

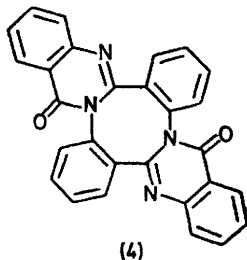
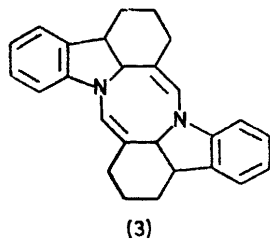
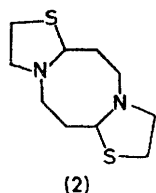
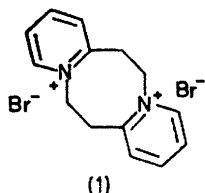
Synthesis, Spectra, and Crystal Structure of 6,7,14,15-Tetrahydrobis-benzimidazo[1,2-*a*;1',2'-*e*][1,5]diazocine

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2-[2-(4-Methylpyridinio)ethyl]benzimidazole (7a) and its 5,6-dimethyl derivative (7b) are converted by pyridine into cyclic dimers (8a and b), the spectra of which are described. An X-ray diffraction study of the tetrahydrobis-benzimidazodiazocine (8a) has verified the molecular structure.

THE 1,5-diazocine system has been described several times since its first synthesis,¹ but it is rare for each nitrogen atom to belong to another heterocyclic ring; the literature reports four such examples [(1),² (2),³ (3),⁴ and (4)⁵].



3-(4-Methylpyridinio)propionic acid bromide (5) reacted with *o*-phenylenediamine (6a) to yield the benz-

imidazole derivative (7a). Heating this under reflux in pyridine or acetonitrile gave a sparingly soluble high-melting product shown to be the pentacyclic diazo-octane derivative (8a). The mass spectrum shows the molecular ion peak at *m/e* 288. The u.v. spectrum shows absorptions at 248, 253.5, 268, 275, and 282.5 nm, characteristic of a benzimidazole derivative.⁶ The n.m.r. spectrum shows an aromatic multiplet (8 H, four different protons) together with two triplets at τ 4.95 (4 H) and 6.00 (4 H) (*J* 6.5 Hz) characteristic of the CH₂-CH₂ structure. Given the molecular weight, this evidence strongly indicates structure (8a).

4,5-Dimethyl-1,2-phenylenediamine (6b) reacted similarly to give, *via* the intermediate (7b), the tetramethyl analogue (8b).

Methylation of (8a) with methyl toluene-*p*-sulphonate gave the toluene-*p*-sulphonate salt of 1-methyl-2-vinylbenzimidazole (10) instead of the expected quaternary salt (9). 2-Vinylbenzimidazole has been obtained by oxidative condensation of acrylaldehyde and *o*-phenylenediamine (yield 2%);⁷ other methods lead to a polymer.⁷ In consequence (8) must be formed directly from (7) and not through a 2-vinylbenzimidazole intermediate.

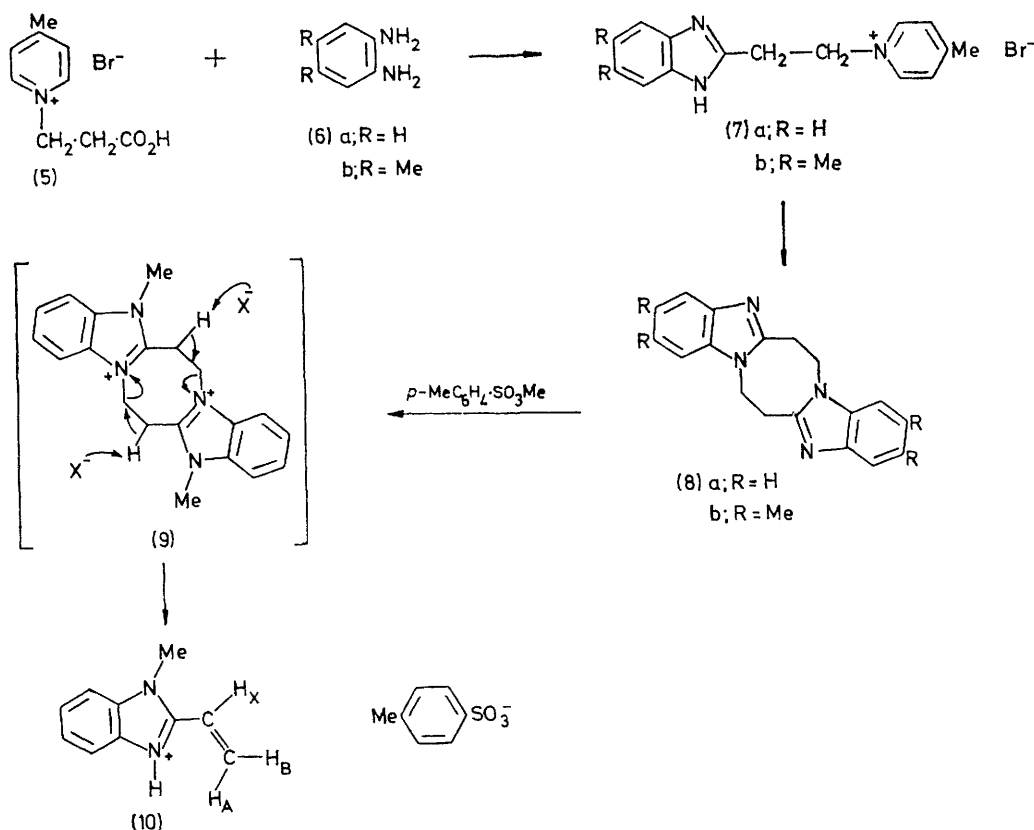
The molecular structure of (8a) has been confirmed by

¹ C. C. Howard and W. Marckwald, *Ber.*, 1899, **32**, 2038.
² V. Boekelheide and W. Feely, *J. Amer. Chem. Soc.*, 1958, **80**, 2217.
³ D. A. Johnson and C. A. Panetta, *J. Org. Chem.*, 1964, **29**, 1826.

⁴ K. Bernauer, *Helv. Chim. Acta*, 1963, **46**, 197.
⁵ A. Chatterjee and M. Ganguly, *J. Org. Chem.*, 1968, **33**, 3358.
⁶ N. F. Cheetham, W. F. Forbes, D. J. Kew, and P. F. Nelson, *Austral. J. Chem.*, 1963, **16**, 729.
⁷ C. G. Overberger, B. Kösters, and T. St. Pierre, *J. Polymer Sci.*, 1967, Part A-1, **5**, 1987.

an X-ray single-crystal diffraction study. The crystal structure consists of discrete molecules situated across crystallographic inversion centres such that only one-half of the atoms in the molecule are included in the

deviation from the plane being 0.005(2) Å; the methylene carbon atoms, C(1) and C(4), deviate from this plane by only 0.008(2) and 0.069(2) Å, respectively. The diazacyclo-octane ring exists in the chair conformation.

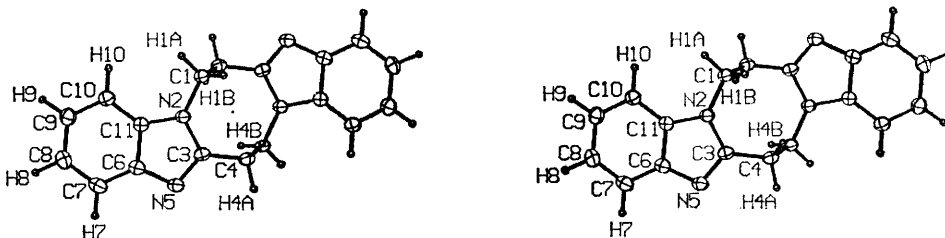


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asymmetric unit. A stereodrawing of the molecule with the atom labelling scheme is presented in the Figure. The intramolecular bond distances and angles are given in Table I; no unusual values were found. For example,

EXPERIMENTAL

M.p.s were measured on a Gallenkamp capillary apparatus. N.m.r. spectra were recorded on a Perkin-Elmer R12 instrument with tetramethylsilane as external standard.



Stereoview of the molecule (8a) with the atom-labelling scheme; the molecule resides across a crystallographic centre of symmetry

the values within the benzimidazole unit are in excellent agreement with those for benzimidazole itself,⁸ with the exception of the N(2)-C(3) bond length which has increased from 1.346(4) to 1.373(2) Å, evidently reflecting the bulkier nature of the methylene substituents. The benzimidazole system is near planar, with the largest

Mass spectral data were obtained on a Hitachi-Perkin-Elmer RMU-6E low resolution instrument. U.v. spectra (ethanol) were measured on a Pye-Unicam SP 800A instrument. Microanalyses were performed by Mr. A. W. R. Saunders (University of East Anglia).

⁸ C. J. Dik-Edixhouen, H. Schenk, and H. van der Meer, *Cryst. Struct. Comm.*, 1973, **2**, 23.

3-(4-Methylpyridinio)propionic Acid Bromide (5).—3-Bromopropionic acid (7.65 g, 5×10^{-2} mol) and 4-methylpyridine (4.70 g, 5×10^{-2} mol) were heated under reflux in acetonitrile (30 ml) for 3 h. Acetonitrile was removed by

TABLE 1

Bond distances (Å) and angles (deg) for 6,7,14,15-tetrahydrobisbenzimidazo[1,2-a;1',2'-e][1,5]diazocine, with estimated standard deviations in parentheses

Atoms	Distance	Atoms	Distance
C(1)–N(2)	1.457(2)	C(6)–C(7)	1.391(3)
C(1)–C(4')	1.536(3)	C(6)–C(11)	1.398(2)
C(1)–H(1A)	0.96(2)	C(7)–C(8)	1.378(2)
C(1)–H(1B)	1.00(2)	C(7)–H(7)	0.97(2)
N(2)–C(3)	1.373(2)	C(8)–C(9)	1.398(3)
N(2)–C(11)	1.386(2)	C(8)–H(8)	0.99(2)
C(3)–C(4)	1.488(3)	C(9)–C(10)	1.378(3)
C(3)–N(5)	1.315(2)	C(9)–H(9)	1.00(2)
C(4)–H(4A)	1.00(2)	C(10)–C(11)	1.393(3)
C(4)–H(4B)	0.99(2)	C(10)–H(10)	0.99(2)
N(5)–C(6)	1.391(2)		

Atoms	Angle	Atoms	Angle
N(2)–C(1)–C(4')	114.2(2)	N(5)–C(6)–C(7)	130.1(2)
N(2)–C(1)–H(1A)	108(1)	N(5)–C(6)–C(11)	110.0(1)
N(2)–C(1)–H(1B)	108(1)	C(7)–C(6)–C(11)	119.9(2)
C(4)–C(1)–H(1A)	110(1)	C(6)–C(7)–C(8)	118.0(2)
C(4)–C(1)–H(1B)	112(1)	C(6)–C(7)–H(7)	120(1)
H(1A)–C(1)–H(1B)	105(1)	C(8)–C(7)–H(7)	122(1)
C(1)–N(2)–C(3)	127.9(1)	C(7)–C(8)–C(9)	121.4(2)
C(1)–N(2)–C(11)	125.7(1)	C(7)–C(8)–H(8)	119(1)
C(3)–N(2)–C(11)	106.4(1)	C(9)–C(8)–H(8)	119(1)
N(2)–C(3)–C(4)	122.8(2)	C(8)–C(9)–C(10)	121.7(2)
N(2)–C(3)–N(5)	113.2(1)	C(8)–C(9)–H(9)	119(1)
C(4)–C(3)–N(5)	123.9(2)	C(10)–C(9)–H(9)	120(1)
C(3)–C(4)–C(1)'	114.1(2)	C(9)–C(10)–C(11)	116.5(2)
C(3)–C(4)–H(4A)	107(1)	C(9)–C(10)–H(10)	120(1)
C(3)–C(4)–H(4B)	110(1)	C(11)–C(10)–H(10)	124(1)
C(1)–C(4)–H(4A)	109(1)	N(2)–C(11)–C(6)	105.5(1)
C(1)–C(4)–H(4B)	110(1)	N(2)–C(11)–C(10)	132.0(2)
H(4A)–C(4)–H(4B)	106(1)	C(6)–C(11)–C(10)	122.5(2)
C(3)–N(5)–C(6)	104.9(1)		

evaporation under reduced pressure to give the *bromide* (5) (9.8 g, 80%) as prisms (from acetonitrile), m.p. 163–165° (Found: C, 43.8; H, 5.0; N, 5.7. $C_9H_{12}BrNO_2$ requires C, 43.9; H, 4.9; N, 5.7%); τ ($CF_3 \cdot CO_2H$) 1.16 (2 H, d), 2.09 (2 H, d), 5.0 (2 H, t), 6.62 (2 H, t), and 7.29 (3 H, s).

2-[2-(4-Methylpyridinio)ethyl]benzimidazole Bromide (7a).—*o*-Phenylenediamine (1.6 g, 1.5×10^{-2} mol) was added to 3-(4-methylpyridinio)propionic acid bromide (5) (2.5 g, 1×10^{-2} mol) in 2N-hydrobromic acid (30 ml). The mixture was heated under reflux for 5 h, neutralised with aqueous NaHCO₃ and filtered. The solvent was removed under reduced pressure and the product extracted with hot dry acetone (2 × 200 ml). Cooling the acetone extract gave the *bromide* (7a) (0.7 g, 22%) as needles (from acetone), m.p. 104–106° (Found: C, 56.0; H, 5.0; N, 13.0. $C_{15}H_{16}BrN_3$ requires C, 56.6; H, 5.0; N, 13.2%); τ (D_2O) 1.6 (2 H, d), 2.34 (2 H, d), 2.47–3.0 (4 H, m), 5.1 (2 H, t), 6.5 (2 H, t), and 7.5 (3 H, s).

5,6-Dimethyl-2-[2-(4-methylpyridinio)ethyl]benzimidazole Bromide (7b).—A similar reaction with 4,5-dimethyl-1,2-phenylenediamine (2.04 g, 1.5×10^{-2} mol) and a refluxing time of 10 h gave the *bromide* (7b) (0.7 g, 20%) as needles (from acetone-ether), m.p. 154–155° (Found: C, 58.6; H, 5.8; N, 12.2. $C_{17}H_{20}BrN_3$ requires C, 59.0; H, 5.8; N, 12.1%); τ ($CF_3 \cdot CO_2H$) 1.53 (2 H, d), 2.47 (2 H, d), 2.80

(2 H, s), 5.10 (2 H, t), 6.20 (2 H, t), 7.63 (3 H, s), and 7.90 (6 H, s).

6,7,14,15-Tetrahydrobisbenzimidazo[1,2-a;1',2'-e][1,5]-diazocine (8a).—2-[2-(4-Methylpyridinio)ethyl]benzimidazole bromide (7a) (1.59 g, 5×10^{-3} mol) was heated under reflux in pyridine (30 ml) for 3 h, and kept at 20 °C overnight to give the 1,5-diazacyclo-octane (8a) (0.3 g, 42%) as white prisms, m.p. 297–300° (from pyridine) (Found: C, 75.0; H, 5.7; N, 19.4. $C_{18}H_{16}N_4$ requires C, 75.0; H, 5.6; N, 19.4%); m/e 288 (M^+); λ_{max} (EtOH) 248 (ϵ 13 100), 253.5 (13 400), 268sh (8 900), 275 (10 700), and 282.5 nm (11 000); τ ($CF_3 \cdot CO_2H$) 2.4–2.8 (8 H, m), 4.95 (4 H, t), and 6.0 (4 H, t). The same product (8a) was obtained (51%) when the reaction was carried out in acetonitrile.

6,7,14,15-Tetrahydro-2,3,10,11-tetramethylbisbenzimidazo[1,2-a,1',2'-e][1,5]diazocine (8b).—In a similar reaction the bromide (7b) (0.4 g, 1.2×10^{-3} mol) gave the 1,5-diazacyclo-octane (8b) (0.2 g, 95%) as prisms, m.p. 311–314°

TABLE 2

Crystallographic data

(a) Final atomic co-ordinates for the non-hydrogen atoms, with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
C(1)	0.4019(2)	0.4834(4)	0.3643(1)
N(2)	0.3503(1)	0.3666(3)	0.4415(1)
C(3)	0.3785(1)	0.4280(4)	0.5538(1)
C(4)	0.4742(2)	0.6261(4)	0.6166(2)
N(5)	0.3164(1)	0.2842(3)	0.6007(1)
C(6)	0.2416(1)	0.1186(4)	0.5140(1)
C(7)	0.1567(2)	–0.0747(4)	0.5151(2)
C(8)	0.0949(2)	–0.2132(4)	0.4160(2)
C(9)	0.1165(2)	–0.1633(4)	0.3170(2)
C(10)	0.1997(2)	0.0280(4)	0.3136(2)
C(11)	0.2618(1)	0.1668(4)	0.4143(1)

(b) Anisotropic thermal parameters ($\times 10^4$) in the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{23}hkb^*c^*)]$ for the non-hydrogen atoms

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	323(10)	339(11)	219(9)	6(9)	92(8)	11(9)
N(2)	300(8)	330(8)	237(7)	6(7)	108(6)	15(6)
C(3)	295(9)	315(10)	246(9)	72(9)	102(7)	10(8)
C(4)	367(11)	332(11)	259(9)	16(9)	145(8)	–32(9)
N(5)	324(8)	395(9)	285(8)	25(7)	144(7)	23(7)
C(6)	273(9)	337(10)	312(9)	58(8)	118(8)	52(8)
C(7)	355(11)	462(12)	378(11)	32(10)	179(9)	96(10)
C(8)	316(10)	376(12)	391(11)	6(9)	103(9)	–26(9)
C(9)	314(11)	389(12)	483(12)	–38(10)	135(9)	31(10)
C(10)	307(10)	363(11)	310(10)	35(9)	118(8)	0(9)
C(11)	257(9)	282(10)	285(9)	40(8)	102(7)	16(8)

(c) Positional and thermal parameters for the hydrogen atoms

Atom	x/a	y/b	z/c	U
H(1A)	0.350(1)	0.443(4)	0.288(2)	0.029(5)
H(1B)	0.401(1)	0.693(4)	0.371(1)	0.023(4)
H(4A)	0.468(1)	0.660(4)	0.692(2)	0.034(5)
H(4B)	0.462(1)	0.811(4)	0.578(1)	0.027(5)
H(7)	0.142(2)	–0.106(4)	0.584(2)	0.042(5)
H(8)	0.035(2)	–0.354(4)	0.415(2)	0.042(5)
H(9)	0.070(1)	–0.268(4)	0.247(2)	0.036(5)
H(10)	0.213(1)	0.058(4)	0.243(1)	0.035(5)

(pyridine) (Found: C, 76.2; H, 6.8; N, 16.2. $C_{22}H_{24}N_4$ requires C, 76.7; H, 6.9; N, 16.3%); m/e 344 (M^+); λ_{max} (EtOH) 251.5 (ϵ 11 700), 257 (11 400), 276.5 sh (9 200), 281.5 (11 600), 285 (11 200), and 291 nm (11 700); τ ($CF_3 \cdot CO_2H$) 2.88 (2 H, s), 3.0 (2 H, s), 5.32 (4 H, t), 6.22 (4 H, t, J 6.5 Hz), 7.93 (6 H, s), and 8.0 (6 H, s).

1-Methyl-2-vinylbenzimidazolium *Toluene-p-sulphonate* (10).—The bisbenzimidazodiazocine (8a) (0.4 g, 1.4×10^{-3} mol) was stirred at 240 °C in methyl toluene-*p*-sulphonate (5 ml) for 0.5 h. Ether (150 ml) was added to remove the excess of tosylate. The insoluble brown residue was dissolved in acetone (20 ml), and ether (200 ml) was added to give the *toluene-p-sulphonate* (10) (88%) as plates, m.p. 175–178° (from acetone-ether) (Found: C, 61.8; H, 5.9; N, 8.4. $C_{17}H_{16}N_2O_3S$ requires C, 61.8; H, 5.5; N, 8.5%); τ (D_2O) 2.5 (4 H, m), 2.6 (2 H, d), 3.1 (2 H, d), 6.22 (3 H, s), and 7.9 (3 H, s); vinyl system τ_A 3.23 (q), τ_B 3.70 (q), τ_X 3.85 (q); J_{AB} 1, J_{AX} 18, J_{BX} 12 Hz (the chemical shifts are close to those for 2-vinylbenzimidazole⁹).

Crystal Structure of the Bisbenzimidazodiazocine (8a).—*Crystal Data.* $C_{18}H_{16}N_4$, $M = 288.36$. Monoclinic, space group $P2_1/c$, $a = 12.228(4)$, $b = 4.756(1)$, $c = 12.717(4)$ Å, $\beta = 111.45(3)^\circ$, $U = 688.4$ Å³, $D_m = 1.37$ g cm⁻³, $Z = 2$, $D_c = 1.391$ g cm⁻³, at -40 °C. Mo- K_α radiation, $\mu = 0.93$ cm⁻¹. A colourless crystal of dimensions *ca.* 0.12 × 0.26 × 0.35 mm was grown by sublimation and mounted on a Syntex $P2_1$ diffractometer equipped with a low-temperature apparatus which cooled the crystal to -40 °C. The radiation employed throughout was Mo- K_α (0.710 69 Å), with a graphite crystal monochromator. The unit cell parameters were refined from the Bragg angles (as determined by the Syntex centring routine) of 42 reflections.

Intensity data for 1 079 unique reflections ($4^\circ < 2\theta < 48^\circ$) were collected by using the ω -scan technique. Scans of 1.0°

* Structure amplitudes are included in Supplementary Publication No. SUP 21571 (8 pp.). For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin I*, 1974, Index issue.

were used with scan rates which ranged from 1.0 to 5.0° min⁻¹ depending on the number of counts measured in a rapid preliminary scan. Backgrounds were measured at both ends of the scan with ω displaced 1.0° from the K_α peak. The intensities of four standard reflections were monitored after every 96 reflections; only statistical variations were noted. The intensities were corrected for Lorentz and polarization effects but not for absorption.*

Solution and Refinement.—The structure was solved by direct methods (MULTAN). Refinement of the structure by the full-matrix least-squares method was carried out by using only those 867 reflections for which $I > 2\sigma(I)$. A difference map was used to locate the hydrogen atoms. Refinement of all positional and thermal (anisotropic for the non-hydrogen atoms and isotropic for the hydrogen atoms) parameters converged at a conventional R value of 0.034. The largest parameter shift in the final cycle of the refinement was 0.07 σ . The largest peak in the final difference Fourier had a height of 0.10 e Å⁻³ and was located between C(10) and C(11). The refined positional and thermal parameters are given in Table 2. The scattering factors and computer programs used in this study are noted elsewhere.⁹

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[5/1247 Received, 25th June, 1975]

⁹ R. L. Harlow, W. J. Wells, tert., G. W. Watt, and S. H. Simonsen, *Inorg. Chem.*, 1974, **13**, 2106.