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(11*R*)-(–)-*N*,*N*′-Dimethylcinchonidinium diiodide

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Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.007 Å
R factor = 0.050
wR factor = 0.084
Data-to-parameter ratio = 21.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, (−)-4-[hydroxy(1-methyl-5-vinyl-1-azoniabicyclo[2.2.2]oct-2-yl)methyl]-1-methylquinolinium diiodide, $C_{21}H_{28}N_2O^{2+}\cdot 2I^-$, is formed from optically active (11*R*)-(−)-cinchonidine and methyl iodide. The N—Me bond lengths are in the range of 1.476 (7)–1.497 (6) Å.

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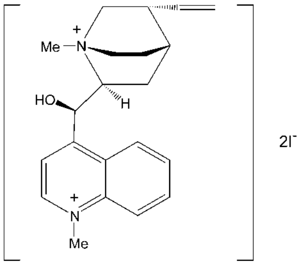
Comment

Since an obvious property of a protein surface is chirality, stereoselective bimolecular electron transfer (ET) with hemoprotein now becomes one of the significant research interests. To date, methylviologen, quinones, and inorganic complexes have been utilized as organic and inorganic quenchers (Barboy & Feitelson, 1987; Tsukahara *et al.*, 1994; Satoh *et al.*, 1997). However, no experiments on the stereoselectivity in the photoinduced ET reactions between metalloprotein and a chiral organic agent have been conducted so far, except for ours (Tsukahara *et al.*, 1997). One of the reasons is a lack of systematic synthesis of such chiral molecules. We have recently reported the design, synthesis, crystal structures and photophysical properties of a variety of chemically modified quinolinium ions and viologens and some of them are attached to optically active 1-(1-naphthyl)/1-phenyl/1-cyclohexylcarbamoylmethyl groups (Tsukahara *et al.*, 1997). They certainly acted as good electron acceptors for the excited triplet state of ZnMb, ^{3}(ZnMb)*, and demonstrated the stereoselective quenching and back ET reactions. However, it is rather difficult to discuss the detailed mechanism of how stereoselectivity was achieved in the bimolecular ET reaction and further design of new optically active agents is still needed to construct more apparent stereoselective ET systems (Takashima *et al.*, 2003). In this study, we describe the structure of the new chiral title compound, (I), as a candidate for new chiral electron acceptors.



(I)

The crystal structure of (I) consists of a discrete $C_{21}H_{28}N_2O^{2+}$ cation and two iodide anions. The N1—C and the N2—C bond lengths are in the ranges 1.332 (6)–1.476 (7) and 1.497 (6)–1.547 (5) Å, respectively. The C—N1—C and C—N2—C angles are in the ranges 119.6 (4)–120.7 (4) and

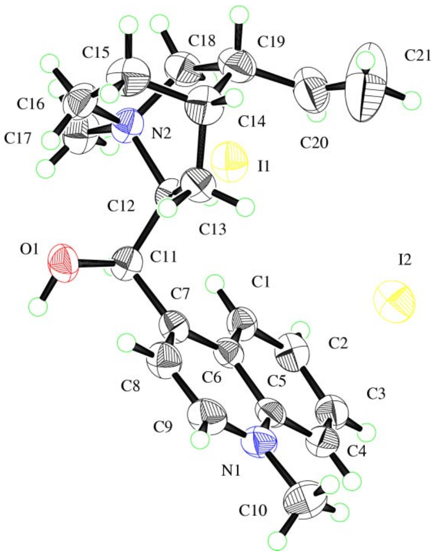


Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids.

105.6 (3)–113.3 (3)°, respectively, which compare well with the values published for (11*S*)-(+)-*N*,*N*′-dimethylcinchoninium diiodide (Yoshikawa *et al.*, 2004). The H1⋯I1 distance of 3.035 Å suggests a weak hydrogen bond.

Experimental

The title compound was prepared from optically active (11*R*)-(−)-cinchonidine. In a 200 ml flask, cinchonidine (0.79 g, 2.7 mmol) was dissolved in 100 ml of *N*,*N*-dimethylformamide at 353 K. Methyl iodide (1.8 g, 13 mmol) was added to the solution and the mixture was reacted for 48 h at 353 K. After removal of the solvent, the crude residue was dissolved in methanol and then reprecipitated by adding ether. The yellow solid was collected by filtration and washed with cold ether. Recrystallization from acetonitrile gave yellow single crystals. The specific rotation, $[\alpha]_D$, at 298 K is −58° (c = 1.0 g per 100 ml, CH_3OH).

Crystal data

$C_{21}H_{28}N_2O^{2+}\cdot 2I^-$
$M_r = 578.27$
Orthorhombic, $P2_12_12_1$
$a = 11.3103$ (4) Å
$b = 13.3106$ (3) Å
$c = 14.9280$ (5) Å
$V = 2247.4$ (1) Å^3
$Z = 4$
$D_x = 1.709$ Mg m^{-3}

Mo Kα radiation
Cell parameters from 29792 reflections
$\theta = 1.4$–$30.5°$
$\mu = 2.81$ mm^{-1}
$T = 296.2$ K
Prism, yellow
0.20 × 0.16 × 0.10 mm

Data collection

Rigaku R-AXIS RAPID Imaging Plate diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{\min} = 0.619$, $T_{\max} = 0.755$
26613 measured reflections

6680 independent reflections
5056 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.046$
$\theta_{\max} = 30.5°$
$h = -15 \rightarrow 16$
$k = -18 \rightarrow 18$
$l = -21 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.084$
$S = 1.10$
5056 reflections
235 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.013$
$\Delta\rho_{\max} = 1.76$ e Å^{-3}
$\Delta\rho_{\min} = -0.39$ e Å^{-3}
Absolute structure: Flack (1983), 2857 Friedel pairs
Flack parameter = 0.01 (2)

Table 1
Selected geometric parameters (Å, °).

O1—C11	1.411 (5)	N2—C12	1.547 (5)
N1—C5	1.376 (6)	N2—C16	1.529 (6)
N1—C9	1.332 (6)	N2—C17	1.497 (6)
N1—C10	1.476 (7)	N2—C18	1.501 (6)
C11—O1—H11	109.0	C12—N2—C17	113.3 (3)
C5—N1—C9	120.7 (4)	C12—N2—C18	105.6 (3)
C5—N1—C10	119.7 (4)	C16—N2—C17	108.6 (3)
C9—N1—C10	119.6 (4)	C16—N2—C18	108.4 (3)
C12—N2—C16	111.5 (3)	C17—N2—C18	109.2 (3)

All H atoms were positioned geometrically (O—H = 0.95, C—H = 0.94–0.98 Å), with $U_{\rm iso}$(H) values derived from the $U_{\rm eq}$ values of the parent atom atoms. The maximum electron-density peaks is 0.06 Å from atom I1 and H11.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *TEXSAN* (Molecular Structure Corporation, 2000); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

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