C(4)···C(9a^{ii})	3.429 (3)	C(2)···C(4a^{iii})	3.463 (3)
N(5)···C(10a^{ii})	3.434 (3)	C(3)···C(10a^{iii})	3.506 (3)
C(1)···C(4^{iii})	3.482 (3)		

C(2)—C(1)—C(10a)	120.1 (2)	C(8)—C(9)—C(9a)	120.3 (2)
C(1)—C(2)—C(3)	120.6 (2)	C(5a)—C(9a)—C(9)	119.8 (2)
C(2)—C(3)—C(4)	120.0 (2)	C(5a)—C(9a)—N(10)	117.6 (2)
C(3)—C(4)—C(4a)	122.0 (2)	C(9)—C(9a)—N(10)	122.6 (1)
C(4)—C(4a)—N(5)	119.3 (1)	C(9a)—N(10)—C(10a)	120.4 (1)
C(4)—C(4a)—C(10a)	117.0 (2)	C(9a)—N(10)—C(1′)	120.7 (2)
N(5)—C(4a)—C(10a)	123.7 (2)	C(10a)—N(10)—C(1′)	118.7 (2)
C(4a)—N(5)—C(5a)	117.0 (1)	C(1)—C(10a)—C(4a)	120.2 (2)
N(5)—C(5a)—C(6)	118.6 (1)	C(1)—C(10a)—N(10)	122.2 (1)
N(5)—C(5a)—C(9a)	123.7 (2)	C(4a)—C(10a)—N(10)	117.5 (2)
C(6)—C(5a)—C(9a)	117.7 (2)	C(4′)—N(4′)—O(4″*A*)	118.3 (2)
C(5a)—C(6)—C(7)	121.7 (2)	C(4′)—N(4′)—O(4″*B*)	118.3 (2)
C(6)—C(7)—C(8)	119.6 (2)	O(4″*A*)—N(4′)—O(4″*B*)	123.4 (2)
C(7)—C(8)—C(9)	121.0 (2)		

C(5a)—C(9a)—N(10)—C(1′)	173.1 (1)
C(1′)—N(10)—C(10a)—C(4a)	−171.6 (1)
C(9a)—N(10)—C(1′)—C(2′)	72.3 (2)
C(10a)—N(10)—C(1′)—C(6′)	66.6 (2)

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

The phase problem was solved by direct methods: 259 reflections with $E > 180$ were included and four starting reflections, in addition to the three origin-fixing reflections, were used. An initial difference Fourier map revealed the half benzene molecule located on the inversion centre at the origin. All H atoms could be found in a further difference map. In the refinement, several cycles of a full-matrix least-squares procedure lead to a convergence at $R = 0.034$; positions of non-H atoms were included with anisotropic and H-atom positions with isotropic displacement parameters.

Data collection and cell refinement: *CAD*-4 *Software* (Enraf–Nonius, 1992). Data reduction: *DATA* (Enraf–Nonius, 1990). Structure refinement: *LSFM* (Enraf–Nonius, 1990). Structure solution: *SIR*88 (Burla, Camalli, Cascarano, Giacovazzo, Polidori & Viterbo, 1989). Molecular graphics: *ORTEP*II (Johnson, 1990).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and bond distances involving H atoms have been deposited with the IUCr (Reference: JZ1027). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). C**51**, 1423–1425

An Intermediate for Chloroquine Analogs: (*E*)-2-(4,7-Dichloro-2-quinolinyl)-3-(dimethylamino)-2-propenal

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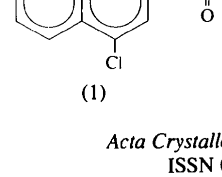
Abstract

The title compound, $C_{14}H_{12}Cl_2N_2O$, has been shown to have an *E* configuration about the double bond in the propenal moiety. Significant delocalization of the lone pair on the N atom of the dimethylamino group into the π system of this moiety is indicated by the planarity about this N atom.

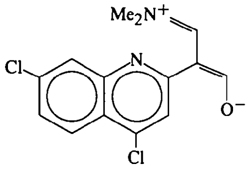
Comment

The increasing resistance observed in *Plasmodium falciparum* to the traditional antimalarial chloroquine [4-(7-chloro-4-quinolinylamino)-1-(diethylamino)-pentane] (Krogstad, Gluzman, Kyle, Oduoula, Martin, Milhous & Schlesinger, 1987; Peters, 1990) has stimulated a search for more effective analogs. As part of our effort in this area, we required chemically reactive derivatives of 4,7-dichloroquinoline that could be used for the synthesis of heterocyclic chloroquine analogs. An attractive intermediate is (1) which has been synthesized in good yield (De, Mague, Byers & Krogstad, 1995).

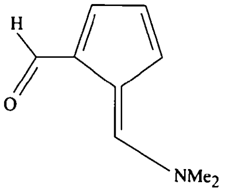


(1)

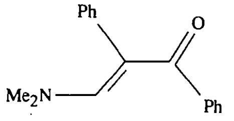
As the stereochemistry about the double bond in the propenal moiety could not be ascertained from NMR studies, the structure of (1) was determined. This shows unequivocally that the double bond in question has the *E* configuration. The most notable features of (1) are the virtual planarity of the dimethylamino group (Table *S*5, deposited), the accompanying short N(2)—C(12) distance of 1.318 (3) Å and the C(10)—C(12)—N(2) angle of 132.6 (2)°. All are consistent with a significant contribution of the resonance form (2) to the bonding description. A comparable situation has been found in (3) (Ammon, 1974), (4) (Arriortua, Urtiaga, Dominguez, Igartua, Iriondo & Solans, 1992), (5) (Carugo, Castellani & Rizzi, 1990) and (6) (Niederhauser, Sterchi & Neuenschwander, 1976). In particular, the distances and angles in the 3-(dimethylamino)-2-propenal moiety compare well with those found in the corresponding parts of (3) and (6). This moiety is twisted relative to the mean plane of the quinoline unit as indicated by the N(1)—C(9)—C(10)—C(12) torsion angle of −50.7 (4)°. Other distances and angles appear normal and there are no unusual intermolecular contacts.



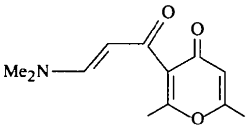
(2)



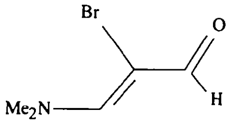
(3)



(4)



(5)



(6)

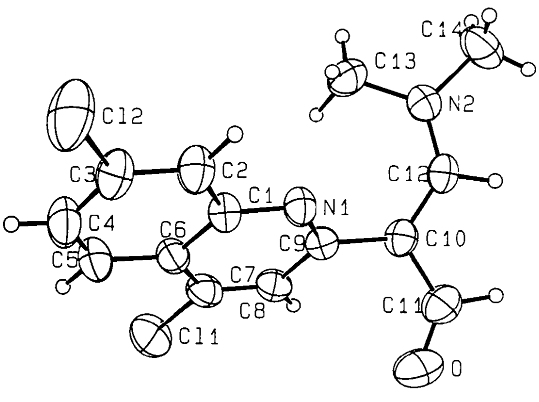


Fig. 1. Molecular structure showing 50% probability displacement ellipsoids for non-H atoms. H atoms are drawn as spheres of arbitrary radii.

Experimental

The pale yellow compound was prepared by the reported method (De, Mague, Byers & Krogstad, 1995) and recrystallized by the slow diffusion of diethyl ether into a chloroform solution.

Crystal data

$C_{14}H_{12}Cl_2N_2O$
$M_r = 295.17$
Triclinic
$P\bar{1}$
$a = 8.2796\,(9)$ Å
$b = 8.644\,(1)$ Å
$c = 11.336\,(1)$ Å
$\alpha = 97.84\,(1)°$
$\beta = 104.36\,(1)°$
$\gamma = 115.03\,(1)°$
$V = 684.7\,(2)$ Å^3
$Z = 2$
$D_x = 1.43$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 23 reflections
$\theta = 11.01–16.91°$
$\mu = 0.46$ mm^{-1}
$T = 293$ K
Triclinic prism
0.53 × 0.43 × 0.17 mm
Pale yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical, ψ scan (North, Phillips & Mathews, 1968)
$T_{\min} = 0.8987$, $T_{\max} = 0.9988$
2581 measured reflections
2389 independent reflections

1567 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int} = 0.018$
$\theta_{\max} = 25.0°$
$h = 0 \rightarrow 9$
$k = -10 \rightarrow 10$
$l = -13 \rightarrow 13$
2 standard reflections frequency: 120 min intensity decay: −1.8%

Refinement

Refinement on F
$R = 0.038$
$wR = 0.049$
$S = 1.56$
1567 reflections
220 parameters
H atoms refined isotropically
$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{\max} = 0.05$
$\Delta\rho_{\max} = 0.05$ e Å^{-3}
$\Delta\rho_{\min} = -0.19$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$B_{\rm eq} = (8\pi^2/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	$B_{\rm eq}/B_{\rm iso}$
Cl(1)	0.8660 (1)	0.11070 (9)	0.90276 (8)	5.47 (2)
Cl(2)	0.2690 (1)	−0.4944 (1)	1.15541 (7)	6.59 (2)
O	0.2894 (3)	−0.0432 (2)	0.5232 (2)	5.51 (6)
N(1)	0.2823 (2)	−0.3673 (2)	0.7351 (2)	3.07 (5)
N(2)	0.1830 (3)	−0.6411 (2)	0.4559 (2)	3.48 (5)

C(1)	0.3795 (3)	−0.3151 (3)	0.8621 (2)	3.15 (6)
C(2)	0.2911 (3)	−0.4167 (3)	0.9369 (2)	3.83 (7)
C(3)	0.3795 (4)	−0.3694 (3)	1.0639 (2)	4.16 (7)
C(4)	0.5585 (4)	−0.2198 (4)	1.1235 (3)	4.83 (8)
C(5)	0.6465 (4)	−0.1231 (3)	1.0535 (3)	4.38 (7)
C(6)	0.5621 (3)	−0.1658 (3)	0.9213 (2)	3.22 (6)
C(7)	0.6409 (3)	−0.0712 (3)	0.8402 (3)	3.44 (6)
C(8)	0.5458 (3)	−0.1209 (3)	0.7147 (2)	3.28 (6)
C(9)	0.3644 (3)	−0.2733 (3)	0.6635 (2)	2.81 (5)
C(10)	0.2586 (3)	−0.3275 (3)	0.5265 (2)	2.99 (5)
C(11)	0.2310 (3)	−0.1989 (3)	0.4704 (3)	4.10 (7)
C(12)	0.1719 (3)	−0.4958 (3)	0.4451 (2)	3.09 (5)
C(13)	0.3110 (4)	−0.6496 (3)	0.5651 (3)	4.86 (7)
C(14)	0.0656 (4)	−0.8036 (4)	0.3523 (3)	5.06 (8)
H(2)	0.172 (3)	−0.519 (3)	0.893 (2)	4.4 (6)*
H(4)	0.608 (4)	−0.194 (3)	1.209 (2)	5.5 (7)*
H(5)	0.766 (4)	−0.026 (3)	1.096 (3)	6.4 (8)*
H(8)	0.591 (3)	−0.063 (3)	0.657 (2)	4.3 (6)*
H(11)	0.148 (3)	−0.251 (3)	0.377 (2)	5.5 (7)*
H(12)	0.093 (3)	−0.510 (3)	0.361 (2)	3.2 (5)*
H(13*a*)	0.336 (3)	−0.739 (3)	0.548 (2)	5.0 (6)*
H(13*b*)	0.253 (4)	−0.665 (4)	0.626 (3)	7.7 (9)*
H(13*c*)	0.432 (4)	−0.536 (4)	0.597 (3)	7.0 (8)*
H(14*a*)	−0.000 (5)	−0.782 (5)	0.281 (4)	11 (1)*
H(14*b*)	−0.020 (4)	−0.884 (4)	0.374 (3)	8.0 (9)*
H(14*c*)	0.127 (4)	−0.853 (4)	0.328 (3)	9 (1)*

* Atoms were refined isotropically.

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

C(9)—C(10)	1.476 (3)	C(12)—N(2)	1.318 (3)
C(10)—C(11)	1.425 (4)	C(13)—N(2)	1.450 (4)
C(11)—O	1.220 (4)	C(14)—N(2)	1.458 (4)
C(10)—C(12)	1.380 (4)		
C(9)—C(10)—C(11)	118.5 (2)	C(10)—C(12)—N(2)	132.6 (2)
C(9)—C(10)—C(12)	126.7 (2)	C(12)—N(2)—C(13)	123.7 (2)
C(11)—C(10)—C(12)	114.7 (2)	C(12)—N(2)—C(14)	119.6 (3)
C(10)—C(11)—O	126.9 (3)	C(13)—N(2)—C(14)	116.7 (3)

The space group $P\bar{1}$ was assumed and confirmed by the successful refinement. The majority of the non-H atoms were obtained from the initial E map (*SIR*88; Burla, Camalli, Cascarano, Giacovazzo, Polidori, Spagna & Viterbo, 1989) and the remainder were located in a $\Delta\rho$ map following initial full-matrix least-squares refinement (*MolEN*; Fair, 1990). All H atoms were located in a $\Delta\rho$ map following refinement of all non-H atoms with anisotropic displacement parameters and were refined with individual isotropic displacement parameters.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SIR*88 (Burla, Camalli, Cascarano, Giacovazzo, Polidori, Spagna & Viterbo, 1989). Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976).

This work was supported by NIH Grant AI 25136 (National Institute of Allergy and Infectious Diseases) and TDR Grant 900131 (World Bank/UNDP/WHO Special Programme for Research and Training in Tropical Diseases) (DJK) and by the Chemistry Department of Tulane University (JTM).

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: CR1173). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2-Carboxypyridinium Chloride Monohydrate

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Abstract

The structure of the monohydrated polymorph of picolinic acid hydrochloride, $C_6H_6NO_2^+.Cl^-.H_2O$, has been determined and the role of the lattice water in the hydrogen bonding to the chloride ion considered. In the anhydrous complex of the same compound, an interaction between the chloride and the pyridinium proton is found [Cl···N 3.144 (2) Å]. In addition, the water of hydration forms bridging links between chloride ions [O—H···Cl 3.086 (2), 3.111 (2) Å] and with a carboxylic acid H atom [O···H—O 2.563 (3) Å]. An intramolecular hydrogen bond between the carboxyl O atom and the H atom of the pyridinium moiety is also found [O···H—N 2.669 (4) Å].

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