

Fig. 2. The unit cell of the title compound looking down the *b* axis. C, O and N atoms are represented by crossed, dashed, and dotted circles respectively. Broken lines represent hydrogen bonds.

that in all the reported similar structures, where N1 is involved in forming an intermolecular hydrogen bond with the neighbouring carbonyl O atom(s). This shows that the presence of the water molecule in the title compound has totally altered its hydrogen bonding.

We thank Dr Y. S. Sadanandam and Dr (Mrs) Meera Shetty, Organic Chemistry Division, IICT, Hyderabad, for supplying the compound, and Miss Madhavi Bhogaraju for assistance.

Acta Cryst. (1992). C48, 1630–1633

Structure of 5 β ,10 α ,10 β -Triethylthebaine Hydrochloride

BY R. H. WOUDEBERG, T. S. LIE, H. VAN KONINGSVELD AND L. MAAT

Laboratory of Organic Chemistry and Catalysis, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands

(Received 18 November 1991; accepted 21 January 1992)

Abstract. (–)-6,7,8,14-Tetradehydro-4,5 α -epoxy-5 β ,10 α ,10 β -triethyl-3,6-dimethoxy-17-methylmorphinan hydrochloride, C₂₅H₃₄NO₃⁺·Cl[–], *M_r* = 432.00, monoclinic, *P*2₁, *a* = 9.304 (2), *b* = 10.987 (2), *c* = 11.833 (2) Å, β = 109.65 (1)°, *V* = 1139.2 Å³, *Z* = 2, *D_x* = 1.26 g cm^{–3}, λ (Mo *K* α) = 0.71073 Å, μ = 1.986 cm^{–1}, *F*(000) = 464, *T* = 293 K, *R* = 0.064 for 2966 observed reflections. The piperidine ring is in a chair conformation. In contrast to other morphinan derivatives, the *N*-methyl group is in an axial posi-

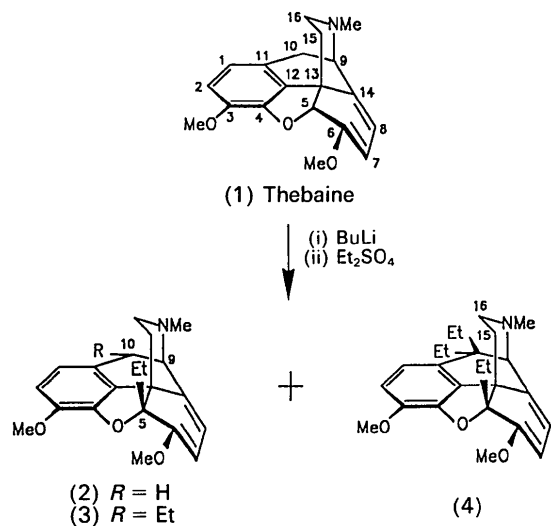
tion. Apparently, the ethyl group at the 10 β position forces the *N*-methyl group into this position.

Introduction. Compounds obtained through appropriate modification of the Diels–Alder adducts of the opium alkaloid (–)-thebaine (1) are well known for their high analgesic potency (Bentley, 1971). In order to investigate the influence of a 5 β -alkyl substituent on the course of the Diels–Alder reaction and its influence on the analgesic potency of the adducts,

References

- BERNTSSON, P. & CARTER, R. E. (1981). *Acta Pharm. Suec.* **18**, 221–225.
- DUAX, W., WEEKS, C. M. & ROHRER, D. C. (1976). *Top. Stereochem.* **9**, 271–283.
- FONSECA, I., MARTÍNEZ-CARRERA, S. & GARCÍA-BLANCO, S. (1986). *Acta Cryst.* C**42**, 1792–1794.
- FORTIER, S., FRASER, M. E., MOORE, N. J., PARK, Y. S., WHITNEY, R. A. & MARKS, G. S. (1985). *Acta Cryst.* C**41**, 411–413.
- FOSSHEIM, R. (1985). *Acta Chem. Scand. Ser. B*, **39**, 785–790.
- FOSSHEIM, R. (1986). *J. Med. Chem.* **29**, 305–307.
- FOSSHEIM, R., SVARTENG, K., MOSTAGD, A., ROMMING, C., SHEFTER, E. & TRIGGLE, D. J. (1982). *J. Med. Chem.* **25**, 126–131.
- HEMPEL, A. & GUPTA, M. P. (1978). *Acta Cryst.* B**34**, 3815–3817.
- JANIS, R. A. & TRIGGLE, D. J. (1983). *J. Med. Chem.* **26**, 775–785.
- KOKUBUN, S. & REUTER, H. (1984). *Proc. Natl Acad. Sci. USA*, **81**, 4824–4827.
- KRAJEWSKI, J. W., URBANCZYK-LIPKOWSKA, Z. & GLUZINSKI, P. (1977a). *Acta Cryst.* B**33**, 2967–2969.
- KRAJEWSKI, J. W., URBANCZYK-LIPKOWSKA, Z. & GLUZINSKI, P. (1977b). *Cryst. Struct. Commun.* **6**, 787–791.
- LANGS, D. A. & TRIGGLE, D. J. (1985). *Mol. Pharmacol.* **27**, 544–548.
- NARDELLI, M. (1983). *Comput. Chem.* **7**, 95–98.
- SCHAUER, C. K., ANDERSON, O. P., NATALE, N. R. & QUINCY, D. A. (1986). *Acta Cryst.* C**42**, 884–886.
- SHELDRICK, G. M. (1990). *SHELXTL-Plus*. Revision 4.11/V. Siemens Analytical X-ray Instruments, Inc., Application Laboratory, Single Crystal, Siemens AG, AUT V353, Karlsruhe, Germany.
- TAMAZWA, K., ARIMA, H., KOJIMA, T., ISOMURA, Y., OKADA, M., FUJITA, S., FURUYA, T., TAKENAKA, T., INAGAKI, O. & TERAI, M. (1986). *J. Med. Chem.* **29**, 2501–2511.
- TRIGGLE, A. M., SHEFTER, E. & TRIGGLE, D. J. (1980). *J. Med. Chem.* **23**, 1442–1445.
- WANG, S. D., HERBETTE, L. G. & RHODES, D. G. (1989). *Acta Cryst.* C**45**, 1748–1751.

thebaine (1) was deprotonated, employing 3.2 equivalents of butyllithium, and reacted with diethyl sulfate to give the 5β -alkyl substituted thebaine analogues (Boden, Gates, Ho & Sundararaman, 1982; Woudenberg, Lie & Maat, 1990). Two products were obtained in a ratio of 6:1 (high performance liquid chromatography) (Woudenberg, Oosterhoff, Lie & Maat, 1992), namely $5\beta,10\alpha$ -diethylthebaine (3) and $5\beta,10\alpha,10\beta$ -triethylthebaine (4). In the ^1H NMR spectrum of (4), H(16)_{ax} was



shifted 0.40 p.p.m. downfield, and H(15)_{eq} 0.49 p.p.m. upfield, whereas the geminal coupling of H(16) changed from approximately 13 to 14.5 Hz, compared to 5β -ethylthebaine (2). Neither ^1H NMR nor ^{13}C NMR could provide us with sufficient information about the exact conformation of the piperidine moiety. Therefore, we performed a single-crystal X-ray analysis of (4).HCl, which gave unambiguous proof for the chair conformation of the piperidine ring with the *N*-methyl substituent in an axial position. To our knowledge, this is the first reported single-crystal X-ray study of a morphinan hydrochloride with an axial methyl group. The *N*-methyl group is usually found in an equatorial position (Gylbert, 1973; Darling, Kolb, Mandel & Mandel, 1982).

Experimental. The title compound was synthesized in our laboratory starting from natural (-)-thebaine with known absolute configuration (Woudenberg, Oosterhoff, Lie & Maat, 1992). Crystals were grown from ethanol/diethyl ether; m.p. 508–510 K (dec.); D_m not measured. A crystal of dimensions 0.40 × 0.25 × 0.25 mm was used for data collection on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation at room temperature using the ω/θ -scan mode [width = (0.85 +

0.35tan θ)°] to a 2θ maximum of 30°. 3475 independent reflections were measured within the range $0 \leq h \leq 13$, $0 \leq k \leq 15$, $-16 \leq l \leq 16$ of which 2970 with $I \geq 1.0\sigma(I)$ were used for all calculations. Three standard reflections were measured every 2 h of X-ray measuring time. No decay was detected. Cell constants were refined from 25 reflections in the range $12 < \theta < 14^\circ$. Lorentz and polarization corrections were applied; no corrections were made for absorption. The structure was solved by direct methods using *MULTAN* (Germain, Main & Woolfson, 1971). Full-matrix least-squares refinement on F of anisotropic heavy atoms and non-methyl H atoms with fixed isotropic thermal parameters (methyl H atoms were not included) carried out using *XRAY72* (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). The final cycle of refinement included 319 variable parameters and converged to $R = 0.064$, $wR = 0.063$ with $w = 1$, $S = 0.97$, maximum shift/e.s.d. = 0.6 and average shift/e.s.d. = 0.08 for 2966 observed reflections (four strong low-order reflections left out). The final ΔF map showed some residual electron density near the Cl atom ($\sim 0.45 \text{ e } \text{\AA}^{-3}$) and at positions ($\leq 0.40 \text{ e } \text{\AA}^{-3}$) where some methyl H atoms might be expected; $\Delta\rho_{\text{min}} = -0.40 \text{ e } \text{\AA}^{-3}$. Atomic scattering factors were provided by *XRAY72*. Dispersion factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV, p. 166).

Discussion. The molecular structure is shown in Fig. 1, together with the atom numbering. The final atomic parameters are listed in Table 1.* Bond lengths and bond angles are given in Table 2. As can be seen from Fig. 1, the piperidine ring is in a chair conformation, which is usual for morphinans. The average torsion angle in the ring is 55.5° with minimum and maximum values of 50.4 [N(17)—C(16)—C(15)—C(13)] and 60.0° [C(13)—C(14)—C(9)—N(17)], respectively. The *N*-methyl group is in an axial position, which differs from the equatorial position usually found in other morphinan hydrochlorides (Gylbert, 1973; Darling, Kolb, Mandel & Mandel, 1982). Apparently, the *N*-methyl group is forced into an axial position by the introduction of an ethyl group at the 10β position. Thus, the changes in the ^1H NMR spectrum may be explained by the change of the position of the lone pair of the N atom (Crabb & Katritzky, 1984). Protons H(16) are now *gauche* to the N-atom lone pair. This position of the lone pair influences the geminal coupling

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, and bond lengths and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55070 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL0550]

Table 1. Positional parameters of non-H atoms and equivalent isotropic thermal parameters (\AA^2)
$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
Cl	0.8411 (2)	-0.11297†	1.0494 (2)	0.109
C(1)	0.3478 (5)	0.2596 (4)	0.7218 (4)	0.039
C(2)	0.2305 (5)	0.2625 (4)	0.6117 (4)	0.038
C(3)	0.2561 (4)	0.2424 (4)	0.5026 (4)	0.033
C(4)	0.4046 (4)	0.2137 (4)	0.5098 (3)	0.030
C(5)	0.6274 (4)	0.1861 (4)	0.4683 (3)	0.030
C(6)	0.6989 (5)	0.3070 (4)	0.4548 (4)	0.033
C(7)	0.8100 (5)	0.3603 (4)	0.5443 (4)	0.037
C(8)	0.8542 (4)	0.3163 (5)	0.6673 (4)	0.037
C(9)	0.7869 (4)	0.1944 (5)	0.8209 (4)	0.036
C(10)	0.6389 (4)	0.2456 (5)	0.8418 (3)	0.037
C(11)	0.4972 (4)	0.2313 (4)	0.7287 (3)	0.032
C(12)	0.5157 (4)	0.2018 (4)	0.6210 (3)	0.027
C(13)	0.6589 (4)	0.1546 (4)	0.6036 (3)	0.028
C(14)	0.7850 (4)	0.2217 (4)	0.6953 (3)	0.031
C(15)	0.6702 (5)	0.0160 (4)	0.6263 (4)	0.038
C(16)	0.6872 (6)	-0.0140 (5)	0.7542 (5)	0.044
N(17)	0.8109 (4)	0.0571 (4)	0.8421 (4)	0.045
C(18)	0.1319 (6)	0.1744 (7)	0.2996 (5)	0.057
C(19)	0.6686 (6)	0.0897 (5)	0.3905 (4)	0.040
C(20)	0.8401 (6)	0.0765 (6)	0.4140 (5)	0.057
C(21)	0.7319 (7)	0.4417 (5)	0.3090 (5)	0.060
C(22)	0.6702 (6)	0.3854 (6)	0.8607 (5)	0.051
C(23)	0.5641 (7)	0.4587 (6)	0.9078 (5)	0.065
C(24)	0.6140 (6)	0.1868 (6)	0.9524 (4)	0.052
C(25)	0.7480 (7)	0.2079 (8)	1.0719 (4)	0.073
C(26)	0.9687 (6)	0.0227 (7)	0.8422 (5)	0.064
O(1)	0.1377 (3)	0.2582 (4)	0.3965 (3)	0.046
O(2)	0.4583 (3)	0.1964 (3)	0.4166 (2)	0.034
O(3)	0.6509 (4)	0.3420 (3)	0.3379 (3)	0.042

† Parameter kept fixed during refinement.

Table 2. Bond lengths (\AA) and bond angles ($^\circ$)

C(1)—C(2)	1.390 (5)	C(9)—N(17)	1.534 (7)
C(1)—C(11)	1.400 (6)	C(10)—C(11)	1.539 (5)
C(2)—C(3)	1.406 (7)	C(10)—C(22)	1.565 (8)
C(3)—C(4)	1.392 (6)	C(10)—C(24)	1.546 (7)
C(3)—O(1)	1.375 (5)	C(11)—C(12)	1.380 (6)
C(4)—C(12)	1.380 (5)	C(12)—C(13)	1.507 (6)
C(4)—O(2)	1.369 (6)	C(13)—C(14)	1.497 (5)
C(5)—C(6)	1.517 (6)	C(13)—C(15)	1.543 (6)
C(5)—C(13)	1.567 (6)	C(15)—C(16)	1.505 (8)
C(5)—C(19)	1.534 (7)	C(16)—N(17)	1.487 (6)
C(5)—O(2)	1.488 (4)	N(17)—C(26)	1.516 (7)
C(6)—C(7)	1.341 (5)	C(18)—O(1)	1.458 (8)
C(6)—O(3)	1.358 (5)	C(19)—C(20)	1.532 (8)
C(7)—C(8)	1.456 (6)	C(21)—O(3)	1.434 (8)
C(8)—C(14)	1.322 (7)	C(22)—C(23)	1.517 (10)
C(9)—C(10)	1.582 (7)	C(24)—C(25)	1.557 (6)
C(9)—C(14)	1.510 (6)		
C(2)—C(1)—C(11)	120.7 (5)	C(22)—C(10)—C(24)	111.3 (4)
C(1)—C(2)—C(3)	122.3 (4)	C(1)—C(11)—C(12)	115.4 (3)
C(2)—C(3)—C(4)	116.8 (3)	C(1)—C(11)—C(10)	124.8 (4)
C(2)—C(3)—O(1)	119.2 (4)	C(10)—C(11)—C(12)	119.4 (4)
C(4)—C(3)—O(1)	124.0 (4)	C(4)—C(12)—C(11)	124.9 (4)
C(3)—C(4)—C(12)	119.3 (4)	C(4)—C(12)—C(13)	108.4 (3)
C(3)—C(4)—O(2)	127.3 (3)	C(11)—C(12)—C(13)	126.7 (3)
C(12)—C(4)—O(2)	113.3 (3)	C(12)—C(13)—C(5)	101.2 (3)
C(6)—C(5)—C(13)	111.3 (3)	C(12)—C(13)—C(14)	104.2 (3)
C(6)—C(5)—C(19)	109.6 (4)	C(12)—C(13)—C(15)	109.1 (4)
C(6)—C(5)—O(2)	109.3 (3)	C(5)—C(13)—C(14)	117.6 (4)
C(13)—C(5)—C(19)	117.5 (4)	C(5)—C(13)—C(15)	112.0 (3)
C(13)—C(5)—O(2)	104.2 (3)	C(14)—C(13)—C(15)	111.7 (3)
C(19)—C(5)—O(2)	104.4 (3)	C(8)—C(14)—C(9)	123.9 (4)
C(5)—C(6)—O(3)	110.5 (3)	C(8)—C(14)—C(13)	122.3 (4)
C(5)—C(6)—C(7)	123.3 (4)	C(9)—C(14)—C(13)	111.2 (4)
C(7)—C(6)—O(3)	125.6 (4)	C(13)—C(15)—C(16)	111.7 (4)
C(6)—C(7)—C(8)	121.8 (4)	C(15)—C(16)—N(17)	112.6 (5)
C(7)—C(8)—C(14)	121.0 (4)	C(9)—N(17)—C(16)	111.5 (3)
C(10)—C(9)—C(14)	111.1 (3)	C(9)—N(17)—C(26)	109.4 (4)
C(10)—C(9)—N(17)	114.3 (4)	C(16)—N(17)—C(26)	113.0 (5)
C(14)—C(9)—N(17)	108.0 (4)	C(5)—C(19)—C(20)	114.3 (4)
C(9)—C(10)—C(11)	111.3 (3)	C(10)—C(22)—C(23)	117.4 (5)
C(9)—C(10)—C(22)	104.0 (4)	C(10)—C(24)—C(25)	113.9 (5)
C(9)—C(10)—C(24)	111.7 (4)	C(3)—O(1)—C(18)	116.4 (4)
C(11)—C(10)—C(22)	106.8 (4)	C(4)—O(2)—C(5)	107.6 (3)
C(11)—C(10)—C(24)	111.4 (4)	C(6)—O(3)—C(21)	116.1 (3)

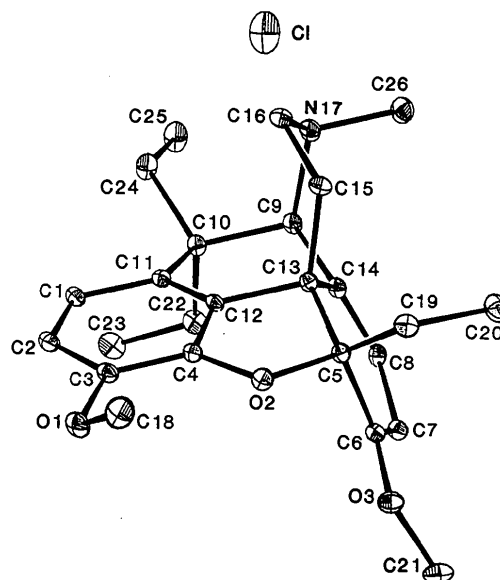


Fig. 1. ORTEP plot (Johnson, 1970) of the title compound. Boundary surfaces are drawn to enclose 50% probability.

of the adjacent two H(16) protons (Chivers & Crabb, 1970), which changes from approximately 13 to 14.5 Hz. The lower field position found for H(16)_{ax} may be explained by the deshielding effect of the N-atom lone pair. No explicit effects can be given for the change of the position of H(15)_{eq}; minor structural changes in the morphinan skeleton are probably involved. A rather strong hydrogen bond exists: the N(17)⋯Cl and H(17)⋯Cl distances are 3.020 (5) and 2.16 (6) \AA , respectively. The N(17)—H(17)⋯Cl angle is 140 (3) $^\circ$. The plane of the aromatic ring and the ring formed by the atoms C(5) through C(8), C(13) and C(14) are nearly planar. The maximum deviations from the least-squares planes are 0.05 [C(12)] and 0.10 \AA [C(5)]. The 3- and 6-methoxy groups are out of these ring planes: C(4)—C(3)—O(1)—C(25) and C(7)—C(6)—O(3)—C(24) torsion angles are 36.6 and 5.5 $^\circ$, respectively.

References

- BENTLEY, K. W. (1971). *The Alkaloids*, Vol. XIII, edited by R. H. F. MANSKE, pp. 75–123. New York: Academic Press.
- BODEN, R. M., GATES, M., HO, S. P. & SUNDARARAMAN, P. (1982). *J. Org. Chem.* **47**, 1347–1349.
- CHIVERS, P. J. & CRABB, T. A. (1970). *Tetrahedron*, **26**, 3389–3399.
- CRABB, T. A. & KATRITZKY, A. R. (1984). *Adv. Heterocycl. Chem.* **36**, 1–173.
- DARLING, S. D., KOLB, V. M., MANDEL, G. S. & MANDEL, N. S. (1982). *J. Pharm. Sci.* **71**, 763–767.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
- GYLBERT, L. (1973). *Acta Cryst.* **B29**, 1630–1635.
- JOHNSON, C. K. (1970). *ORTEP*. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee, USA.

STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. W. & HALL, S. R. (1972). The XRAY72 system – version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.

WOUDENBERG, R. H., LIE, T. S. & MAAT, L. (1990). *Recl Trav. Chim. Pays-Bas*, **109**, 353–357.

WOUDENBERG, R. H., OOSTERHOFF, B. E., LIE, T. S. & MAAT, L. (1992). *Recl Trav. Chim. Pays-Bas*, **111**, 119–125.

Acta Cryst. (1992). **C48**, 1633–1635

Acenaphtho[1,2-*a*]acenaphthylene at 178 K

BY PETER G. JONES AND PETER BUBENITSCHKEK

Institut für Anorganische und Analytische Chemie der Technischen Universität, Hagenring 30, W-3300 Braunschweig, Germany

GEORGE M. SHELDRIK

Institut für Anorganische Chemie der Universität, Tammannstrasse 4, W-3400 Göttingen, Germany

AND GERALD DYKER

Institut für Organische Chemie der Technischen Universität, Hagenring 30, W-3300 Braunschweig, Germany

(Received 2 December 1991; accepted 31 January 1992)

Abstract. C₂₂H₁₂, $M_r = 276.3$, monoclinic, $P2_1/c$, $a = 10.946$ (4), $b = 5.817$ (2), $c = 10.551$ (4) Å, $\beta = 94.15$ (3)°, $V = 670.0$ Å³, $Z = 2$, $D_x = 1.370$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.08$ mm⁻¹, $F(000) = 288$, $T = 178$ K, $R = 0.049$ for 711 reflections. The molecule possesses crystallographic inversion symmetry and is planar to within 0.004 Å. The molecular strain is apparent, for example, in C—C—C bond angles as high as 141°. The quantitative agreement of bond lengths with those calculated by Dasgupta & Dasgupta [*J. Mol. Struct.* (1975), **27**, 113–116] is only moderate; in particular, the central C—C bond at 1.390 (5) Å is 0.02 Å longer than predicted.

Introduction. Acenaphtho[1,2-*a*]acenaphthylene is an interesting target for calculations (Bose, 1966; Dasgupta & Dasgupta, 1975) and synthetic studies (Mitchell, Fyles & Ralph, 1977) because of its ring strain and its spectroscopic properties. The semi-benzenoid hydrocarbon is rationally and efficiently prepared from 1,8-diiodonaphthalene and acenaphthylene by a new palladium-catalyzed annelation reaction (Dyker, 1991). We have determined the crystal structure in order to characterize the molecular geometry of the hexacyclic $(4n + 2)\pi$ system and to compare the experimental parameters with calculated values (*op. cit.*).

Experimental. Single crystals in the form of red prisms and plates were obtained from chloroform. Intensity data were collected from two crystals, (1) $0.38 \times 0.24 \times 0.22$ mm, (2) $0.42 \times 0.40 \times 0.18$ mm, mounted on glass fibres with inert oil and transferred

to the cold gas stream of a Siemens R3 diffractometer with LT-2 low-temperature attachment. Intensities were measured to $2\theta_{\text{max}} = 50^\circ$ using monochromated Mo $K\alpha$ radiation. Of 1398 reflections (1), 2356 reflections (2), 1184 were unique ($R_{\text{int}} = 0.038$ after application of a refined scale factor, index ranges $h - 12$ to 13, $k 0$ to 6, $l 0$ to 12) and 711 $> 3\sigma(F)$ were considered observed. The cell constants were refined from setting angles of 50 reflections in the 2θ range 20–23°. Three check reflections showed no significant intensity variation. No absorption correction was applied.

The structure was solved by direct methods; the solution with the second best combined figure-of-merit proved to be correct, the apparently best solution consisting of 'chicken wire'. Full-matrix anisotropic least-squares refinement on F was then performed. H atoms were included using a riding model. The weighting scheme was $w^{-1} = \sigma^2(F) + 0.00025F^2$; final $R = 0.049$, with $wR = 0.048$; 100 parameters; $S = 1.5$; maximum $\Delta/\sigma = 0.001$, maximum, minimum $\Delta\rho = 0.16, -0.17$ e Å⁻³. The program system used was *SHELXTL-Plus* (Sheldrick, 1989), which contained the atomic scattering factors and f' , f'' values. Final atom coordinates are given in Table 1, with derived bond lengths and angles in Table 2.*

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55118 (6 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA0107]