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3,3-(Oxydiethyl)-1,2-di(*o*-methylphenyl)guanidinium Chloride Monohydrate

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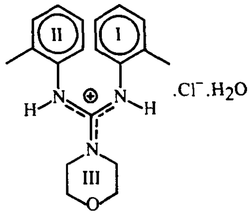
Abstract

In the title compound, bis(2-methylphenylamino)(morpholino)methylium chloride hydrate, $C_{19}H_{24}N_3O^+.Cl^-.H_2O$, the guanidinium moiety is protonated; the three C—N bond lengths are therefore almost identical. Steric strain as a result of the bulky substituents leads to distortions of the guanidinium skeleton. The co-crystallized water molecule accepts no conventional hydrogen bonds but only weak C—H···O interactions.

Comment

The agrochemical and pharmaceutical activities of guanidines are well established in the literature (Molina, Alajarin & Saez, 1983). The conformation of the title compound, (1), as observed in the crystal structure is shown in Fig. 1. Since (1) has been crystallized as a chloride, the guanidine moiety is protonated (*i.e.* N8 and N10 both carry an H atom). The three guanidyl C—N bond lengths are identical within their e.s.d.s [1.337 (2), 1.335 (2) and 1.335 (2) Å for C9—N8, C9—N10 and C9—N11, respectively], indicating delocalization of the positive charge. The conformation around N11 is planar with a sum of valence angles of 360.0 (2)°. This contrasts with the geometry of related uncharged molecules such as 3,3-(oxydiethyl)-1,2-diphenylguanidine where the guanidine C—N bonds are unequal with a defined C═N double bond [1.291 (9) Å], and a significantly pyramidal geometry of the N atom to which the oxydiethyl moiety is bonded (Sudha *et al.*, 1995*b*).



(1)

The N11-oxydiethyl moiety represents a morpholino group which is in a chair conformation. Generally, the pyramidality of morpholino N atoms may cover wide ranges between 337 and 360° (Wong-Ng, Nyburg, Awwal, Jankie & Kresge, 1982). If N is part of an uncharged guanidine group, we have found sums of angles of 351.8 (9) (Sudha *et al.*, 1995*b*) and 358.2 (6)° (Sudha *et al.*, 1995*a*). Both phenyl rings are oriented roughly perpendicular to the guanidine plane [dihedral angle 79.1 (1)° for ring I and 71.7 (1)° for ring II]; the dihedral angle between the phenyl rings is 32.5 (1)°. Steric conflict of the bulky methylphenyl substituents leads to significant distortion of the guanidine moiety, in particular to opening of the angles at N8, C9 and N10 [C9—N8—C1 = 125.2 (2), N8—C9—N10 = 121.4 (2),

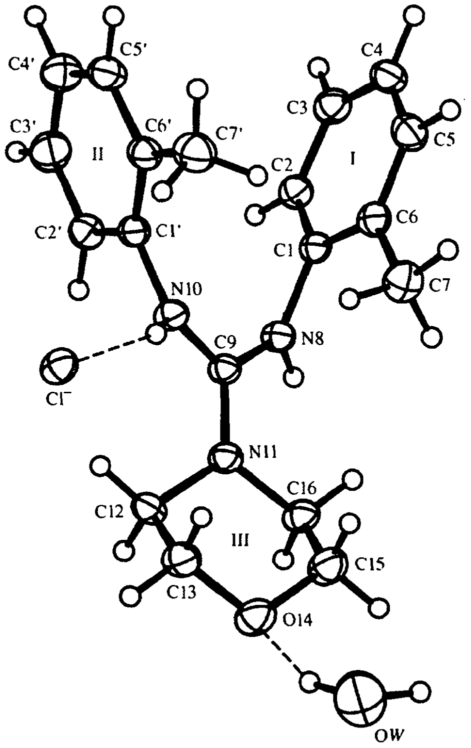


Fig. 1. Molecular structure and atom labelling of the title compound shown in a minimal overlap projection. Displacement ellipsoids are drawn at the 30% probability level.

C9—N10—C1′ = 123.8 (2)°]. Despite this opening, the phenyl-C atoms C1 and C1′ approach a very short intramolecular distance of 2.956 (2) Å.

Both guanidyl N—H groups donate hydrogen bonds to symmetry-related chloride ions (Table 3). The co-crystallized water molecule donates a further hydrogen bond to Cl^- and an additional one to the oxydiethyl O atom. This leaves no more conventional hydrogen-bond donors to satisfy the acceptor potential of the water molecule. Instead, the lone-pair region of the water molecule is oriented towards the positively charged guanidinium moiety, with a short contact to N11 [*OW*···N11(*x* − 1, *y*, *z*) = 3.114 (2) Å]. This is associated with C—H···*OW* interactions involving C12—H and C2′—H. This is quite a typical example of a water molecule that accepts no conventional hydrogen bonds but only C—H···O interactions (numerous examples compiled by Steiner, 1995). The resulting configuration of intermolecular interactions around the cation of (1) is shown in Fig. 2.

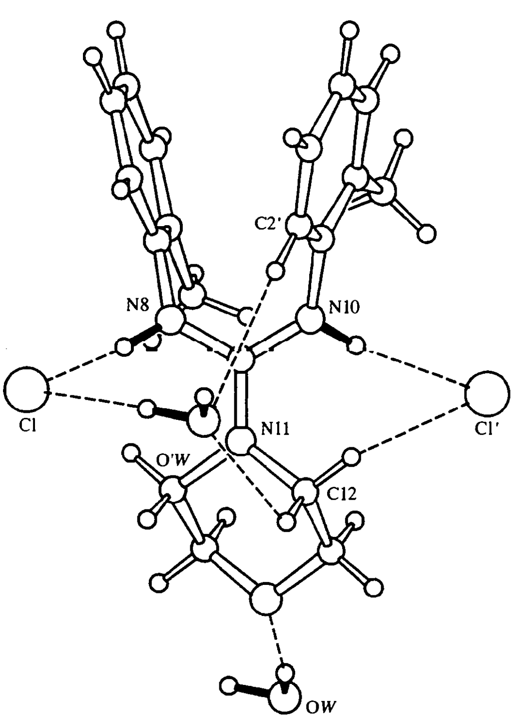


Fig. 2. The hydrogen-bond configuration around the cation of (1), shown in a projection onto the guanidine plane.

Experimental

The title compound, (1), was synthesized at, and supplied from, the SPIC Science Foundation, Madras, India. The method desulfurizes 1,3-diaryl thioureas in the presence of an appropriate amine (Ramadas & Srinivasan, 1995). Chloride crystals were grown from MeOH.

Crystal data

$C_{19}H_{24}N_3O^+.Cl^-.H_2O$
$M_r = 363.88$
Monoclinic
$P2_1/c$
$a = 7.970 (2)$ Å
$b = 14.544 (3)$ Å
$c = 16.502 (4)$ Å
$\beta = 100.58 (5)°$
$V = 1880.3 (8)$ Å^3
$Z = 4$
$D_x = 1.285$ Mg m^{-3}
D_m not measured

Cu *K*α radiation
$\lambda = 1.54176$ Å
Cell parameters from 25 reflections
$\theta = 10.9–36.1°$
$\mu = 1.934$ mm^{-1}
$T = 293 (2)$ K
Irregular plate
0.6 × 0.5 × 0.1 mm
Colourless

Data collection

Enraf–Nonius Turbo CAD-4 diffractometer
$\omega–2\theta$ scans
Absorption correction: ψ-scan (North, Phillips & Mathews, 1968)
$T_{min} = 0.54$, $T_{max} = 0.82$
3101 measured reflections
2777 independent reflections

2634 observed reflections [$I > 2\sigma(I)$]
$R_{int} = 0.0444$
$\theta_{max} = 59.87°$
$h = -8 \rightarrow 8$
$k = 0 \rightarrow 16$
$l = -1 \rightarrow 18$
3 standard reflections
frequency: 60 min
intensity decay: −1.8%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0389$
$wR(F^2) = 0.1118$
$S = 1.036$
2777 reflections
238 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.0665P)^2 + 0.8109P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.254$ e Å^{-3}
$\Delta\rho_{min} = -0.193$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0020 (3)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Cl	−0.20585 (6)	0.40458 (3)	0.22177 (3)	0.0477 (2)
O*W*	−0.8067 (3)	0.0806 (2)	0.15756 (15)	0.0970 (7)
C1	0.1611 (2)	0.10681 (12)	0.43939 (11)	0.0343 (4)
C2	0.3355 (2)	0.09739 (13)	0.46417 (12)	0.0405 (5)
C3	0.4101 (3)	0.10979 (14)	0.54607 (13)	0.0474 (5)
C4	0.3093 (3)	0.13221 (15)	0.60227 (13)	0.0505 (5)
C5	0.1351 (3)	0.14036 (15)	0.57790 (13)	0.0494 (5)
C6	0.0555 (2)	0.12683 (13)	0.49611 (12)	0.0392 (4)
C7	−0.1359 (3)	0.1292 (2)	0.4723 (2)	0.0564 (6)
C1′	0.1860 (2)	0.28189 (12)	0.35144 (11)	0.0375 (4)
C2′	0.3306 (3)	0.25924 (15)	0.32004 (12)	0.0470 (5)
C3′	0.4869 (3)	0.2974 (2)	0.35457 (15)	0.0599 (6)
C4′	0.4951 (3)	0.3584 (2)	0.41926 (15)	0.0644 (7)
C5′	0.3510 (3)	0.3817 (2)	0.44923 (14)	0.0576 (6)
C6′	0.1914 (3)	0.34412 (14)	0.41591 (12)	0.0444 (5)
C7′	0.0354 (3)	0.3708 (2)	0.4490 (2)	0.0620 (6)
N8	0.0888 (2)	0.09009 (10)	0.35461 (9)	0.0374 (4)
C9	0.0001 (2)	0.15129 (12)	0.30336 (10)	0.0341 (4)
N10	0.0250 (2)	0.24154 (10)	0.31425 (9)	0.0380 (4)
N11	−0.1186 (2)	0.12048 (11)	0.24147 (10)	0.0397 (4)
C12	−0.1773 (3)	0.17032 (15)	0.16410 (11)	0.0439 (5)
C13	−0.3680 (3)	0.17906 (15)	0.14953 (13)	0.0502 (5)
O14	−0.4469 (2)	0.09091 (11)	0.14906 (10)	0.0605 (5)
C15	−0.3906 (3)	0.0445 (2)	0.22549 (15)	0.0575 (6)
C16	−0.2006 (3)	0.03039 (14)	0.24207 (13)	0.0474 (5)

Table 2. *Selected geometric parameters (Å, °)*

C1—N8	1.433 (2)	C9—N11	1.335 (2)
C1′—N10	1.442 (2)	N11—C16	1.465 (3)
N8—C9	1.337 (2)	N11—C12	1.468 (2)
C9—N10	1.335 (2)		
C9—N8—C1	125.2 (2)	C9—N11—C16	123.3 (2)
N10—C9—N11	120.0 (2)	C9—N11—C12	124.6 (2)
N10—C9—N8	121.4 (2)	C16—N11—C12	112.1 (2)
N11—C9—N8	118.6 (2)	C13—O14—C15	110.7 (2)
C9—N10—C1′	123.8 (2)		
C1—N8—C9—N10	27.0 (3)	N10—C9—N11—C16	−155.7 (2)
C2—C1—N8—C9	−120.6 (2)	N8—C9—N11—C16	22.6 (3)
C1—N8—C9—N11	−151.3 (2)	N10—C9—N11—C12	26.9 (3)
N11—C9—N10—C1′	−151.8 (2)	N8—C9—N11—C12	−154.9 (2)
N8—C9—N10—C1′	30.0 (3)	C9—N11—C12—C13	−126.3 (2)
C2′—C1′—N10—C9	53.1 (2)	C9—N11—C16—C15	126.3 (2)

Table 3. *Selected hydrogen-bond parameters (Å, °)*

Data for normalized H-atom positions are based on bond lengths of O—H = 0.98, N—H = 1.04 and C—H = 1.09 Å.

	D···*A*	H(norm)···*A*	*D*—H(norm)···*A*
O*W*—H1*W*···Cl^{i}	3.233 (2)	2.26	175
O*W*—H2*W*···O14	2.901 (3)	1.97	159
N8—HN8···Cl^{ii}	3.189 (2)	2.17	165
N10—HN10···Cl	3.210 (2)	2.25	153
C12—H12*A*···O*W*^{iii}	3.250 (3)	2.73	109
C12—H12*B*···Cl	3.556 (2)	2.71	134
C2′—H2′···O*W*^{iii}	3.750 (4)	2.71	160
C7′—H7′1···O*W*^{iv}	3.513 (3)	2.59	142

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

H atoms bonded to C atoms were refined in the default riding model of *SHELXL*93 (Sheldrick, 1993), with torsion angles of methyl groups refined. H atoms bonded to N and O*W* could be located from difference Fourier calculations; those bonded to N were subsequently treated in the riding model with *U* allowed to vary, and those bonded to O*W* were refined isotropically. Since the isotropic displacement parameters of H(N) and H(O) refined to realistic values of $0.06 < U < 0.1$ Å^2, this treatment can be regarded as sensible.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CAD*-4 *Software*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: TA1111). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2α,3α:7α,8α-Diépoxy-*cis*-himachalane

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Abstract

The stereochemistry of the major isomer resulting from the epoxidation of γ-*cis*-himachalene has been established as 2α,3α:7α,8α-diepoxy-γ-*cis*-himachalene, $C_{15}H_{24}O_2$. Hence, the configurations of the two resulting derivatives have been deduced. The seven-membered ring is twist-chair shaped while the six-membered ring adopts a 1,2-diplanar conformation.

Commentaire

Le γ-*cis*-himachalène, (1), est le constituant sesquiterpénique minoritaire de l'huile essentielle du cèdre de l'Atlas (*Cedrus Atlantica*), isolé par Plattier & Teisseire (1974). La littérature ne rapporte qu'une seule réaction concernant l'oxydation de ce sesquiterpène (Plattier, Rouillier & Teisseire, 1974), il s'agit de son hydroboration. Dans le but d'étudier le comportement de (1) vis à vis de l'acide *m*-chloroperbenzoïque (*m*CPBA), comme ses isomères: l'α-*cis*- (Chiaroni, Riche, Benhar-