

N(1)—O(2) distance is 2.85 (2) Å, whilst the N(2)—O(1) distance is 2.88 (2) Å. In both cases the hydrogen-bond distance is less than 3.0 Å, hence these bonds play an important role in the packing of the molecules in a unit cell. The unit cell consists of four molecules with Cl(1) and Cl(2) as terminal atoms. The molecules are arranged in two pairs held by van der Waals forces of attraction and form columns along the screw axis as a result of the intermolecular hydrogen-bond system.

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References

- ADAMS, M. J., BLUNDELL, T. L., DODSON, E. J., DODSON, G. G., VIJAYAN, M., BAKER, E. N., HARDING, M. M., HODGKIN, D. C., RIMMER, B. & SHEAT, S. (1969). *Nature (London)*, **224**, 491–495.
- DICKERSON, R. E. & GEIS, I. (1969). *The Structure of Proteins*. New York: Harper & Row.
- FRENZ, B. A. (1978). *Computing in Crystallography*, edited by H. SCHENK, R. OLTJOF-HAZEKAMP, H. VAN KONINGSVELD & G. C. BASSI, 64–71. Delft Univ. Press.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.
- KAGAN, H. (1979). *Organic Stereochemistry*, pp. 28–29. London: Edward Arnold.
- LEE, J. D. & BRYANT, M. W. R. (1969). *Acta Cryst.* **B25**, 2094–2101.
- MAIN, P., LESSINGER, L., WOOLFSON, M. M., GERMAIN, G. & DECLERCQ, J.-P. (1977). *MULTAN77. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- MAIRE, J. C., KAPOOR, T. S., BACHLAS, B. P. & VINCENT, E. J. (1984). *Tetrahedron Lett.* In the press.
- MEYER, K. P. (1977). 7th Proc. Int. Congr. Vac. Technol. Vol. 2, pp. 1085–1088.
- RICCI, J. S. & BERNAL, I. (1969). *J. Am. Chem. Soc.* **91**, 4078–4082.
- RICCI, J. S. & BERNAL, I. (1970). *J. Chem. Soc. B*, pp. 806–811.

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Structure of the Twofold Addition Product Tetramethyl 6-Diethylamino-3,7a,10,11b-tetrahydro-7H-dipyridazino[4,5-*b*:4',5'-*d*]azepine-1,4,8,11-tetracarboxylate, C₂₂H₂₈N₆O₈

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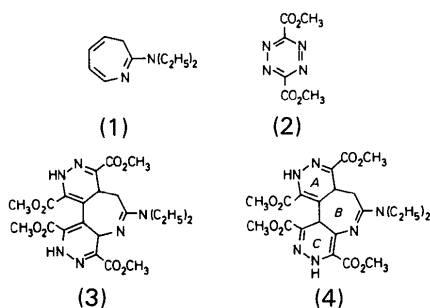
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Abstract. $M_r = 504.51$, triclinic, $P\bar{1}$, $a = 9.565$ (2), $b = 13.699$ (3), $c = 9.463$ (2) Å, $\alpha = 96.95$ (2), $\beta = 97.12$ (2), $\gamma = 97.05$ (2)°, $V = 1209.34$ Å³, $Z = 2$, $D_x = 1.385$ Mg m⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu(\text{Cu } K\alpha)$

$= 0.863$ mm⁻¹, $F(000) = 532$, $T = 290$ (1) K, $R = 0.072$ for 2469 observed reflections. The molecule contains a seven-membered azepine ring which adopts a distorted boat conformation such that the dihedral angle between the best planes through the two dihydropyridazino rings is 88.5° and thus reduces the crowding of the ester groups on these rings.

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Introduction. There is continued interest in reactions of conjugated, seven-membered heterocyclic compounds. In particular, their ability to act as two, four or six π systems, or in some cases to react *via* a valence tautomer, has led to a remarkable variety of cyclo-addition reactions, which have recently been reviewed (Mukai, Kumagi & Yamashita, 1981). While oxepines, 1*H*-azepines, and 1*H*-1,2-diazepines have been extensively studied, the 3*H*-azepine ring system has received far less attention, although many simple derivatives are now readily accessible. Recently two of us reported that 2-diethylamino-3*H*-azepine (1) reacts with the electron-deficient tetrazine (2) to yield a product assigned structure (3) on the basis of ¹H NMR data (Seitz, Kämpchen & Overheu, 1978). This provides the only report to date of twofold addition to a seven-membered heterocycle. An X-ray crystal study was undertaken to confirm the presence of the novel bisdihydropyridazino[4,5-*b*:4',5'-*d*]azepine ring system, and to study the geometry the molecule adopts in order to relieve crowding of the ester groups on the 1,3-butadiene moiety of (3).



Experimental. Yellow prisms from methanol. Crystal 0.12 × 0.32 × 0.37 mm. Hilger & Watts Y290 computer-controlled four-circle diffractometer. Unit cell: 22 reflections, least-squares refinement. No absorption correction. Intensity measurements by $\omega/2\theta$ scans, count time per step 1 s, range of each scan 0.9°; $\theta_{\max} = 60^\circ$, $h = -10$ to 10, $k = -15$ to 15, $l = 0$ to 10; 4510 reflections recorded including some Friedel pairs, 3545 unique, 1076 with $I < 2\sigma(I)$ classified as unobserved, $R_{\text{int}} = 0.0293$. Intensity variation of three standard reflections (510, 080, 333) < 1%. Structure solved by direct methods using *MULTAN80* (Main *et al.*, 1980). Structure refined (on *F*) by full-matrix least squares using *SHELX76* (Sheldrick, 1976). Final refinement cycle included anisotropic thermal parameters for the non-hydrogen atoms; all H atoms determined from a difference Fourier map but included at calculated positions, riding on their parent atoms; methyls treated as rigid groups. Final $R = 0.072$, $R_w = 0.074$ for 2469 observed reflections, $w = 8.134/[\sigma^2(F_o) + 0.0025(F_o)^2]$. Atomic scattering factors and values of f' and f'' from *International Tables for X-ray Crystallography* (1974).

Max. Δ/σ generally < 0.1 for both positional and thermal parameters. Max. and min. heights in final difference Fourier map 0.378 and $-0.353 \text{ e } \text{\AA}^{-3}$. No secondary-extinction correction applied. All calculations performed on the University of York DEC 10 computer. Least-squares planes and torsion angles calculated using *XANADU* (Roberts & Sheldrick, 1975). Figures drawn using *ARTIST* (Valley, 1983).

Discussion. The final atomic coordinates for the non-hydrogen atoms are listed in Table 1 and bond lengths and angles in Table 2.* The molecular structure of (4) is shown in Fig. 1 with the atomic numbering used in the structure analysis. The structure determination has shown that (3) exists as its tautomer (4). The seven-membered ring *B* exists in a distorted boat conformation relative to the best plane (maximum deviation 0.035 Å) through atoms C(1), N(7), C(8) and C(15), with C(6), C(9) and C(10) lying -0.585 , -0.927 and -1.183 \AA respectively from this plane, the average value of the standard deviations being 0.006 Å. The double bond is definitely localized at N(7)–C(8). The endocyclic torsion angles for the azepine ring are given in Fig. 2. The structural angles α and β are given in Fig. 2. The structural angles α and β are the plane through C(1), N(7), C(8), C(15) and the two planes C(1), C(6), N(7) and C(8), C(9), C(10), C(15) are 50.7 (4) and 51.5 (4)° respectively (Fig. 2). These compare with the values of 57 (1) and 32 (1)° observed in two substituted 3*H*-azepines (Carstensen-Oeser, 1972). The conformation of the azepine ring has been determined in several other molecules and generally adopts a distorted boat conformation although the corresponding endocyclic torsion angles with the azepine group vary considerably (Paul, Johnson, Paquette, Barrett & Maluska, 1968; Mattia, Mazzarella & Puliti, 1982; Barnes, Golnazarians, Iball, Paton, Paterson & Suschitzky, 1983). The dihedral angles between the mean plane through the atoms C(1), N(7), C(8), C(15) of the azepine ring and the dihydropyridazine rings *A* and *C* are 75.9 (3) and 46.1 (3)° respectively. The conformation of ring *B* is such that rings *A* and *C* are approximately perpendicular [the angle between the normals to the best planes through *A* and *C* is 91.5 (4)°].

The dihydropyridazine rings *A* and *C* are both non-planar. C(10) and N(13) are 0.41 (1) and 0.21 (1) Å out of the mean plane through C(11), N(12), C(14) and C(15) (ring *A*) and C(1) and N(4) are 0.16 (1) and 0.06 (1) Å from the mean defined by C(2), N(3), C(5) and C(6) (ring *C*).

* Lists of structure factors, anisotropic thermal parameters, torsion angles and details of mean planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39612 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\times 10^4$) with e.s.d.'s in parentheses

$$U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33} + 2U_{23}\cos\alpha + 2U_{13}\cos\beta + 2U_{12}\cos\gamma).$$

	x	y	z	$U_{eq}(\text{\AA}^2)$
C(1)	3442 (4)	3577 (3)	1071 (4)	392
C(2)	3955 (4)	3687 (3)	-346 (4)	383
N(3)	4953 (3)	3249 (2)	-851 (4)	432
N(4)	5532 (4)	2588 (3)	-133 (4)	489
C(5)	5033 (4)	2266 (3)	1088 (5)	406
C(6)	4008 (4)	2689 (3)	1691 (5)	418
N(7)	3503 (4)	2440 (3)	2907 (4)	461
C(8)	2216 (4)	2059 (3)	2948 (4)	407
C(9)	1101 (5)	1703 (3)	1656 (5)	484
C(10)	1215 (4)	2302 (3)	375 (5)	394
C(11)	-250 (4)	2284 (3)	-426 (4)	360
N(12)	-1093 (3)	2922 (2)	-75 (4)	421
N(13)	-561 (3)	3680 (3)	988 (4)	455
C(14)	918 (4)	3980 (3)	1334 (5)	405
C(15)	1828 (4)	3366 (3)	941 (4)	350
C(16)	3411 (4)	4438 (3)	-1185 (5)	408
O(17)	2717 (3)	5042 (2)	-688 (3)	549
O(18)	3794 (3)	4408 (2)	-2495 (4)	589
C(19)	3265 (6)	5117 (4)	-3364 (6)	687
C(20)	5679 (4)	1430 (3)	1623 (5)	489
O(21)	5470 (4)	1080 (3)	2693 (4)	830
O(22)	6521 (3)	1072 (2)	720 (4)	661
C(23)	7171 (6)	227 (4)	1090 (6)	709
C(24)	-799 (4)	1471 (3)	-1576 (4)	394
O(25)	-103 (3)	828 (2)	-1931 (4)	609
O(26)	-2141 (3)	1468 (2)	-2150 (3)	531
C(27)	-2776 (6)	630 (4)	-3223 (7)	717
C(28)	1221 (4)	5001 (3)	2142 (5)	445
O(29)	288 (3)	5495 (2)	2326 (4)	749
O(30)	2563 (3)	5286 (2)	2674 (3)	511
C(31)	2939 (5)	6299 (3)	3405 (5)	528
N(32)	1812 (4)	1925 (3)	4244 (4)	546
C(33)	385 (5)	1487 (4)	4449 (6)	633
C(34)	-597 (7)	2275 (5)	4639 (9)	1079
C(35)	2844 (6)	2275 (4)	5554 (5)	661
C(36)	3735 (8)	1492 (5)	5958 (7)	978

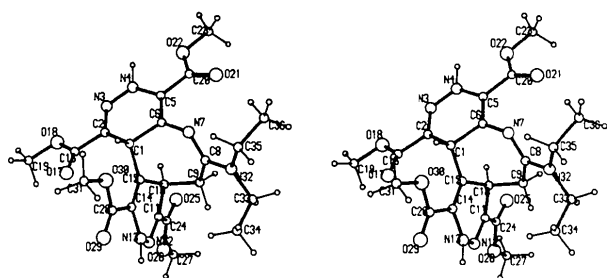


Fig. 1. Stereoview of the molecular structure showing the atomic numbering scheme.

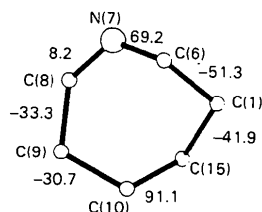


Fig. 2. Endocyclic torsion angles ($^\circ$) (e.s.d.'s $\sim 0.4^\circ$) of the seven-membered azepine ring.

The crystal-packing diagram (Fig. 3) shows the presence of intermolecular hydrogen bonding between N(4) \cdots N(12) [N(12) at $x-1, y, z$] and N(13) \cdots O(17) [O(17) at $-x, 1-y, -z$] with hydrogen-bonding distances of 3.20 (1) and 2.87 (1) \AA respectively. There are also a number of intramolecular contacts which

Table 2. Interatomic distances (\AA) and angles ($^\circ$)

C(1)–C(2)	1.502 (6)	C(14)–C(15)	1.336 (6)
C(1)–C(6)	1.540 (6)	C(14)–C(28)	1.487 (5)
C(1)–C(15)	1.522 (5)	C(16)–O(17)	1.210 (5)
C(2)–N(3)	1.298 (5)	C(16)–O(18)	1.333 (6)
C(2)–C(16)	1.478 (6)	O(18)–C(19)	1.445 (7)
C(3)–N(4)	1.330 (5)	C(20)–O(21)	1.199 (7)
C(5)–C(6)	1.350 (6)	C(20)–O(22)	1.337 (6)
C(5)–C(20)	1.478 (6)	O(22)–C(23)	1.438 (7)
C(6)–N(7)	1.366 (6)	C(24)–O(25)	1.208 (5)
N(7)–C(8)	1.284 (5)	C(24)–O(26)	1.330 (5)
C(8)–C(9)	1.508 (5)	O(26)–C(27)	1.454 (6)
C(8)–N(32)	1.357 (6)	C(28)–O(29)	1.202 (5)
C(9)–C(10)	1.552 (6)	C(28)–O(30)	1.312 (5)
C(10)–C(11)	1.504 (5)	O(30)–C(31)	1.455 (5)
C(10)–C(15)	1.509 (5)	N(32)–C(33)	1.467 (6)
C(11)–N(12)	1.301 (5)	N(32)–C(35)	1.475 (6)
C(11)–C(24)	1.457 (5)	C(33)–C(34)	1.523 (9)
N(12)–N(13)	1.357 (4)	C(35)–C(36)	1.507 (10)
N(13)–C(14)	1.410 (5)		
N(4)–C(5)	1.402 (6)		
C(6)–C(1)–C(2)	110.1 (3)	N(13)–C(14)–C(28)	110.6 (3)
C(15)–C(1)–C(2)	112.8 (3)	C(15)–C(14)–C(28)	129.2 (3)
C(15)–C(1)–C(6)	106.0 (3)	N(13)–C(14)–C(15)	120.2 (3)
C(16)–C(2)–C(1)	118.3 (4)	C(10)–C(15)–C(14)	117.2 (3)
C(16)–C(2)–N(3)	115.6 (4)	C(1)–C(15)–C(10)	114.3 (3)
N(3)–C(2)–C(1)	125.7 (4)	C(1)–C(15)–C(14)	128.5 (3)
N(4)–N(3)–C(2)	119.3 (4)	C(2)–C(16)–O(17)	121.9 (4)
N(3)–N(4)–C(5)	123.2 (4)	C(2)–C(16)–O(18)	114.2 (4)
N(4)–C(5)–C(6)	121.0 (4)	C(16)–O(18)–C(19)	116.1 (4)
N(4)–C(5)–C(20)	115.5 (4)	C(5)–C(20)–O(21)	126.4 (4)
C(6)–C(5)–C(20)	123.5 (4)	C(5)–C(20)–O(22)	110.8 (4)
C(1)–C(6)–C(5)	119.1 (4)	O(21)–C(20)–O(22)	122.8 (4)
C(1)–C(6)–N(7)	116.2 (4)	C(20)–O(22)–C(23)	116.3 (4)
C(5)–C(6)–N(7)	124.4 (4)	C(11)–C(24)–O(25)	122.2 (3)
C(6)–N(7)–C(8)	124.2 (3)	C(11)–C(24)–O(26)	114.7 (3)
N(7)–C(8)–C(9)	125.4 (4)	O(25)–C(24)–O(26)	122.9 (3)
N(7)–C(8)–N(32)	118.6 (4)	C(24)–O(26)–C(27)	116.9 (4)
C(9)–C(8)–N(32)	116.0 (4)	C(14)–C(28)–O(29)	121.7 (3)
C(8)–C(9)–C(10)	114.9 (3)	C(14)–C(28)–O(30)	114.4 (4)
C(9)–C(10)–C(15)	109.3 (3)	O(29)–C(28)–O(30)	123.8 (4)
C(9)–C(10)–C(11)	109.0 (3)	C(28)–O(30)–C(31)	117.0 (3)
C(11)–C(10)–C(15)	108.7 (3)	C(8)–N(32)–C(33)	124.4 (4)
C(10)–C(11)–N(12)	123.0 (3)	C(8)–N(32)–C(35)	118.7 (4)
C(10)–C(11)–C(24)	118.7 (3)	C(33)–N(32)–C(35)	116.8 (4)
N(12)–C(11)–C(24)	118.1 (3)	N(32)–C(33)–C(34)	111.6 (4)
C(11)–N(12)–N(13)	117.4 (3)	N(32)–C(35)–C(36)	112.2 (4)
N(12)–N(13)–C(14)	120.9 (3)	O(17)–C(16)–O(18)	123.8 (4)

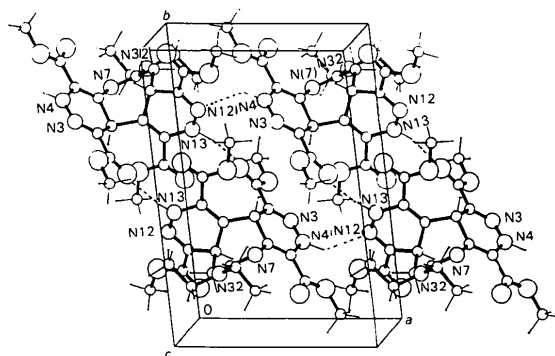


Fig. 3. View of the packing in the unit cell. The dotted lines indicate intermolecular hydrogen bonds.

play an important role in the molecular packing. There are five intramolecular contacts between the ring N atoms and the O atoms of the ester groups: N(3)···O(18) 2·601 (7), N(4)···O(22) 2·560 (8), N(7)···O(21) 2·814 (9), N(12)···O(26) 2·627 (6) and N(13)···O(29) 2·633 (8) Å. In addition there is a short contact between O(17) and O(30) [3·182 (6) Å] of the ester groups of rings *A* and *C* respectively.

References

BARNES, J. C., GOLNAZARIANS, W., IBALL, J., PATON, J. D., PATERSON, T. McC. & SUSCHITZKY, H. (1983). *Acta Cryst.* **C39**, 1410–1412.
 CARSTENSEN-OESER, E. (1972). *Chem. Ber.* **105**, 982–990.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
 MATTIA, C. A., MAZZARELLA, L. & PULITI, R. (1982). *Acta Cryst.* **B38**, 2513–2515.
 MUKAI, T., KUMAGI, T. & YAMASHITA, Y. (1981). *Heterocycles*, **15**, 1569.
 PAUL, I. C., JOHNSON, S. M., PAQUETTE, L. A., BARRETT, J. H. & MALUSKA, R. J. (1968). *J. Am. Chem. Soc.* **90**, 5023–5024.
 ROBERTS, P. & SHELDRIK, G. M. (1975). *XANADU*. Program for crystallographic calculations. Univ. of Cambridge, England.
 SEITZ, G., KÄMPCHEN, T. & OVERHEU, W. (1978). *Arch. Pharm.* **311**, 786–795.
 SHELDRIK, G. M. (1976). *SHELX76*. Program system for crystal structure determination. Univ. of Cambridge, England.
 VALLELY, D. G. (1983). *ARTIST*. A program for plotting molecular structures and electron density maps. Univ. of York, England.

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Reinvestigation of the Structure of Thiourea *S,S*-Dioxide, CH₄N₂O₂S

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Abstract. $M_r = 432.46$, orthorhombic, *Pnma*, $a = 10.644$ (2), $b = 10.106$ (3), $c = 3.9348$ (4) Å, $V = 423.27$ Å³, $Z = 4$, $D_m = 1.66$, $D_x = 1.697$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7093$ Å, $\mu = 5.89$ cm⁻¹, $F(000) = 224$, $T = 298$ K, $R = 0.046$ for 562 observed reflections. The C–S bond length 1.8615 (4) Å, close to that of the previous investigation, is much longer than that in thiourea at 123 K [1.716 (8) Å]. This indicates weakening of the C–S bond upon the oxidation of thiourea. The two crystallographically independent N–H···O hydrogen bonds are roughly equal [2.84 Å].

Introduction. The structure of the title compound has been determined by Sullivan & Hargreaves (1962) using Weissenberg photographs. This work presents the redetermination using a CAD-4 diffractometer in order to obtain better parameters. We are interested in the rather long C–S bond length, –SO₂ conformation and the intermolecular hydrogen bondings.

Experimental. Sample prepared by oxidation of thiourea using hydrogen peroxide. Crystals grown from water, 0.4 × 0.47 × 0.13 mm, CAD-4 diffractometer, unit cell: 20 reflections, 2θ range 15 to 40°. D_m by flotation (CHCl₃/CHBr₃). $2\theta_{\text{max}} = 60^\circ$. Two equivalent sets hkl , $\bar{h}\bar{k}\bar{l}$ averaged to yield 649 unique reflection

data with $\sum(\Delta I/\bar{I})$ of 0.6%, where ΔI indicates the difference between the sets, \bar{I} the arithmetic average intensity of the equivalent sets; the summation is over all the reflections measured. $h \leq 14$, $k \leq 14$, $l \leq 4$. Three standard reflections monitored every 0.5 h; variation 2%. 562 observed with $I \geq \sigma(I)$. Empirical absorption correction based on ψ scans from four reflections with 2θ values from 8 to 42°. H atoms (from ΔF map) refined isotropically, remainder anisotropically, function minimized $\sum w(F_o - F_c)^2$; $R = 0.046$, $R_w = 0.027$, $S = 3.89$; weighting scheme from counting statistics. $(\Delta/\sigma)_{\text{max}} = 0.9$ (for H atom). Peaks on final $\Delta\rho$ map 0.95 e Å⁻³ (around S atom). Secondary-extinction coefficient 0.241 (length in μm). Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Computing programs: NRCC SDP PDP-11 package (Gabe & Lee, 1981).

Discussion. The atomic coordinates and isotropic temperature factors are shown in Table 1.† The bond lengths and angles are approximately the same as those of the previous work (Sullivan & Hargreaves, 1962). The only significant differences are in the hydrogen

† Lists of anisotropic thermal parameters and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39624 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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