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

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The title compound, $C_{14}H_{21}N_2O^+ \cdot ClO_4^-$, a methoxy-1-arylated vinamidinium salt, has been found to crystallize in the monoclinic space group $P2_1/c$ at room temperature. The vinamidinium plane forms a dihedral angle of 61.2 (1)° with the benzene ring. The molecular packing is stabilized by C—H···O interactions.

Comment

The title compound, (I), a 1-methoxy-arylated vinamidinium salt, was studied, as a member of a series of vinamidinium systems, in order to explore the possibility of these compounds showing non-linear optical properties.
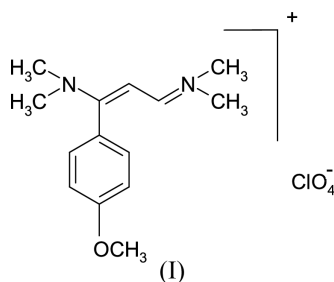

(I)

Fig. 1 shows the structure of the title compound. The sums of the valence angles (Table 1) around atoms N1 and N2 indicate that these atoms are sp^2-hybridized. As observed in related vinamidinium systems (Girija *et al.*, 2004*a,b*), the amino and imino groups are not clearly distinguishable, due to the delocalization of the electrons. The vinamidinium plane (N1/C1/C2/C3/N2; r.m.s. deviation 0.136 Å) forms a dihedral angle of 61.2 (1)° with the benzene ring, indicating the non-coplanar disposition of the aryl ring with respect to the vinamidinium moiety. The exocyclic angles around atom C7 show considerable asymmetry, with O5—C7—C6 [124.5 (2)°] being wider than O5—C7—C8 [115.3 (2)°], as observed in a related structure (Fun *et al.*, 1996). This may be due to the steric repulsion between the methyl group and the benzene ring (H6···H14*C* = 2.23 Å). The C14—O5—C7—C6 [2.1 (4)°] and C14—O5—C7—C8 [−178.4 (3)°] torsion angles indicate that the methoxy group is almost coplanar with the benzene ring. The crystal structure is stabilized by C—H···O interactions (see Table 2). The compound does not exhibit second harmonic generation (SHG), since it has crystallized in a centrosymmetric space group.

Experimental

A formylating agent was obtained by the action of phosphoryl chloride and dimethylformamide in chloroform. To this reagent, *p*-methoxyacetophenone, 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 from ethanol at room temperature by slow evaporation

Crystal data

$C_{14}H_{21}N_2O^+ \cdot ClO_4^-$	D_m not measured
$M_r = 332.78$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 15
$a = 8.239\ (3)$ Å	reflections
$b = 12.399\ (2)$ Å	$\theta = 6.9–8.0°$
$c = 16.152\ (3)$ Å	$\mu = 0.26$ mm^{-1}
$\beta = 93.10\ (2)°$	$T = 293\ (2)$ K
$V = 1647.5\ (7)$ Å^3	Prism, colourless
$Z = 4$	$0.3 \times 0.2 \times 0.1$ mm
$D_x = 1.342$ Mg m^{-3}	

Data collection

Rigaku AFC-7S diffractometer	$h = 0 \rightarrow 8$
ω–2θ scans	$k = 0 \rightarrow 14$
4573 measured reflections	$l = -19 \rightarrow 19$
2632 independent reflections	3 standard reflections
2165 reflections with $I > 2\sigma(I)$	every 150 reflections
$R_{int} = 0.033$	intensity decay: 2.9%
$\theta_{max} = 25.0°$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0694P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.050$	$+ 1.1572P]$
$wR(F^2) = 0.148$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} < 0.001$
2632 reflections	$\Delta\rho_{max} = 0.50$ e Å^{-3}
204 parameters	$\Delta\rho_{min} = -0.41$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

N1—C1	1.332 (3)	N2—C12	1.462 (4)
N1—C10	1.466 (4)	C1—C2	1.402 (4)
N1—C11	1.470 (4)	C1—C4	1.486 (3)
N2—C3	1.321 (3)	C2—C3	1.374 (4)
N2—C13	1.459 (4)		
C1—N1—C10	122.1 (2)	C3—N2—C13	120.9 (3)
C1—N1—C11	123.5 (2)	C3—N2—C12	121.7 (2)
C10—N1—C11	113.7 (2)	C13—N2—C12	117.3 (2)
N1—C1—C4—C5	−123.3 (3)	N1—C1—C4—C9	58.1 (3)
C2—C1—C4—C5	58.0 (4)	C2—C1—C4—C9	−120.5 (3)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C3—H3$\cdots$O5^i	0.93	2.59	3.325 (4)	136
C10—H10$C\cdots$O3^{ii}	0.96	2.59	3.379 (5)	140
C11—H11$A\cdots$O1^{iii}	0.96	2.55	3.251 (5)	130
C11—H11$B\cdots$O3^{ii}	0.96	2.59	3.393 (6)	141
C12—H12$C\cdots$O2^{iv}	0.96	2.59	3.506 (4)	160

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

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 at $1.5U_{eq}$(C) for the methyl H atoms and at $1.2U_{eq}$(C) for the other H atoms. A rotating group model was used for the methyl groups.
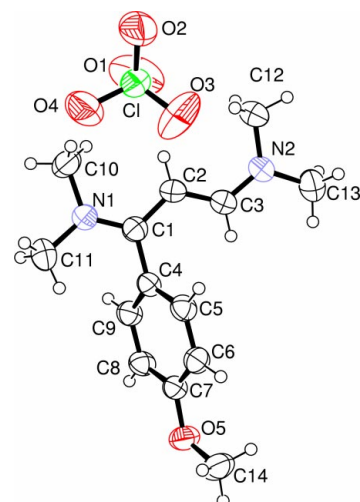

Figure 1
ORTEP-3 (Farrugia, 1997) diagram of the title compound, showing 50% probability displacement ellipsoids and the atom-numbering scheme.
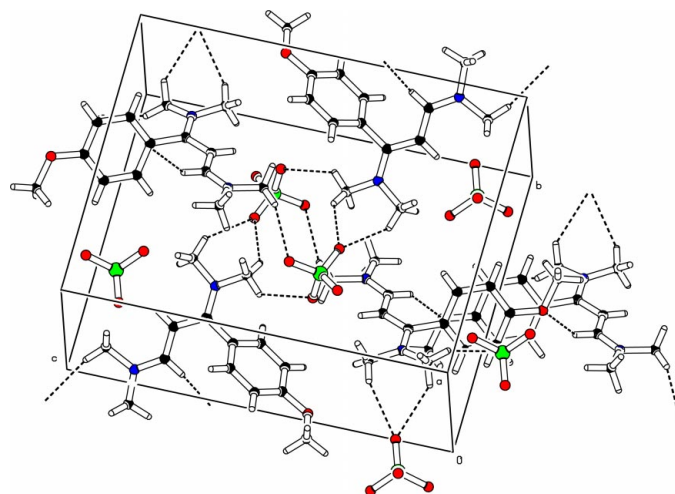

Figure 2
Packing diagram of the title compound, viewed approximately down the b axis.

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