

Crystal structure of 3,6-bis(dimethylamino)acridine hydroperchloride (acridine orange•HClO₄)

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Abstract

Single crystals of 3,6-bis(dimethylamino)acridine hydroperchloride (acridine orange•HClO₄) was prepared and molecular structure was crystallographically determined.

Key words: Acridine orange, Crystal structures

1 Introduction

Acridine orange is quite useful biological dyes for nucleic acids and polysaccharides.¹ The interaction of acridine derivatives with DNA has been studied extensively. The central N atom of the acridine ring can hydrogen bond to a hydrogen bond acceptor such as an ionized phosphate group. The protonated mode is interested in their actions as antibacterial agents since that is only active as bacteriostats. Some structural determinations for acridine orange derivatives have been carried out. The crystal structure of acridine orange

hydrochloride mono-hydrate,^{2,3} acridine orange hydroiodide,³ acridine orange tetrachlorozincate⁴ and acridine orange hexafluorosilicate⁵ have been reported. In this study orange single crystals of 3,6-bis(dimethylamino)acridine hydroperchloride (acridine orange•HClO₄) (**1**) were by chance obtained from methanol solution of [Pd₂(μ-dppm)₂Cl₂] (dppm=bis(diphenylphosphino)methane), AgClO₄ and acridine orange base, and the crystal structure was determined.

2 Experimental

A orange crystal of **1** was attached to the end of a glass fiber and was mounted on a Rigaku AFC-5R diffractometer with a graphite mono-chromated Mo K α radiation ($\lambda=0.71069\text{\AA}$). The detailed measurement conditions and the crystal data are listed in Table 1. The intensity data were collected

Table 1 Crystal and experimental data

Formula : ClO ₄ N ₃ C ₁₇ H ₂₀
Formula weight : 365.82
Crystal system : monoclinic
Space group : <i>P2₁/c</i> , <i>Z</i> =4
<i>a</i> =7.2997(9) \AA
<i>b</i> =10.912(2) \AA
<i>c</i> =22.066(3) \AA
β =98.21(1) $^\circ$
<i>V</i> =1739.5(5) \AA^3
<i>D_c</i> =1.397 g/cm ³
<i>R</i> =0.061, <i>R_w</i> =0.064
No. of reflections used=857 (<i>I</i> >3 σ (<i>I</i>))
Measurement : Rigaku AFC-5R
Program system : TEXSAN
Structure determination : Direct Method (<i>MITHRIL</i>)
Refinement : Full-matrix least-square

at 23°C using the ω -2 θ scan technique to a maximum 2 θ of value of 55.0°. Of the 3810 reflections which were collected, 3489 were unique. The intensities of three representative reflections which were measured after every 150 reflections remained constant through data collection, indicative of crystal and electronic stability. No decay correction was applied. The linear absorption coefficient for Mo K α is 2.4 cm⁻¹. Azimuthal scans of several reflections indicated no need for an absorption correction. The data were corrected for Lorentz and polarization effects.

The structures were solved by a direct method (*MITHRIL*).⁶ The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located by Fourier difference synthesis. The final cycle of the full-matrix least squares refinement was based on 857 observed reflections (*I*>3 σ (*I*)), and 226 variable parameters. Reliability factors are defined

as $R=\Sigma(|F_o|-|F_c|)/\Sigma|F_c|$ and $R_w=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, where $w=4F_o^2/\sigma(F_o^2)$. The final *R* and *R_w* values were 0.061 and 0.064, respectively. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.34 and -0.24 e \AA^{-3} , respectively. Atomic scattering factors and anomalous dispersion terms were taken from the International Tables for X-ray Crystallography, Vol. IV.⁷ All calculations were performed using the program TEXSAN crystallographic software package.⁸

Table 2 Selective atomic coordinate and equivalent isotropic thermal parameters *B_{eq}* (\AA^3) of non-hydrogen atoms

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B_{eq}</i>
Cl(1)	0.7699(7)	0.1994(3)	0.6435(2)	6.9(2)
O(1)	0.712(2)	0.314(1)	0.6517(5)	16(1)
O(2)	0.843(2)	0.1390(8)	0.6939(4)	13.1(7)
O(3)	0.624(2)	0.134(1)	0.6182(7)	21(1)
O(4)	0.884(2)	0.207(2)	0.6040(8)	23(1)
N(1)	0.744(1)	0.4760(7)	0.5331(3)	3.8(5)
N(2)	0.869(1)	0.185(1)	0.3831(4)	5.7(6)
N(3)	0.618(1)	0.7463(9)	0.6918(4)	5.5(5)
C(1)	0.703(1)	0.589(1)	0.5536(5)	3.8(6)
C(2)	0.678(1)	0.609(1)	0.6131(5)	4.3(6)
C(3)	0.642(1)	0.725(1)	0.6341(5)	4.5(6)
C(4)	0.630(1)	0.824(1)	0.5902(6)	5.3(6)
C(5)	0.650(1)	0.804(1)	0.5311(5)	5.1(6)
C(6)	0.690(1)	0.686(1)	0.5091(5)	4.0(5)
C(7)	0.723(2)	0.662(1)	0.4508(5)	4.9(6)
C(8)	0.763(1)	0.545(1)	0.4323(5)	4.2(6)
C(9)	0.800(1)	0.513(1)	0.3735(5)	5.4(7)
C(10)	0.832(2)	0.399(1)	0.3565(5)	5.4(7)
C(11)	0.836(1)	0.300(1)	0.4001(5)	4.8(6)
C(12)	0.809(1)	0.328(1)	0.4597(5)	4.2(6)
C(13)	0.774(1)	0.446(1)	0.4753(5)	3.9(6)
C(14)	0.909(2)	0.151(1)	0.3221(6)	8.1(8)
C(15)	0.875(2)	0.082(1)	0.4259(6)	7.5(8)
C(16)	0.588(2)	0.868(1)	0.7151(5)	7.0(7)
C(17)	0.644(2)	0.649(1)	0.7368(5)	6.9(7)

$$B_{eq}=(4/3)\Sigma_i\Sigma_jB_{ij}a_i\cdot a_j.$$

3 Results and discussion

The molecular structure of **1** was shown in Fig. 1, together with the atomic labeling scheme. The framework of acridine ring system is nearly planar within the standard deviation. The acridine molecule

is mono-cationized with the H(1) atom bonded at the N(1) atom of the central ring system. The H(1) atom forms a hydrogen bond to the O(1) atom of ClO₄ anion [N(1)-O(1)=3.19(1) \AA ; N(1)-

H(1)=1.135Å]. The C(1)-N(1)-C(13) angle of 126.9(8)° is typical of a protonated pyridine nitrogen.^{3,5} On the other hand the adjacent N(1)-C(1)-C(6) and N(1)-C(13)-C(8) angles of 116.1(9)° and 115.9(9)° are lower than those of an unprotonated pyridine system. The 3- and 6-dimethylamino groups have a slight but significant influence on the fused ring geometry:³ the pairs of {C(2)-C(3) and C(3)-C(4)} bond and of {C(10)-C(11) and C(11)-C(12)} bond show an increased single-bond character compared with the unsubstituted compounds. On the other hand there is a bond shortening (increased double-bond character) for the pairs of {C(4)-C(5) and C(3)-C(4)} bond and of {C(9)-C(10) and C(11)-C(12)} bond.

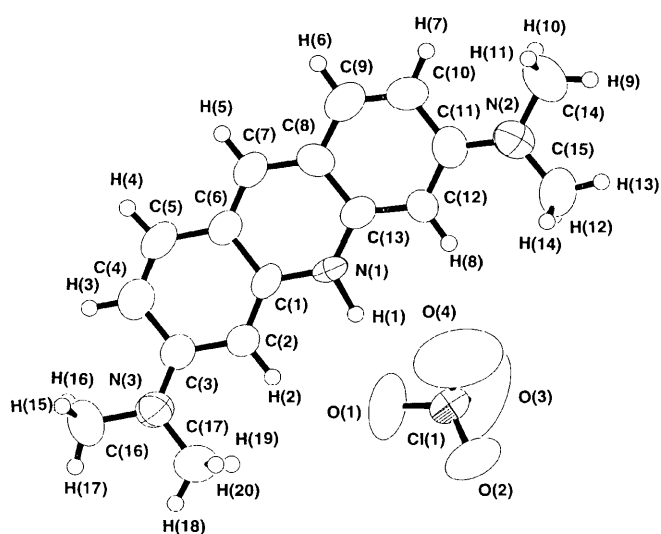


Figure 1 Molecular Structure of **1** and the atomic labeling scheme.

The crystal packing along the *b*-axis is shown in Fig. 2. The acridine rings are almost in parallel stacking along the *a*-axis. The separation of 3.45Å

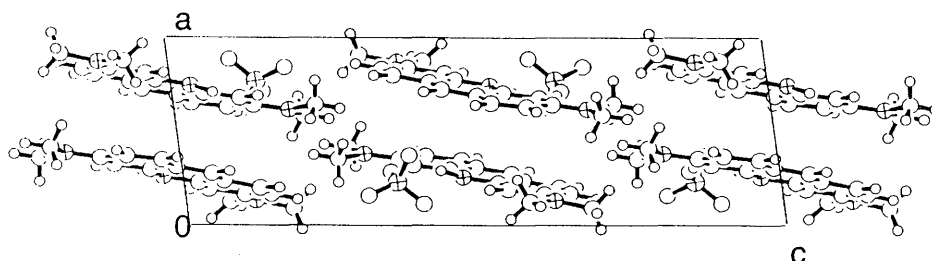


Figure 2 Crystal packing of **1** along the *b*-axis.

between the acridine rings is close to those (3.45-3.51Å) found in other acridine orange derivatives,^{2,5} indicative of the occurrence of the π - π stacking.

Table 3 Selected bond distances(Å) and bond angles(°)

N(1)-C(1)	1.36(1)	N(1)-C(13)	1.37(1)
N(2)-C(11)	1.34(1)	N(2)-C(14)	1.47(1)
N(2)-C(15)	1.46(1)	N(3)-C(3)	1.33(1)
N(3)-C(16)	1.46(1)	N(3)-C(17)	1.44(1)
C(1)-C(2)	1.37(1)	C(1)-C(6)	1.44(1)
C(2)-C(3)	1.39(1)	C(3)-C(4)	1.44(1)
C(4)-C(5)	1.35(1)	C(5)-C(6)	1.42(1)
C(6)-C(7)	1.37(1)	C(7)-C(8)	1.39(1)
C(8)-C(9)	1.41(1)	C(8)-C(13)	1.43(1)
C(9)-C(10)	1.33(1)	C(10)-C(11)	1.45(1)
C(11)-C(12)	1.39(1)	C(12)-C(13)	1.36(1)
N(1)-H(1)	1.135	N(1)-O(1)	3.19(1)
C(1)-N(1)-C(13)	126.9(8)	C(11)-N(2)-C(14)	124(1)
C(11)-N(2)-C(15)	122(1)	C(14)-N(2)-C(15)	114(1)
C(3)-N(3)-C(16)	123(1)	C(3)-N(3)-C(17)	121(1)
C(16)-N(3)-C(17)	116.1(9)	N(1)-C(1)-C(2)	121.9(9)
N(1)-C(1)-C(6)	116(1)	C(2)-C(1)-C(6)	122(1)
C(1)-C(2)-C(3)	122(1)	N(3)-C(3)-C(2)	122(1)
N(3)-C(3)-C(4)	121(1)	C(2)-C(3)-C(4)	117(1)
C(3)-C(4)-C(5)	122(1)	C(4)-C(5)-C(6)	122(1)
C(1)-C(6)-C(5)	115.5(9)	C(1)-C(6)-C(7)	120(1)
C(5)-C(6)-C(7)	125(1)	C(6)-C(7)-C(8)	122(1)
C(7)-C(8)-C(9)	125(1)	C(7)-C(8)-C(13)	120(1)
C(9)-C(8)-C(13)	115(1)	C(8)-C(9)-C(10)	124(1)
C(9)-C(10)-C(11)	120(1)	N(2)-C(11)-C(10)	120(1)
N(2)-C(11)-C(12)	122(1)	C(10)-C(11)-C(12)	118(1)
C(11)-C(12)-C(13)	120(1)	N(1)-C(13)-C(8)	115.9(9)
N(1)-C(13)-C(12)	122(1)	C(8)-C(13)-C(12)	123(1)

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