the molecule. As expected, the values of some torsion angles differ considerably from those calculated for the chair–boat conformation of dimethylcyclodeca-1,5-diene (Guy, Sim & White, 1976), especially those for C(1) and C(10) involved in the *cis* fusion of the ten-membered ring with the O(1) five-membered ring.

The two five-membered rings which form a spiro-[4.4] system *via* C(12) show different conformations. The one containing O(1) can be described as a distorted C(10) half-chair with the asymmetry parameter $\Delta C_2 = 5.2$, and the other a distorted O(2) envelope with $\Delta C_s = 1.1$ [O(2) deviates from the plane through C(12), C(13), C(14) and C(15) by 0.10 Å] (Duax & Norton, 1975). For the ideal envelope conformation, $\Delta C_s = 0$, while for the ideal half-chair, $\Delta C_2 = 0$.

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Structures of 2,2′-Polymethylene-1,1′-biisoquinolinium Dibromides

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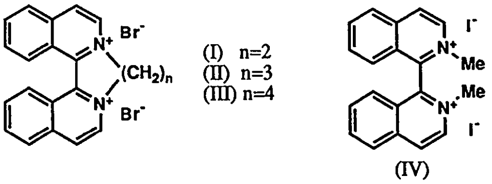
Abstract. 2,2′-Dimethylene-1,1′-biisoquinolinium dibromide (I), $C_{20}H_{16}N_2^{2+}.2Br^-$, $M_r = 444.15$, tetragonal, $I4_1/a$ (origin is located on $\bar{1}$), $a = 14.696$ (3), $c = 15.853$ (3) Å, $V = 3423.6$ (12) Å^3, $Z = 8$, $D_x = 1.72$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71068 Å, $\mu = 46.9$ cm^{-1}, $F(000) = 1760$, $T = 294$ K, $R = 0.041$ for 1201 unique observed reflections. 2,2′-Trimethylene-1,1′-biisoquinolinium dibromide monohydrate (II), $C_{21}H_{18}N_2^{2+}.2Br^-.H_2O$, $M_r = 476.17$, triclinic, $P\bar{1}$, $a = 9.934$ (2), $b = 13.285$ (3), $c = 7.969$ (1) Å, $\alpha = 95.32$ (1), $\beta = 92.64$ (2), $\gamma = 114.70$ (2)°, $V = 947.1$ (3) Å^3, $Z = 2$, $D_x = 1.67$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71068 Å, $\mu = 42.5$ cm^{-1}, $F(000) = 476$, $T = 294$ K, $R = 0.051$ for 3337 unique observed reflections. (I) shows C_2 symmetry and the molecular axis coincides with the crystallographic twofold axis, while the dication of (II) adopts a nearly C_2 symmetrical conformation. The dihedral angles between the two isoquinoline rings of (I) and (II) are 49.1 (1) and 61.9 (1)°, respectively.



Introduction. Bridged bisquaternary salts of 1,1′-biisoquinolines (I)–(IV) are known to produce a blue chemiluminescence in hydroxylic solvents by addition of base, and the efficiency of the chemiluminescence falls in the series of (I) > (II) > (III) > (IV) (Mason & Roberts, 1967). It was reported that (I) was reduced electrochemically or chemically to the radical cation and further to the neutral olefin, which was oxidized to biisoquinolone accompanying light emission (Heller, Henry & Fritsch, 1973). Redox properties and the chemiluminescence efficiency of these biisoquinolinium salts are expected to be greatly influenced by the degree of conjugation between the two heteroaromatic rings and the conformational flexibility. It was reported that reduction potentials of bisquaternary salts of 2,2′-biimidazoles are related to the dihedral angles between the two imidazole rings (Thummel, Goulle & Chen, 1989). In this study we have determined the crystal structures

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Table 1. *Final atomic coordinates with their e.s.d.'s* ($\times 10^4$, *for* Br $\times 10^5$) *and equivalent isotropic thermal parameters*, B_{eq} ($Å^2$), *for non-*H *atoms of* (I) *and* (II)

$$B_{eq} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

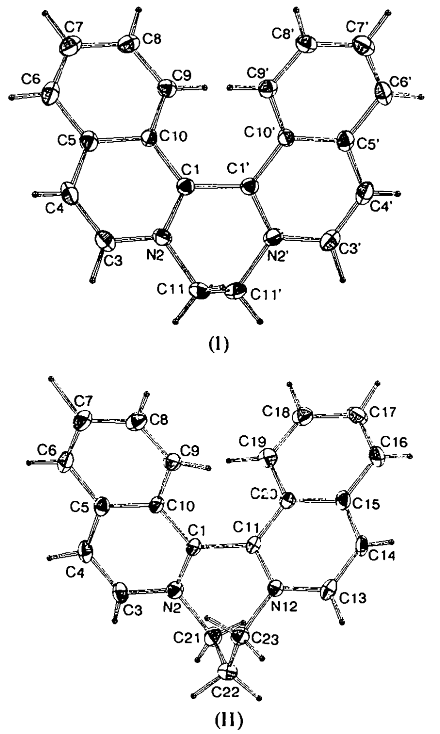
	x	y	z	B_{eq}
Compound (I)				
C(1)	4643 (3)	2862 (3)	1329 (3)	2.3
N(2)	4543 (2)	3336 (2)	609 (2)	2.7
C(3)	4004 (3)	4089 (3)	558 (3)	3.1
C(4)	3521 (3)	4356 (3)	1232 (3)	3.2
C(5)	3490 (3)	3825 (3)	1970 (3)	2.6
C(6)	2893 (3)	4020 (3)	2646 (3)	3.1
C(7)	2849 (3)	3457 (3)	3326 (3)	3.3
C(8)	3370 (3)	2659 (3)	3353 (3)	2.8
C(9)	3963 (3)	2447 (3)	2716 (3)	2.4
C(10)	4060 (3)	3036 (3)	2016 (3)	2.2
C(11)	5035 (4)	3007 (3)	−147 (3)	3.8
Br	92509 (3)	48872 (3)	−32670 (3)	3.7
Compound (II)				
C(1)	2801 (4)	7358 (3)	982 (5)	1.9
N(2)	3409 (4)	7585 (3)	2589 (4)	2.1
C(3)	4549 (4)	7329 (4)	3072 (6)	2.4
C(4)	5150 (5)	6869 (4)	1918 (6)	2.8
C(5)	4566 (4)	6602 (3)	206 (5)	2.2
C(6)	5133 (5)	6093 (4)	−1046 (7)	3.0
C(7)	4470 (6)	5777 (4)	−2644 (7)	3.1
C(8)	3147 (5)	5924 (4)	−3082 (6)	2.8
C(9)	2593 (5)	6434 (4)	−1927 (5)	2.3
C(10)	3303 (4)	6805 (3)	−264 (5)	2.1
C(11)	1620 (4)	7744 (3)	540 (5)	2.0
N(12)	381 (4)	7354 (3)	1360 (4)	2.1
C(13)	−757 (5)	7644 (4)	1037 (6)	2.7
C(14)	−693 (5)	8319 (4)	−175 (6)	2.7
C(15)	587 (5)	8780 (3)	−1026 (5)	2.4
C(16)	725 (6)	9524 (4)	−2258 (6)	2.9
C(17)	2018 (6)	10003 (4)	−2963 (6)	3.4
C(18)	3258 (6)	9782 (4)	−2508 (6)	2.9
C(19)	3159 (5)	9048 (4)	−1379 (6)	2.4
C(20)	1810 (4)	8517 (3)	−615 (5)	1.9
C(21)	2778 (6)	8088 (4)	3923 (6)	2.7
C(22)	1240 (6)	7256 (5)	4270 (6)	3.1
C(23)	255 (5)	6612 (4)	2670 (6)	2.6
Br(1)	15596 (5)	44139 (4)	25260 (7)	3.2
Br(2)	33962 (5)	9463 (4)	28602 (6)	3.1
O	2311 (5)	2794 (4)	5080 (5)	4.9

of (I) and (II) as part of our investigation on the redox properties and photochemical behaviour of (I)–(IV).

Experimental. (I) was obtained by heating 1,1′-biisoquinoline (Tiecco, Testaferri, Tingoli, Chianelli & Montanucci, 1984) and a large excess of 1,2-dibromoethane around 373 K. (II) was synthesized by a similar procedure using 1,3-dibromopropane.

(I) Brown plate-like crystal obtained from an ethanol solution, crystal dimensions 0.2 × 0.15 × 0.1 mm. Rigaku AFC-5 diffractometer, graphite-monochromated Mo $K\alpha$ radiation; cell parameters were refined by least squares on the basis of 17 independent 2θ values ($25 < 2\theta < 30°$); intensity data were collected up to $2\theta = 55°$ ($h = -17 \rightarrow 0$, $k = -17 \rightarrow 17$, $l = 0 \rightarrow 20$) using the ω–2θ scan technique; scan speed 4° min^{-1} in θ, scan width $(1.0 + 0.35\tan\theta)°$; background counts were accumulated 5 s before and after each scan, three standard reflections (608, 394, 952) were monitored every 50 reflections, no significant variation in intensities; 3169 reflections were measured, of which 1474 were unique, $R_{int} = 0.036$; 1201 reflections with $|F_o| > 3\sigma(|F_o|)$ were considered as observed and used for structure determination; corrections for Lorentz and polarization were made, absorption was ignored. The position of the bromide anion was determined by direct methods, and other non-H atoms were located by weighted Fourier calculations (*MULTAN*78; Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), subsequent difference Fourier map calculations, full-matrix least-squares refinement (*SHELX*76; Sheldrick, 1976) with anisotropic thermal parameters for non-H atoms and isotropic for H atoms; some H atoms were located on difference Fourier maps, other H-atom positions were calculated geometrically and then refined; $\sum w(|F_o| - |F_c|)^2$ minimized, where $w = [\sigma^2(|F_o|) + 0.00012|F_o|^2]^{-1}$; final $R = 0.041$ and $wR = 0.036$ for 1201 unique observed reflections and 141 refined parameters; $S = 1.69$; $(\Delta/\sigma)_{max} = 0.13$; final difference map showed $-0.36 < \Delta\rho < 0.47$ e Å^{-3}.

(II) Yellow plate-like crystal obtained from an MeOH–EtOH solution, crystal dimensions 0.35 × 0.2 × 0.15 mm; cell parameters were refined on the basis of 20 independent 2θ values ($25 < 2\theta < 30°$); inten-



(I)

(II)

Fig. 1. *ORTEP* plots (Johnson, 1965) of the biisoquinolinium ions with the atom numbering. The anisotropic ellipsoids for non-H atoms enclose 30% probability.

Table 2. *Bond distances* (Å), *bond angles* (°) *and selected torsion angles* (°) *for* (I) *and* (II)

Compound (I)		Compound (II)			
C(1)—N(2)	1.344 (5)	C(1)—N(2)	1.342 (6)	C(11)—N(12)	1.346 (6)
C(1)—C(10)	1.410 (6)	C(1)—C(10)	1.411 (6)	C(11)—C(20)	1.402 (6)
C(1)—C(1′)	1.494 (6)	C(1)—C(11)	1.504 (6)		
N(2)—C(3)	1.364 (6)	N(2)—C(3)	1.361 (6)	N(12)—C(13)	1.360 (6)
N(2)—C(11)	1.481 (7)	N(2)—C(21)	1.499 (7)	N(12)—C(23)	1.476 (6)
C(3)—C(4)	1.343 (7)	C(3)—C(4)	1.352 (7)	C(13)—C(14)	1.363 (7)
C(4)—C(5)	1.407 (7)	C(4)—C(5)	1.410 (7)	C(14)—C(15)	1.399 (7)
C(5)—C(6)	1.415 (7)	C(5)—C(6)	1.420 (7)	C(15)—C(16)	1.428 (7)
C(5)—C(10)	1.432 (6)	C(5)—C(10)	1.429 (6)	C(15)—C(20)	1.430 (6)
C(6)—C(7)	1.360 (7)	C(6)—C(7)	1.351 (8)	C(16)—C(17)	1.349 (9)
C(7)—C(8)	1.402 (7)	C(7)—C(8)	1.440 (8)	C(17)—C(18)	1.420 (8)
C(8)—C(9)	1.371 (7)	C(8)—C(9)	1.361 (7)	C(18)—C(19)	1.364 (7)
C(9)—C(10)	1.415 (6)	C(9)—C(10)	1.414 (7)	C(19)—C(20)	1.425 (7)
C(11)—C(11′)	1.495 (8)				
		C(21)—C(22)	1.522 (8)	C(22)—C(23)	1.516 (8)
N(2)—C(1)—C(10)	119.7 (4)	N(2)—C(1)—C(10)	120.3 (4)	C(1)—C(11)—N(12)	117.2 (4)
N(2)—C(1)—C(1′)	116.4 (4)	N(2)—C(1)—C(11)	118.3 (4)	N(12)—C(11)—C(20)	120.6 (4)
C(10)—C(1)—C(1′)	123.8 (4)	C(10)—C(1)—C(11)	121.3 (4)	C(1)—C(11)—C(20)	122.1 (4)
C(1)—N(2)—C(3)	122.3 (4)	C(1)—N(2)—C(3)	122.1 (4)	C(11)—N(12)—C(13)	121.6 (4)
C(1)—N(2)—C(11)	117.7 (4)	C(1)—N(2)—C(21)	119.6 (4)	C(11)—N(12)—C(23)	119.7 (4)
C(3)—N(2)—C(11)	120.0 (4)	C(3)—N(2)—C(21)	118.3 (4)	C(13)—N(12)—C(23)	118.6 (4)
N(2)—C(3)—C(4)	119.9 (5)	N(2)—C(3)—C(4)	120.5 (4)	N(12)—C(13)—C(14)	120.6 (5)
C(3)—C(4)—C(5)	121.1 (5)	C(3)—C(4)—C(5)	120.6 (5)	C(13)—C(14)—C(15)	120.3 (5)
C(4)—C(5)—C(6)	122.5 (4)	C(4)—C(5)—C(6)	122.8 (4)	C(14)—C(15)—C(16)	122.2 (5)
C(4)—C(5)—C(10)	118.2 (4)	C(4)—C(5)—C(10)	118.3 (4)	C(14)—C(15)—C(20)	118.8 (4)
C(6)—C(5)—C(10)	119.2 (4)	C(6)—C(5)—C(10)	118.9 (4)	C(16)—C(15)—C(20)	119.0 (4)
C(5)—C(6)—C(7)	120.4 (5)	C(5)—C(6)—C(7)	120.7 (5)	C(15)—C(16)—C(17)	120.0 (5)
C(6)—C(7)—C(8)	120.5 (5)	C(6)—C(7)—C(8)	120.0 (5)	C(16)—C(17)—C(18)	121.3 (6)
C(7)—C(8)—C(9)	121.0 (5)	C(7)—C(8)—C(9)	120.8 (5)	C(17)—C(18)—C(19)	120.7 (5)
C(8)—C(9)—C(10)	120.2 (4)	C(8)—C(9)—C(10)	119.8 (5)	C(18)—C(19)—C(20)	119.7 (5)
C(1)—C(10)—C(5)	117.6 (4)	C(1)—C(10)—C(5)	117.9 (4)	C(11)—C(20)—C(15)	117.8 (4)
C(1)—C(10)—C(9)	123.8 (4)	C(1)—C(10)—C(9)	122.5 (4)	C(11)—C(20)—C(19)	123.0 (4)
C(5)—C(10)—C(9)	118.5 (4)	C(5)—C(10)—C(9)	119.6 (4)	C(15)—C(20)—C(19)	119.2 (4)
N(2)—C(11)—C(11′)	106.9 (4)				
		N(2)—C(21)—C(22)	111.2 (4)	N(12)—C(23)—C(22)	111.1 (4)
		C(21)—C(22)—C(23)	113.1 (5)		
N(2)—C(1)—C(1′)—N(2′)	37.3 (5)	N(2)—C(1)—C(11)—N(12)	−59.7 (6)	C(1)—N(2)—C(21)—C(22)	69.1 (6)
N(2)—C(11)—C(11′)—N(2′)	64.3 (5)			C(11)—N(12)—C(23)—C(22)	73.2 (6)
		N(2)—C(21)—C(22)—C(23)	−43.6 (6)		
C(1)—N(2)—C(11)—C(11′)	40.4 (6)	N(12)—C(23)—C(22)—C(21)	−43.1 (6)		

sity data were collected up to $2\theta = 55°$ ($h = -12\rightarrow12$, $k = -17\rightarrow17$, $l = -10\rightarrow0$) by methods similar to those used for (I); three standard reflections ($\bar{5}6\bar{3}$, $2\bar{5}\bar{4}$, $2\bar{8}\bar{1}$) were monitored, no significant variation in intensities; 4663 reflections were measured, of which 3991 were unique, $R_{\text{int}} = 0.013$; 3337 reflections with $|F_o| > 3\sigma(|F_o|)$ were considered as observed and used for structure determination; direct methods (*SHELXS*86; Sheldrick, 1986); subsequent refinement was carried out by similar procedures to those for (I). $w = [\sigma^2(|F_o|) + 0.007|F_o|^2]^{-1}$; final $R = 0.051$ and $wR = 0.058$ for 3337 unique observed reflections and 307 refined parameters; $S = 0.81$; $(\Delta/\sigma)_{\max} = 0.14$; $-1.28 < \Delta\rho < 1.45$ e Å^{-3} (near the Br atoms). Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Calculations were carried out on a HITAC M-680 computer at the Computer Centre of the University of Tokyo and on an IBM 4381-R24 computer at Ochanomizu University. ^{1}H NMR spectra were obtained in D_2O solution with a JEOL JNM-GX270 spectrometer.

Discussion. The final atomic coordinates for non-H atoms are given in Table 1.* Fig. 1 shows the structure of the biisoquinolinium dications in (I) and (II) with the atomic numbering. Table 2 lists the bond distances, bond angles and selected torsion angles. In the crystal (I) is located on the crystallographic twofold axis; that is, the asymmetric unit contains one half of the dication and one bromide ion. ^{1}H NMR spectra of (I) and (II) in D_2O solution show non-equivalence of geminal N^+—CH_2 protons [δ 5.58, 5.42 (4H, ABq) for (I); δ 5.07 (*m*, 2H) and 4.45 (*m*, 2H) for (II)], indicating that both (I) and (II) exist in C_2 conformations in solution and that the conformational conversion is slow on the NMR

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* Lists of anisotropic thermal parameters for non-H atoms, positional and thermal parameters for H atoms, bond distances and angles, equations of least-squares planes, and observed structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54743 (25 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS0544]

time scale at room temperature. The chemically equivalent bond distances and angles of (II) are in good agreement with each other, which is consistent with the NMR spectral data. In both (I) and (II) the bond N(2)—C(3) is slightly longer than C(1)—N(2), suggesting that the canonical structure shown in the scheme is more dominant than the others. The corresponding bond distances and angles of (I) and (II) are almost the same within the experimental error. In the case of (I), however, the bond angle C(10)—C(1)—C(1′) [123.8 (4)°] is somewhat enlarged, while N(2)—C(1)—C(1′) is reduced to 116.4 (4)°. Although the isoquinoline rings in (I) and (II) are almost planar, maximum deviations from the least-squares plane composed of C(1)–C(10) are 0.11, 0.08 and 0.07 Å at C(1) in (I), C(1) and C(11) in (II), respectively. As a whole, the deviations of the atoms in (I) are larger than those in (II). Furthermore, C(1′) and C(11) in (I) are shifted from the plane by 0.30 and 0.32 Å in opposite directions, while the corresponding values for (II) are 0.26 [C(11)] and 0.05 Å [C(21)] or 0.16 [C(1)] and 0.07 Å [C(23)]. These results clearly indicate that the isoquinolinium moiety in (I) is more strained than that in (II) due to large steric repulsion between H(9) and H(9′). The two isoquinoline rings in (II) are rotated more from each other than those in (I). The difference in the dihedral angle of the two rings between (I) and (II) [49.1 (1) *vs* 61.9 (1)°] is probably a reflection of the different redox properties of those salts such as reduction potentials and reactivity to reductants, which will be discussed elsewhere. The out-of-plane deformation of the isoquinoline rings also may influence the electronic state of these salts.

Heller *et al.* (1973) reported that the sample of (I) was obtained as the monohydrate, but we obtained crystals of (I) without water of crystallization. On the other hand, the crystal of (II) contains water molecules in the ratio 1:1. The water molecule is hydrogen bonded to two bromide ions (Fig. 2). The distances Br(1)—O and Br(2)—O are 3.368 (5) and 3.449 (5) Å, respectively, and the angle Br(1)—O—Br(2) is 111.7 (2)°. Although the dication in (II) almost adopts a C_2 conformation as already described, the two bromide ions and one water molecule are not symmetrically located about the approximate C_2 axis passing through C(22) and the midpoint of C(1) and C(11). There is no significant intermolecular short contact both in (I) and (II).

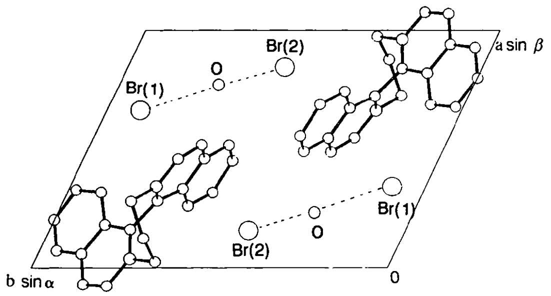

Fig. 2. Crystal structure of (II) viewed along the *c* axis. The broken lines indicate hydrogen bonds.

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The First Structure of a Benzo[*b*][1,4]diazocine

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Abstract. 1-Ethyl-1,2-dihydro-3-methyl-5-phenylbenzo[*b*][1,4]diazocin-2-one, $C_{19}H_{18}N_2O$, $M_r = 290.4$, monoclinic, $P2_1/c$, $a = 9.714$ (3), $b = 10.087$ (5), $c = 15.758$ (8) Å, $\beta = 91.67$ (4)°, $V = 1543.4$ Å^3, $Z = 4$, $D_x = 1.25$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu = 0.73$ cm^{-1}, $F(000) = 616$, $T = 295$ K, $R = 0.033$

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