

1-Dimethylamino-3-dimethylimino-1-phenylprop-1-ene perchlorate

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Key indicators

Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(\text{C}-\text{C}) = 0.005$ Å
 R factor = 0.057
 wR factor = 0.204
Data-to-parameter ratio = 14.9For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound, $\text{C}_{13}\text{H}_{19}\text{N}_2^+\cdot\text{ClO}_4^-$, a 1-arylated vinamidinium salt, has been found to crystallize in monoclinic space group $P2_1/n$ at room temperature. The dihedral angle between the planar vinamidinium moiety and the aryl ring is $81.2(1)^\circ$. The molecular packing is stabilized by $\text{C}-\text{H}\cdots\text{O}$ interactions.

Comment

The title compound, (I), a 1-arylated vinamidinium salt, has been studied as part of a series of vinamidinium systems that are prospective non-linear optical materials (Hawn & Bloor, 1989). These compounds have all the necessary molecular features to satisfy the conditions for a material to exhibit high second-harmonic generation (SHG), such as extensive charge delocalization, where the amino and imino groups at the two ends of the conjugated structure function as electron donor and electron acceptor, respectively. These compounds were chosen for X-ray crystallographic study and the structural details were extrapolated to the possible behaviour of the materials with regard to their SHG effects. Vinamidinium salts are also sources of vinylogous amidines, which are reactive towards nucleophiles, leading to the formation of pyrroles, pyrazoles, oxazoles, diazepines, quinolines, quinazolines *etc.* (Lloyd & Nab, 1976; Jutz, 1978; Gupton *et al.*, 1990).

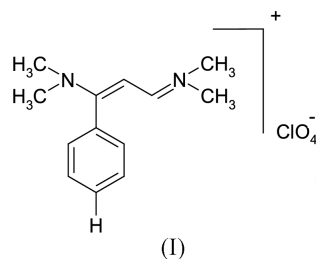


Fig. 1 shows the molecular structure of (I). The $\text{N1}-\text{C1}$ [$1.327(4)$ Å] and $\text{N2}-\text{C3}$ [$1.314(4)$ Å] bond distances are almost equal, indicating the partial double-bond character prevailing in these compounds. The amine and imine groups are not clearly distinguishable, as the bond lengths of both the groups are of the same order, indicating delocalization of the electrons. The dihedral angle between the vinamidinium plane ($\text{N1}/\text{C1}/\text{C2}/\text{C3}/\text{N2}$) and the aryl ring is $81.2(1)^\circ$.

The crystal packing is stabilized by intermolecular $\text{C}-\text{H}\cdots\text{O}$ interactions between O atoms of the perchlorate group and C atoms of the vinamidinium moiety.

The compound does not exhibit non-linear optical activity, since it crystallizes in a centrosymmetric space group. However, substitution at the 2-position of the propene moiety

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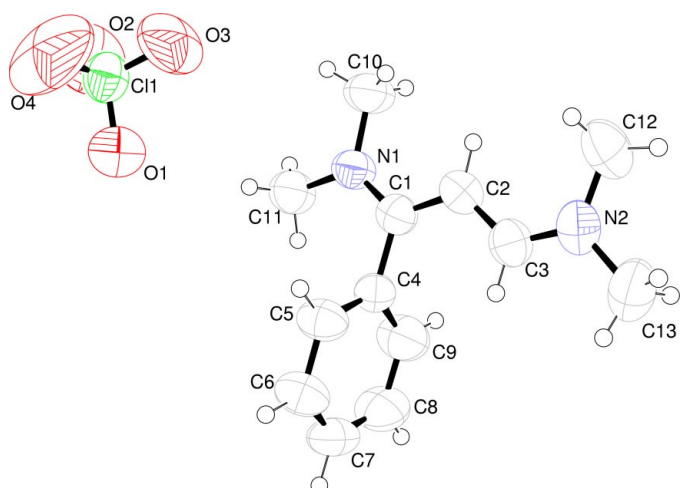


Figure 1
A view of the title compound, showing 50% probability displacement ellipsoids and the atom-numbering scheme.

results in a symmetrically placed phenyl ring and the resulting 2-arylated vinamidinium salts show SHG effects (Girija & Begum, 2004).

Experimental

A formylating agent was obtained by the reaction of phosphoryl chloride and dimethyl formamide in chloroform medium. To this reagent, acetophenone dissolved in the same solvent was added. The mixture was heated under reflux, extracted with chloroform and treated with a saturated solution of sodium perchlorate in water. The compound was filtered off and dried over P_2O_5 (Holy *et al.*, 1965). Crystals were grown at room temperature by slow evaporation, using ethanol as a solvent.

Crystal data

$C_{13}H_{19}N_2^+ \cdot ClO_4^-$	$D_x = 1.289 \text{ Mg m}^{-3}$
$M_r = 302.75$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 16 reflections
$a = 11.3858 (18) \text{ \AA}$	$\theta = 6.9\text{--}7.8^\circ$
$b = 7.7718 (14) \text{ \AA}$	$\mu = 0.26 \text{ mm}^{-1}$
$c = 18.194 (3) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 104.374 (12)^\circ$	Prism, colourless
$V = 1559.6 (5) \text{ \AA}^3$	$0.3 \times 0.2 \times 0.1 \text{ mm}$
$Z = 4$	

Data collection

Rigaku AFC-7S diffractometer	$h = 0 \rightarrow 13$
$\omega/2\theta$ scans	$k = 0 \rightarrow 9$
2899 measured reflections	$l = -21 \rightarrow 20$
2753 independent reflections	3 standard reflections
1834 reflections with $I > 2\sigma(I)$	every 150 reflections
$R_{\text{int}} = 0.010$	intensity decay: 0.7%
$\theta_{\text{max}} = 25.0^\circ$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.108P)^2 + 0.6901P]$
$R[F^2 > 2\sigma(F^2)] = 0.057$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.204$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.05$	$\Delta\rho_{\text{max}} = 0.36 \text{ e \AA}^{-3}$
2753 reflections	$\Delta\rho_{\text{min}} = -0.28 \text{ e \AA}^{-3}$
185 parameters	
H-atom parameters constrained	

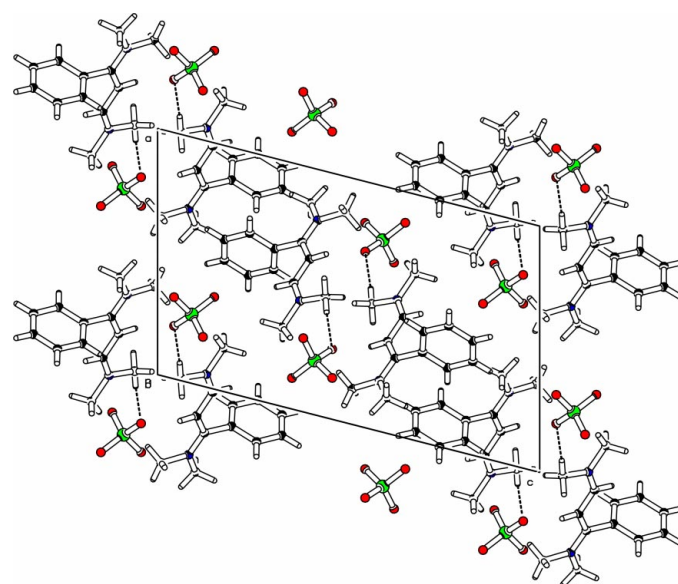


Figure 2
The molecular packing in the unit cell, viewed down the b axis.

Table 1

Selected geometric parameters (\AA , $^\circ$).

N1—C1	1.327 (4)	N2—C13	1.473 (5)
N1—C11	1.462 (4)	C1—C2	1.387 (4)
N1—C10	1.463 (4)	C1—C4	1.495 (4)
N2—C3	1.314 (4)	C2—C3	1.382 (5)
N2—C12	1.456 (5)		
C1—N1—C11	123.8 (3)	C3—N2—C13	120.9 (3)
C1—N1—C10	121.8 (3)	C12—N2—C13	117.7 (3)
C11—N1—C10	114.2 (3)	N1—C1—C2	123.2 (3)
C3—N2—C12	121.2 (3)	N1—C1—C4	116.8 (3)
C10—N1—C1—C2	0.7 (5)	N1—C1—C4—C9	96.8 (4)
N1—C1—C2—C3	−176.6 (3)	C2—C1—C4—C9	−83.3 (4)
C12—N2—C3—C2	1.2 (5)	N1—C1—C4—C5	−82.0 (4)
C1—C2—C3—N2	177.1 (3)	C2—C1—C4—C5	97.9 (4)

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
C10—H10A \cdots O3 ⁱ	0.96	2.52	3.374 (5)	148
C11—H11C \cdots O1	0.96	2.57	3.417 (5)	147
C12—H12C \cdots O2 ⁱⁱ	0.96	2.38	3.331 (7)	173

Symmetry codes: (i) $1 - x, 1 - y, -z$; (ii) $1 + x, 1 + y, z$.

H atoms were positioned geometrically ($C\text{---}H = 0.93\text{--}0.96 \text{ \AA}$) and allowed to ride on their parent atoms, with $U_{\text{iso}}(H)$ set to $1.5U_{\text{eq}}(C)$ for the methyl H atoms and $1.2U_{\text{eq}}(C)$ for the other H atoms.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1995); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics:

ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: PLATON (Spek, 1990).

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