

2-Amino-4,6-diphenyl-4*H*-1,3-oxazinium trifluoroacetate

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The 2-amino-4,6-diphenyl-4*H*-1,3-oxazinium trifluoroacetate ion pairs in the title compound, $C_{16}H_{15}N_2O^+ \cdot C_2F_3O_2^-$, are held together by two $N-H \cdots O$ hydrogen bonds [$N_{\text{amino}}-H \cdots O$ and $N_{\text{oxazinium}}-H \cdots O$], and adjacent ion pairs are linked into helical chains by a third and substantially weaker $N_{\text{amino}}-H \cdots O$ hydrogen bond.

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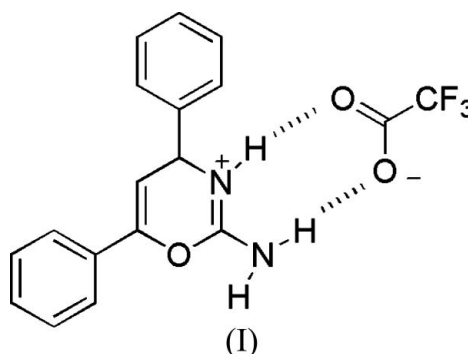
Key indicators

Single-crystal X-ray study
 $T = 296$ K
 Mean $\sigma(C-C) = 0.003$ Å
 Disorder in solvent or counterion
 R factor = 0.045
 wR factor = 0.115
 Data-to-parameter ratio = 12.0

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Comment

Domino (Tietze, 1996; Armstrong *et al.*, 1996; Tietze & Modi, 2000) and multicomponent (Dömling & Ugi, 2000; Kappe, 2000; Bienaymé *et al.*, 2000; Jacobi von Wangelin *et al.*, 2003; Simon *et al.*, 2004) reactions (MCRs) are powerful strategies in current organic synthesis. Consistently, several reported MCRs feature Diels–Alder chemistry with heterodiene (Batey *et al.*, 1999; Taylor & Hall, 2000; Touré *et al.*, 2003; Tietze & Rachkelmann, 2004; Strübing *et al.*, 2005) building blocks for the synthesis of heterocyclic six-membered rings. Recently, we synthesized a series of 2-amino-4*H*-1,3-oxazines and 2-amino-4*H*-1,3-thiazines (Huang *et al.*, 2005). 4*H*-1,3-Oxazines and 4*H*-1,3-thiazines are important synthetic intermediates in organic synthesis (Schmidt, 1972; Jochims *et al.*, 1990; Vanier *et al.*, 2004), and these skeletons have been found in a few biologically relevant compounds (Ilyuchenok *et al.*, 1979; Eckstein & Urbanski, 1963; Eckstein & Urbanski, 1978; Sondhi *et al.*, 2000) and vulcanization accelerators (Gridunov *et al.*, 1972). Since the Diels–Alder reaction may yield other stereoisomers, we wished to confirm the structure of a product of the reaction, 2-amino-4,6-diphenyl-4*H*-1,3-oxazine. Unfortunately, we have not obtained any crystals. Therefore, we prepared crystals of its salt with trifluoroacetic acid, namely the title compound, (I).



There are two independent ion pairs (Fig. 1). The C–O bond lengths of the anions [1.215 (2)–1.227 (2) Å] indicate that the original trifluoroacetic group turns out to be the trifluoroacetate, with full delocalization of electrons. Similarly,

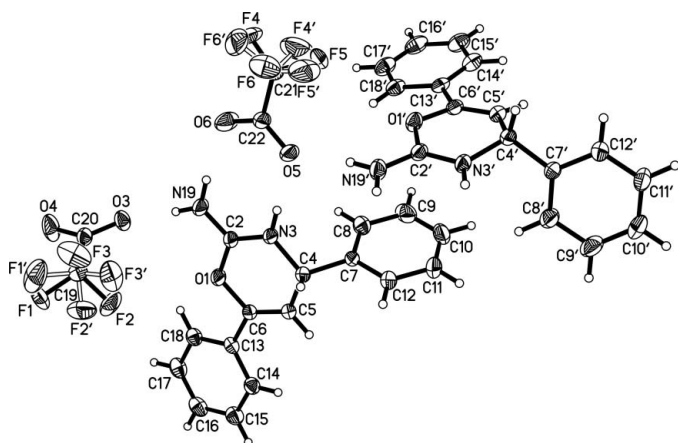


Figure 1
A view of (I), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Both disorder components are shown.

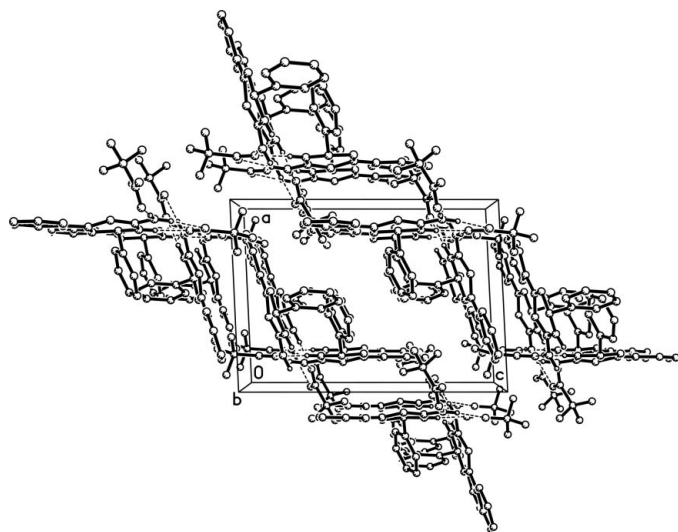


Figure 2
The crystal packing of (I), viewed down the *b* axis. Hydrogen bonds are indicated by dashed lines. H atoms not involved in hydrogen bonding have been omitted.

the N3–C2/N3'–C2' [1.299 (2) and 1.307 (2) Å] and N19–C2/N19'–C2' bond lengths [1.297 (3) and 1.296 (3) Å], and the angles of the heterocyclic rings, are consistent with the iminium tautomer and suggest protonation of the heterocycle.

A network of intermolecular N–H...O interactions (Fig. 2) provide strong packing directives in (I). The ion pairs are held together by two N–H...O hydrogen bonds [Table 2; N...O = 2.766 (2)–2.778 (3) Å], and adjacent ion-pairs are linked into helical chains by a third and substantially weaker N–H...O hydrogen bond [N...O = 2.820–2.823 (2) Å].

Experimental

2-Amino-4,6-diphenyl-4*H*-1,3-oxazine was prepared as described by Huang *et al.* (2005). Crystals of (I) appropriate for data collection were obtained by slow evaporation of an *N,N*-dimethylformide (3 ml) and trifluoroacetic acid (1 ml) solution of 2-amino-4,6-diphenyl-4*H*-1,3-oxazine (20 mg) at room temperature over a period of a week.

Crystal data

$C_{16}H_{15}N_2O^+ \cdot C_2F_3O_2^-$
 $M_r = 364.32$
 Triclinic, $P\bar{1}$
 $a = 10.341$ (2) Å
 $b = 11.867$ (2) Å
 $c = 14.409$ (3) Å
 $\alpha = 90.62$ (2)°
 $\beta = 92.68$ (2)°
 $\gamma = 91.03$ (2)°
 $V = 1765.9$ (6) Å³

$Z = 4$
 $D_x = 1.370$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 30 reflections
 $\theta = 6.6$ – 13.7 °
 $\mu = 0.12$ mm⁻¹
 $T = 296$ (2) K
 Block, colourless
 $0.58 \times 0.50 \times 0.42$ mm

Data collection

Siemens P4 diffractometer
 ω scans
 Absorption correction: none
 7215 measured reflections
 6591 independent reflections
 3495 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.012$

$\theta_{max} = 25.5$ °
 $h = 0 \rightarrow 12$
 $k = -14 \rightarrow 14$
 $l = -17 \rightarrow 17$
 3 standard reflections
 every 97 reflections
 intensity decay: 2.8%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.045$
 $wR(F^2) = 0.115$
 $S = 0.94$
 6591 reflections
 548 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.056P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.24$ e Å⁻³
 $\Delta\rho_{min} = -0.18$ e Å⁻³
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.0093 (9)

Table 1

Selected geometric parameters (Å, °).

O1–C2	1.333 (2)	N3'–C2'	1.307 (2)
O1–C6	1.407 (2)	N3'–C4'	1.463 (3)
N3–C2	1.299 (2)	N19'–C2'	1.296 (3)
N3–C4	1.460 (2)	O3–C20	1.227 (2)
N19–C2	1.297 (3)	O4–C20	1.216 (2)
O1'–C2'	1.327 (2)	O5–C22	1.222 (2)
O1'–C6'	1.409 (2)	O6–C22	1.215 (2)
C2–O1–C6	119.49 (15)	C2'–O1'–C6'	119.15 (16)
C2–N3–C4	124.65 (17)	C2'–N3'–C4'	123.66 (19)
N19–C2–N3	124.0 (2)	N19'–C2'–N3'	123.8 (2)
N19–C2–O1	114.44 (18)	N19'–C2'–O1'	114.67 (19)
N3–C2–O1	121.54 (18)	N3'–C2'–O1'	121.5 (2)
C4–N3–C2–N19	171.3 (2)	C4'–N3'–C2'–N19'	–168.2 (2)
C4–N3–C2–O1	–7.3 (3)	C4'–N3'–C2'–O1'	11.5 (3)
C4–C5–C6–O1	1.6 (3)	C4'–C5'–C6'–O1'	–0.7 (3)
N3–C4–C7–C8	–33.2 (3)	N3'–C4'–C7'–C8'	35.2 (3)
O1–C6–C13–C18	11.2 (3)	O1'–C6'–C13'–C18'	–10.7 (3)

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
N3–H3N...O5	0.87 (1)	1.90 (1)	2.772 (2)	178 (2)
N19–H19A...O3	0.87 (1)	1.95 (1)	2.823 (2)	179 (2)
N19–H19B...O6	0.88 (1)	1.90 (1)	2.778 (3)	173 (2)
N3'–H3'N...O3 ⁱ	0.87 (1)	1.90 (1)	2.766 (2)	177 (2)
N19'–H19D...O4 ⁱ	0.87 (1)	1.90 (1)	2.770 (3)	174 (2)
N19'–H19C...O5	0.88 (1)	1.95 (1)	2.820 (2)	174 (2)

Symmetry code: (i) *x*, *y* + 1, *z*.

The CF₃ groups of the anions are disordered, with three of the F atoms distributed over two sites (F1/F2/F3 and F1'/F2'/F3'; F4/F5/F6 and F4'/F5'/F6'), their occupation factors being 50% each estimated on the basis of U_{eq} values. The disordered parts of the anions were constrained to a chemically reasonable geometry. H atoms bonded to the N atoms were located in difference Fourier maps and their parameters were refined with N–H distances restrained to 0.86 (1) Å. The positions of the C-bound H atoms were calculated geometrically and refined using a riding model, with C–H = 0.93–0.98 Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *SHELXTL/PC* (Siemens, 1991); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL/PC*; software used to prepare material for publication: *SHELXTL/PC*.

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