

# 1-Dimethylamino-3-dimethyliminio-2-(*p*-methoxyphenyl)prop-1-ene perchlorate

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## Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean  $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$

$R$  factor = 0.043

$wR$  factor = 0.113

Data-to-parameter ratio = 16.7

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

The title compound,  $\text{C}_{14}\text{H}_{21}\text{N}_2\text{O}^+\cdot\text{ClO}_4^-$ , is an organic non-linear optical material. It crystallizes in the monoclinic space group  $P2_1$  and exhibits second-harmonic generation equivalent to that of urea. The structural study shows extensive electron delocalization in the vinamidinium moiety. The dihedral angle between the vinamidinium moiety and the benzene ring is  $81.6(1)^\circ$ .

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## Comment

The title compound, (I), is found to be of interest as an organic non-linear optical (NLO) material. The crystals show optical second-harmonic generation (SHG) with the fundamental beam ( $\lambda = 1064\text{ nm}$ ) of a Nd-YAG laser, with an SHG effect equivalent to that of urea. We report here the crystal structure of (I).

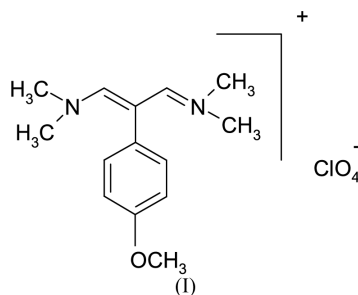
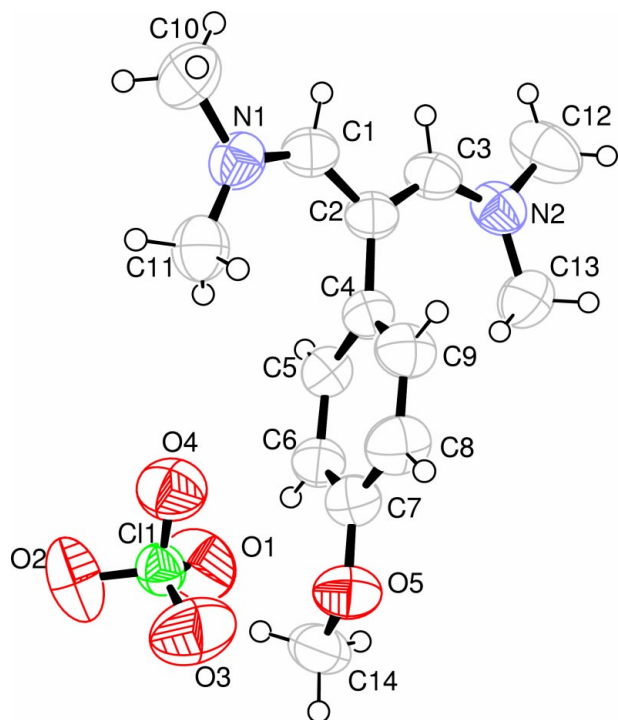


Fig. 1 shows the asymmetric unit of (I). The torsion angles about the C4(benzene)–C2(propene) bond (Table 1) indicate an almost perpendicular disposition of the aryl ring with respect to the vinamidinium moiety. The amino and imino groups are not clearly distinguishable, as the bond lengths of both groups are of the same order (Table 1). Hence there is extensive electron delocalization.

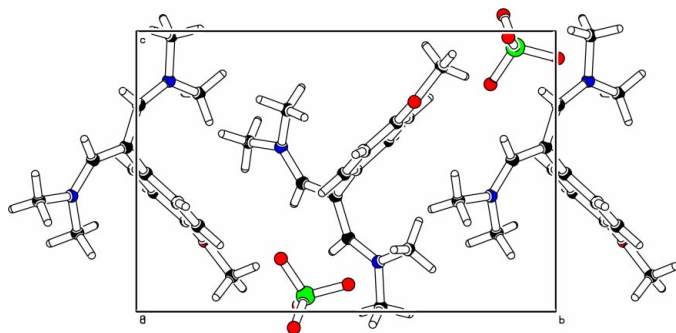
A short H1...H3 contact of  $1.99\text{ \AA}$  is observed in the molecular structure of (I). No classical hydrogen bonds are observed. A view of the molecular packing in the unit cell is shown in Fig. 2. The packing in (I) is stabilized by C–H...O interactions (Table 2) and van der Waals forces.

## Experimental

The title compound was prepared by heating a mixture of dimethylformamide (11 g),  $\text{POCl}_3$  (4.6 g) and *p*-methoxyphenylacetic acid (0.01 mol) for 2 h under constant stirring (Arnold & Holy, 1967). A solution of 70% aqueous perchloric acid mixed with a small quantity of ethanol was added dropwise, resulting in precipitation of (I). Crystals of (I) suitable for a single-crystal X-ray diffraction study were grown at ambient temperature by slow evaporation of a chloroform solution.



**Figure 1**  
A view of the cation and anion of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme.



**Figure 2**  
A view, down the *a* axis, of the molecular packing in the unit cell of (I).

#### Crystal data

$C_{14}H_{21}N_2O^+ \cdot ClO_4^-$   
 $M_r = 332.79$   
 Monoclinic,  $P2_1$   
 $a = 7.295$  (2) Å  
 $b = 13.117$  (3) Å  
 $c = 8.793$  (2) Å  
 $\beta = 92.228$  (5)°  
 $V = 840.7$  (4) Å<sup>3</sup>  
 $Z = 2$

$D_x = 1.315$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 8589 reflections  
 $\theta = 2.3$ – $27.4$ °  
 $\mu = 0.25$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
 Prism, pale yellow  
 $0.3 \times 0.2 \times 0.1$  mm

#### Data collection

Bruker SMART CCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: none  
 8565 measured reflections  
 3404 independent reflections

2910 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.026$   
 $\theta_{max} = 27.3$ °  
 $h = -9 \rightarrow 8$   
 $k = -16 \rightarrow 16$   
 $l = -11 \rightarrow 10$

#### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.043$   
 $wR(F^2) = 0.113$   
 $S = 1.08$   
 3404 reflections  
 204 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0634P)^2 + 0.0303P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} < 0.001$   
 $\Delta\rho_{max} = 0.17$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.13$  e Å<sup>-3</sup>  
 Absolute structure: Flack (1983);  
 1577 Friedel pairs  
 Flack parameter =  $-0.01$  (6)

**Table 1**

Selected geometric parameters (Å, °).

N1—C1	1.307 (3)	N2—C13	1.462 (4)
N1—C11	1.462 (4)	C1—C2	1.406 (4)
N1—C10	1.467 (4)	C2—C3	1.383 (4)
N2—C3	1.317 (3)	C2—C4	1.496 (3)
N2—C12	1.456 (4)		
C1—N1—C11	126.2 (2)	C12—N2—C13	114.9 (3)
C1—N1—C10	119.2 (3)	C3—C2—C1	112.1 (2)
C11—N1—C10	114.3 (3)	C3—C2—C4	125.3 (2)
C3—N2—C12	119.4 (2)	C1—C2—C4	122.6 (2)
C3—N2—C13	125.7 (2)		
C3—C2—C4—C5	-83.8 (3)	C3—C2—C4—C9	98.9 (3)
C1—C2—C4—C5	97.7 (3)	C1—C2—C4—C9	-79.7 (3)

**Table 2**

Hydrogen-bonding 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>
C11—H11C...O2 <sup>i</sup>	0.96	2.46	3.341 (5)	152

Symmetry code: (i)  $1 - x, y - \frac{1}{2}, 1 - z$ .

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

Data collection: SMART (Bruker, 1998); cell refinement: SMART; data reduction: SAINT (Bruker, 1998); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); 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, 2003).

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