

Table 7. Intermolecular distances (Å) in TMAIXN shorter than or equal to the sum of the corresponding van der Waals radii

S(1)...C(9) ^{VI}	3.61 (2)	C(9)...C(16) ^{VII}	3.86 (3)
S(4)...C(3) ^{II}	3.75 (1)	C(10)...C(19) ^{III}	3.85 (2)
O(1)...C(9) ^{VI}	3.43 (2)	C(10)...C(15) ^{VIII}	3.95 (1)
O(3)...C(18) ^I	3.40 (1)	C(11)...C(18) ^I	3.60 (2)
C(1)...C(9) ^{VI}	3.53 (2)	C(12)...C(18) ^I	3.74 (1)
C(1)...C(15) ^{VII}	3.69 (1)	C(12)...C(4) ^{II}	3.93 (1)
C(2)...C(15) ^{VII}	3.86 (1)	C(14)...C(16) ^{II}	3.90 (3)
C(5)...C(15) ^{IV}	3.63 (2)	C(14)...C(17) ^{III}	3.84 (2)
C(8)...C'(9) ^V	3.75 (2)		

Symmetry code

(I)	x,	y,	z	(V)	-x,	-y,	1-z
(II)	x-1,	y,	z	(VI)	-x,	$\frac{1}{2}+y,$	$\frac{1}{2}-z$
(III)	-x,	1-y,	1-z	(VII)	-x,	$y-\frac{1}{2},$	$\frac{1}{2}-z$
(IV)	-x,	1-y,	-z	(VIII)	-x-1,	$y-\frac{1}{2},$	$\frac{1}{2}-z$

that of N, indicating that the thermal motion of the C atoms consists mainly of rotational vibrations about the central atom. For this reason their H atoms could not be located.

Fig. 3 is a clinographic projection of the structure showing the molecular packing of TMAIXN in the unit cell. The roughly planar IXN anions form layers, approximately parallel to (104), being interconnected by the tetramethylammonium cations, which are distributed both in and between the layers. Moreover, van der Waals anion-anion interactions are observed. In Table 7 some of the more interesting intermolecular distances shorter than 4.0 Å are given.

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The Crystal and Molecular Structures of 2,3-Dihydrobenzimidazole-2-spirocyclohexane (at 193 K) and of the (1:1) Complex of 2,3-Dihydrobenzimidazole-2-spirocyclohexane with 5,6-(*N,N'*-Dipiperidino)isobenzimidazole-2-spirocyclohexane

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The structures of the title compounds have been refined to $R = 0.049$ and 0.082 respectively. 2,3-Dihydrobenzimidazole-2-spirocyclohexane is orthorhombic, with $a = 24.073$ (8), $b = 20.363$ (6), $c = 8.520$ (8) Å, $Z = 16$, space group $Fdd2$. The complex is monoclinic, with $a = 19.98$ (3), $b = 8.72$ (3), $c = 21.40$ (4) Å, $\beta = 122.38^\circ$, $Z = 4$, space group $P2_1/c$. In both structures the dihydrobenzimidazole molecules are linked into chains by hydrogen bonds. The isobenzimidazole molecules in the complex are hydrogen-bonded to this chain at right angles, precluding electronic interaction between the molecules.

Introduction

Isobenzimidazole-2-spirocyclohexane reacts with 2,3-dihydrobenzimidazole to give black crystals of a 1:1 complex (Herbert & Suschitzky, 1973). Similar complexes are formed with substituted benzimidazoles. Increasing substitution gives less strongly coloured complexes. Satisfactory crystals have not yet been obtained for any of the dark complexes. The example reported here has piperidine substituents and is the orange product of the pale-yellow components shown in Fig. 1.

Experimental

For each sample, data were collected on Weissenberg photographs, from which intensities were measured by the Science Research Laboratory Microdensitometer Service.

Crystal data

(I) 2,3-Dihydrobenzimidazole-2-spirocyclohexane, yellow needles with the needle axis parallel to *c* and well developed (110) and (1 $\bar{1}$ 0) faces. Data were collected at 193 K with a Stoe low-temperature goniometer and crystals set about *a* and *c* and the *bc* diagonal. Only 610 unique reflections were observed above background because of the high symmetry of the space group. $C_{12}H_{16}N_2$, $M_r = 188.27$, $a = 24.073$ (8), $b = 20.363$ (6), $c = 8.520$ (8) Å, $U = 4176.3$ Å³, $Z = 16$, $D_x = 1.20$ g cm⁻³; $\lambda = 1.5418$ Å, $F(000) = 1632$, $\mu(\text{Cu } K\alpha) = 4.8$ cm⁻¹. Space group *Fdd2* (from systematic absences), $T = 193 \pm 5$ K.

(II) Complex of 5,6-(*N,N'*-dipiperidino)isobenzimidazole-2-spirocyclohexane (*A*) and 2,3-dihydrobenzimidazole-2-spirocyclohexane (*B*), orange-yellow plates. Data were collected from crystals mounted about *a* and *c* of a cell in space group *B2₁/c*, corresponding to easily recognized directions in the crystal. All subsequent calculations were performed after transformation into the standard space group *P2₁/c*. 1643

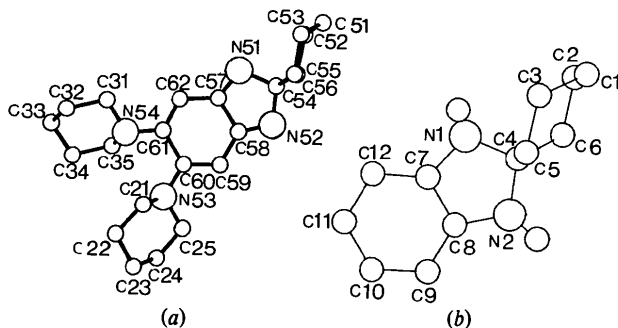


Fig. 1. (a) 5,6-(*N,N'*-Dipiperidino)isobenzimidazole-2-spirocyclohexane. (b) 2,3-Dihydrobenzimidazole-2-spirocyclohexane.

reflections were observed above background. $C_{34}H_{48}N_6$, $M_r = 540$, $a = 19.98$ (3), $b = 8.72$ (3), $c = 21.40$ (4) Å, $\beta = 122.38$ (4)°, $U = 3148.71$ Å³, $Z = 4$, $D_x = 1.14$ g cm⁻³; $\lambda = 1.5418$ Å, $F(000) = 1136$, $\mu(\text{Cu } K\alpha) = 4.6$ cm⁻¹. Space group *P2₁/c* (from systematic absences), $T = 293 \pm 3$ K.

Structure determination and refinement

All calculations were performed with *SHELX 76* (Sheldrick, 1976). Both structures were solved with the direct-methods program *TANG*. In each case the best *E* map showed almost all the non-hydrogen atoms. The remainder were revealed on Fourier maps during full-matrix least-squares refinement with isotropic thermal parameters which reduced *R* to 0.13 (I) and 0.15 (II). Scattering factors were from *International Tables for X-ray Crystallography* (1974).

For (I) the introduction of anisotropic thermal parameters and the removal of 18 planes for which $|F_o - F_c| > 0.5F_c$ gave convergence at $R = 0.081$, at which point a difference map located all the H atoms. The inclusion of these H atoms with isotropic thermal parameters allowed *R* to converge at 0.051 with 195 parameters, with unsatisfactory bond lengths and angles for the protons of the cyclohexane ring. As an alternative the positions of all the H atoms attached to C atoms were calculated and refined with a riding model and C-H = 1.04 Å. Three isotropic thermal parameters were used to describe the benzene, cyclohexane and N protons respectively. Convergence was obtained at $R = 0.049^*$ for 135 parameters (4.5

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33388 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. 2,3-Dihydrobenzimidazole-2-spirocyclohexane: atomic coordinates ($\times 10^4$) with e.s.d.'s

	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	614 (4)	9225 (4)	4080 (14)
C(2)	273 (4)	9056 (3)	5541 (13)
C(3)	-44 (3)	8418 (3)	5266 (12)
N(1)	-2 (2)	7261 (2)	4514 (11)
N(2)	653 (2)	7624 (2)	6219 (10)
C(4)	332 (2)	7857 (3)	4830 (11)
C(5)	707 (3)	8026 (4)	3455 (11)
C(6)	1010 (4)	8668 (4)	3735 (12)
C(7)	300 (2)	6720 (3)	5074 (10)
C(8)	710 (2)	6943 (3)	6064 (11)
C(9)	1070 (2)	6525 (3)	6839 (11)
C(10)	1006 (3)	5850 (3)	6569 (12)
C(11)	591 (3)	5629 (3)	5568 (12)
C(12)	237 (3)	6066 (3)	4783*

* Fixed parameter to define origin.

Table 2. Complex of 2,3-dihydrobenzimidazole-2-spirocyclohexane with 5,6-(*N,N'*-dipiperidino)isobenzimidazole-2-spirocyclohexane: atomic coordinates ($\times 10^4$) with *e.s.d.*'s

	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>
C(1)	694 (7)	4594 (8)	4624 (6)	N(51)	7359 (4)	-2938 (5)	511 (3)
C(2)	1303 (5)	5011 (8)	4439 (4)	N(52)	6163 (4)	-4421 (6)	82 (4)
C(3)	876 (5)	5345 (7)	3588 (4)	C(57)	6905 (4)	-2343 (7)	711 (4)
C(4)	381 (4)	3997 (7)	3119 (4)	C(58)	6169 (5)	-3233 (7)	451 (4)
C(5)	-209 (5)	3500 (8)	3324 (4)	C(59)	5598 (5)	-2744 (7)	619 (4)
C(6)	203 (6)	3186 (8)	4158 (5)	C(60)	5750 (4)	-1442 (7)	1024 (4)
N(1)	-30 (4)	4329 (6)	2314 (3)	C(61)	6486 (4)	-497 (7)	1289 (4)
N(2)	895 (4)	2663 (5)	3180 (3)	C(62)	7036 (5)	-945 (7)	1140 (4)
C(7)	991 (4)	2798 (6)	2564 (4)	N(53)	5209 (4)	-895 (6)	1224 (3)
C(8)	1523 (5)	2035 (7)	2441 (5)	C(21)	4394 (5)	-1442 (9)	756 (5)
C(9)	1463 (5)	2338 (8)	1767 (5)	C(22)	3823 (6)	-425 (9)	838 (5)
C(10)	897 (6)	3358 (9)	1250 (5)	C(23)	4059 (6)	-423 (11)	1644 (6)
C(11)	378 (5)	4111 (7)	1394 (4)	C(24)	4960 (6)	30 (12)	2177 (5)
C(12)	426 (5)	3821 (7)	2041 (4)	C(25)	5482 (6)	-981 (10)	2010 (5)
C(51)	7968 (5)	-5692 (8)	-342 (5)	N(54)	6589 (4)	854 (6)	1688 (3)
C(52)	8184 (5)	-5737 (8)	449 (5)	C(31)	6019 (5)	2086 (8)	1237 (5)
C(53)	7422 (5)	-5739 (7)	486 (5)	C(32)	6044 (6)	3350 (9)	1734 (6)
C(54)	6903 (5)	-4336 (7)	79 (4)	C(33)	6883 (6)	3958 (10)	2232 (6)
C(55)	6716 (6)	-4226 (10)	-703 (5)	C(34)	7461 (6)	2697 (10)	2680 (6)
C(56)	7457 (6)	-4271 (10)	-746 (5)	C(35)	7416 (5)	1414 (9)	2140 (5)

reflections per parameter). Examination of a weighting scheme did not justify departure from unit weights.

With (II) the use of anisotropic thermal parameters, the removal of 16 reflections for which $|F_o - F_c| > 0.5F_c$ and the introduction of H atoms at calculated positions with an isotropic thermal parameter for the protons of each ring gave convergence at $R = 0.082$ for 385 parameters (4.2 reflections per parameter). The final weighting scheme was $w = 1/(\sigma_F^2 + 0.019096F^2)$.

Results and discussion

Tables 1 and 2 list the atomic positional parameters of the non-hydrogen atoms. Table 3 compares the bond lengths and angles in the isobenzimidazole (*A*) with the two determinations of the dihydrobenzimidazole (*B*) and those in benzimidazole itself (Dik-Edixhaven, Schenk & van der Meer, 1973). In (I) and (II), the *B* molecules are connected by hydrogen bonds to form chains about the screw axes parallel to *c* in (I) and *b* in (II) (Figs. 2, 3). A similar arrangement is found in benzimidazole. In (II) the *B*-*B* hydrogen bond uses the proton of N(1) and the lone pair of electrons of N(2) while the proton of N(2) forms a hydrogen bond to N(51), linking the *A* molecules to the *B* chain. The benzimidazole rings of the *A* and *B* molecules are packed at 92° to each other.

There are no significant differences between the geometries of *B* in (I) and (II). Since C(4) is tetrahedrally bonded, C(4)-N(1) and C(4)-N(2) are single bonds (average 1.497 Å) in both *A* and *B*, breaking the delocalization observed in the five-membered ring in benzimidazole. In the non-planar ring of *B* these long bonds reduce N(1)-C(4)-N(2) to 100.0° compared

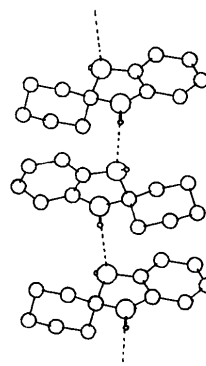


Fig. 2. Hydrogen bonding in 2,3-dihydrobenzimidazole-2-spirocyclohexane, *a*-axis projection.

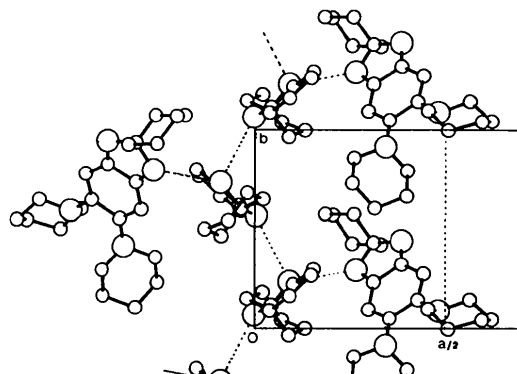


Fig. 3. Hydrogen bonding in the complex, *c*-axis projection.

with 108.4° in the planar *A* and 114.0° in benzimidazole. In *B*, C(7)-N(1) and C(8)-N(2) are not significantly longer than in benzimidazole (average

Table 3. Bond lengths (Å) and angles (°), with *e.s.d.*'s

	(I) <i>B</i>	(II) <i>B</i>	(II) <i>A</i> *	Benzimidazole†
C(1)—C(2)	1.530 (12)	1.512 (19)	1.507 (15)	
C(2)—C(3)	1.524 (9)	1.570 (11)	1.566 (16)	
C(3)—C(4)	1.504 (9)	1.518 (8)	1.538 (9)	
C(4)—C(5)	1.518 (9)	1.523 (15)	1.509 (14)	
C(5)—C(6)	1.517 (10)	1.538 (12)	1.533 (19)	
C(6)—C(1)	1.511 (13)	1.554 (11)	1.542 (11)	
C(4)—N(1)	1.482 (7)	1.487 (10)	1.506 (8)	1.346
C(4)—N(2)	1.491 (7)	1.511 (10)	1.482 (14)	1.311
C(7)—N(1)	1.403 (7)	1.393 (14)	1.300 (13)	1.372
C(8)—N(2)	1.399 (7)	1.435 (13)	1.299 (10)	1.395
C(7)—C(8)	1.377 (7)	1.403 (8)	1.482 (11)	1.392
C(8)—C(9)	1.382 (7)	1.393 (14)	1.433 (15)	1.389
C(9)—C(10)	1.401 (7)	1.408 (16)	1.360 (10)	1.386
C(10)—C(11)	1.389 (9)	1.399 (11)	1.506 (11)	1.401
C(11)—C(12)	1.401 (9)	1.394 (16)	1.356 (14)	1.378
C(12)—C(7)	1.362 (8)	1.359 (14)	1.463 (9)	1.401
C(60)—N(53)			1.441 (13)	
C(61)—N(54)			1.404 (9)	
N(1)—N(2)'	3.223 (9)	3.256 (15)	3.134 (15)‡	2.90
Molecule <i>A</i> , piperidine rings§				
	<i>X</i>		<i>Y</i>	
N—C(1)	1.462 (10)		1.485 (9)	
C(1)—C(2)	1.527 (16)		1.514 (14)	
C(2)—C(3)	1.525 (16)		1.521 (14)	
C(3)—C(4)	1.581 (14)		1.510 (12)	
C(4)—C(5)	1.545 (18)		1.576 (15)	
C(5)—N	1.465 (12)		1.480 (11)	
	(I) <i>B</i>	(II) <i>B</i>	(II) <i>A</i> *	Benzimidazole†
C(1)—C(2)—C(3)	109.5 (7)	109.6 (7)	110.8 (7)	
C(2)—C(3)—C(4)	112.6 (5)	112.3 (6)	110.4 (8)	
C(4)—C(5)—C(6)	111.1 (6)	111.7 (7)	113.1 (7)	
C(5)—C(6)—C(1)	111.9 (7)	111.4 (7)	110.9 (9)	
C(6)—C(1)—C(2)	109.2 (6)	110.0 (1.0)	110.9 (9)	
C(3)—C(4)—C(5)	112.1 (5)	111.2 (8)	111.7 (8)	
C(3)—C(4)—N(1)	109.9 (5)	112.0 (6)	107.1 (5)	
C(3)—C(4)—N(2)	110.9 (5)	111.5 (6)	109.2 (7)	
C(5)—C(4)—N(1)	116.5 (5)	110.9 (6)	109.8 (7)	
C(5)—C(4)—N(2)	112.2 (5)	110.6 (6)	110.6 (6)	
N(1)—C(4)—N(2)	99.5 (4)	100.2 (7)	108.4 (7)	114.0
C(4)—N(1)—C(7)	107.4 (4)	110.2 (6)	103.0 (7)	106.6
C(4)—N(2)—C(8)	107.0 (5)	106.1 (5)	106.1 (6)	104.2
N(1)—C(7)—C(8)	108.7 (5)	107.1 (8)	113.2 (6)	105.8
N(2)—C(8)—C(7)	108.3 (5)	109.9 (8)	109.3 (9)	109.5
N(1)—C(7)—C(12)	130.4 (5)	131.6 (6)	128.2 (7)	131.9
N(2)—C(8)—C(9)	128.8 (5)	128.6 (6)	129.9 (7)	130.0
C(7)—C(8)—C(9)	122.6 (5)	121.5 (9)	120.9 (6)	120.6
C(8)—C(9)—C(10)	117.1 (5)	116.7 (7)	118.2 (8)	117.8
C(9)—C(10)—C(11)	119.9 (6)	121.3 (1.1)	122.4 (9)	120.9
C(10)—C(11)—C(12)	121.6 (6)	120.5 (1.0)	120.3 (6)	122.3
C(11)—C(12)—C(7)	117.8 (6)	118.8 (7)	119.6 (7)	116.1
C(12)—C(7)—C(8)	120.9 (5)	121.3 (9)	118.6 (9)	122.4
C(9)—C(10)—N(3)			121.3 (8)	
C(11)—C(10)—N(3)			116.3 (6)	
C(10)—C(11)—N(4)			119.0 (8)	
C(12)—C(11)—N(4)			120.8 (7)	

* Atoms numbered (50 + *n*).† Dik-Edixhaven *et al.* (1973).

‡ N(1)⋯N(52).

§ Ring *X* is N(53), C(21)—C(25); ring *Y* is N(54), C(31)—C(35).

Table 3 (cont.)

Molecule *A*, piperidine rings

	<i>X</i>	<i>Y</i>
C—N—C(1)	115.2 (7)	115.0 (8)
C—N—C(5)	116.5 (6)	113.5 (5)
C(1)—N—C(5)	111.3 (8)	112.7 (6)
N—C(1)—C(2)	111.0 (7)	110.1 (7)
C(1)—C(2)—C(3)	109.4 (7)	110.9 (1.0)
C(2)—C(3)—C(5)	111.0 (1.1)	111.9 (7)
C(3)—C(4)—C(5)	109.9 (8)	109.1 (8)

Table 4. Selected mean planes in (II)

Molecule *B*Plane *L*: C(4), N(1), N(2), C(7)—C(12)

$$10.3246x + 6.5210y + 1.6107z = 3.2874$$

Plane *M*: C(2), C(3), C(5), C(6)

$$-13.1911x + 6.5092y + 9.0672z = 5.5720$$

Molecule *A*Plane *N*: N(51), N(52), C(57)—C(62)

$$0.4150x - 4.6686y + 15.0215z = 2.4422$$

Plane *O*: C(21), C(22), C(24), C(25)

$$10.3703x + 6.98037y - 11.3648z = 2.7031$$

Plane *P*: C(31), C(32), C(34), C(35)

$$12.4612x + 5.7084y - 14.8678z = 6.8596$$

Plane *Q*: C(52), C(53), C(55), C(56)

$$0.6833x + 7.4675y + 8.9196z = -3.3344$$

Angles between planes (°)

<i>L—M</i>	75.42	<i>N—P</i>	134.28
<i>L—N</i>	92.16	<i>O—P</i>	12.64
<i>N—O</i>	132.16	<i>N—Q</i>	91.30

1.40 Å). This is a typical value for N adjacent to an aromatic ring, identical with C(60)—N(53) and C(61)—N(54) for the piperidine substituents in *A*. In *A* C(57)—N(51) and C(58)—N(52) are much shorter (1.300 Å) and C(57)—C(58) and C(60)—C(61)

average 1.494 Å, indicating little or no conjugation between the diene systems C(60)=C(59)—C(58)=N(52) and C(61)=C(62)—C(58)=N(51). N(51), N(52), C(51)—C(62) are all within 0.007 Å of the mean plane containing them; C(54) is 0.015 Å out of this plane.

One piperidine group lies on either side of the benzimidazole ring in *A*, connected to it equatorially. N(53) and N(54) are 0.031 Å above and below the benzimidazole plane. The normals to the mean planes C(21), C(22), C(24), C(25) and C(31), C(32), C(34), C(35) intersect at 12.6° and make angles to that of the benzimidazole plane of 134.3 and 132.1° respectively.

Equations for selected mean planes are given in Table 4.

Fig. 3 shows that there is no possibility of electronic interaction between the π systems of *A* and *B* in (II). In the related black complexes the absence of the bulky piperidine rings must allow the molecular planes of donor and acceptor to be parallel rather than at right angles as observed in (II).

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The Crystal Structure of Guanidinium Pyrophosphate Monoperhydrate Sesquihydrate

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[C(NH₂)₃]₄P₂O₇·H₂O₂·1½H₂O crystallizes in space group *P2₁/a* with *a* = 17.84 (3), *b* = 14.15 (2), *c* = 17.72 (3) Å, β = 116.8 (2)°; each asymmetric unit consists of twice the above formula. The crystals are extremely stable carriers of hydrogen peroxide. There are two types of hydrogen-bonded chain in the structure: (···P₂O₇···H₂O···)_n and (···P₂O₇···H₂O₂···)_n. The remaining water molecules and the guanidinium ions hold these chains together. Each H₂O₂ molecule donates two hydrogen bonds and receives three.