5$ 117.5 (3) $O15-S13-C16$ 109.0 (1)2864 measured reflections3 standard reflections $C4-C5-N6$ 124.8 (3) $S13-C16-C17$ 120.0 (2)2749 independent reflectionsfrequency: 166 min $C4-C5-N6$ 117.8 (2) $S13-C16-C21$ 118.8 (2)1988 observed reflectionsfrequency: 166 min $N6-C5-C8$ 117.3 (2) $C17-C16-C21$ 112.8 (2) $[I > 3.0\sigma(I)]$ intensity variation: none $C5-N6-C7$ 118.4 (2) $C16-C17-C18$ 119.6 (3) $Refinement$ $Refinement$ $N6-C7-C7a$ 120.9 (3) $C18-C19-C22$ 120.9 (3) $Refinement$ on F $(\Delta/\sigma)_{max} = 0.04$ $C5-C8-O9$ 123.1 (3) $C19-C20-C21$ 128.43) $R = 0.043$ $\Delta \rho_{max} = 0.22$ e Å ⁻³ $C5-C8-O9$ 123.1 (3) $C19-C20-C21$ 118.2 (3) $wR = 0.065$ $\Delta \rho_{min} = -0.38$ e Å ⁻³ $C5-C8-O10$ 113.5 (2) $C16-C21-C20$ 118.2 (3) $S = 1.35$ Extinction correction: none $C2-N1-S13-C16$ -88.3 (2) $N1-S13-C16-C21$ 85.3 (2) 1983 reflectionsAtomic scattering factorsH atoms of the methyl group of C22 were disordered		$n = -5 \rightarrow 5$	C3—C3a—C	.7a	107.3 (3)	014\$13015	122.1 (1)
none $l = 0 \rightarrow 17$ $C_{3a}-C4-C5$ 117.5 (3) $015-S13-C16$ 109.0 (1)2864 measured reflections3 standard reflections $C4-C5-N6$ 124.8 (3) $S13-C16-C17$ 120.0 (2)2749 independent reflectionsfrequency: 166 min intensity variation: none $requency: 166 min$ intensity variation: none $C4-C5-C8$ 117.5 (2) $S13-C16-C21$ 118.8 (2)1988 observed reflectionsfrequency: 166 min intensity variation: none $N6-C5-C8$ 117.3 (2) $C17-C16-C21$ 121.2 (3) $[I > 3.0\sigma(I)]$ $N6-C7-C7a$ 120.9 (3) $C17-C18-C19$ 120.9 (3) <i>Refinement</i> $Refinement$ on F $(\Delta/\sigma)_{max} = 0.04$ $C5-C8-O9$ 123.1 (3) $C19-C20-C21$ 121.8 (3) $R = 0.043$ $\Delta \rho_{max} = 0.22$ e Å ⁻³ $C5-C8-O9$ 123.1 (3) $C19-C20-C21$ 121.8 (3) $wR = 0.065$ $\Delta \rho_{min} = -0.38$ e Å ⁻³ $C2-N1-S13-C16$ -88.3 (2) $N1-S13-C16-C17$ -95.0 (2) $S = 1.35$ Extinction correction: none $C2-N1-S13-C16$ 75.8 (2) $N1-S13-C16-C21$ 85.3 (2) 1983 reflectionsAtomic scattering factors $Farming factors$ H atoms of the methyl group of C22 were disordered	Absorption correction:	$k = -13 \rightarrow 12$	C4—C3a—C	C7a	117.4 (3)	O14-S13-C16	108.8 (1)
2864 measured reflections 2749 independent reflections 1988 observed reflections $[I > 3.0\sigma(I)]$ 3 standard reflections 	none	$l = 0 \rightarrow 17$	C3a—C4—C	25	117.5 (3)	O15-S13-C16	109.0(1)
2749 independent reflections 1988 observed reflections [$I > 3.0\sigma(I)$]frequency: 166 min intensity variation: none $C4-C5-C8$ N6-C7-C7 $117.8(2)$ ($17.8(2)$ $S13-C16-C21$ ($17.8(2)$ $118.8(2)$ ($217-C16-C21$ $118.8(2)$ ($212.2(3)$ <i>Refinement</i> Refinement on F $R = 0.043$ $(\Delta/\sigma)_{max} = 0.04$ $\Delta\rho_{max} = 0.22$ e Å ⁻³ $N6-C7-C7a$ ($2-C7a-C7a$ $120.9(3)$ ($21-C7a-C7a$ $C17-C18-C19-C20$ ($120.9(3)$ $118.4(2)$ ($21-C18-C19-C20$ $118.4(2)$ ($21-C18-C19-C20$ <i>Refinement</i> $R = 0.043$ $\Delta\rho_{max} = 0.04$ $\Delta\rho_{min} = -0.38$ e Å ⁻³ $C5-C8-O9$ ($C2-N1-S13-C16$ $C19-C20-C21$ ($212.1(3)$ $212.1(3)$ ($21-C21-C20$ <i>R</i> = 0.065 $S = 1.35$ $\Delta\rho_{min} = -0.38$ e Å ⁻³ Atomic scattering factors $C2-N1-S13-C16$ ($C7a-N1-S13-C16$ $N1-S13-C16-C17$ ($75.8(2)$ $N1-S13-C16-C21$ ($85.3(2)$)1983 reflections ($217-crametric construction correction: none(217-crametric construction correction correctio$	2864 measured reflections	3 standard reflections	C4C5N6	5	124.8 (3)	\$13-C16-C17	120.0 (2)
1988 observed reflections $[I > 3.0\sigma(I)]$ intensity variation: none $N_{0C_{3-}-C_{3}}$ $117.3 (2)$ $C1/-C16-C21$ $121.2 (3)$ $[I > 3.0\sigma(I)]$ intensity variation: none $N_{0C_{3-}-C_{3-}}$ $120.9 (3)$ $C17-C16-C17-C18$ $119.6 (3)$ Refinement $Refinement$ $N_{0C_{3-}-C_{3-}}$ $107.1 (2)$ $C18-C19-C20$ $118.4 (3)$ Refinement on F $(\Delta/\sigma)_{max} = 0.04$ $C_{3C_{3-}-C_{7-}$ $120.9 (3)$ $C17-C18-C19-C22$ $121.0 (3)$ $R = 0.043$ $\Delta \rho_{max} = 0.22$ e Å ⁻³ $C_{5-C8-O9}$ $123.1 (3)$ $C19-C20-C21$ $121.8 (3)$ $wR = 0.065$ $\Delta \rho_{min} = -0.38$ e Å ⁻³ $C_{5-C8-O10}$ $113.5 (2)$ $C16-C17-C17$ $120.9 (3)$ $S = 1.35$ Extinction correction: none $C_{2-N1-S13-C16}$ $-88.3 (2)$ $N1-S13-C16-C17$ $-95.0 (2)$ $S = 1.35$ Atomic scattering factorsH atoms of the methyl group of C22 were disordered	2749 independent reflections	frequency: 166 min	C4C5C8	3	117.8 (2)	\$13-C16-C21	118.8 (2)
$ \begin{bmatrix} I > 3.0\sigma(I) \end{bmatrix} $ $ \begin{bmatrix} I$	1988 observed reflections	intensity variation: none	N6-C5-C	5	117.3 (2)	C1/-C16-C21	121.2 (3)
$(1 > 3.00 (1)]$ $N0 = -1/a$ $120.9 (3)$ $C1/a = C19$ $120.9 (3)$ Refinement $N1 = -C7a = C3a$ $107.1 (2)$ $C18 = C19 = C20$ $118.4 (3)$ Refinement on F $(\Delta/\sigma)_{max} = 0.04$ $C5 = C8 = 09$ $123.1 (3)$ $C19 = C20$ $118.4 (3)$ $R = 0.043$ $\Delta \rho_{max} = 0.22$ e Å ⁻³ $C5 = C8 = 09$ $123.1 (3)$ $C19 = C20 = C21$ $121.8 (3)$ $wR = 0.065$ $\Delta \rho_{min} = -0.38$ e Å ⁻³ $C5 = C8 = 010$ $113.5 (2)$ $C16 = C21 = C20$ $118.2 (3)$ $S = 1.35$ Extinction correction: none $C7a = N1 = S13 = C16$ $75.8 (2)$ $N1 = S13 = C16 = C21$ $85.3 (2)$ 1983 reflectionsAtomic scattering factorsH atoms of the methyl group of C22 were disordered	$[I > 3.0\sigma(D)]$	intensity furnations none	N6 C7 C	/	118.4 (2)	C10 - C17 - C18	119.0 (3)
RefinementN1-C7a-C7132.0 (3)C18-C19-C22113.4 (3)Refinement on F $(\Delta/\sigma)_{max} = 0.04$ $C_{3-C7a-C7}$ 120.9 (3)C20-C19-C22121.0 (3) $R = 0.043$ $\Delta\rho_{max} = 0.22 e Å^{-3}$ $C_{5-C8-O9}$ 123.1 (3)C19-C20-C21121.8 (3) $wR = 0.065$ $\Delta\rho_{min} = -0.38 e Å^{-3}$ $C_{5-C8-O10}$ 113.5 (2)C16-C21-C20118.2 (3) $S = 1.35$ Extinction correction: none $C_{7a-N1-S13-C16}$ -88.3 (2)N1-S13-C16-C17-95.0 (2)1983 reflectionsAtomic scattering factorsfactorsH atoms of the methyl group of C22 were disordered	[1 > 3.00(1)]		N1-C72-C	7a 73a	120.9(3) 1071(2)	C17 - C10 - C19	120.9(3)
Refinement $(\Delta/\sigma)_{max} = 0.04$ $(\Delta/\sigma)_{max} = 0.22 \text{ e} \text{ Å}^{-3}$ $(\Delta/\sigma)_{max} = 0.22 \text{ e} \text{ A}^{-3}$ $(\Delta/\sigma)_{max} = 0.22 \text{ e}$	D - f		$N1 - C7_{2} - C$.5a 77	107.1(2) 1320(3)	C18 - C19 - C20	1710(3)
Refinement on F $(\Delta/\sigma)_{max} = 0.04$ C5-C8-O9123.1 (3)C19-C20-C21121.8 (3) $R = 0.043$ $\Delta\rho_{max} = 0.22 \text{ e} \text{ Å}^{-3}$ C5-C8-O10113.5 (2)C16-C21-C20118.2 (3) $wR = 0.065$ $\Delta\rho_{min} = -0.38 \text{ e} \text{ Å}^{-3}$ C2-N1-S13-C16-88.3 (2)N1-S13-C16-C17-95.0 (2) $S = 1.35$ Extinction correction: noneC7a-N1-S13-C1675.8 (2)N1-S13-C16-C2185.3 (2)1983 reflectionsAtomic scattering factorsH atoms of the methyl group of C22 were disordered	Kejinemeni		C3a-C7a-	C 7	1209(3)	C_{20} C_{19} C_{22}	120.6(3)
$R = 0.043$ $\Delta \rho_{max} = 0.22 \text{ e } \text{\AA}^{-3}$ $C5-C8-O10$ $113.5(2)$ $C16-C21-C20$ $118.2(3)$ $wR = 0.065$ $\Delta \rho_{min} = -0.38 \text{ e } \text{\AA}^{-3}$ $C2-N1-S13-C16$ $-88.3(2)$ $N1-S13-C16-C17$ $-95.0(2)$ $S = 1.35$ Extinction correction: none $C7a-N1-S13-C16$ $75.8(2)$ $N1-S13-C16-C21$ $85.3(2)$ 1983 reflectionsAtomic scattering factorsH atoms of the methyl group of C22 were disordered	Refinement on F	$(\Delta/\sigma)_{\rm max} = 0.04$	C5-C8-O	9	123.1(3)	C19 - C20 - C21	121.8 (3)
$wR = 0.065$ $\Delta \rho_{min} = -0.38 \text{ e} \text{ Å}^{-3}$ $C2-N1-S13-C16$ $-88.3(2)$ $N1-S13-C16-C17$ $-95.0(2)$ $S = 1.35$ Extinction correction: none $C7a-N1-S13-C16$ $75.8(2)$ $N1-S13-C16-C21$ $85.3(2)$ 1983 reflectionsAtomic scattering factorsH atoms of the methyl group of C22 were disordered	R = 0.043	$\Delta \rho_{\rm max} = 0.22 \text{ e} \text{ Å}^{-3}$	C5-C8-01	10	113.5 (2)	C16-C21-C20	118.2 (3)
S = 1.35Extinction correction: none $C7a - N1 - S13 - C16$ $75.8 (2)$ $N1 - S13 - C16 - C21$ $85.3 (2)$ 1983 reflectionsAtomic scattering factors1983 reflectionsfrom international Tables1984 H atoms of the methyl group of C22 were disordered	wR = 0.065	$\Delta \rho_{\rm min} = -0.38 \ {\rm e} \ {\rm \AA}^{-3}$	C2-N1-S1	13—C16	-88.3 (2)	N1-S13-C16-C17	-95.0 (2)
1983 reflections Atomic scattering factors H atoms of the methyl group of C22 were disordered	S = 1.35	Extinction correction: none	C7a—N1—S	613—C16	75.8 (2)	N1-S13-C16-C21	85.3 (2)
from International Tables in atoms of the methyl group of C22 were disordered	1983 reflections	Atomic scattering factors	U atoma	of the	athul ana	in of C22 wars	licordorad
217 parallelets found millional radies Two positions were found with an occurrency factor of	217 parameters	from International Tables	Two posi	tions were	found "	ip of C22 were to	factor

H atoms of the methyl group of C22 were disordered. Two positions were found with an occupancy factor of 0.50 each. The isotropic displacement parameters of the H atoms were set equal to $1.10U_{eq}$ of the parent atom. Data collection: Enraf–Nonius CAD-4 software. Data reduction: *NONIUS* (Riche, 1989). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELX76* (Sheldrick, 1976). Molecular graphics: *R3M* (Riche, 1983); *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *ACTACIF* (Riche, 1992).

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

for X-ray Crystallography

(1974, Vol. IV)

$U_{\rm eq} = (1/3)$	$\Sigma_i \Sigma_j U_{ij} a_i^* a_j$	$_{j}^{*}\mathbf{a}_{i}.\mathbf{a}_{j}.$
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H-atom parameters not

 $w = 1/[\sigma^2(F) + 0.0072F^2]$

Calculated weights

refined

	x	у	Z	U_{eq}
N1	0.4317 (5)	0.6094 (2)	0.2586 (2)	0.047(2)
C2	0.4612 (7)	0.6849 (3)	0.2036 (2)	0.060 (4)
C3	0.6202 (8)	0.6347 (3)	0.1371 (2)	0.066 (4)
C3a	0.7071 (6)	0.5232 (2)	0.1492 (2)	0.048 (3)
C4	0.8762 (6)	0.4336 (3)	0.1051 (2)	0.050 (3)
C5	0.9105 (6)	0.3377 (2)	0.1390 (2)	0.041 (3)
N6	0.7893 (5)	0.3230 (2)	0.2104 (2)	0.044 (2)
C7	0.6286 (6)	0.4073 (2)	0.2531 (2)	0.045 (3)
C7a	0.5876 (5)	0.5093 (2)	0.2257 (2)	0.041 (3)
C8	1.0978 (6)	0.2433 (2)	0.0942(2)	0.045 (3)
09	1.2249 (5)	0.2499 (2)	0.0325 (2)	0.066 (3)
O10	1.1135 (4)	0.1528 (2)	0.1300(1)	0.056 (2)
C11	1.3021 (7)	0.0620 (3)	0.0914 (3)	0.060 (3)
C12	1.2735 (7)	-0.0382(3)	0.1325 (3)	0.068 (4)
S13	0.2934 (1)	0.6534 (1)	0.3608(1)	0.045 (1)
014	0.2025 (4)	0.5419 (2)	0.3714 (2)	0.056 (2)
015	0.1176 (4)	0.7433 (2)	0.3514 (2)	0.060(2)
C16	0.5541 (5)	0.7261 (2)	0.4535 (2)	0.042 (3)
C17	0.6848 (6)	0.6600 (3)	0.5037 (2)	0.055 (3)
C18	0.8886(7)	0.7179 (3)	0.5763 (2)	0.061 (4)
C19	0.9616 (6)	0.8424 (3)	0.6004 (2)	0.051 (3)

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: PA1098). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Product of a Paterno–Büchi Reaction of Pentafluorobenzaldehyde and 4-*tert*-Butyl-1-acetoxycyclohexene

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Abstract

The stereochemistry of the product of the photoaddition of pentafluorobenzaldehyde to 4-*tert*-butyl-1acetoxycyclohexene, 4-*tert*-butyl-8-pentafluorophenyl-7-oxabicyclo[4.2.0]oct-1-yl acetate, $C_{19}H_{21}F_5O_3$, has been established. The ring fusion is *cis*, and the aryl and acetoxy substitutents are *trans* to the tertiary butyl group.

Comment

In the course of developing a synthesis for the 3acetoxyoxetane subunit in the antineoplastic agent taxol (Wani, Taylor, Wall, Coggan & McPhail, 1971), we examined the prospects for using a Paterno–Büchi reaction (Paterno & Chietti, 1909; Büchi, Imman & Lipinsky, 1954) of enol acetates and benzaldehydes to introduce this particular moiety. The success of the methodology would depend upon the yields of the photoaddition reaction as well as of the subsequent oxidative degradation of the aromatic ring and a decarboxylation. Prior reports of the photoaddition reactions of enol ethers and trimethylsilyl enol ethers with aromatic aldehydes suggested that the regiochemistry desired in the taxol situation was favored (Jones, 1981). The photolysis of variously substituted benzaldehydes with enol acetates had not, however, been investigated (Vasudevan, Brock, Watt & Morita, 1994). The photolysis of 4-*tert*-butyl-1-acetoxycyclohexene (1) and pentafluorobenzaldehyde (2) gave preferentially a 2-aryl-3-acetoxyoxetane with the expected *cis* relationship between the pentafluorophenyl and acetoxy groups. It was difficult, however, to resolve the remaining stereochemical issue regarding the selectivity of the facial attack by (2): attack on the diastereotopic faces of (1) would lead either to the oxetane (3) or the oxetane (4). The structure determination confirmed that the product was, in fact, the oxetane (3).



In forming the oxetane (3) rather than (4), the pentafluorobenzaldehyde (2) underwent a preferential syn addition with respect to the tert-butyl group in the enol acetate (1). The factors which guide this unexpected diastereospecificity in this situation are unclear, but the steric influence of the tert-butyl group on attack by the triplet state of (2) would appear to be minimal. A kinetic preference for addition to the re face of the enol acetate (1) may reflect a transition state in which the acetyl group preferentially shields the si face. Molecular-mechanics calculations for 4-tert-butyl-1-acetoxycyclohexene (1) suggested that a conformation with the acetyl group twisted toward the si face (i.e. syn to the tert-butyl group) was more stable than other conformations with the acetyl in a quadrant above the re face. This same preference, if present in the transition state, would favor the formation of (3).



Fig. 1. Perspective drawing showing the molecular structure and the atom-numbering scheme. The shapes of the ellipsoids correspond to 50% probability contours of atomic displacement. The H atoms have been omitted for the sake of clarity.

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