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.

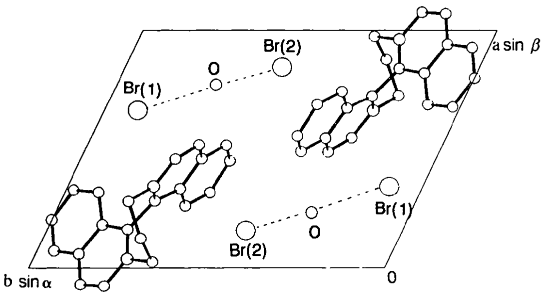

Fig. 2. Crystal structure of (II) viewed along the *c* axis. The broken lines indicate hydrogen bonds.

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).

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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, $R = 0.033$

for 1806 observed reflections. This novel ring system, prepared by an unprecedented ring expansion of a benzimidazole, has a chiral 'tub' structure.

Introduction. The reaction of 1-ethylbenzimidazole (1) with the electron-deficient alkyne (2) in refluxing toluene gives a 1:1 adduct as the only product. This substance was tentatively assigned structure (4) to satisfy spectral data, most notably the H,CH_3 coupling constant of 1.6 Hz in the ^1H NMR spectrum, the low carbonyl stretching frequency (1662 cm^{-1}) and the lack of absorptions at wavelengths greater than 330 nm in the ultraviolet spectrum (Acheson, Wallis & Woollard, 1979). However, this structure could only be produced by a unprecedented ring-expansion process proceeding *via* the intermediate (3) as shown in the scheme below. [Attack on (3) by a trace of water could, in principle, effect the conversion too.] To confirm this structure, which is related to the important anxiolytic benzodiazepine drug valium, the X-ray crystal structure analysis was undertaken.

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (4) *with e.s.d.'s in parentheses*

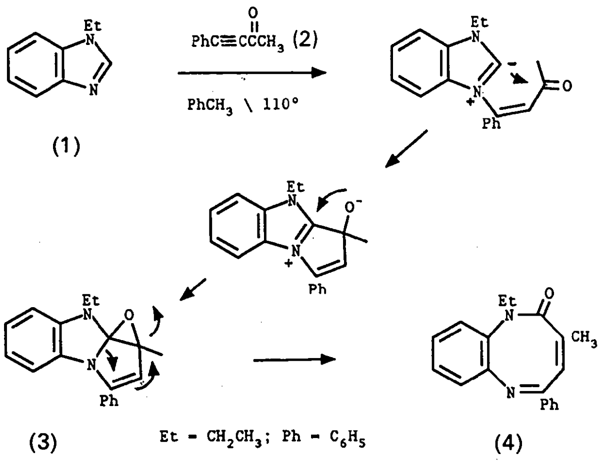
$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
O(21)	0.7049 (2)	−0.0924 (2)	0.03233 (8)	0.054 (1)
N(1)	0.8097 (2)	−0.0752 (2)	0.16177 (9)	0.038 (1)
N(6)	0.7944 (2)	−0.3321 (2)	0.2447 (1)	0.040 (1)
C(2)	0.7016 (2)	−0.1059 (2)	0.1097 (1)	0.037 (1)
C(3)	0.5724 (2)	−0.1545 (2)	0.1492 (1)	0.040 (1)
C(4)	0.5679 (2)	−0.2741 (2)	0.1843 (1)	0.042 (1)
C(5)	0.6903 (2)	−0.3615 (2)	0.1964 (1)	0.039 (1)
C(6a)	0.7971 (2)	−0.2118 (2)	0.2907 (1)	0.039 (1)
C(7)	0.7996 (2)	−0.2187 (3)	0.3791 (1)	0.050 (1)
C(8)	0.8062 (3)	−0.1054 (3)	0.4275 (1)	0.058 (1)
C(9)	0.8127 (3)	0.0175 (3)	0.3896 (1)	0.057 (1)
C(10)	0.8123 (2)	0.0265 (2)	0.3017 (1)	0.048 (1)
C(10a)	0.8041 (2)	−0.0876 (2)	0.2525 (1)	0.037 (1)
C(11)	0.9403 (2)	−0.0316 (2)	0.1259 (1)	0.047 (1)
C(12)	1.0355 (3)	−0.1455 (3)	0.1103 (2)	0.071 (1)
C(31)	0.4500 (3)	−0.0655 (3)	0.1373 (2)	0.058 (1)
C(51)	0.6901 (2)	−0.4928 (2)	0.1530 (1)	0.040 (1)
C(52)	0.5721 (3)	−0.5436 (3)	0.1136 (2)	0.056 (1)
C(53)	0.5739 (3)	−0.6680 (3)	0.0756 (2)	0.063 (1)
C(54)	0.6925 (3)	−0.7408 (2)	0.0755 (2)	0.057 (1)
C(55)	0.8112 (3)	−0.6900 (2)	0.1128 (2)	0.062 (1)
C(56)	0.8099 (2)	−0.5672 (2)	0.1518 (2)	0.052 (1)

Table 2. *Bond lengths* (Å) *and bond angles* (°) *for* (4) *with e.s.d.'s in parentheses*

O(21)—C(2)	1.228 (2)	C(6a)—C(10a)	1.393 (3)
N(1)—C(2)	1.350 (3)	C(7)—C(8)	1.374 (4)
N(1)—C(10a)	1.438 (2)	C(8)—C(9)	1.378 (4)
N(1)—C(11)	1.471 (3)	C(9)—C(10)	1.388 (3)
N(6)—C(5)	1.282 (3)	C(10)—C(10a)	1.389 (3)
N(6)—C(6a)	1.413 (3)	C(11)—C(12)	1.500 (4)
C(2)—C(3)	1.499 (3)	C(51)—C(52)	1.386 (3)
C(3)—C(4)	1.329 (3)	C(51)—C(56)	1.385 (3)
C(3)—C(31)	1.497 (4)	C(52)—C(53)	1.391 (4)
C(4)—C(5)	1.489 (3)	C(53)—C(54)	1.366 (4)
C(5)—C(51)	1.490 (3)	C(54)—C(55)	1.377 (4)
C(6a)—C(7)	1.393 (3)	C(55)—C(56)	1.384 (4)

C(2)—N(1)—C(10a)	122.2 (2)	C(6a)—C(7)—C(8)	120.8 (2)
C(2)—N(1)—C(11)	120.0 (2)	C(7)—C(8)—C(9)	120.7 (2)
C(10a)—N(1)—C(11)	117.8 (2)	C(8)—C(9)—C(10)	119.5 (2)
C(5)—N(6)—C(6a)	120.4 (2)	C(9)—C(10)—C(10a)	120.1 (2)
O(21)—C(2)—N(1)	122.4 (2)	N(1)—C(10a)—C(6a)	120.8 (2)
O(21)—C(2)—C(3)	119.6 (2)	N(1)—C(10a)—C(10)	118.7 (2)
N(1)—C(2)—C(3)	118.0 (2)	C(6a)—C(10a)—C(10)	120.4 (2)
C(2)—C(3)—C(4)	120.5 (2)	N(1)—C(11)—C(12)	112.1 (2)
C(2)—C(3)—C(31)	115.0 (2)	C(5)—C(51)—C(52)	121.6 (2)
C(4)—C(3)—C(31)	124.1 (2)	C(5)—C(51)—C(56)	119.8 (2)
C(3)—C(4)—C(5)	123.8 (2)	C(52)—C(51)—C(56)	118.5 (2)
N(6)—C(5)—C(4)	123.5 (2)	C(51)—C(52)—C(53)	120.4 (2)
N(6)—C(5)—C(51)	117.9 (2)	C(52)—C(53)—C(54)	120.4 (2)
C(4)—C(5)—C(51)	118.5 (2)	C(53)—C(54)—C(55)	119.7 (2)
N(6)—C(6a)—C(7)	118.0 (2)	C(54)—C(55)—C(56)	120.3 (2)
N(6)—C(6a)—C(10a)	123.4 (2)	C(51)—C(56)—C(55)	120.6 (2)
C(7)—C(6a)—C(10a)	118.5 (2)		



Experimental. Small colourless blocks of (4) were grown from methanol, m.p. 491.5–492.5 K, Enraf–Nonius CAD-4 diffractometer; Mo $K\alpha$ radiation, graphite monochromator; ω scans; crystal dimensions 0.3 × 0.3 × 0.25 mm, unit-cell dimensions by least-squares fit to setting angles of 12 automatically centred reflections with $10 < \theta < 12°$. Room-temperature measurement, no absorption correction, max. $(\sin\theta)/\lambda$ in intensity measurements 0.64 Å^{-1}, two standard reflections monitored (no change in intensity), 3323 reflections measured, 2847 unique, $R_{int} = 0.01$, 1806 counted as observed [$I > 3\sigma(I)$], index range h −11/11, k 0/12, l 0/20. $0k0$ reflections absent for k = odd, $h0l$ absent for l = odd. Structure solved in $P2_1/c$ (*MULTAN*80) and refined on F by full-matrix least-squares analyses including anisotropic displacement parameters for non-H atoms (*SHELX*76). H-atom positions located and allowed to refine isotropically. An extinction parameter (5.92) was refined and included in the refinement (*XRAY*), 272 parameters refined. A modified weighting scheme (Dunitz & Seiler, 1973) with $r = 4.0$ Å^2 was used. The model converged to $R = 0.033$, $wR = 0.039$. Max. Δ/σ in final cycle for positional parameters: 0.004; for displacement parameters: 0.01. Max. and min. residual electron density in final difference Fourier synthesis 0.21 and $-0.20\,e\,Å^{-3}$. Computer programs: *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), *SHELX*76 (Sheldrick, 1976) and *XRAY* (Stewart, Kruger, Ammon, Dickinson & Hall, 1972); molecular illustrations with *PLUTO* (Motherwell & Clegg, 1978). Atomic scattering factors for O, N, C from Cromer & Mann (1968), for H from Stewart, Davidson & Simpson (1965).

Discussion. The structure (4) was confirmed and this is the first structural report on a benzo[*b*][1,4]diazocine. Fractional atomic coordinates and equivalent isotropic displacement parameters are given in Table 1* and bond lengths and angles in Table 2. The illustrations of the molecule in Figs. 1 and 2 clearly show the chiral 'tub' structure adopted by the eight-membered ring. Both enantiomers are present in the crystal. The fused benzene ring forms part of one side of the 'tub' and lies at 130 (1)° to the base of the 'tub' [N(1), C(2), C(5) and N(6)]. The other side of the tub [C(2), C(3), C(4) and C(5)] makes a similar angle [127 (1)°] to the base and the two sides lie at 78 (1)° to one another. The eight-membered ring does not deviate too far from *mm* symmetry; the torsion angles about N(1)—C(2) and C(5)—N(6) round the ring are both less than 1°. The bonding about the amide and imine groups is planar and there is no significant deviation from the normal bonding geometry associated with these groups (Chakrabati & Dunitz, 1982). The ring structure directs the ethyl and phenyl substituents behind the cavity of the 'tub'. The methylene H atoms are diastereotopic due to the chiralty of the ring structure and are non-equivalent in the ^{1}H NMR spectrum of a $CDCl_3$ solution (δ 3.16 and 4.18). The phenyl group lies at 55 (1)° to the base of the 'tub' and not far from coplanarity with the imine bond [torsion angles N(6)—C(5)—C(51)—C(52) 167 (1), N(6)—C(5)—C(51)—C(56) −13 (1)°]. The ring structure is similar to that of benzocyclooctatetraene (Li, Chiu, Mak & Huang, 1983) though the latter has a slightly more open 'tub' [both side/base angles 139 (1)°]. Apart from the amide C,N bond, the bond lengths in the diazocine ring show no signs of π-electron delocalization, as expected for an 8π system. The crystal packing is shown in Fig. 2. The molecules are packed in interlocking layers perpendicular to the *a* axis with the fused benzene rings lying in the *bc* plane. Only one intermolecular contact is shorter than the sum of the appropriate van der Waals radii: O(21)···H(71)(x, $-y-0.5$, $z-0.5$) 2.450 (4) Å.

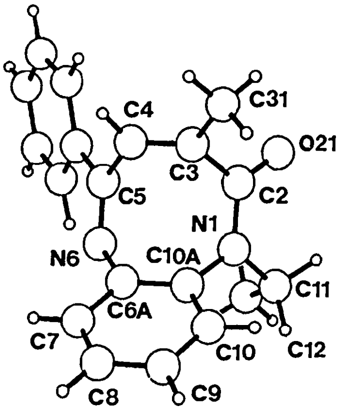


Fig. 1. View of (4) with atom-numbering scheme. The phenyl ring is numbered from C(51) to C(56) starting from the substituted carbon.

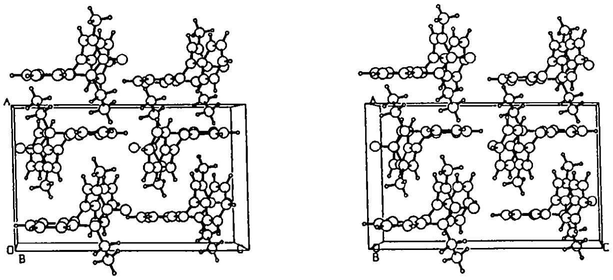


Fig. 2. Crystal packing of (4) viewed down the *b* axis.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54775 (27 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL0503]

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