

Acta Cryst. (1996). **C52**, 2216–2218

Trimethyl[2-(2-methyl-2-propenoxy)-ethyl]ammonium Iodide (Methacryloylcholine Iodide)

OLYANA ANGELOVA,^a JOSEF MACÍČEK,^{a*} KRASIMIR KOSSEV^a AND NELY KOSEVA^b

^aBulgarian Academy of Sciences, Central Laboratory of Mineralogy and Crystallography, Rakovski Str. 92, 1000 Sofia, Bulgaria, and ^bSofia University, Department of Chemistry, J. Baucher 1, 1027 Sofia, Bulgaria. E-mail: jmacicsek@bgcict.acad.bg

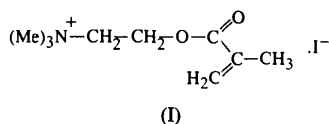
(Received 22 November 1995; accepted 27 February 1996)

Abstract

The structure of the title compound, C₉H₁₈NO₂⁺.I⁻, has been refined in the centrosymmetric space group *Pnma*, with the two ions set on a mirror plane and one choline methylene C atom statistically disordered on both sides of this plane. The acryloyl fragment and the choline chain are in antiperiplanar and intermediate between anticlinal and antiperiplanar conformations, respectively. The crystal packing is forced by interionic interactions only. The four C atoms of the quaternary ammonium groups and iodide anions are ordered in a dual tetrahedral fashion.

Comment

Methacryloylcholine is a homologue of the natural neurotransmitter acetylcholine. In a series of structural investigations of agonists of acetylcholine (Gieren & Kokkinidis, 1986*b,c*), structure–activity relationships have been discussed and a model correlating the X-ray structures and the pharmacological activity of the cholinergic agonists has been speculated. On this basis, preliminary information about the crystal structure of any new homologue can be used to predict its potential activity and application. In addition, methacryloylcholine is a widely used monomer for the preparation of polymers with valuable properties (Askarov, Muhitdinov & Nazarov, 1977; Askarov, 1986). The structure of methacryloylcholine iodide, (I), is presented here.



Bond lengths and angles in the methacryloylcholine cation are similar to those found in related derivatives (Gieren & Kokkinidis, 1982*a*, 1986*a*; Jagner & Jensen, 1977; Svinning & Sørum, 1975; Craven & Hite, 1973). The shortening of the C5—C6 bond from the typical value of 1.49 (6) to 1.360 (6) Å is the exception and is most likely due to the model of disorder including the

C6 atom only. Analysis of the shape of the displacement ellipsoids of all the atoms showed that atoms C5, O1, O2, C1 and C4 have quite elongated ellipsoids [with longest principal axes of 0.216 (6), 0.166 (3), 0.166 (3), 0.140 (4) and 0.129 (4) Å², respectively, with respect to an average shortest axis of 0.052 (4) Å²], the direction of elongation being perpendicular to the mirror plane. This fact indicates a positional flexibility of these atoms beyond the mirror symmetry imposed by the space group.

The most interesting feature of the molecular geometry is the twist of the choline chain. The three torsion angles at the C6—N bond (Table 2) show a twist of the trimethylammonium group to a synclinal (*gauche*) conformation. The following two twists along the chain, $\tau_2(\text{C5—C6})$ and $\tau_3(\text{O—C5})$ as defined by Gieren & Kokkinidis (1982*a,b*), are intermediate between anticlinal and antiperiplanar (deviations of 28.0 and 36.9° from anticlinal and of 32.0 and 23.1° from antiperiplanar). This is a significant difference with respect to the acetylcholine agonists, which exhibit a predominantly synclinal τ_2 conformation (Gieren & Kokkinidis, 1982*a*). The last twist, $\tau_4(\text{C3—O1})$, is imposed by symmetry to give an antiperiplanar (*trans*) conformation. The acryloyl fragment is fixed in the more stable *trans* conformation with respect to the C2—C3 bond (Sato & Hirai, 1991).

The intramolecular O1···N and O2···N distances of 3.641 (3) and 5.165 (4) Å, respectively, widely discussed earlier as related to the cholinergic activity of the acetylcholine agonists (Gieren & Kokkinidis, 1986*c*), correspond to very weak interactions, if any, which are shielded by the immediate H5 and H62 atoms at distances of 2.44 (4) and 2.17 (4) Å, respectively (Fig. 1). Thus, it seems that the title compound should not exhibit a pronounced cholinergic activity in case it retains in solution the conformation found in the crystal structure. On the other hand, both O atoms are in close contact with H atoms (calculated positions) from the methacryloyl fragment of the cation; O1···H12 2.40 (4) Å, O1···H12—C1 101 (3)° and O2···H41 2.69 (4) Å, O2···H41—C4 97 (4)°. This geometry may indicate the existence of specific intra-

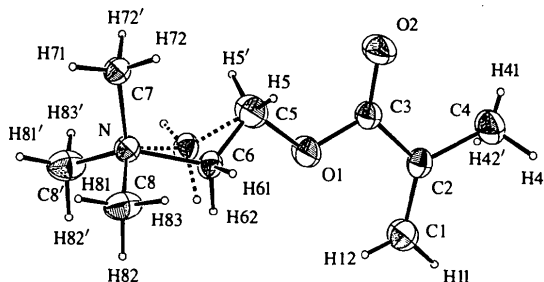


Fig. 1. A view of the methacryloylcholine cation showing the disordered C6 atom and the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

molecular interactions which would explain the ability of acrylates to polymerize.

In the crystal, each quaternary ammonium group is surrounded by four anions in a regular tetrahedral environment and *vice versa* (Fig. 2). Thus, all geometrically distinct face types of the ammonium tetrahedron (Gieren & Kokkinidis, 1982a) are occupied. The I...C interatomic distances are grouped in Table 3 according to the face types. It can be seen that there is one short and two long distances in faces A and C and one long and two short distances in the two B faces.

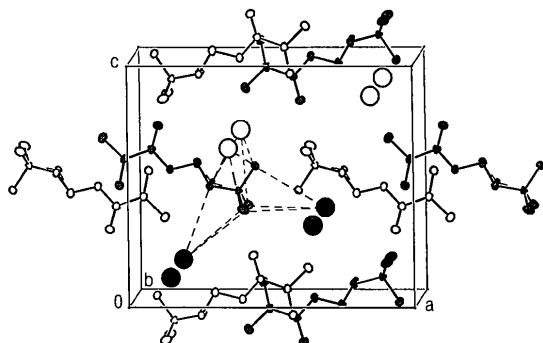


Fig. 2. A packing diagram in the unit cell viewed along the *b* axis. Ions at *y* = 0.25 and *y* = 0.75 are designated by open and shaded ellipsoids, respectively. The tetrahedral arrangement of the iodide anions around the quaternary N atom is denoted by dashed lines. H atoms have been omitted for clarity.

Experimental

The quaternization of 2-(2-methyl-2-propenyloxy)ethyl-dimethylamine (Fluka) with methyl iodide (Fluka) (1:1) was carried out under an air atmosphere in the absence of solvent. Methyl iodide was added dropwise with continuous stirring and cooling of the reaction mixture. After the addition of methyl iodide, the mixture was stirred at room temperature for 30 min. Diethyl ether was added and the quaternary salt which formed was filtered off. The product was purified by recrystallization from ethanol and dried under reduced pressure. Single crystals were grown by slow evaporation from water or ethanol solution.

Crystal data

C₉H₁₈NO₂⁺.I⁻

M_r = 299.15

Orthorhombic

Pnma

a = 14.467 (2) Å

b = 7.391 (4) Å

c = 11.868 (3) Å

V = 1268.9 (9) Å³

Z = 4

D_x = 1.565 Mg m⁻³

D_m not measured

Data collection

Enraf-Nonius CAD-4 diffractometer

Continuous scan profiles

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 22 reflections

θ = 20.23–21.53°

μ = 2.47 mm⁻¹

T = 292 K

Prismatic

0.33 × 0.20 × 0.20 mm

Colourless

1594 observed reflections [*I* > 3σ(*I*)]

R_{int} = 0.031

Absorption correction:

empirical *via* ψ scan

(North, Phillips & Mathews, 1968)

T_{min} = 0.817, *T_{max}* = 1.000

4138 measured reflections

1943 independent reflections

Refinement

Refinement on *F*

R = 0.026

wR = 0.041

S = 0.979

1594 reflections

80 parameters

H atoms refined as riding

w = 1/[σ²(*F*) + (0.030*F*)²]

(Δ/σ)_{max} = 0.337

Δρ_{max} = 0.313 e Å⁻³

Δρ_{min} = -0.616 e Å⁻³

θ_{max} = 30.0°

h = 0 → 10

k = 0 → 16

l = -20 → 20

3 standard reflections

frequency: 120 min

intensity decay: 0.5%

Extinction correction:

Stout & Jensen (1968); formula 17.16

Extinction coefficient:

9.56 × 10⁻⁷

Atomic scattering factors

from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
I	0.34205 (1)	1/4	0.64261 (2)	0.05624 (6)
O1	-0.1137 (2)	1/4	0.4833 (2)	0.0898 (9)
O2	-0.0745 (2)	1/4	0.3027 (2)	0.098 (1)
N	-0.3544 (2)	1/4	0.5728 (2)	0.0582 (7)
C1	0.0625 (3)	1/4	0.5498 (3)	0.088 (1)
C2	0.0440 (2)	1/4	0.4406 (3)	0.0588 (8)
C3	-0.0516 (3)	1/4	0.4004 (3)	0.0618 (9)
C4	0.1174 (4)	1/4	0.3535 (3)	0.090 (2)
C5	-0.2103 (3)	1/4	0.4558 (4)	0.113 (2)
C6	-0.2559 (3)	0.1811 (6)	0.5463 (4)	0.054 (1)
C7	-0.4126 (2)	1/4	0.4685 (3)	0.0591 (8)
C8	-0.3768 (3)	0.4106 (5)	0.6412 (2)	0.0860 (9)

Table 2. Selected geometric parameters (Å, °)

O1—C3	1.332 (4)	N—C8	1.474 (4)
O1—C5	1.434 (5)	C1—C2	1.323 (5)
O2—C3	1.206 (4)	C2—C3	1.463 (5)
N—C6	1.546 (5)	C2—C4	1.482 (6)
N—C7	1.497 (4)	C5—C6	1.360 (6)
C3—O1—C5	119.2 (3)	C1—C2—C4	122.5 (4)
C6—N—C7	110.5 (3)	C3—C2—C4	116.8 (3)
C6—N—C8	125.4 (3)	O1—C3—O2	121.6 (3)
C6—N—C8'	92.8 (3)	O1—C3—C2	113.4 (3)
C7—N—C8	109.4 (2)	O2—C3—C2	124.9 (3)
C8—N—C8'	107.3 (3)	O1—C5—C6	107.0 (4)
C1—C2—C3	120.7 (3)	N—C6—C5	119.0 (3)
C3—O1—C5—C6	156.9 (2)	C8'—N—C6—C5	159.7 (3)
C7—N—C6—C5	47.8 (4)	O1—C5—C6—N	148.0 (3)
C8—N—C6—C5	-86.7 (4)		

Symmetry code: (i) *x*, ½ - *y*, *z*.

Table 3. The shortest distances (Å) between atoms of the NC₄ tetrahedron and the face-adjacent I atoms

Face†	C...I _{min}	C...I _{av}	C...I _{max}	N...I ⁿ	<i>n</i>
A (C7, C8, C8')	4.107 (3)	4.237 (5)	4.237 (5)	4.468 (3)	(ii)
B1 (C7, C6, C8')	4.054 (1)	4.089 (4)	4.229 (3)	4.496 (2)	(iii)
B2 (C7, C6, C8)	4.055 (1)	4.091 (4)	4.231 (3)	4.498 (2)	(iv)
C (C6, C8', C8)	3.988 (4)	4.244 (4)	4.245 (4)	4.415 (3)	(v)

Symmetry codes: (i) *x*, ½ - *y*, *z*; (ii) *x* - 1, *y*, *z*; (iii) -*x*, *y* - ½, 1 - *z*; (iv) -*x*, *y* + ½, 1 - *z*; (v) *x* - ½, ½ - *y*, ½ - *z*.

† Face labelling according to Gieren & Kokkinidis (1982a).

The structure was solved manually by the Patterson method. The initial refinement in the noncentrosymmetric *Pn2₁a* (No. 33) space group converged to $R = 0.024$ and $wR = 0.039$, but gave unsatisfactory molecular geometry in the choline part of the cation. The structure was then refined in the centrosymmetric *Pnma* (No. 62) space group, with positioning of the ions on a mirror plane and allowing one methylene C atom to be statistically disordered on both sides of the plane. The positions of all H atoms, except the methyl H atoms, were calculated and included in the refinement with a riding geometry. Methyl H atoms were found in difference Fourier maps and their positions were normalized and included in the refinement as riding.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Data reduction: *Structure Determination Package* (Enraf–Nonius, 1985). Program(s) used to refine structure: *Structure Determination Package*. Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *KAPPA* (Macíček, 1992).

This work was supported by the Bulgarian National Science Fund (Project Ch-402) and the Bulgarian National ‘Young Scientists’ Fund (Project 3-4-OPS/94).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry, torsion angles and r.m.s. amplitudes have been deposited with the IUCr (Reference: NA1215). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Askarov, M. A. (1986). Editor. *Ionic Polymers*, pp. 3–8. Tashkent, UzSSR: FAN.
- Askarov, M. P., Muhitdinov, N. A. & Nazarov, A. (1977). In *Polymerization of Aminoalkyl Acrylates*. Tashkent, UzSSR: FAN.
- Craven, B. M. & Hite, G. (1973). *Acta Cryst.* B29, 1132–1136.
- Enraf–Nonius (1985). *Structure Determination Package. SDP/PDP User's Guide*. Version 3.0. Enraf–Nonius, Delft, The Netherlands.
- Enraf–Nonius (1989). *CAD-4 Software*. Version 5. Enraf–Nonius, Delft, The Netherlands.
- Gieren, A. & Kokkinidis, M. (1982a). *Z. Naturforsch. Teil C*, 37, 282–288.
- Gieren, A. & Kokkinidis, M. (1982b). *Z. Naturforsch. Teil C*, 37, 977–984.
- Gieren, A. & Kokkinidis, M. (1986a). *Z. Naturforsch. Teil C*, 41, 618–626.
- Gieren, A. & Kokkinidis, M. (1986b). *Z. Naturforsch. Teil C*, 41, 627–640.
- Gieren, A. & Kokkinidis, M. (1986c). *Z. Naturforsch. Teil C*, 41, 641–646, and references therein.
- Jagner, S. & Jensen, B. (1977). *Acta Cryst.* B33, 2757–2762.
- Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
- Macíček, J. (1992). *KAPPA. Program for the Preparation of Material for Publication from a CIF File*. Bulgarian Academy of Sciences, Bulgaria.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A24, 351–359.
- Sato, K. & Hirai, H. (1991). *J. Polym. Sci. A*, 29, 1507–1514.
- Stout, G. H. & Jensen, H. (1968). In *X-ray Structure Determination*. New York: MacMillan.
- Svinning, A. & Sørum, H. (1975). *Acta Cryst.* B31, 1581–1586.

Acta Cryst. (1996). C52, 2218–2220

Crystalline Complexes Involving Amino Acids. II. (*R*)-(-)-1-Phenylglycinium Hydrogen Squarate Monohydrate

OLYANA ANGELOVA,^a ROSICA PETROVA,^a VALENTINA RADOMIRSKA^b AND TSONKO KOLEV^b

^aBulgarian Academy of Sciences, Central Laboratory of Mineralogy and Crystallography, Rakovski str. 92, 1000 Sofia, Bulgaria, and ^bBulgarian Academy of Sciences, Institute of Organic Chemistry, Acad. G. Bonchev str. Build 9, 1113 Sofia, Bulgaria. E-mail: jmacicek@bgcict.acad.bg

(Received 7 March 1996; accepted 15 May 1996)

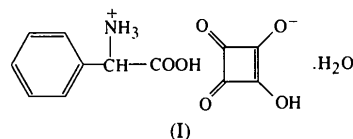
Abstract

The title compound, C₈H₁₀NO₂⁺.C₄HO₄⁻.H₂O, crystallizes in the orthorhombic space group *P2₁2₁2₁* in a layered structure of charged phenylglycinium and squarate/water layers stacked along the *c* axis and held together by an extensive hydrogen-bonding network. The amino group of the phenylglycine molecule adopts a proton from the squaric acid. The C—C bond lengths within the squarate anion are consistent with a delocalized double bond around the hydroxyl-bearing C atom: 1.414 (3) and 1.431 (3) Å versus 1.481 (3) and 1.494 (3) Å for the opposite bonds in the ring.

Comment

The structure determination reported here was undertaken as part of a project investigating the non-linear optical properties of new classes of organic compounds involving salts of optically active amino acids, amines and guanidine derivatives with ‘oxocarbons’ (West, 1980) – deltic, squaric, croconic and rhodisonic acids as well as its sulfur derivatives. The series has been started with the structure of the L-argininium hydrogen squarate (Angelova, Velikova, Radomirska & Kolev, 1996).

The title structure (I) is built up from layers of phenylglycinium cations and squarate anions stacked along the *c* axis. The phenyl and squarate rings are almost coplanar, the dihedral angle between them being 5.7 (3)°. The closest distance between their planes is 3.305 (2) Å.



The α-amino group in phenylglycine is protonated and the corresponding C2—N bond length is 1.503 (3) Å, similar to those found in the crown ether inclusion complexes with phenylglycine methyl (Goldberg, 1977; Courtois, Masdouri, Genin & Gross, 1986)