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Crystallographic evidence of the formation of an *N*-alkylated enammonium salt: 5-ethoxycarbonylmethyl-1-ethyl-2,3,6,7-tetrahydro-4*H*,12*H*-indolo[2,3-*a*]quinolizin-5-ium trifluoromethanesulfonate

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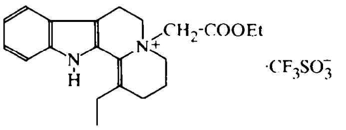
Abstract

The structure determination of the title compound, $C_{21}H_{27}N_2O_2^+\cdot CF_3SO_3^-$, substantiates the possibility of a reaction in which the alkylation process of Wenkert enamines unexpectedly gives rise to an *N*-alkylated enammonium salt. The study of the molecular packing reveals that the small trifluoromethanesulfonate anions are located between the sheets of the cations, thus enjoying relatively high freedom of motion in their cavities.

Comment

The so-called Wenkert enamine is a widely used intermediate in the synthesis of vinca alkaloids (Szántay & Nemes, 1994). In the alkylation process of this Wenkert enamine, activated alkyl halides usually provide easier access to *C*-alkylated products as opposed to *N*-alkylated ones. However, with the use of ethoxycarbonylmethyl trifluoromethanesulfonate, an *N*-alkylated enammonium salt was unexpectedly obtained (Lukács *et al.*, 1996). The crystal structure determination of the title compound, (I), proves the inverted reactivity of C1 as opposed to the enamine. The exploitation of this *umpolung* (the inverted reactivity) is reported in detail by Lukács *et al.* (1998).



(I)

The molecular structure with displacement ellipsoids is depicted in Fig. 1. The molecule is built up from a planar indole and a puckered tetrahydro-4*H*,12*H*-quinolizine moiety. Deviations of atoms pertaining to the tetrahydro-4*H*,12*H*-quinolizine moiety from the best plane of the indole ring [given by the equation $-10.834\,(7)x + 4.891\,(8)y + -6.968\,(8)z = -14.814\,(3)$] are as follows: C1 = −0.282 (2), C2 = −0.268 (2), C3 = 0.203 (2), C4 = −0.311 (2), N5 = 0.243 (3), C6 = −0.481 (3), C7 = −0.011 (3) and C12b = −0.063 (3) Å. Ring *C* has a half-chair shape with puckering parameters of $Q = 0.492\,(2)$ Å, $\theta = 49.8\,(2)°$, $\varphi = 35.0\,(3)°$ (Cremer & Pople, 1975), whilst ring *D* is an envelope with C4 on the flap [$Q = 0.501\,(3)$ Å, $\theta = 129.6\,(3)°$, $\varphi = 252.6\,(3)°$]. The quaternary ammonium base formed around N5 is characterized by a mean C—N bond length of 1.522 (9) Å and a mean tetrahedral bond angle of 109.5 (3)°. The atom S20($2 - x, -y, 1 - z$) is 5.267 (5) Å from the nearest N5 atom. The shortest distance between the positively charged N5 atom and one of the O atoms of the trifluoromethanesulfonate anion, O23($\frac{3}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$), is 4.006 (4) Å. The relatively small trifluoromethanesulfonate anions are located between the sheets of the cations (Fig. 2). Therefore, as shown by their large anisotropic displacement parameters, they have substantial freedom of motion in their cavities. The terminal ethyl group of the long ethoxy-

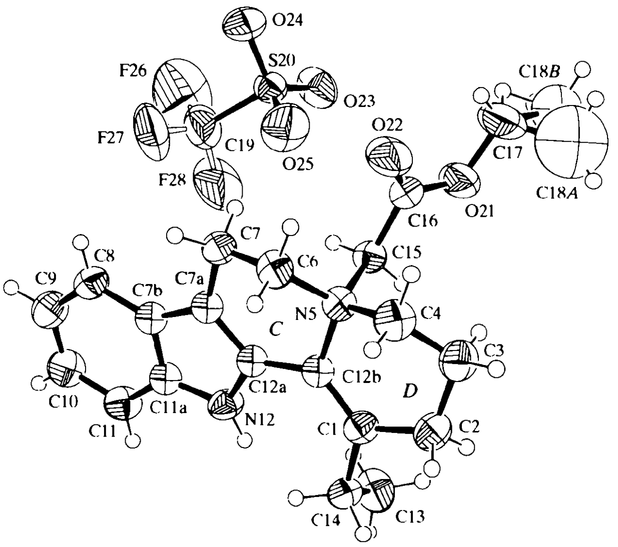


Fig. 1. *ORTEP* (Johnson, 1965) diagram of the compound showing atomic displacement parameters at the 50% probability level, atomic numbering and ring indicators. The two disordered positions of C18 are indicated.

carbonylmethyl side chain has also vigorous thermal vibration (C18 is split into two disordered positions in the refinement). Only one N···O contact can be regarded as a hydrogen bond with parameters N12···O24(x, $y-1$, z) = 2.920 (3), H12···O24 = 2.204 (2) Å and N12—H12···O24 = 140.7 (1)°.

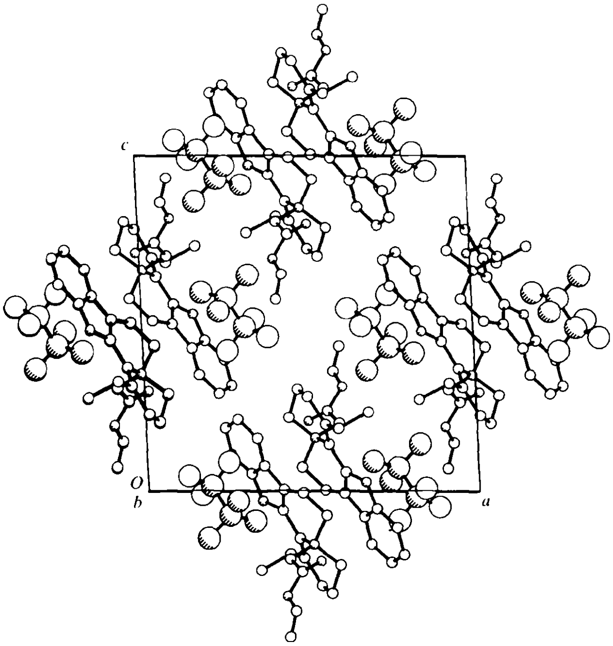


Fig. 2. The packing motif in the unit cell shows the arrangement of trifluoromethanesulfonate anions among the sheets of the cations viewed from the direction of the crystallographic b axis. O, S and C atoms are partly shaded while F atoms are unshaded. H atoms are omitted and C18 positions are not split for clarity.

Experimental

Details of the preparation and analytical investigations (IR, ^{1}H and ^{13}C NMR, MS) of the compound are reported elsewhere (Lukács *et al.*, 1996).

Crystal data

$C_{21}H_{27}N_2O_2^+ \cdot CF_3SO_3^-$
$M_r = 488.52$
Monoclinic
$P2_1/n$
$a = 14.910\,(2)$ Å
$b = 10.299\,(1)$ Å
$c = 15.184\,(1)$ Å
$\beta = 92.93\,(1)°$
$V = 2328.6\,(4)$ Å^3
$Z = 4$
$D_x = 1.393$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 25 reflections
$\theta = 2.92–77.01°$
$\mu = 1.774$ mm^{-1}
$T = 293\,(2)$ K
Block
0.45 × 0.24 × 0.18 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (*MolEN*; Fair, 1990)
$T_{min} = 0.624$, $T_{max} = 0.727$
5026 measured reflections
4839 independent reflections

3995 reflections with $I > 2\sigma(I)$
$R_{int} = 0.022$
$\theta_{max} = 75.71°$
$h = 0 \rightarrow 18$
$k = 0 \rightarrow 12$
$l = -19 \rightarrow 19$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.051$
$wR(F^2) = 0.154$
$S = 1.159$
4839 reflections
313 parameters
H atoms: see text
$w = 1/[\sigma^2(F_o^2) + (0.0890P)^2 + 1.1142P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.050$

$\Delta\rho_{max} = 0.389$ e Å^{-3}
$\Delta\rho_{min} = -0.390$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0020 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å)*

C4—N5	1.521 (3)	N12—C12a	1.391 (3)
N5—C15	1.516 (3)	C16—O22	1.190 (3)
N5—C12b	1.518 (3)	C16—O21	1.309 (3)
N5—C6	1.533 (3)	O21—C17	1.452 (4)
C11a—N12	1.373 (3)		

H atoms were introduced into calculated positions and refined riding on the respective C and N atoms. H atoms were included in structure-factor calculations but they were not refined

Data collection: *CAD*-4 (Enraf–Nonius, 1992). Cell refinement: *CAD*-4. Data reduction: *HELENA* (Spek, 1995). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1208). Services for accessing these data are described at the back of the journal.

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