Table 3. *Selected bond distances* (Å) *and bond angles* (°)

	(I)	(II)*	(III)
N—O	1·397 (4)	1·411 (7)	1·403 (6)
N—C*c*†	1·481 (5)	1·459 (10)	1·490 (7)
N—C*v*†	1·292 (5)	1·319 (10)	1·362 (7)
C*v*═C*v*	1·378 (6)	1·368 (10)	1·328 (8)
C—CN	1·430 (6) 1·413 (6)	1·425 (10)	1·440 (9)
C≡N	1·139 (5) 1·136 (6)	1·148 (10)	1·131 (8)
C*v*—S	—	1·760 (8)	1·763 (5)
O—N—C*c*	113·9 (3)	113·2 (6)	113·1 (4)
O—N—C*v*	118·2 (3)	116·4 (6)	113·9 (4)
C*c*—N—C*v*	127·9 (3)	124·9 (6)	121·3 (5)
C*c*—O—N	108·9 (3)	109·3 (5)	114·6 (4)
N—C*v*—C*v*	129·5 (4)	129·7 (6)	129·8 (5)
C*v*—C*v*—CN	117·0 (4) 126·9 (4)	125·8 (7)	124·9 (5)
C*v*—C*v*—S	—	118·2 (5)	119·8 (4)

* Mean values over the three independent molecules.
† C*c* for C of the ring, C*v* for C of the vinyl part.

C8, 63, −25, −28, 46, −6 and −47°. Because of the bridge, the six-membered ring is inevitably a boat conformation but it is highly distorted in the C5—O6—N7 region. Concerning the two seven-membered rings, that with a C8—C9 double bond has a nearly regular boat conformation (Hendrickson's theoretical values: −30·9, −57·5, 57·5, 30·9, −69·9, 0, 69·9°) while that containing N—O is a distorted chair, particularly around N—O (theoretical values: 83·5, −63·8, 63·8, −83·5, 66·1, 0, −66·1°) (Hendrickson, 1967).

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Structure of 4,5,6,7-Tetrahydro-1,3-benzimidazole-2-thione

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Abstract. $C_7H_{10}N_2S$, $M_r = 154{\cdot}23$, tetragonal, $P4_32_12$, $a = 7{\cdot}1519(6)$, $c = 14{\cdot}3532(6)$ Å, $V = 734{\cdot}2$ Å^3, $Z = 4$, $D_m = 1{\cdot}40$, $D_x = 1{\cdot}395$ Mg m^{-3}, $\lambda(\mathrm{Cu}\,K\alpha) = 1{\cdot}5418$ Å, $\mu = 3{\cdot}19$ mm^{-1}, $F(000) = 328$, $T = 296$ K, final $R = 0{\cdot}026$ for 520 observed reflections. The molecule has a crystallographic two-fold axis of symmetry. Both the S and the C atom bonded to it lie on this twofold axis, which also bisects the C(2)—C(2′) and C(4)—C(4′) bonds. The exocyclic C—S forms the thione structure in the solid state. The five-membered imidazole ring is planar, with the S atom also lying in this plane, whereas the cyclohexene ring has a distorted half-chair conformation. There is a relatively weak but linear hydrogen bond from the N—H group to the S atom of an adjacent molecule along **c**. Each S atom, because of its location on a twofold axis, is involved in two such bonds.

Introduction. The imidazolethione system has been a subject of interest on account of its wide-ranging pharmacological activity (Kohn, Kohn, Steenberg & Buckley, 1977; Gosselin, Imbach, Townsend & Panzica, 1979) and its effective inhibition of metallic corrosion (Donnelly, Downie, Grzeskowiak, Hamburg & Short, 1978). 4,5,6,7-Tetrahydro-1,3-benzimidazole-2-thione is one such compound newly synthesized by the reaction between potassium thiocyanate and 2-aminocyclohexanone oxime; the latter's amino N atom, acting as an electrophile, and its C atom bonded to the hydroxyimino group, acting

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as a nucleophile, enter into a variety of reactions (Sato, Imamura & Kitano, 1984; Sato, Imamura, Kitano, Kanda & Ashida, 1984). We report here the crystal and molecular struture of the compound as established by X-ray diffraction.

Experimental. Colorless prismatic crystals from isopropanol. The density was measured by flotation in a chloroform–cyclohexane solution. Rigaku AFC5R automated four-circle diffractometer, graphite-monochromated Cu $K\alpha$ radiation with a 12 kW rotating-anode generator; crystal size 0·2 × 0·2 × 0·4 mm. Unit-cell dimensions obtained from a least-squares refinement of angular settings of 25 reflections in the range $75 < 2\theta < 80°$. 2θ–ω scan, scan range $\Delta\omega = (1{\cdot}52 + 0{\cdot}30\tan\theta)°$ up to $2\theta = 120°$, scan rate 6·0° $\min^{-1}$ in ω, $-8 \leq h \leq 8$, $-5 \leq k \leq 5$, $-16 \leq l \leq 16$. Weak reflections $[I < 10\sigma(I)]$ rescanned (maximum of two scans) and the counts accumulated to assure good counting statistics, background counts on each side of reflections, the ratio of peak counting time to background counting time was 2:1.

The intensities of three monitor reflections measured after every 150 reflections declined by 1·05% so a linear correction factor was applied to the data; 746 reflections collected, 551 were unique; $R_{\rm int} = 0{\cdot}018$, equivalent reflections were merged. Corrections for Lorentz–polarization, absorption (empirical absorption correction, transmission factors ranging from 0·85 to 1·09) and secondary extinction (coefficient $0{\cdot}132 \times 10^{-3}$). Structure determination by direct methods (*MITHRIL*; Gilmore, 1984), H atoms positioned from a difference map, full-matrix least-squares refinement with anisotropic thermal parameters for non-H atoms and isotropic for H atoms.

The absolute configuration was examined by measuring a complete set of Bijvoet pairs. Of the pairs of reflections, 176 had non-equivalent calculated structure factors for the two reflections; the most significant of these ratios are listed in Table 1.* Space group $P4_32_12$ was chosen over the enantiomorphic space group $P4_12_12$ on the basis of the lower weighted R value (0·026 as opposed to 0·035) and the differences in $F_{\rm obs}$ for the Bijvoet pairs.

Function minimized $\sum w(|F_o| - |F_c|)^2$ with $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma(F_o^2)$ is standard deviation based on counting statistics. Final refinement based on 520 observed reflections $[I > 3\sigma(I)]$ and 68 variable parameters gave $R = 0{\cdot}026$, $wR = 0{\cdot}030$, $S = 1{\cdot}47$, $\Delta/\sigma = 0{\cdot}00$, maximum and minimum peaks on the final difference map corresponded to 0·11 and $-0{\cdot}18$ e Å^{-3}, respectively. Neutral-atom scattering factors and $\Delta f'$, $\Delta f''$ from *International Tables for X-ray Crystallography* (1974, Vol. IV). The VAX-based *TEXSAN* (Molecular Structure Corporation, 1985) system was used for calculations.

Table 1. *Ratios of the Bijvoet pairs with the most significant dispersion effect*

h	k	l	$\Delta I/I_{\rm obs}$	$\Delta I/I_{\rm calc}$
4	3	2	+0·25	+0·04
4	1	8	−0·16	−0·01
5	3	1	−0·15	−0·01
5	2	5	−0·15	−0·11
6	1	3	−0·17	−0·13
5	4	1	+0·14	+0·16
5	2	8	+0·14	+0·01
6	3	1	+0·22	+0·27
6	2	6	+0·19	+0·06
5	4	6	+0·16	+0·05
6	3	5	+0·19	+0·07

Table 2. *Atomic positional and thermal parameters with their e.s.d.'s in parentheses*

$B_{\rm eq}$ is the equivalent isotropic temperature factor calculated from the anisotropic temperature coefficients (Hamilton, 1959).

	x	y	z	$B_{\rm eq}$(Å^2)
S(1)	0·25149 (7)	0·2515	0	2·8 (2)
N(1)	0·4173 (3)	0·5827 (2)	−0·0460 (1)	2·3 (8)
C(1)	0·4186 (3)	0·4186	0	2·0 (6)
C(2)	0·5809 (3)	0·6839 (3)	−0·0289 (1)	2·0 (8)
C(3)	0·6284 (4)	0·8725 (3)	−0·0635 (2)	2·9 (1)
C(4)	0·7938 (3)	0·9442 (3)	−0·0057 (2)	3·2 (1)

Table 3. *Bond lengths* (Å), *bond angles* (°) *and selected torsion angles* (°) *with e.s.d.'s in parentheses*

A prime denotes an atom related by a crystallographic twofold axis.

S(1)—C(1)	1·690 (3)	C(2)—C(3)	1·477 (3)
N(1)—C(1)	1·347 (2)	C(3)—C(4)	1·533 (3)
N(1)—C(2)	1·397 (3)	C(4)—C(4′)	1·530 (5)
C(2)—C(2′)	1·331 (4)		
S(1)—C(1)—N(1)	127·7 (1)	N(1)—C(2)—C(3)	127·3 (2)
C(1)—N(1)—C(2)	111·1 (2)	C(2′)—C(2)—C(3)	126·0 (1)
N(1)—C(1)—N(1′)	104·6 (2)	C(2)—C(3)—C(4)	107·5 (2)
N(1)—C(2)—C(2′)	106·6 (1)	C(3)—C(4)—C(4′)	111·4 (2)
C(3)—C(2)—C(2′)—C(3′)	−5·4 (5)	C(2′)—C(2)—C(3)—C(4)	−11·7 (3)
C(2)—C(3)—C(4)—C(4′)	45·1 (3)	C(3)—C(4)—C(4′)—C(3′)	−65·7 (4)
N(1)—C(2)—C(3)—C(4)	164·8 (2)	C(1)—N(1)—C(2)—C(3)	−177·4 (2)

Discussion. The refined atomic parameters for the correct space group $P4_32_12$ are listed in Table 2.*

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* The statistics for the comparison of Bijvoet pairs for the selected space group are as follows:

	Number	Sum$\lvert\Delta F_c\rvert$
F_c difference agrees with F_o	136	45·45
F_c difference disagrees with F_o	40	2·85
$F(hkl) = F(\bar{h}kl)$ reflections	183	0·00

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and mean-planes calculations have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53668 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The bond distances, bond angles and selected torsion angles are listed in Table 3. An *ORTEP* drawing (Johnson, 1976) of a molecule with the numbering scheme is shown in Fig. 1.

The molecule has a crystallographic twofold axis of symmetry through the origin along **a** + **b**. Both the S(1) atom and the C atom bonded to it, C(1), lie on this twofold axis, which also bisects the C(2)—C(2′) and C(4)—C(4′) bonds. The C(1)—S(1) distance of 1·690 (3) Å along with the protonated N atom confirms the presence of the thione tautomer in the solid state. Similar thione forms were observed in 2-mercaptobenzimidazole (Form, Raper & Downie, 1976) and 1-methyl-4-imidazoline-2-thione (Raper, Creighton, Oughtred & Nowell, 1983). The significant shortening of the C(1)—N(1) bond and lengthening of the C(2)—N(1) bond within the heterocycle, including the short distance between adjacent C(2) and C(2′) atoms, as compared with the values for 2-mercaptobenzimidazole [C(1)—N(1) = 1·362, C(2)—N(1) = 1·383, C(2)—C(2′) = 1·400 Å] and 1-methyl-4-imidazoline-2-thione [av. C(1)—N(1) = 1·348, C(2)—N(1) = 1·381, C(2)—C(2′) = 1·333 Å] explains the failure to form the delocalized aromatic bond system which might be expected for this molecule.

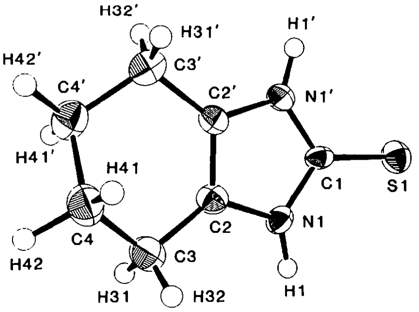

Fig. 1. Molecular structure and atomic numbering. Thermal ellipsoids are drawn at the 50% probability level and H atoms are given arbitrary thermal parameters for clarity. A prime represents one half of the molecule related by a crystallographic twofold axis.

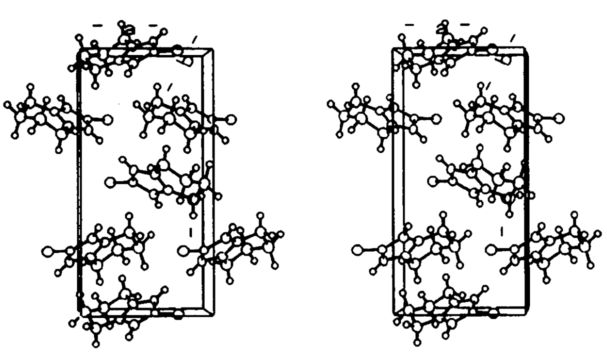

Fig. 2. Stereoview of the crystal packing of the molecules viewed along **b**.

The five-membered imidazole ring is planar, with the S atom also lying in this plane, whereas the cyclohexene ring has a distorted half-chair conformation. Four of the atoms in the six-membered ring are nearly coplanar, C(2), C(2′), C(3) and C(3′), while the other two atoms, C(4) and C(4′), lie above (−0·38 Å) and below (0·38 Å) this plane, respectively.

The bond distances and angles in the cyclohexene ring are consistent with the corresponding values found for 5-(4,5,6,7-tetrahydrobenzimidazol-2-yl)valeronitrile (Kitano, Sato, Imamura & Ashida, 1983) and 4,5,6,7-tetrahydrobenzimidazole hydrochloride (Carlström, Hacksell & Jönsson, 1981) except for the short distance of C(2)—C(2′) (1·331 Å) and the long distance of C(4)—C(4′) (1·530 Å) as compared with the values (av. 1·355, 1·44 Å) and (av. 1·340, 1·507 Å) for 5-(4,5,6,7-tetrahydrobenzimidazol-2-yl)valeronitrile and 4,5,6,7-tetrahydrobenzimidazole hydrochloride, respectively.

The molecular arrangement in the crystal viewed along **b** is illustrated in Fig. 2. There is a relatively weak but nearly linear hydrogen bond from the imide H to the S atom of an adjacent molecule along **c** with the following parameters: N···S 3·392 (2), H···S 2·66 (2) Å, N—H···S 150 (2)°. Each S atom, because of its location on a twofold axis, receives two such bonds with an H···S···H angle of 150 (2)°.

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