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Structure of Diiodide Salts of *N*-Heteroaromatic Dications

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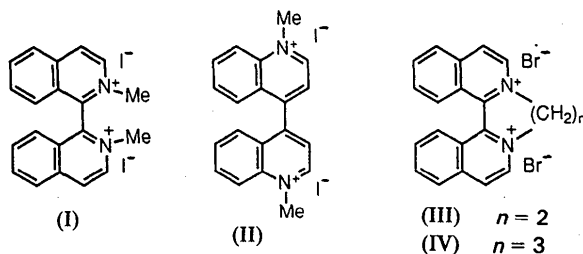
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Abstract

The structures of 2,2'-dimethyl-1,1'-biisoquinolinium diiodide monohydrate (I) and 1,1'-dimethyl-4,4'-biquinolinium diiodide (II) have been determined. Both biisoquinolinium and biquinolinium dications have a twofold rotation axis. The two *N*-heteroaromatic planes in (I) are twisted from each other to a greater extent than those in (II); this can be explained by steric repulsion of the *N*-methyl groups in (I). In both crystals each I⁻ anion is in a relatively close contact with one of the positively charged N atoms of the dications. These interionic interactions seem to be responsible for the deep red color of the crystals.

Comment

Biisoquinolinium salt (I) and polymethylene-bridged analogs (III) and (IV) are reported to produce blue chemiluminescence in hydroxylic solvents by addition of base (Mason & Roberts, 1967). Heller, Henry



& Fritsch (1973) proposed that the chemiluminescence reaction involved two-electron reduction of the biisoquinolinium dications and subsequent oxygenation and then cleavage to yield excited carbonyl compounds. Recently, with interest in the relationship between structure and chemiluminescence efficiency and electronic redox property, we determined crystal structures of (III) and (IV) (Mori, Matsuyama, Yamada & Maeda, 1992). In these crystals the biisoquinolinium dications adopt a C_2 conformation. Unlike (I), (III) or (IV), biquinolinium salt (II) produced no chemiluminescence in the same alkaline solution. (II) showed a charge-transfer (CT) absorption band around 460 nm in dimethylformamide (DMF) (Ishii, 1986), while (I) showed a weak CT absorption band around 440 nm in DMF and the intensity of the CT band increased in less polar media such as DMF–dichloromethane (3:1 *v/v*) mixed solvent. These spectral properties indicate that the organic dication and I⁻ form a CT complex in the ground state in both (I) and (II). The characteristic red color of the crystal may be a result of the CT interaction. It has been reported, however, that in the crystal of 1-ethyl-2-methylquinolinium iodide, interionic interaction is weak and an ion-pair does not exist (Sakanoue, Kai, Yasuoka, Kasai & Kakudo, 1970). In the present study, structures of (I) and (II) have been determined to investigate conformational features and interaction between the ions.

As shown in Fig. 1, both (I) and (II) show C_2 symmetry and the molecular axes coincide with the crystallographic twofold axes. In (I), a water molecule also is located on the C_2 axis. Most of the bond distances and angles in (I) are similar to the corresponding ones in (III) and (IV) (Mori, Matsuyama, Yamada & Maeda, 1992). The C(1)—N(2)—C(11) angle is somewhat enlarged, while C(3)—N(2)—C(11) is significantly narrower than 120°. The isoquinoline ring of (I) is almost planar with maximum deviation of 0.022 Å at C(8); the *N*-methyl C atom C(11) deviates by only 0.054 Å from the plane. The two N atoms N(2) and N(2') are located on opposite

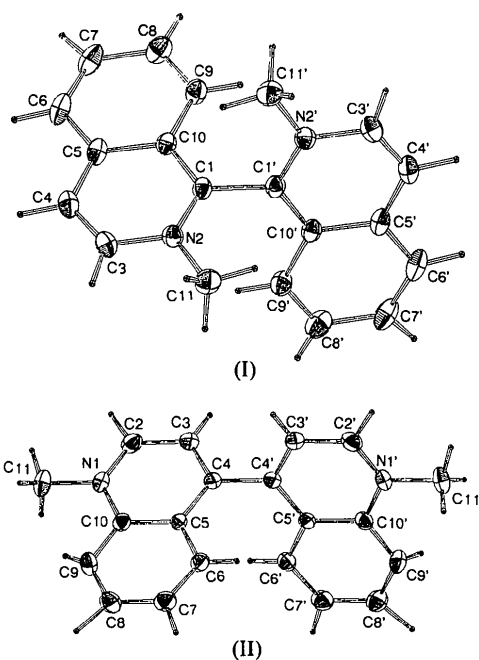


Fig. 1. ORTEP plots (Johnson, 1965) of the bisoquinolinium cation in (I) and the biquinolinium cation in (II) with the atom numbering. The anisotropic ellipsoids for non-H atoms enclose 30% probability.

sides across the C(1)—C(1') bond. The dihedral angle between the two isoquinoline rings of (I) is larger than those in (III) and (IV). This indicates that the isoquinoline moiety in (I) is less strained than those in (III) and (IV), although conjugation between the two *N*-heteroaromatic groups seems to be smaller. These conformational features of (I) may influence its chemiluminescence and redox properties.

The quinoline moiety in (II) is almost planar with maximum deviation of 0.028 Å at C(2) and C(4); the deviation of the *N*-methyl C atom C(11) from the plane is 0.050 Å. The C(4)—C(4') distance in (II) is shorter than C(1)—C(1') in (I). The torsion angle C(3)—C(4)—C(4')—C(3') in (II) is smaller than N(2)—C(1)—C(1')—N(2') in (I). This results from the smaller steric repulsion between the two *N*-heteroaromatic rings of (II) than that of (I).

Fig. 2 shows the crystal structures of (I) and (II). In both crystals the I⁻ anion is in close contact with the N atom of one organic cation with an interatomic distance of 3.828 (3) Å in (I) and 3.745 (3) Å in (II). This interionic interaction seems to contribute to the deep red color of these crystals. The I⁻ anion interacts with cations at other sites with distances of ca 4.0 Å. Parallel stacking of *N*-heteroaromatic cations was not observed in either (I) or (II). In (I), a water molecule is hydrogen bonded with two I⁻ anions. The I(1)⋯O distance is 3.521 (5) Å and the angle I(1)⋯O⋯I(1') is 94.1 (1)°.

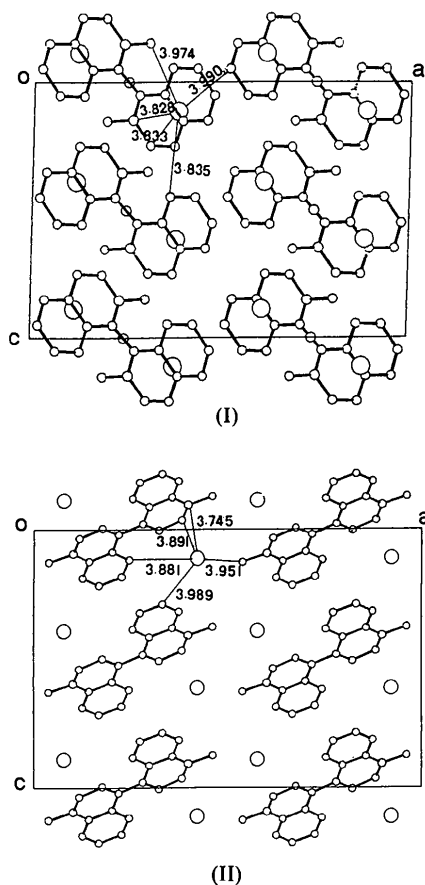


Fig. 2. Crystal structures of (I) and (II) viewed along the *b* axis. Selected interatomic distances (Å) are given.

Experimental

Compound (I)

Crystal data

C₂₀H₁₈N₂²⁺·2I⁻·H₂O

M_r = 558.2

Monoclinic

*A*2/*a*

a = 17.099 (5) Å

b = 10.091 (3) Å

c = 11.386 (4) Å

β = 92.09 (3)°

V = 1963.5 (11) Å³

Z = 4

D_x = 1.888 Mg m⁻³

Mo *K*α radiation

λ = 0.71068 Å

Cell parameters from 19 reflections

θ = 13–15°

μ = 3.22 mm⁻¹

T = 294 K

Plate

0.25 × 0.15 × 0.15 mm

Red

Crystal source: synthesized from 1,1'-bisisoquinoline and methyl iodide

Data collection

Rigaku AFC-5 diffractometer

ω/2θ scans

Absorption correction:

none

*R*_{int} = 0.02

θ_{max} = 27.5°

h = 0 → 23

k = 0 → 14

l = -14 → 14

2325 measured reflections
2124 independent reflections
1915 observed reflections
[$F > 3\sigma(F)$]

Refinement

Refinement on F
Final $R = 0.035$
 $wR = 0.039$
 $S = 1.428$
1915 reflections
139 parameters
All H-atom parameters re-
fined

Compound (II)**Crystal data**

$C_{20}H_{18}N_2^{2+} \cdot 2I^-$
 $M_r = 540.1$
Monoclinic
 $A2/a$
 $a = 21.867(5) \text{ \AA}$
 $b = 6.119(1) \text{ \AA}$
 $c = 14.470(4) \text{ \AA}$
 $\beta = 90.52(3)^\circ$
 $V = 1936.2(8) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.852 \text{ Mg m}^{-3}$
Mo $K\alpha$ radiation
 $\lambda = 0.71068 \text{ \AA}$

Data collection

Rigaku AFC-5 diffractome-
ter
 $\omega/2\theta$ scans
Absorption correction:
none
2300 measured reflections
2136 independent reflections
2016 observed reflections
[$F > 3\sigma(F)$]

Refinement

Refinement on F
Final $R = 0.039$
 $wR = 0.040$
 $S = 1.401$
2016 reflections
145 parameters
All H-atom parameters re-
fined

3 standard reflections
monitored every 50
reflections
intensity variation: $< 2\%$

$$w = 1/[\sigma^2(F) + 0.0005F^2]$$

$$(\Delta/\sigma)_{\max} = 0.36$$

$$\Delta\rho_{\max} = 0.96 \text{ e \AA}^{-3}$$

$$\Delta\rho_{\min} = -0.69 \text{ e \AA}^{-3}$$

Atomic scattering factors
from *International Tables*
for *X-ray Crystallography*
(1974, Vol. IV)

Cell parameters from 17
reflections

$$\theta = 13-15^\circ$$

$$\mu = 3.22 \text{ mm}^{-1}$$

$$T = 294 \text{ K}$$

Plate

$$0.3 \times 0.3 \times 0.15 \text{ mm}$$

Red

Crystal source: synthesized
by the method of Craw-
ford & Ingle (1971)

$$R_{\text{int}} = 0.016$$

$$\theta_{\max} = 27.5^\circ$$

$$h = -28 \rightarrow 28$$

$$k = 0 \rightarrow 8$$

$$l = 0 \rightarrow 19$$

3 standard reflections
monitored every 50
reflections
intensity variation: $< 1\%$

$$w = 1/[\sigma^2(F) + 0.001F^2]$$

$$(\Delta/\sigma)_{\max} = 0.09$$

$$\Delta\rho_{\max} = 1.48 \text{ e \AA}^{-3}$$

$$\Delta\rho_{\min} = -1.64 \text{ e \AA}^{-3}$$

Atomic scattering factors
from *International Tables*
for *X-ray Crystallography*
(1974, Vol. IV)

C(4)	0.3759 (2)	0.4615 (4)	0.2503 (3)	0.043
C(5)	0.3964 (2)	0.5333 (3)	0.1508 (3)	0.037
C(6)	0.4633 (2)	0.6160 (4)	0.1498 (4)	0.048
C(7)	0.4801 (2)	0.6841 (4)	0.0514 (4)	0.053
C(8)	0.4326 (2)	0.6718 (4)	-0.0514 (4)	0.049
C(9)	0.3668 (2)	0.5959 (4)	-0.0540 (3)	0.041
C(10)	0.3467 (2)	0.5247 (3)	0.0476 (3)	0.032
C(11)	0.1955 (2)	0.2857 (4)	0.1517 (4)	0.047
I(1)	0.61640 (2)	0.44038 (3)	0.38740 (2)	0.056
O	0.25	0.3220 (5)	0.5	0.076

Compound (II)

N(1)	0.1019 (1)	0.4355 (5)	0.0937 (2)	0.037
C(2)	0.1178 (2)	0.5861 (6)	0.0353 (3)	0.044
C(3)	0.1767 (2)	0.5934 (6)	-0.0047 (3)	0.042
C(4)	0.2190 (2)	0.4402 (5)	0.0202 (2)	0.033
C(5)	0.2027 (1)	0.2775 (5)	0.0868 (2)	0.030
C(6)	0.2451 (2)	0.1179 (6)	0.1179 (2)	0.037
C(7)	0.2269 (2)	-0.0353 (7)	0.1813 (3)	0.047
C(8)	0.1676 (2)	-0.0393 (7)	0.2141 (3)	0.053
C(9)	0.1258 (2)	0.1130 (8)	0.1860 (3)	0.047
C(10)	0.1423 (1)	0.2752 (5)	0.1229 (2)	0.034
C(11)	0.0379 (2)	0.4324 (9)	0.1268 (3)	0.053
I(1)	0.57798 (1)	0.42751 (4)	0.38814 (2)	0.046

Table 2. Bond distances (\AA), bond angles ($^\circ$) and selected torsion angles ($^\circ$) for (I) and (II)

Compound (I)

C(1)—N(2)	1.331 (4)	C(5)—C(10)	1.428 (5)
C(1)—C(10)	1.410 (5)	C(6)—C(7)	1.355 (7)
N(2)—C(3)	1.378 (5)	C(7)—C(8)	1.406 (7)
N(2)—C(11)	1.479 (5)	C(8)—C(9)	1.360 (6)
C(3)—C(4)	1.362 (6)	C(9)—C(10)	1.415 (5)
C(4)—C(5)	1.400 (5)	C(1)—C(1')	1.502 (6)
C(5)—C(6)	1.416 (6)		
N(2)—C(1)—C(10)	120.7 (3)	C(4)—C(5)—C(10)	118.3 (3)
N(2)—C(1)—C(1')	118.8 (3)	C(6)—C(5)—C(10)	119.1 (3)
C(10)—C(1)—C(1')	120.3 (3)	C(5)—C(6)—C(7)	120.1 (4)
C(1)—N(2)—C(3)	121.4 (3)	C(6)—C(7)—C(8)	120.7 (4)
C(1)—N(2)—C(11)	122.2 (3)	C(7)—C(8)—C(9)	121.3 (4)
C(3)—N(2)—C(11)	116.3 (3)	C(8)—C(9)—C(10)	119.6 (4)
N(2)—C(3)—C(4)	120.6 (4)	C(1)—C(10)—C(5)	118.5 (3)
C(3)—C(4)—C(5)	120.5 (4)	C(1)—C(10)—C(9)	122.4 (3)
C(4)—C(5)—C(6)	122.5 (4)	C(5)—C(10)—C(9)	119.1 (3)
N(2)—C(1)—C(1')—N(2')		-107.9 (4)	
C(10)—C(1)—C(1')—C(10')		-96.5 (4)	

Compound (II)

N(1)—C(2)	1.299 (5)	C(5)—C(10)	1.426 (5)
N(1)—C(10)	1.384 (4)	C(6)—C(7)	1.373 (6)
N(1)—C(11)	1.482 (6)	C(7)—C(8)	1.384 (7)
C(2)—C(3)	1.417 (6)	C(8)—C(9)	1.365 (7)
C(3)—C(4)	1.364 (5)	C(9)—C(10)	1.398 (6)
C(4)—C(5)	1.434 (5)	C(4)—C(4')	1.480 (7)
C(5)—C(6)	1.416 (5)		
C(2)—N(1)—C(10)	121.9 (3)	C(4)—C(5)—C(10)	119.3 (3)
C(2)—N(1)—C(11)	118.5 (4)	C(6)—C(5)—C(10)	118.9 (3)
C(10)—N(1)—C(11)	119.6 (3)	C(5)—C(6)—C(7)	119.3 (3)
N(1)—C(2)—C(3)	122.5 (4)	C(6)—C(7)—C(8)	121.3 (4)
C(2)—C(3)—C(4)	119.2 (4)	C(7)—C(8)—C(9)	120.8 (5)
C(3)—C(4)—C(5)	118.9 (3)	C(8)—C(9)—C(10)	120.2 (4)
C(3)—C(4)—C(4')	121.2 (3)	N(1)—C(10)—C(5)	118.2 (3)
C(5)—C(4)—C(4')	119.9 (3)	N(1)—C(10)—C(9)	122.3 (3)
C(4)—C(5)—C(6)	121.8 (3)	C(5)—C(10)—C(9)	119.5 (3)
C(3)—C(4)—C(4')—C(3')		73.1 (5)	
C(5)—C(4)—C(4')—C(5')		73.4 (4)	

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2) for (I) and (II)

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

Compound (I)	x	y	z	U_{eq}
C(1)	0.2793 (2)	0.4444 (3)	0.0507 (3)	0.032
N(2)	0.2633 (2)	0.3763 (3)	0.1471 (2)	0.034
C(3)	0.3110 (2)	0.3833 (4)	0.2471 (3)	0.043

In structure (I) the methyl group was treated as a rigid group. H atoms in the water molecule were not included. Other H atoms were refined isotropically. Program(s) used to solve structure: *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Program(s) used to refine structure: *SHELX76* (Sheldrick, 1976).

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, complete bond distances and angles, and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71024 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS1030]

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Structure of 2-Ethyl-2-nitroindan-1,3-dione

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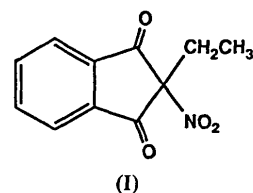
Abstract

The indan-1,3-dione system is slightly non-planar, with the tetrahedral C atom lying 0.149 (2) Å out of the best plane of the other eight C and two O atoms.

The terminal C atom of the ethyl group is directed *anti* to the nitro group and *gauche* to the carbonyl C atoms, forming C—C—C torsion angles of 53.3 (2) and –64.3 (2)°. The nitro group is nearly coplanar with the ethyl substituent, forming an O—N—C torsion angle of 175.9 (2)°. The C=O distances are 1.194 (2) and 1.204 (2) Å.

Comment

The crystal structures of a number of substituted indan-1,3-diones have been studied over the last 20 years on account of the well known anticoagulant activity of the parent compound in vitamin K dependent biosynthesis (Ernster, Lind & Rase, 1972; Bravic, Gaultier & Hauw, 1974; Csöregi & Eckstein, 1979). The crystal structure determination of the title compound (I), which was unexpectedly prepared by reacting 2-ethyl-1-inden-3-one-1-yl acetate with a



nitric acid–sulfuric acid 1:1 mixture (Garcia & Enas, 1992), affording colorless crystals when crystallized from slow cooling and evaporation of ethanol, is part of a program of structure analysis of some new derivatives of indan-1,3-dione. Structural data for 2-nitroindan-1,3-dione dihydrate (Selenius & Lundgren, 1980) and 2-(2-nitrobenzylidene)indan-1,3-dione (Varghese, Srinivasan, Ramadas & Padmanabhan, 1986) are in agreement with those of the title compound.

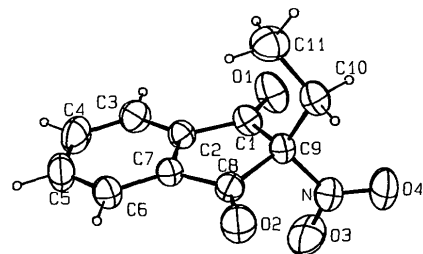


Fig. 1. ORTEP drawing (Johnson, 1965) of the molecule, representing heavy atoms as 40% probability ellipsoids and H atoms as circles of arbitrary radii.

Experimental

Crystal data

C₁₁H₉NO₄
M_r = 219.2
Monoclinic

D_x = 1.386 Mg m⁻³
Cu Kα radiation
λ = 1.54184 Å