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N,*N*-Dimethyl-*N*′-phenylformamidinium perchlorate

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Key indicators

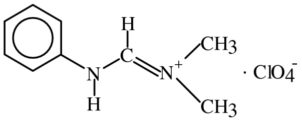
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.051
wR factor = 0.153
Data-to-parameter ratio = 18.9

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

The molecular structure of the title compound, $C_9H_{13}N_2^+\cdot ClO_4^-$, consists of an *N*,*N*-dimethyl–*N*′-phenylformamidinium cation and a perchlorate anion. The latter forms five hydrogen bonds with three different formamidinium cations, using three O atoms. The cations and anions are linked through C—H···O and N—H···O hydrogen bonds, forming a ring; the centrosymmetrically related rings form a staircase *via* C—H···O hydrogen bonds.

Comment

There is considerable interest in the chemistry and structure of iminium salts, because of their importance in organic synthesis (Boehme & Viehe, 1976). The chromophores of visual pigments contain polyunsaturated iminium salts (Uhl & Abrahamson, 1981; Brige, 1981). The iminium salts exhibit optical properties and the position of the counterion plays a role in determining the optical properties of the iminium cation (Arnaboldi *et al.*, 1979).



(I)

The cation of the title compound, (I), is nearly planar and the dihedral angle between the phenyl ring and the Schiff base chain is 7.7 (1)°. Protonation occurs at N9, and the positive charge is delocalized between atoms N9 and N7, as evidenced by the bond distances N7—C8 [1.316 (3) Å] and C8═N9 [1.294 (3) Å]. This is confirmed by the coplanarity of atoms C1, N7, C8, N9, C10 and C11 [maximum deviation is 0.031 (4) Å for C10]. The perchlorate anion accepts five hydrogen bonds from three different formamidinium cations, using three O atoms. One of the perchlorate O atoms (O4) acts as an acceptor in three hydrogen bonds and this O atom is also characterized by an extended bond of length 1.426 (2) Å. The cations and anions are linked through N7—H7···O4^{i} and C8—H8···O3^{ii} hydrogen bonds and form a ring, which is further reinforced by two C2—H2···O4^{i} and C11—H11*D*···O4^{i} hydrogen bonds. The centrosymmetrically related rings are linked *via* C11—H11*E*···O1^{iii} interactions and form a staircase, which runs parallel to the *b* axis (see Table 2 for symmetry codes).

Experimental

Aniline (0.05 mol) was dissolved in 6 ml DMF and kept under ice-cold conditions. To this, 1.4 ml $POCl_3$ (0.035 ml) was added dropwise for 15 min with stirring at 273 K. The reaction mixture was stirred at room temperature for 30 minutes and then at 303 K for 15 h. The

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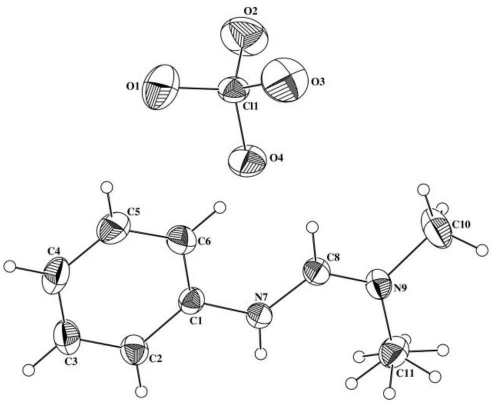

Figure 1
The molecular structure of the title compound, (I), showing 35% probability displacement ellipsoids.

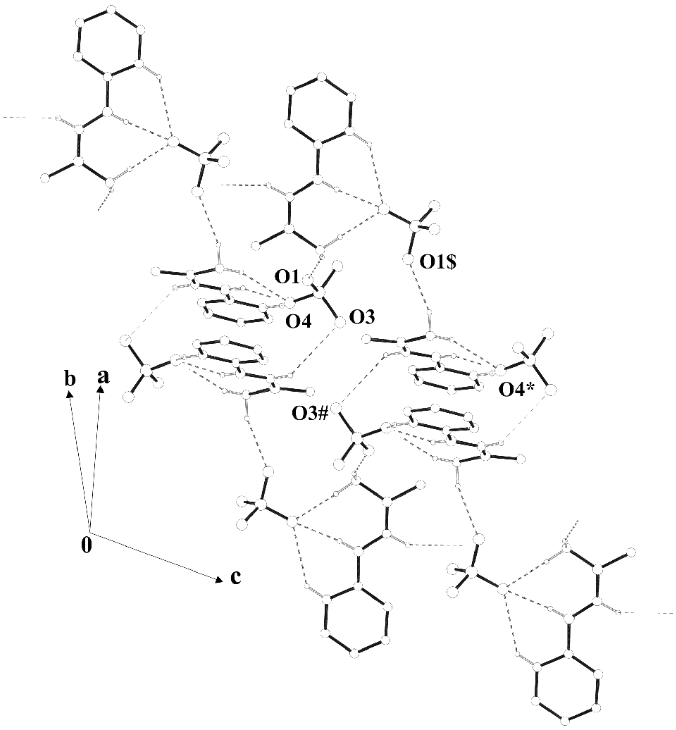

Figure 2
Part of the crystal packing of the title compound, showing hydrogen-bonded networks of cations and anions. Atoms marked with a dollar ($), hash (#) or asterisk (*) are at the symmetry positions ($1 - x$, $-y$, $-z$), ($1 - x$, $-y$, $1 - z$) and ($1 - x$, $y - \frac{1}{2}$, $\frac{1}{2} - z$), respectively.

reaction mixture was finally poured into crushed ice and treated with sodium perchlorate or dilute perchloric acid. The resulting creamy yellow precipitate was filtered, washed with water and dried. This crude product was recrystallized using $CHCl_3$ to give pure title compound.

Crystal data

$C_9H_{13}N_2ClO_4$
$M_r = 248.66$
Monoclinic, $P2_1/c$
$a = 7.8382$ (2) Å
$b = 17.5688$ (6) Å
$c = 9.1123$ (2) Å
$\beta = 113.269$ (1)°
$V = 1152.77$ (6) Å^3
$Z = 4$

$D_x = 1.433$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3903 reflections
$\theta = 2.3$–28.3°
$\mu = 0.33$ mm^{-1}
$T = 293$ (2) K
Prism, pale yellow
0.28 × 0.16 × 0.12 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Siemens, 1996)
$T_{min} = 0.913$, $T_{max} = 0.961$
7777 measured reflections

2854 independent reflections
1917 reflections with $I > 2\sigma(I)$
$R_{int} = 0.039$
$\theta_{max} = 28.3°$
$h = -10 \rightarrow 8$
$k = -15 \rightarrow 23$
$l = -11 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.153$
$S = 1.02$
2854 reflections
151 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0752P)^2 + 0.2933P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.34$ e Å^{-3}
$\Delta\rho_{min} = -0.22$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.007 (2)

Table 1
Selected geometric parameters (Å, °).

Cl1—O1	1.406 (3)	N7—C8	1.316 (3)
Cl1—O2	1.407 (2)	C8—N9	1.294 (3)
Cl1—O3	1.419 (2)	N9—C10	1.465 (3)
Cl1—O4	1.426 (2)	N9—C11	1.466 (3)
C1—N7	1.422 (3)		
C2—C1—N7	117.6 (2)	C8—N9—C10	120.0 (2)
C6—C1—N7	122.6 (2)	C8—N9—C11	123.2 (2)
C8—N7—C1	125.3 (2)	C10—N9—C11	116.7 (2)
N9—C8—N7	126.0 (2)		
C2—C1—N7—C8	173.9 (2)	N7—C8—N9—C10	177.0 (2)
C6—C1—N7—C8	−6.5 (4)	N7—C8—N9—C11	−0.7 (4)
C1—N7—C8—N9	−179.9 (2)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C11—H11D···N7	0.96	2.47	2.875 (3)	105
N7—H7···O4^{i}	0.82 (3)	2.09 (3)	2.877 (3)	160 (3)
C2—H2···O4^{i}	0.93	2.56	3.295 (3)	134
C11—H11D···O4^{i}	0.96	2.41	3.329 (3)	160
C8—H8···O3^{ii}	0.93	2.40	3.174 (4)	140
C11—H11E···O1^{iii}	0.96	2.38	3.310 (4)	162

Symmetry codes: (i) $1 - x, -y, -z$; (ii) $1 - x, -y, 1 - z$; (iii) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$.

The H atom on N7 was located in a difference Fourier map and refined, while all other H atoms were positioned geometrically and were allowed to ride on their attached atoms. One of the methyl groups (C11) was found to be disordered; it was treated as an idealized disordered methyl group, with two positions rotated from each other by 60°, and the site-occupation factors were fixed at 0.5.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT*; data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ZORTEP* (Zsolnai, 1997) and *PLUTON* (Spek, 1990); software used to prepare material for publication: *SHELXL*97 and *PARST* (Nardelli, 1995).

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References

Arnaboldi, M., Motto, M. G., Tsujimoto, K., Balogh-Nair, V. & Nakanishi, K. (1979). *J. Am. Chem. Soc.* **101**, 7082–7084.

Boehme, H. & Viehe, H. G. (1976). *Iminium Salts in Organic Chemistry*. New York: Wiley.

Brige, R. R. (1981). *Ann. Rev. Biophys. Bioeng.* **10**, 315–354.

Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Siemens (1996). *SADABS*, *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34.

Uhl, R. & Abrahamson, E. W. (1981). *Chem. Rev.* **81**, 1291–1312.

Zsolnai, L. (1997). *ZORTEP*. University of Heidelberg, Germany.