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# (11*S*)-(+)-*N*,*N*′-Dimethylcinchoninium diiodide

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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*S*)-(+)-cinchonine and methyl iodide. The N—Me bond lengths are in the range 1.48 (1)–1.49 (1) Å.

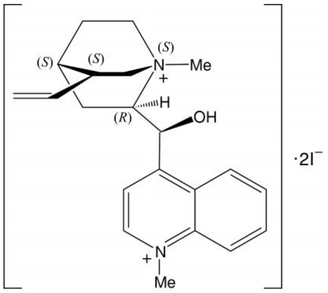
**Key indicators**

Single-crystal X-ray study
$T$ = 296 K
Mean $\sigma$(C–C) = 0.010 Å
$R$ factor = 0.049
$wR$ factor = 0.107
Data-to-parameter ratio = 19.8

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

## Comment

Photo-induced electron-transfer (ET) reaction between hemoproteins, containing hemes as cofactors, and small molecules to transport the electron initiated by the light energy has received considerable attention in the fields of both chemistry and biochemistry. Many experiments have been made on the intermolecular photo-induced ET reactions by using zinc-substituted hemoproteins, because the photo-excited triplet state can act as a strong reductant having a lifetime of several milliseconds (Zemel & Hoffman, 1981). 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). Since an obvious property of the protein surface is chirality, stereoselective bimolecular ET with hemoproteins is now a significant research interest. However, no experiments on the stereoselectivity in the photo-induced ET reactions between metalloproteins and a chiral organic agent have been conducted so far, with the exception of Tsukahara *et al.* (1997). One of the reasons is the lack of systematic syntheses of such chiral molecules. In this study, we describe the structure of a new chiral title compound, (I), as a candidate for new chiral electron acceptors.



(I)

The asymmetric unit of (I) consists of a discrete $C_{21}H_{28}N_2O^{2+}$ cation and two iodide anions. The N1—C and N2—C bond lengths are in the ranges 1.33 (1)–1.48 (1) and 1.50 (1)–1.531 (7) Å, respectively. The C—N1—C and C—N2—C angles are in the ranges 118.6 (7)–120.8 (6) and 106.1 (5)–112.8 (5)°, respectively. The O1$\cdots$I2($x+1$, $y$, $z$) distance of 3.350 (3) Å suggests a weak hydrogen bond.

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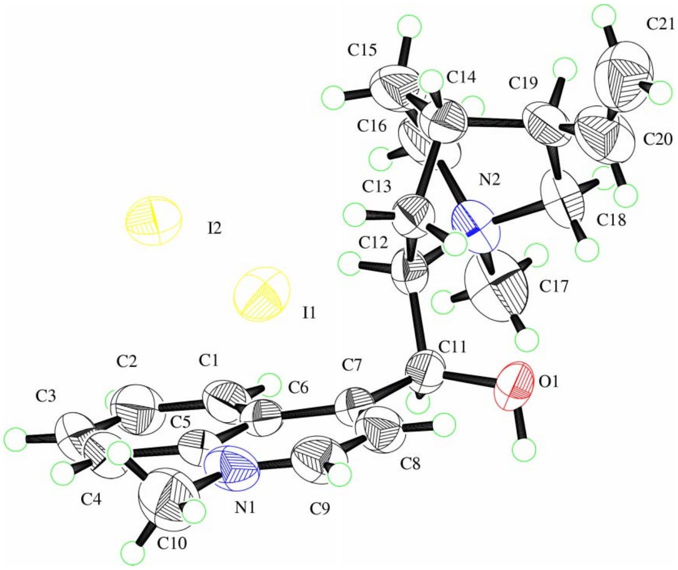

**Figure 1**
The molecular structure of (I), showing 50% probability displacement ellipsoids.

## Experimental

The title compound, (I), was prepared from optically active (11*S*)-(+)-cinchonine. In a 200 ml flask, cinchonine (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 heated 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 of (I). The specific rotation, $[\alpha]_D$, at 295 K is +123° ($c$ = 1.00, $CH_3OH$ where $c$ is a concentration of units g per 100 $cm^{-3}$).

### *Crystal data*

$C_{21}H_{28}N_2O^{2+}\cdot2I^-$
$M_r$ = 578.27
Monoclinic, $P2_1$
$a$ = 8.8608 (5) Å
$b$ = 10.9102 (4) Å
$c$ = 12.2876 (5) Å
$\beta$ = 106.018 (2)°
$V$ = 1141.76 (9) Å$^3$
$Z$ = 2

$D_x$ = 1.682 Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 14933 reflections
$\theta$ = 1.7–30.5°
$\mu$ = 2.77 mm$^{-1}$
$T$ = 296.2 K
Prism, yellow
0.20 × 0.15 × 0.10 mm

### *Data collection*

Rigaku R-AXIS RAPID Imaging Plate diffractometer
$\omega$ scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min}$ = 0.559, $T_{max}$ = 0.758
13 000 measured reflections

5957 independent reflections
4656 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.027
$\theta_{max}$ = 30.5°
$h$ = −12 → 12
$k$ = −13 → 15
$l$ = −17 → 17

### *Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.107
$S$ = 1.48
5957 reflections
235 parameters
H-atom parameters not refined

$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.081
$\Delta\rho_{max}$ = 1.34 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.45 e Å$^{-3}$
Absolute structure: Flack (1983), 2305 Friedel pairs
Flack parameter = −0.02 (3)

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| O1—C11 | 1.406 (7) | N2—C12 | 1.529 (7) |
| N1—C5 | 1.37 (1) | N2—C16 | 1.507 (9) |
| N1—C9 | 1.331 (10) | N2—C17 | 1.49 (1) |
| N1—C10 | 1.48 (1) | N2—C18 | 1.507 (8) |
| | | | |
| C5—N1—C9 | 121.1 (5) | C12—N2—C18 | 111.7 (4) |
| C5—N1—C10 | 121.0 (6) | C16—N2—C17 | 107.3 (5) |
| C9—N1—C10 | 117.9 (7) | C16—N2—C18 | 107.8 (4) |
| C12—N2—C16 | 106.3 (5) | C17—N2—C18 | 110.5 (6) |
| C12—N2—C17 | 112.9 (5) | | |

All the H atoms bonded to carbon were placed at calculated positions, and fixed (C—H = 0.93–1.02 Å). The positional parameters of the hydroxyl H atom could not be derived from a difference-density map; they were calculated geometrically. The maximum and minimum electron-density peaks are 0.04 and 2.09 Å from atoms I2 and I1, respectively.

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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