O1	0.7987 (4)	−0.2248 (2)	0.1005 (2)	4.43 (7)
O2	0.8192 (4)	−0.2765 (2)	0.2439 (2)	5.31 (9)
O3	0.6980 (4)	0.2884 (2)	0.2828 (2)	5.38 (8)
O4	0.4245 (3)	0.1730 (2)	0.3175 (1)	4.15 (7)
N1	1.0082 (4)	−0.2872 (2)	0.0815 (2)	4.39 (9)
N2	0.5621 (4)	−0.1433 (2)	0.2183 (2)	3.71 (8)
N3	0.6136 (4)	0.0711 (2)	0.1810 (2)	3.76 (8)
N4	0.4042 (5)	0.2958 (2)	0.4052 (2)	4.62 (9)
C1	1.2150 (6)	−0.4038 (4)	−0.0530 (4)	5.1 (1)
C2	0.844 (1)	−0.4522 (5)	−0.2425 (3)	6.4 (2)
C3	1.0033 (5)	−0.3426 (2)	−0.0203 (2)	3.73 (9)
C4	0.7377 (5)	−0.2203 (2)	0.1925 (2)	3.71 (9)
C5	0.4579 (7)	−0.1412 (4)	0.3097 (3)	4.8 (1)
C6	0.8039 (7)	0.0723 (4)	0.1233 (3)	4.9 (1)
C7	0.5893 (5)	0.1879 (3)	0.2627 (2)	3.9 (1)
C8	0.2457 (5)	0.2793 (3)	0.4534 (2)	4.0 (1)
C9	0.2054 (9)	0.3984 (3)	0.5481 (3)	5.7 (1)
C10	−0.1158 (8)	0.1677 (5)	0.5058 (3)	5.9 (2)

Table 2. *Selected geometric parameters* (Å, °)

S1—N2	1.684 (2)	S1—N3	1.677 (2)
S2—C2	1.813 (4)	S3—C10	1.803 (4)
S2—C3	1.730 (3)	S3—C8	1.732 (3)
O1—N1	1.455 (3)	O4—N4	1.447 (3)
O1—C4	1.347 (3)	O4—C7	1.364 (3)
O2—C4	1.188 (3)	O3—C7	1.190 (3)
N1—C3	1.277 (4)	N4—C8	1.278 (4)
N2—C4	1.374 (3)	N3—C7	1.374 (3)
N2—C5	1.472 (4)	N3—C6	1.476 (4)
C1—C3	1.495 (4)	C8—C9	1.503 (4)
N2—S1—N3	105.7 (1)	S1—N3—C7	124.2 (2)
S1—N2—C4	124.1 (2)	S1—N3—C6	120.1 (2)
S1—N2—C5	118.5 (2)	S3—C8—N4	123.2 (2)
S2—C3—N1	122.9 (2)	S3—C8—C9	121.4 (2)
S2—C3—C1	122.0 (3)	N4—O4—C7	110.5 (2)
N1—O1—C4	111.4 (2)	O4—N4—C8	109.0 (2)
O1—N1—C3	108.6 (2)	O3—C7—O4	124.8 (3)
O1—C4—O2	125.5 (3)	O4—C7—N3	110.8 (2)
O1—C4—N2	110.6 (2)	O3—C7—N3	124.3 (3)
O2—C4—N2	123.9 (3)	N4—C8—C9	115.4 (3)
N1—C3—C1	115.1 (3)	C8—S3—C10	103.4 (2)
C2—S2—C3	103.6 (2)	C6—N3—C7	115.7 (2)
C4—N2—C5	117.0 (2)		
S1—N2—C4—O1	0.3 (3)	O3—C7—N3—C6	6.1 (5)
S1—N2—C4—O2	−178.3 (2)	N1—O1—C4—N2	170.4 (2)
S2—C3—N1—O1	−3.1 (3)	N1—C3—S2—C2	−173.1 (3)
O1—N1—C3—C1	176.0 (2)	N2—S1—N3—C6	90.3 (3)
O1—C4—N2—C5	173.0 (3)	N2—S1—N3—C7	−90.9 (2)
O2—C4—O1—N1	−11.0 (4)	C1—C3—S2—C2	7.8 (3)
O2—C4—N2—C5	−5.7 (4)	C3—N1—O1—C4	150.4 (2)
S1—N3—C7—O3	−172.8 (3)	N3—C7—O4—N4	178.5 (2)
S1—N3—C7—O4	7.2 (4)	N4—C8—S3—C10	−177.5 (3)
S3—C8—N4—O4	−0.8 (4)	N3—S1—N2—C5	104.9 (2)
O4—N4—C8—C9	179.2 (3)	N3—S1—N2—C4	−82.5 (2)
O4—C7—N3—C6	−173.8 (3)	C9—C8—S3—C10	2.5 (4)
O3—C7—O4—N4	−1.4 (4)	C7—O4—N4—C8	178.7 (2)

The θ scan width was $1.5(0.83 + 0.14\tan\theta)^\circ$. The scan was recorded as 96 steps with the two outermost 16-step blocks for background determination. The θ scan speed was 5.49–2.06° min^{-1}. Correction for dispersion was made using *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.3.1).

The structure was solved using *MITHRIL* (Gilmore, 1983). Crystallographic calculations were performed with the *TEXSAN* system (Molecular Structure Corporation, 1987) on Digital Equipment Corporation MicroVAX II and VAXStation II computers. Molecular graphics were prepared using *ORTEP*II (Johnson, 1976) and *ChemDraw* (Cambridge Scientific Computing, 1989). Other material for publication was produced using *PLOTMD* (Luo, Ammon & Gilliland, 1989).

The instrumentation used in this work was obtained in part with grants from the National Science Foundation (CHE-84-02155) and the National Institutes of Health (RR-03354).

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: CR1160). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Aranda, G., Gauvrit, C., Cesario, M., Guilhem, J., Pascard, C. & Tran Huu Dau, M. M. (1983). *Phytochemistry*, **22**, 2431–2435.

Cambridge Scientific Computing (1989). *ChemDraw. Desktop Publishing for Chemists.* Version 2.1.3. Cambridge Scientific Computing, 875 Massachusetts Ave., Cambridge, MA, USA.

Dewar, M. J. S., Zoebisch, E. G., Healy, E. F. & Stewart, J. J. P. (1985). *J. Am. Chem. Soc.* **107**, 3902–3909.

D'Silva, T. J. (1971). US Patent 3 576 834.

D'Silva, T. J. (1985). *Recent Advances in the Chemistry of Insect Control*, edited by N. F. James. Special Publication No. 53, 205–227. London: Royal Society of Chemistry.

Gilmore, C. J. (1983). *MITHRIL. A Computer Program for the Automatic Solution of Crystal Structures.* Univ. of Glasgow, Scotland.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Luo, J., Ammon, H. L. & Gilliland, G. (1989). *J. Appl. Cryst.* **22**, 186.

Molecular Structure Corporation (1987). *TEXSAN. Structure Analysis Package.* Version 2.0. Molecular Structure Corporation, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Stewart, J. J. P. (1990). *MOPAC.* Version 6.0. Quantum Chemistry Program Exchange No. 455. Indiana Univ., Indiana, USA.

Takusagawa, F. & Jacobson, R. A. (1977). *J. Agric. Food Chem.* **25**, 577–581.

Waite, M. G. & Sim, G. A. (1971). *J. Chem. Soc. B*, pp. 572–576.

Zachariasen, W. H. (1968). *Acta Cryst.* **A24**, 212–216.

Acta Cryst. (1995). C**51**, 1621–1627

4-Substituted 1-Methyl-1*H*-2,3-benzodiazepine Compounds

ALEXANDER J. BLAKE, MERVYN HARDING AND
JOHN T. SHARP

*Department of Chemistry, The University of Edinburgh,
West Mains Road, Edinburgh EH9 3JJ, Scotland*

(*Received* 24 *November* 1994; *accepted* 24 *January* 1995)

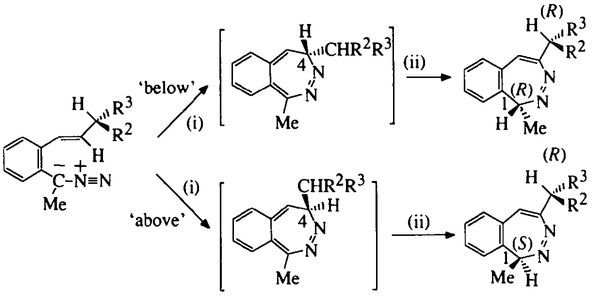
Abstract

The structures of a series of six 1-methyl-1*H*-2,3-benzodiazepine compounds, 1(*R*)-methyl-4-[1(*R*)-phenylethyl]-1*H*-2,3-benzodiazepine ($C_{18}H_{18}N_2$), (1), 1(*R*)-methyl-4-[1(*R*),2,2-trimethylpropyl]-1*H*-2,3-benzo-

diazepine ($C_{16}H_{22}N_2$), (2), 1(*S*)-methyl-4-[1(*S*)-ethyl-2,2-dimethylpropyl]-1*H*-2,3-benzodiazepine ($C_{17}H_{24}N_2$), (3), 1(*R*)-methyl-4-[1(*R*)-methoxybenzyl]-1*H*-2,3-benzodiazepine ($C_{18}H_{18}N_2O$), (4), 1(*S*)-methyl-4-[1(*R*)-methoxy-2,2-dimethylpropyl]-1*H*-2,3-benzodiazepine ($C_{16}H_{22}N_2O$), (5), and 1(*R*)-methyl-4-[1(*R*)-benzoyloxy-2,2-dimethylpropyl]-1*H*-2,3-benzodiazepine ($C_{22}H_{24}N_2O_2$), (6), with differing substituents on the 4-position of the seven-membered diazepine ring, have been determined. [The IUPAC name for the ester (6) is 2,2-dimethyl-1-(1-methyl-1*H*-2,3-benzodiazepin-4-yl)propyl benzoate.]

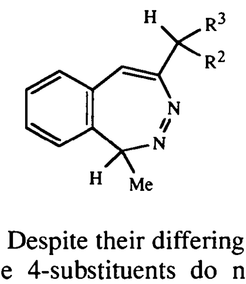
Comment

The main objective of this work was to study the effect of different chiral groups in the diazo compound on the face-selectivity of the 1.7 electrocyclization reaction. The cyclization step leads to the formation of two diastereomeric intermediates; these then rearrange *via* a stereospecific, suprafacial [1,5] H-atom migration to give a pair of diastereomeric 1*H*-2,3-benzodiazepine compounds:



(i) 1.7 electrocyclization
(ii) [1,5] sigmatropic H shift

The ratio of these products was measured by HPLC and NMR. The crystal structure of one of each of these pairs of isomers was determined in order to establish the relative configuration of the two chiral centres and thereby establish which of the alternative cyclization paths was preferred in each case (Blake, Harding & Sharp, 1994).



	R^2	R^3
(1)	Ph	Me
(2)	^{t}Bu	Me
(3)	^{t}Bu	Et
(4)	Ph	OMe
(5)	^{t}Bu	OMe
(6)	^{t}Bu	OCOPh

Despite their differing steric and electronic properties, the 4-substituents do not affect the geometry of the diazepine ring. In all six compounds this ring may be described by reference to two planes (defined by N2–N3–C5*a*–C9*a* and N3–C4–C5–C5*a*), the corresponding interplanar angle and the deviation of C1 from the first plane: the interplanar angles are 31.92 (8), 33.03 (14), 33.34 (18), 32.24 (18), 32.54 (11) and 32.52 (11)° for compounds (1)–(6), respectively, and the corresponding deviations for C1 are 0.792 (3), 0.785 (3), 0.787 (3), 0.799 (5), 0.776 (2) and 0.785 (2) Å.

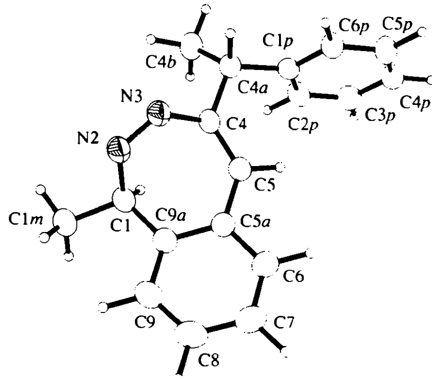


Fig. 1. A view of a molecule of (1) with atom-numbering scheme. Displacement ellipsoids enclose 50% probability surfaces.

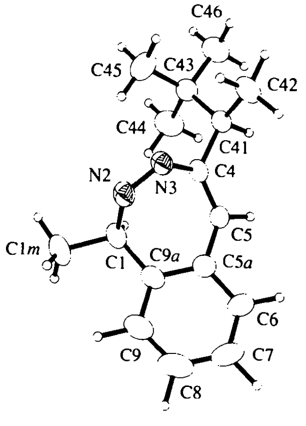


Fig. 2. A view of a molecule of (2) with atom-numbering scheme. Displacement ellipsoids enclose 50% probability surfaces.

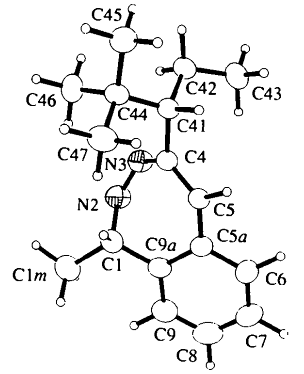


Fig. 3. A view of a molecule of (3) with atom-numbering scheme. Displacement ellipsoids enclose 50% probability surfaces.

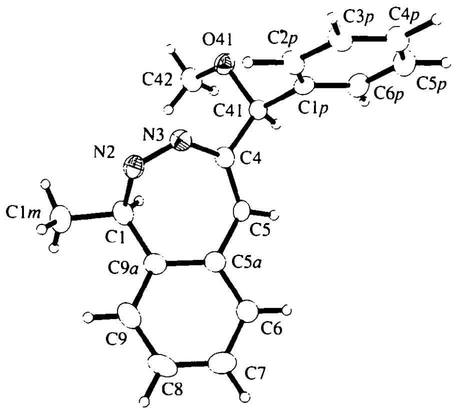


Fig. 4. A view of a molecule of (4) with atom-numbering scheme. Displacement ellipsoids enclose 50% probability surfaces.

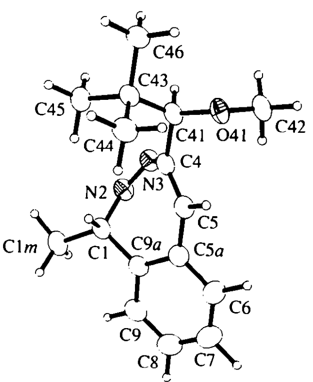


Fig. 5. A view of a molecule of (5) with atom-numbering scheme. Displacement ellipsoids enclose 50% probability surfaces.

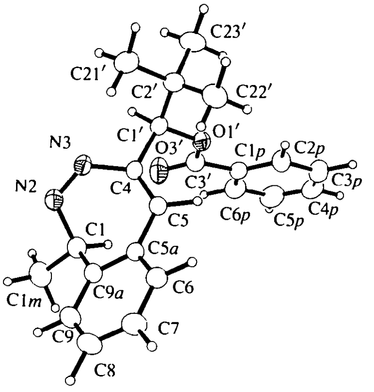


Fig. 6. A view of a molecule of (6) with atom-numbering scheme. Displacement ellipsoids enclose 50% probability surfaces.

Experimental

Compounds (1)–(6) were prepared by 1.7 electrocyclization followed by a [1,5] sigmatropic H shift as shown in the reaction scheme above. Crystals were grown from hexane.

Compound (1)

Crystal data

$C_{18}H_{18}N_2$
$M_r = 262.34$
Monoclinic
$P2_1/n$
$a = 8.502\,(2)$ Å
$b = 21.675\,(13)$ Å
$c = 8.741\,(3)$ Å
$\beta = 115.76\,(2)°$
$V = 1450.8\,(11)$ Å^3
$Z = 4$
$D_x = 1.201$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 11 reflections
$\theta = 13$–$15°$
$\mu = 0.071$ mm^{-1}
$T = 298\,(2)$ K
Plate
0.62 × 0.54 × 0.23 mm
Yellow

Data collection

Stoe Stadi-4 four-circle diffractometer
ω–2θ scans using on-line profile fitting (Clegg, 1981)
Absorption correction: none
1898 measured reflections
1898 independent reflections
1577 observed reflections $[I > 2\sigma(I)]$

$\theta_{\max} = 22.51°$
$h = -9 \rightarrow 8$
$k = 0 \rightarrow 23$
$l = 0 \rightarrow 9$
3 standard reflections frequency: 120 min intensity decay: 6%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0452$
$wR(F^2) = 0.1194$
$S = 1.065$
1895 reflections
170 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0666P)^2 + 0.4158P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.003$
$\Delta\rho_{\max} = 0.21$ e Å^{-3}
$\Delta\rho_{\min} = -0.15$ e Å^{-3}

Extinction correction: *SHELXL93* (Sheldrick, 1993)
Extinction coefficient: 0.024 (4)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (1)

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

	x	y	z	$U_{\rm eq}$
C1	0.2835 (3)	0.04526 (10)	0.2373 (3)	0.0594 (6)
C1*m*	0.2949 (4)	0.02547 (13)	0.0750 (3)	0.0795 (8)
N2	0.1508 (3)	0.09546 (9)	0.1940 (2)	0.0633 (5)
N3	0.1616 (2)	0.13202 (9)	0.3095 (2)	0.0615 (5)
C4	0.2793 (3)	0.12495 (10)	0.4835 (3)	0.0552 (6)
C4*a*	0.3346 (3)	0.18744 (10)	0.5703 (3)	0.0582 (6)
C4*b*	0.4545 (4)	0.22057 (13)	0.5073 (3)	0.0807 (8)
C5	0.3023 (3)	0.07063 (10)	0.5645 (3)	0.0579 (6)
C5*a*	0.2453 (3)	0.01021 (10)	0.4894 (3)	0.0554 (6)
C6	0.2032 (3)	−0.03539 (11)	0.5787 (3)	0.0658 (6)
C7	0.1367 (3)	−0.09122 (12)	0.5061 (4)	0.0731 (7)
C8	0.1100 (3)	−0.10271 (12)	0.3411 (4)	0.0759 (7)
C9	0.1541 (3)	−0.05935 (11)	0.2515 (3)	0.0687 (7)
C9*a*	0.2265 (3)	−0.00277 (10)	0.3250 (3)	0.0559 (6)
C1*p*	0.4122 (2)	0.18394 (7)	0.76314 (12)	0.0544 (6)
C2*p*	0.5827 (2)	0.16324 (7)	0.8579 (2)	0.0660 (6)
C3*p*	0.6491 (2)	0.15775 (7)	1.0339 (2)	0.0702 (7)
C4*p*	0.5449 (2)	0.17296 (8)	1.11523 (12)	0.0727 (7)
C5*p*	0.3743 (2)	0.19365 (8)	1.0205 (2)	0.0747 (7)
C6*p*	0.30799 (15)	0.19914 (7)	0.8444 (2)	0.0630 (6)

Table 2. *Selected geometric parameters* (Å, °) *for* (1)

C1—N2	1.493 (3)	C4—C5	1.344 (3)
C1—C9*a*	1.494 (3)	C5—C5*a*	1.451 (3)
N2—N3	1.255 (2)	C5*a*—C9*a*	1.403 (3)
N3—C4	1.420 (3)		
N2—C1—C9*a*	105.1 (2)	C4—C5—C5*a*	127.5 (2)
N3—N2—C1	118.3 (2)	C9*a*—C5*a*—C5	120.7 (2)
N2—N3—C4	124.4 (2)	C5*a*—C9*a*—C1	117.9 (2)
C5—C4—N3	122.2 (2)		
C9*a*—C1—N2—N3	78.5 (2)	N3—C4—C5—C5*a*	13.3 (4)
C1—N2—N3—C4	−7.5 (3)	C4—C5—C5*a*—C9*a*	28.2 (3)
N2—N3—C4—C5	−45.8 (3)	N2—C1—C9*a*—C5*a*	−71.5 (2)

Compound (2)

Crystal data

$C_{16}H_{22}N_2$
$M_r = 242.36$
Monoclinic
$P2_1/c$
$a = 11.7871\ (9)$ Å
$b = 10.3877\ (7)$ Å
$c = 12.4807\ (8)$ Å
$\beta = 102.276\ (6)°$
$V = 1493.2\ (2)$ Å^3
$Z = 4$
$D_x = 1.078$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 44 reflections
$\theta = 12.5–14.0°$
$\mu = 0.063$ mm^{-1}
$T = 298\ (2)$ K
Plate
0.69 × 0.32 × 0.09 mm
Pale green

Data collection

Stoe Stadi-4 four circle diffractometer
ω–2θ scans with ω width $(0.8 + 0.35\tan\theta)°$
Absorption correction: none
1951 measured reflections
1951 independent reflections
1265 observed reflections $[I > 2\sigma(I)]$

$\theta_{\max} = 22.51°$
$h = -12 \rightarrow 12$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 13$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0435$
$wR(F^2) = 0.1133$
$S = 1.219$
1945 reflections
164 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0640P)^2 + 0.0239P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.13$ e Å^{-3}
$\Delta\rho_{\min} = -0.11$ e Å^{-3}

Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.017 (3)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (2)

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

	x	y	z	$U_{\rm eq}$
C1	0.6171 (2)	0.4349 (2)	0.7211 (2)	0.0628 (7)
C1*m*	0.6145 (3)	0.5381 (3)	0.8073 (2)	0.0982 (9)
N2	0.6563 (2)	0.3125 (2)	0.77993 (14)	0.0646 (6)
N3	0.7028 (2)	0.2281 (2)	0.73198 (14)	0.0587 (5)
C4	0.7105 (2)	0.2348 (2)	0.6208 (2)	0.0491 (6)
C41	0.8141 (2)	0.1641 (2)	0.5949 (2)	0.0558 (6)
C42	0.8097 (2)	0.0221 (2)	0.6280 (2)	0.0829 (8)
C43	0.9328 (2)	0.2307 (2)	0.6374 (2)	0.0641 (7)
C44	0.9265 (2)	0.3675 (3)	0.5930 (3)	0.1028 (10)
C45	0.9681 (2)	0.2336 (3)	0.7621 (2)	0.1037 (10)
C46	1.0267 (2)	0.1595 (3)	0.5918 (3)	0.1023 (10)
C5	0.6189 (2)	0.2687 (2)	0.5418 (2)	0.0541 (6)
C5*a*	0.5105 (2)	0.3233 (2)	0.5560 (2)	0.0558 (6)
C6	0.4074 (2)	0.2963 (3)	0.4794 (2)	0.0751 (7)
C7	0.3035 (2)	0.3428 (3)	0.4948 (3)	0.0929 (9)
C8	0.2994 (3)	0.4178 (3)	0.5840 (3)	0.0988 (11)
C9	0.3980 (3)	0.4485 (3)	0.6586 (2)	0.0798 (8)
C9*a*	0.5049 (2)	0.4031 (2)	0.6449 (2)	0.0577 (6)

Table 4. *Selected geometric parameters* (Å, °) *for* (2)

C1—N2	1.491 (3)	C4—C5	1.345 (3)
C1—C9*a*	1.493 (3)	C5—C5*a*	1.442 (3)
N2—N3	1.252 (2)	C5*a*—C9*a*	1.399 (3)
N3—C4	1.412 (3)		
N2—C1—C9*a*	105.3 (2)	C4—C5—C5*a*	127.3 (2)
N3—N2—C1	118.9 (2)	C9*a*—C5*a*—C5	121.6 (2)
N2—N3—C4	124.2 (2)	C5*a*—C9*a*—C1	116.8 (2)
C5—C4—N3	121.6 (2)		
C9*a*—C1—N2—N3	78.6 (2)	C4—C5—C5*a*—C9*a*	31.5 (3)
C1—N2—N3—C4	−6.9 (3)	C5—C5*a*—C9*a*—C1	3.1 (3)
N2—N3—C4—C5	−45.6 (3)	N2—C1—C9*a*—C5*a*	−69.8 (2)
N3—C4—C5—C5*a*	11.6 (4)		

Compound (3)

Crystal data

$C_{17}H_{24}N_2$
$M_r = 256.38$
Monoclinic
$P2_1/c$
$a = 12.852\ (6)$ Å
$b = 10.605\ (5)$ Å
$c = 12.331\ (6)$ Å
$\beta = 111.07\ (3)°$
$V = 1568.3\ (13)$ Å^3
$Z = 4$
$D_x = 1.086$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 10 reflections
$\theta = 11–12°$
$\mu = 0.064$ mm^{-1}
$T = 298\ (2)$ K
Lath
0.82 × 0.14 × 0.04 mm
Lemon yellow

Data collection

Stoe Stadi-4 four-circle diffractometer
ω–2θ scans with on-line profile fitting (Clegg, 1981)
Absorption correction: none
2030 measured reflections
2027 independent reflections
1245 observed reflections $[I > 2\sigma(I)]$

$R_{\rm int} = 0.0465$
$\theta_{\max} = 22.50°$
$h = 0 \rightarrow 13$
$k = -11 \rightarrow 0$
$l = -12 \rightarrow 12$
3 standard reflections
frequency: 120 min
intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0486$
$wR(F^2) = 0.1251$
$S = 1.208$
2026 reflections

Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.009 (3)

173 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0651P)^2 + 0.1325P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.16$ e Å^{-3}
$\Delta\rho_{\min} = -0.14$ e Å^{-3}

Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 5. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (3)

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

	x	y	z	$U_{\rm eq}$
C1	0.6403 (2)	0.4540 (3)	−0.1505 (2)	0.0647 (8)
C1*m*	0.6333 (3)	0.5652 (4)	−0.2308 (3)	0.1008 (12)
N2	0.6762 (2)	0.3410 (3)	−0.2002 (2)	0.0736 (8)
N3	0.7260 (2)	0.2544 (2)	−0.1317 (2)	0.0681 (7)
C4	0.7381 (2)	0.2494 (2)	−0.0130 (2)	0.0520 (7)
C5	0.6501 (2)	0.2710 (2)	0.0202 (2)	0.0538 (7)
C5*a*	0.5436 (2)	0.3264 (3)	−0.0479 (2)	0.0544 (7)
C6	0.4470 (2)	0.2937 (3)	−0.0265 (3)	0.0676 (9)
C7	0.3450 (3)	0.3447 (3)	−0.0911 (3)	0.0790 (10)
C8	0.3377 (3)	0.4303 (4)	−0.1773 (3)	0.0854 (11)
C9	0.4306 (3)	0.4650 (3)	−0.1986 (3)	0.0737 (9)
C9*a*	0.5345 (2)	0.4162 (3)	−0.1348 (2)	0.0562 (7)
C41	0.8432 (2)	0.1857 (2)	0.0648 (2)	0.0549 (7)
C42	0.8581 (2)	0.0553 (3)	0.0169 (3)	0.0691 (9)
C43	0.7690 (3)	−0.0377 (3)	0.0144 (3)	0.0852 (10)
C44	0.9484 (2)	0.2714 (3)	0.0979 (3)	0.0616 (8)
C45	1.0477 (2)	0.2066 (3)	0.1914 (3)	0.0828 (10)
C46	0.9816 (3)	0.3016 (3)	−0.0069 (3)	0.0873 (10)
C47	0.9259 (3)	0.3944 (3)	0.1503 (3)	0.0875 (11)

Table 6. *Selected geometric parameters* (Å, °) *for* (3)

C1—N2	1.492 (4)	C4—C5	1.352 (3)
C1—C9*a*	1.495 (4)	C5—C5*a*	1.448 (4)
N2—N3	1.257 (3)	C5*a*—C9*a*	1.407 (4)
N3—C4	1.417 (3)		
N2—C1—C9*a*	105.6 (2)	C4—C5—C5*a*	127.8 (3)
N3—N2—C1	117.9 (2)	C9*a*—C5*a*—C5	121.2 (2)
N2—N3—C4	124.2 (2)	C5*a*—C9*a*—C1	116.7 (2)
C5—C4—N3	120.9 (2)		
C9*a*—C1—N2—N3	−80.4 (3)	C4—C5—C5*a*—C9*a*	−30.5 (4)
C1—N2—N3—C4	8.3 (4)	C5—C5*a*—C9*a*—C1	−1.7 (4)
N2—N3—C4—C5	46.5 (4)	N2—C1—C9*a*—C5*a*	69.2 (3)
N3—C4—C5—C5*a*	−14.3 (4)		

Compound (4)

Crystal data

$C_{18}H_{18}N_2O$
$M_r = 278.34$
Orthorhombic
$P2_12_12_1$
$a = 6.350$ (5) Å
$b = 10.954$ (8) Å
$c = 21.118$ (18) Å
$V = 1468.9$ (20) Å^3
$Z = 4$
$D_x = 1.259$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 62 reflections
$\theta = 15$–$16°$
$\mu = 0.079$ mm^{-1}
$T = 150.0$ (2) K
Lath
1.14 × 0.30 × 0.19 mm
Yellow

Data collection

Stoe Stadi-4 four-circle diffractometer
ω–2θ scans with ω width $(1.2 + 0.35\tan\theta)°$

$\theta_{\max} = 25.07°$
$h = -7 \rightarrow 1$
$k = 0 \rightarrow 13$
$l = 0 \rightarrow 25$

Absorption correction: none
1529 measured reflections
1529 independent reflections
1283 observed reflections $[I > 2\sigma(I)]$

3 standard reflections
frequency: 60 min
intensity decay: 1.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0552$
$wR(F^2) = 0.1379$
$S = 1.057$
1523 reflections
179 parameters
$w = 1/[\sigma^2(F_o^2) + (0.1064P)^2 + 0.23P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.008$
$\Delta\rho_{\max} = 0.28$ e Å^{-3}
$\Delta\rho_{\min} = -0.41$ e Å^{-3}

Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.002 (5)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 7. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (4)

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

	x	y	z	$U_{\rm eq}$
C1	0.3500 (6)	−0.2878 (3)	0.1754 (2)	0.0269 (9)
C1*m*	0.5322 (6)	−0.3527 (4)	0.2059 (2)	0.0339 (10)
N2	0.4157 (5)	−0.1582 (3)	0.16369 (15)	0.0260 (7)
N3	0.2747 (5)	−0.0782 (3)	0.15974 (14)	0.0253 (8)
C4	0.0564 (6)	−0.1049 (3)	0.1581 (2)	0.0216 (8)
C5	−0.0280 (6)	−0.1941 (3)	0.1216 (2)	0.0209 (8)
C5*a*	0.0840 (6)	−0.2901 (3)	0.0884 (2)	0.0229 (8)
C6	0.0022 (7)	−0.3387 (3)	0.0324 (2)	0.0268 (9)
C7	0.1133 (7)	−0.4254 (3)	−0.0011 (2)	0.0328 (10)
C8	0.3069 (7)	−0.4650 (3)	0.0202 (2)	0.0334 (10)
C9	0.3893 (7)	−0.4212 (3)	0.0768 (2)	0.0300 (9)
C9*a*	0.2779 (6)	−0.3347 (3)	0.1122 (2)	0.0233 (8)
C41	−0.0823 (6)	−0.0066 (3)	0.1871 (2)	0.0216 (8)
O41	0.0041 (5)	0.0376 (2)	0.24523 (12)	0.0269 (6)
C42	−0.0015 (7)	−0.0534 (4)	0.2934 (2)	0.0332 (9)
C1*p*	−0.1149 (4)	0.1045 (2)	0.14389 (10)	0.0229 (8)
C2*p*	0.0539 (3)	0.1695 (2)	0.11946 (12)	0.0292 (9)
C3*p*	0.0181 (3)	0.2686 (2)	0.08024 (12)	0.0299 (9)
C4*p*	−0.1864 (4)	0.3027 (2)	0.06542 (11)	0.0299 (9)
C5*p*	−0.3552 (3)	0.2377 (2)	0.08985 (13)	0.0326 (10)
C6*p*	−0.3194 (3)	0.1386 (2)	0.12908 (12)	0.0272 (9)

Table 8. *Selected geometric parameters* (Å, °) *for* (4)

C1—N2	1.500 (5)	C4—C5	1.356 (5)
C1—C9*a*	1.502 (5)	C5—C5*a*	1.450 (5)
N2—N3	1.256 (4)	C5*a*—C9*a*	1.416 (5)
N3—C4	1.417 (5)		
N2—C1—C9*a*	105.2 (3)	C4—C5—C5*a*	127.1 (3)
N3—N2—C1	118.2 (3)	C9*a*—C5*a*—C5	120.3 (3)
N2—N3—C4	123.7 (3)	C5*a*—C9*a*—C1	117.5 (3)
C5—C4—N3	123.3 (3)		
C9*a*—C1—N2—N3	79.0 (4)	C4—C5—C5*a*—C9*a*	29.0 (5)
C1—N2—N3—C4	−7.8 (5)	C5—C5*a*—C9*a*—C1	5.8 (5)
N2—N3—C4—C5	−45.4 (6)	N2—C1—C9*a*—C5*a*	−72.0 (4)
N3—C4—C5—C5*a*	12.5 (6)		

Compound (5)

Crystal data

$C_{16}H_{22}N_2O$
$M_r = 258.36$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å

Triclinic
$P\overline{1}$
$a = 7.7357$ (9) Å
$b = 9.4583$ (10) Å
$c = 11.0128$ (13) Å
$\alpha = 102.929$ (8)°
$\beta = 101.797$ (6)°
$\gamma = 100.792$ (5)°
$V = 745.48$ (15) Å^3
$Z = 2$
$D_x = 1.151$ Mg m^{-3}

Cell parameters from 20 reflections
$\theta = 15$–16°
$\mu = 0.072$ mm^{-1}
$T = 298$ (2) K
Tabular
1.23 × 1.04 × 0.46 mm
Colourless

Data collection

Stoe Stadi-4 four-circle diffractometer
ω–2θ scans with ω width $(0.99 + 0.35\tan\theta)$°
Absorption correction: none
2054 measured reflections
1950 independent reflections
1777 observed reflections $[I > 2\sigma(I)]$

$R_{\rm int} = 0.0036$
$\theta_{\rm max} = 22.52$°
$h = -8 \rightarrow 7$
$k = -10 \rightarrow 9$
$l = 0 \rightarrow 11$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0336$
$wR(F^2) = 0.0925$
$S = 1.132$
1942 reflections
173 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0466P)^2 + 0.1211P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.12$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.10$ e Å^{-3}

Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.120 (9)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 9. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (5)

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

	x	y	z	$U_{\rm eq}$
C1	0.2840 (2)	0.5722 (2)	0.43458 (13)	0.0511 (4)
C1*m*	0.2833 (2)	0.6031 (2)	0.57589 (14)	0.0650 (5)
N2	0.1523 (2)	0.64690 (14)	0.37097 (12)	0.0559 (4)
N3	0.1771 (2)	0.68256 (14)	0.27155 (11)	0.0543 (4)
C4	0.3074 (2)	0.6394 (2)	0.20650 (12)	0.0480 (4)
C41	0.3852 (2)	0.7549 (2)	0.14410 (12)	0.0505 (4)
O41	0.39882 (14)	0.68759 (12)	0.01798 (9)	0.0601 (3)
C42	0.2287 (3)	0.6396 (2)	−0.0758 (2)	0.0785 (6)
C43	0.5749 (2)	0.8544 (2)	0.22186 (13)	0.0526 (4)
C44	0.7176 (2)	0.7631 (2)	0.2267 (2)	0.0671 (5)
C45	0.5666 (3)	0.9269 (2)	0.35905 (14)	0.0691 (5)
C46	0.6249 (2)	0.9788 (2)	0.1583 (2)	0.0648 (5)
C5	0.3254 (2)	0.4978 (2)	0.17842 (13)	0.0519 (4)
C5*a*	0.2562 (2)	0.3798 (2)	0.23245 (14)	0.0519 (4)
C6	0.2187 (2)	0.2300 (2)	0.1614 (2)	0.0670 (5)
C7	0.1536 (2)	0.1162 (2)	0.2109 (2)	0.0772 (5)
C8	0.1252 (2)	0.1489 (2)	0.3332 (2)	0.0747 (5)
C9	0.1614 (2)	0.2943 (2)	0.4054 (2)	0.0630 (4)
C9*a*	0.2301 (2)	0.4119 (2)	0.35787 (13)	0.0504 (4)

Table 10. *Selected geometric parameters* (Å, °) *for* (5)

C1—N2	1.492 (2)	C4—C5	1.345 (2)
C1—C9*a*	1.494 (2)	C5—C5*a*	1.446 (2)
N2—N3	1.255 (2)	C5*a*—C9*a*	1.411 (2)
N3—C4	1.419 (2)		
N2—C1—C9*a*	106.38 (11)	C4—C5—C5*a*	127.38 (13)
N3—N2—C1	117.86 (11)	C9*a*—C5*a*—C5	121.29 (13)
N2—N3—C4	124.07 (12)	C5*a*—C9*a*—C1	117.34 (13)
C5—C4—N3	122.05 (13)		
C9*a*—C1—N2—N3	−79.4 (2)	C4—C5—C5*a*—C9*a*	−28.1 (2)
C1—N2—N3—C4	8.5 (2)	C5—C5*a*—C9*a*—C1	−2.4 (2)
N2—N3—C4—C5	46.9 (2)	N2—C1—C9*a*—C5*a*	68.84 (15)
N3—C4—C5—C5*a*	−16.2 (2)		

Compound (6)

Crystal data

$C_{22}H_{24}N_2O_2$
$M_r = 348.43$
Orthorhombic
Pcab
$a = 12.962$ (2) Å
$b = 13.4604$ (8) Å
$c = 22.2464$ (15) Å
$V = 3881.5$ (6) Å^3
$Z = 8$
$D_x = 1.193$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 42 reflections
$\theta = 12.0$–12.5°
$\mu = 0.077$ mm^{-1}
$T = 298$ (2) K
Block
0.78 × 0.57 × 0.42 mm
Pale yellow–green

Data collection

Stoe Stadi-4 four-circle diffractometer
ω–2θ scans using on-line profile fitting (Clegg, 1981)
Absorption correction: none
2541 measured reflections
2541 independent reflections
2139 observed reflections $[I > 2\sigma(I)]$

$\theta_{\rm max} = 22.52$°
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 14$
$l = 0 \rightarrow 23$
3 standard reflections
frequency: 120 min
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0345$
$wR(F^2) = 0.0938$
$S = 1.118$
2538 reflections
236 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0485P)^2 + 0.6225P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.11$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.12$ e Å^{-3}

Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0044 (6)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 11. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (6)

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

	x	y	z	$U_{\rm eq}$
C1	0.13299 (12)	0.33571 (13)	0.58551 (8)	0.0550 (4)
C1*m*	0.04611 (14)	0.3900 (2)	0.55427 (10)	0.0816 (6)
N2	0.14029 (10)	0.23410 (11)	0.55882 (6)	0.0565 (4)
N3	0.18049 (11)	0.16703 (11)	0.59002 (6)	0.0536 (4)
C4	0.22999 (12)	0.18390 (12)	0.64570 (6)	0.0474 (4)

C5	0.29828 (12)	0.25755 (12)	0.65467 (7)	0.0473 (4)
C5*a*	0.31675 (12)	0.34153 (11)	0.61553 (7)	0.0450 (4)
C6	0.41400 (13)	0.38592 (13)	0.61394 (8)	0.0564 (4)
C7	0.43416 (14)	0.46333 (14)	0.57589 (8)	0.0667 (5)
C8	0.35769 (15)	0.49890 (14)	0.53877 (8)	0.0670 (5)
C9	0.26072 (14)	0.45843 (13)	0.54055 (7)	0.0586 (5)
C9*a*	0.23793 (12)	0.38034 (11)	0.57929 (7)	0.0473 (4)
C1′	0.21374 (13)	0.09823 (12)	0.68846 (7)	0.0530 (4)
C2′	0.2944 (2)	0.01413 (13)	0.68940 (8)	0.0656 (5)
C21′	0.3033 (2)	−0.0281 (2)	0.62569 (9)	0.0859 (7)
C22′	0.3998 (2)	0.0500 (2)	0.71081 (10)	0.0874 (7)
C23′	0.2550 (2)	−0.0674 (2)	0.73148 (10)	0.1019 (8)
O1′	0.20741 (8)	0.13609 (8)	0.74953 (5)	0.0542 (3)
C3′	0.11859 (14)	0.17934 (13)	0.76603 (8)	0.0556 (4)
O3′	0.04901 (10)	0.19375 (12)	0.73132 (6)	0.0838 (4)
C1*p*	0.11671 (12)	0.20635 (12)	0.83028 (7)	0.0525 (4)
C2*p*	0.19944 (15)	0.19121 (15)	0.86803 (8)	0.0650 (5)
C3*p*	0.1938 (2)	0.2198 (2)	0.92749 (9)	0.0769 (6)
C4*p*	0.1059 (2)	0.2614 (2)	0.94931 (9)	0.0792 (6)
C5*p*	0.0224 (2)	0.2751 (2)	0.91264 (11)	0.0865 (7)
C6*p*	0.0279 (2)	0.2483 (2)	0.85303 (9)	0.0733 (6)

Table 12. *Selected geometric parameters* (Å, °) *for* (6)

C1—C9*a*	1.493 (2)	C4—C5	1.344 (2)
C1—N2	1.494 (2)	C5—C5*a*	1.447 (2)
N2—N3	1.252 (2)	C5*a*—C9*a*	1.402 (2)
N3—C4	1.413 (2)		
C9*a*—C1—N2	105.89 (13)	C4—C5—C5*a*	126.58 (14)
N3—N2—C1	117.77 (12)	C9*a*—C5*a*—C5	121.10 (14)
N2—N3—C4	123.99 (14)	C5*a*—C9*a*—C1	117.42 (14)
C5—C4—N3	123.20 (14)		
C9*a*—C1—N2—N3	78.8 (2)	C4—C5—C5*a*—C9*a*	29.6 (2)
C1—N2—N3—C4	−7.7 (2)	C5—C5*a*—C9*a*—C1	3.7 (2)
N2—N3—C4—C5	−46.1 (2)	N2—C1—C9*a*—C5*a*	−70.5 (2)
N3—C4—C5—C5*a*	13.5 (3)		

H atoms were placed in fixed calculated positions with $U_{\rm iso}$ = 1.5 × $U_{\rm eq}$(C) for methyl H atoms and $U_{\rm iso}$ = 1.2 × $U_{\rm eq}$(C) for others.

Data collection and cell refinement: *STADI*4 (Stoe & Cie, 1995*a*) for (4), otherwise *DIF*4 (Stoe & Cie, 1990*a*). Data reduction: *X-DATRED* (Stoe & Cie, 1995*b*) for (4), otherwise *REDU*4 (Stoe & Cie, 1990*b*). Program used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL*/*PC* (Sheldrick, 1992).

We thank the SERC for provision of a four-circle diffractometer and for a studentship (to MH).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HA1139). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Blake, A. J., Harding, M. & Sharp, J. T. (1994). *J. Chem. Soc. Perkin Trans.* 1, pp. 3149–3161.
Clegg, W. (1981). *Acta Cryst.* A**37**, 22–28.
Cosier, J. & Glazer, A. M. (1986). *J. Appl. Cryst.* **19**, 105–108.
Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures.* Univ. of Göttingen, Germany.
Sheldrick, G. M. (1992). *SHELXTL/PC.* Version 4.3. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* Univ. of Göttingen, Germany.
Stoe & Cie (1990*a*). *DIF4. Diffractometer Control Program.* Version 7.09/DOS. Stoe & Cie, Darmstadt, Germany.
Stoe & Cie (1990*b*). *REDU4. Data Reduction Program.* Version 7.03/DOS. Stoe & Cie, Darmstadt, Germany.
Stoe & Cie (1995*a*). *STADI4. Data Collection Program for Windows.* Version 1.04. Stoe & Cie, Darmstadt, Germany.
Stoe & Cie (1995*b*). *X-RED. Data Reduction Program for Windows.* Version 1.04. Stoe & Cie, Darmstadt, Germany.

Acta Cryst. (1995). C**51**, 1627–1629

1-Cyclohexyl-3-(2-tolyl)thiourea

R. Akilan, K. Sivakumar[†] and K. Subramanian

Department of Physics, Anna University,
Madras 600025, India

N. Janarthanan and K. Ramadas

Centre for Agrochemical Research, SPIC Science
Foundation, 110 Mount Road, Madras 600032,
India

Hoong-Kun Fun

X-ray Crystallography Laboratory, School of Physics,
Universiti Sains Malaysia, 11800 USM, Penang,
Malaysia

(*Received* 23 *November* 1994; *accepted* 25 *January* 1995)

Abstract

The cyclohexane ring in the title compound, $C_{14}H_{20}N_2S$, is in a chair conformation. There are N—H···S hydrogen bonds present in the structure.

Comment

Unsymmetrical thioureas are found to exhibit agrochemical properties and are commercially interesting compounds (Sarkis & Faisal, 1985; Alder, 1989). The title compound, (I), was synthesized in view of its agrochemical importance and the details of the synthesis have been published elsewhere (Ramadas, Srinivasan & Janarthanan, 1993). There is not much in the literature on the crystal structure determination of disubstituted thioureas and so this prompted us to perform an X-ray investigation on this series of compounds. Also, this forms part of our studies on the structural and insecticidal activities of this class of compounds.

[†] Visiting Post Doctoral Research Fellow, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia.

Acta Crystallographica Section C
ISSN 0108-2701 ©1995