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Acta Cryst. (1998). C**54**, 1718–1720

(*S*)-*N*-Triphenylmethylpyroglutamyl Fluoride†

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(*Received 8 April 1998; accepted 21 May 1998*)

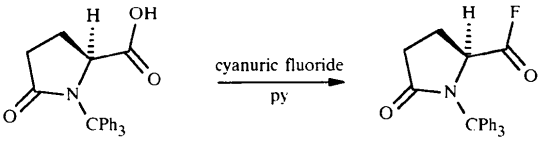
Abstract

The title compound, $C_{24}H_{20}FNO_2$, is the product of the reaction of (*S*)-*N*-triphenylmethylpyroglutamic acid with cyanuric fluoride in the presence of pyridine. The crystal structure determination shows the presence of two crystallographically independent molecules, with the two pyrrolidinyl rings adopting slightly different conformations.

† Alternative name: (*S*)-5-fluoroformyl-1-triphenylmethylpyrrolidin-2-one.

Comment

Treatment of N^{α}-triphenylmethylamino acids with cyanuric fluoride in the presence of pyridine provides access to the corresponding fluorides, which are powerful acylating agents suitable for use in peptide synthesis (Karigiannis *et al.*, 1998). These agents react much faster with amino components than the corresponding benzotriazolyl 'active' esters (Barlos *et al.*, 1984), and thus we decided to determine the structure of the title compound, (II), prepared from the readily available (*S*)-*N*-triphenylmethylpyroglutamic acid, (I) (Papaioannou *et al.*, 1995), using X-ray analysis. Fluoride (II) was the only one of the recently prepared N^{α}-triphenylmethylamino acid fluorides (Karigiannis *et al.*, 1998) which could be obtained in a suitable crystalline form for crystallographic analysis. In addition, in the 200 MHz ^{1}H NMR spectrum of (II), the H5 proton appears at 4.353 p.p.m. as a doublet, with J = 9.21 Hz, although it would be expected to couple with the two vicinal protons at C4 and the F atom.



(I) (II)

The crystal structure determination of (II) shows the presence of two independent molecules in the asymmetric unit, *A* and *B*, with the two pyrrolidinyl rings adopting slightly different conformations. Thus, in molecules *A* and *B*, the C4 atom deviates from the plane defined by the amide function by 0.467 (7) and 0.296 (6) Å, respectively. Furthermore, one of the faces of the fluoroformyl group appears to be screened by one of the phenyl groups of the triphenylmethyl (trityl) function, leaving the other face susceptible to nucleophilic attack. This, at least in part, together with the strong electron-withdrawing character of the F atom and its much smaller size compared to the benzotriazolyloxy group of the corresponding 'active' esters of N^{α}-tritylamino acids, should account for the higher reactivity of the N^{α}-tritylamino acid fluorides towards nucleophiles. On the other hand, the crystal structure of (II) shows that in both independent pyrrolidinyl rings, the conformation about the C4—C5 bond tends to be eclipsed, with a staggering angle of about 20° [C3—C4—C5—N1 = 22.2 (4) and 19.2 (3)° for *A* and *B*, respectively]. Consequently, the torsion angles H4*A*1—C4*A*—C5*A*—H5*A* and H4*B*1—C4*B*—C5*B*—H5*B*, and H4*A*2—C4*A*—C5*A*—H5*A* and H4*B*2—C4*B*—C5*B*—H5*B*, are about −100 and 20°, respectively. Moreover, the orientation of the fluoroformyl substituent can be defined by the C4—C5—C6—F1 torsion angle, whose value is −87.2 (4) and −80.8 (4)° in *A* and *B*, respectively. Thus, the relative orientation of H5 with respect to F1, *i.e.* given

by the H5—C5—C6—F1 torsion angle, corresponds to values of 34 and 40° for this angle in *A* and *B*, respectively. It is thus apparent that the coupling constant between F1 and H5 should be close to 0 Hz, obviously due to the presence of the carbonyl function, to account for the actual appearance of the H5 resonance as a doublet. Furthermore, the crystal structure of (II) shows that the trityl moiety adopts the usual propeller-like conformation in both molecules, which is the established means of reducing steric interactions between the phenyl rings in this group (Destro *et al.*, 1980). However, the orientation of the phenyl ring closest to the fluoroformyl function is slightly different in molecules *A* and *B*, as is apparent from the C5—N1—C7—C8 torsion angle (Table 1). The absolute configuration of (II), which was chosen to agree with the known chirality of the commercially available (*S*)-glutamic acid from which (II) was synthesized, is depicted in Fig. 1.

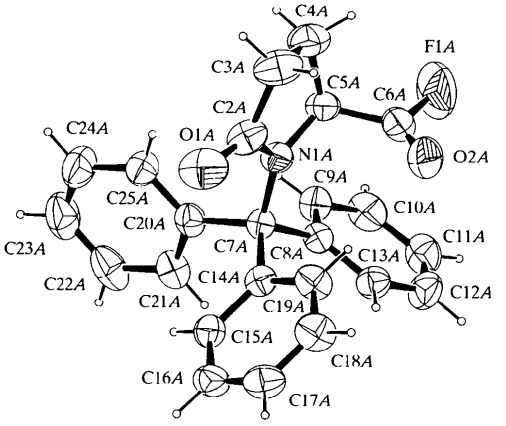


Fig. 1. View of molecule *A* of the title compound, with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as spheres of arbitrary radii.

Experimental

To a cold (263 K) solution of *N*-triphenylmethylpyroglutamic acid (2.23 g, 6 mmol) and dry pyridine (3.4 ml, 42 mmol) in anhydrous dichloromethane (DCM; 8 ml), a solution of cyanuric fluoride (1 ml, 12 mmol) in anhydrous DCM (4 ml) was added dropwise over a period of 15 min, and the resulting reaction mixture was further stirred at that temperature for 45 min. Glacial acetic acid (1.71 ml, 30 mmol) was added and the reaction mixture was stirred for 15 min. Ethyl acetate (60 ml) was then added, and the resulting precipitate filtered off and washed with ethyl acetate. The combined filtrates were then concentrated under reduced pressure and the residue was subjected to flash column chromatography using 20 g silica gel, and toluene–ethyl acetate (8:2) as eluant. The fractions containing the product were pooled and evaporated under reduced pressure to leave a thick oil, which upon adding diethyl ether and after overnight refrigeration gave 1.23 g (55% yield) of crystalline product. Crystals suitable for X-ray analysis were obtained by recrystallization from ethyl acetate–hexane solution.

Crystal data

$C_{24}H_{20}FNO_2$
M_r = 373.41
Triclinic
*P*1
a = 8.3410 (11) Å
b = 9.2516 (11) Å
c = 13.522 (2) Å
α = 81.329 (9)°
β = 84.722 (9)°
γ = 68.050 (7)°
V = 956.1 (2) Å^3
Z = 2
D_x = 1.297 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 65 reflections
θ = 10.0–18.9°
μ = 0.089 mm^{-1}
T = 293 (2) K
Prism
0.6 × 0.4 × 0.2 mm
Colourless

Data collection

Philips PW1100 diffractometer (updated by Stoe)
$\omega/2\theta$ scans
Absorption correction: none
4856 measured reflections
4856 independent reflections
3556 reflections with $I > 2\sigma(I)$

θ_{max} = 28.49°
$h = -11 \rightarrow 11$
$k = -12 \rightarrow 12$
$l = 0 \rightarrow 18$
3 standard reflections
frequency: 120 min
intensity decay: 4.6%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.120
S = 1.062
4856 reflections
505 parameters
H-atom parameters not refined

$w = 1/[\sigma^2(F_o^2) + (0.0683P)^2 + 0.0566P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.174 e Å^{-3}
$\Delta\rho_{min}$ = −0.223 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

N1*A*—C2*A*′	1.377 (4)	N1*B*—C2*B*	1.378 (3)
C2*A*—O1*A*	1.207 (4)	C2*B*—O1*B*	1.209 (3)
C6*A*—O2*A*	1.171 (4)	C6*B*—O2*B*	1.183 (5)
C6*A*—F1*A*	1.325 (4)	C6*B*—F1*B*	1.317 (4)
O1*A*—C2*A*—N1*A*	125.4 (3)	O1*B*—C2*B*—N1*B*	124.6 (2)
O1*A*—C2*A*—C3*A*	126.9 (3)	O1*B*—C2*B*—C3*B*	127.1 (3)
O2*A*—C6*A*—F1*A*	120.2 (3)	O2*B*—C6*B*—F1*B*	120.8 (3)
O2*A*—C6*A*—C5*A*	129.7 (3)	O2*B*—C6*B*—C5*B*	127.7 (3)
F1*A*—C6*A*—C5*A*	109.9 (3)	F1*B*—C6*B*—C5*B*	111.3 (3)
N1*A*—C5*A*—C6*A*—O2*A*	−27.1 (5)	N1*B*—C5*B*—C6*B*—O2*B*	−21.9 (5)
N1*A*—C5*A*—C6*A*—F1*A*	158.1 (3)	N1*B*—C5*B*—C6*B*—F1*B*	163.9 (3)
C5*A*—N1*A*—C7*A*—C8*A*	18.9 (3)	C5*B*—N1*B*—C7*B*—C8*B*	4.3 (3)

H atoms were placed in calculated positions and thereafter allowed to ride on their parent atoms, with U_{iso}(H) = 1.2U_{eq}(C).

Data collection: *DIF*4 (Stoe & Cie, 1987*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1987*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *PLATON* (Spek, 1990). Software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1368). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 1720–1722

Photochromic Properties of Spiro[fluorene–chromenes]

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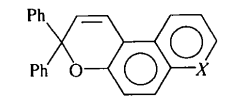
(*Received 10 December 1997; accepted 30 March 1998*)

Abstract

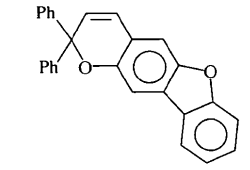
Two annelated spiro[fluorene–chromene] structures, spiro[2*H*-benzo[*h*]chromene-2,9′-fluorene], $C_{25}H_{16}O$, and 9,10,11,12-tetrahydrospiro[3*H*,8*H*-cyclohepta[4,5]furano-[3,2-*f*]chromene-2,9′-fluorene], $C_{28}H_{22}O_2$, have been analysed in order to define the effect of introducing a spiro-C atom into the pyran ring on the photochromic properties of the chromenes. The results are compared with those obtained for previously studied non-spiro 2,2-substituted chromenes.

Comment

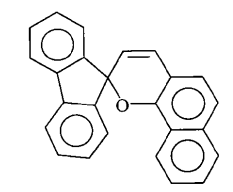
The title compounds, (IV) and (V), were studied and compared with the previously analysed compounds (I), (II) and (III) (see scheme below) (Aldoshin *et al.*, 1995, 1996) in order to define the effect of replacing the C_{sp^3} atom by a spiro atom on the structures and photochromic properties of chromenes.



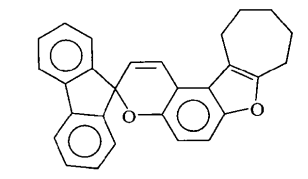
(I) X=N
(II) X=CH



(III)



(IV)



(V)

The characteristic geometric parameters of compounds (I) to (V) are reported in Table 3. In compound (IV), the pyran ring is more planar than in compounds (I), (II) and (III), while in compound (V), the contrary is observed. In compound (V), the longer C15—C16 bond length of 1.470 (2) Å compared with the corresponding bonds in the other compounds [(I) 1.453 (2), (II) 1.454 (2), (III) 1.444 (4) and (IV) 1.448 (3) Å] confirms this assumption.

As a correlation between the strain energy (E_s) of the pyran ring and the photocolourability (A_0) (Miller *et al.*, 1975) has been found (Aldoshin *et al.*, 1996),

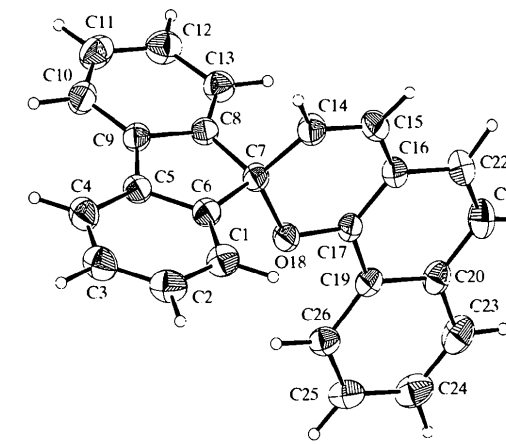


Fig. 1. *ORTEP*II drawing (Johnson, 1976) of compound (IV) with displacement ellipsoids of 50% probability and H atoms drawn as small circles.