

# Synthesis and palladium-catalysed transformation of an annelated barrelene

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Gerald Dyker,<sup>\*,a</sup> Thomas Kerl,<sup>a</sup> Peter G. Jones,<sup>b</sup> Ina Dix<sup>b</sup> and Peter Bubenitschek<sup>c</sup>

<sup>a</sup> Fachbereich 6, Organische/Metallorganische Chemie, Gerhardt-Mercator-Universität-Gesamthochschule Duisburg, Lotharstrasse 1, D-47048 Duisburg, Germany

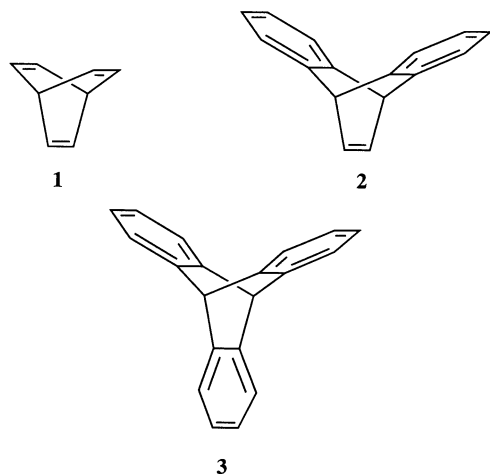
<sup>b</sup> Institut für Analytische und Anorganische Chemie, Technische Universität Braunschweig, Hagenring 30, D-38106 Braunschweig, Germany

<sup>c</sup> Institut für Organische Chemie, Technische Universität Braunschweig, Hagenring 30, D-38106 Braunschweig, Germany

The annelated barrelene **8** is easily accessible in a three-step reaction procedure from simple starting materials. An intermolecular palladium-catalysed arylation at the strained tetrasubstituted double bond of the barrelene finally leads to polycyclic hydrocarbons.

## Introduction

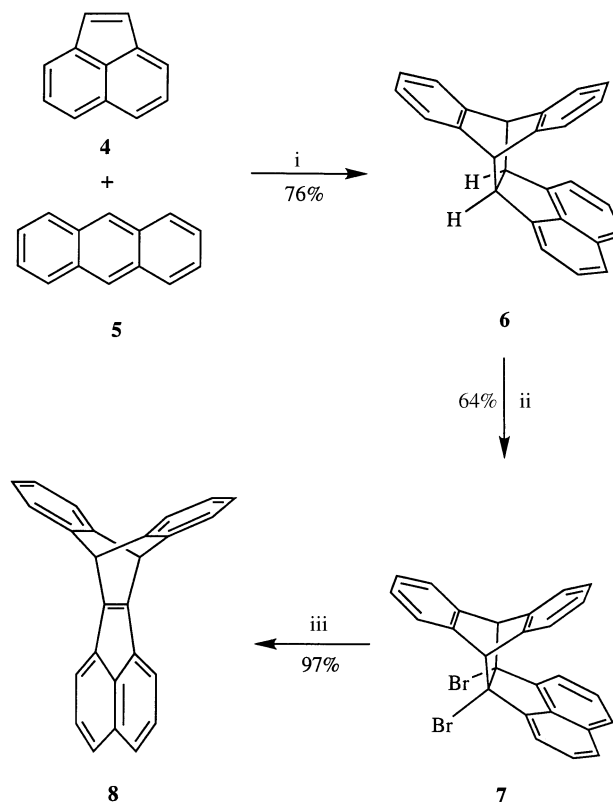
Barrelenes are a group of hydrocarbons with an interesting three-dimensional carbon framework. The parent compound, bicyclo[2.2.2]octa-2,5,7-triene **1**,<sup>1</sup> which lends the group its name because of its barrel-shaped  $\pi$ -electron cloud,<sup>2</sup> shows remarkable reactivity. For example, with dicyanoethyne, the compound is transformed to 1,2-dicyanonaphthalene even at room temperature.<sup>3</sup> Photochemical conversion of **1** into semi-bullvalene with acetone as sensitizer<sup>4</sup> was one of the first examples of the di- $\pi$ -methane rearrangement.<sup>5</sup> Benzoannulation of **1** leads to benzobarrelene (1,4-dihydro-1,4-ethenonaphthalene),<sup>6</sup> dibenzobarrelene **2**<sup>7</sup> and, finally, to triptycene **3**.<sup>8</sup>



The last-mentioned compound is easily accessible by cycloaddition of dehydrobenzene to anthracene.<sup>9</sup> By analogy, the annelated barrelene **8** can be regarded either as a cycloadduct of benzo[*k*]fluoranthene<sup>10</sup> with dehydrobenzene or as an adduct of anthracene with acenaphthylene.<sup>11</sup> The latter is an extremely strained cycloalkyne, which has been observed in an argon matrix, but failed to react with dienes as trapping agents. Therefore, we tested a reaction sequence including the Diels–Alder reaction of acenaphthylene **4** and anthracene **5** followed by dehydrogenation as an alternative approach to the annelated barrelene **8**.

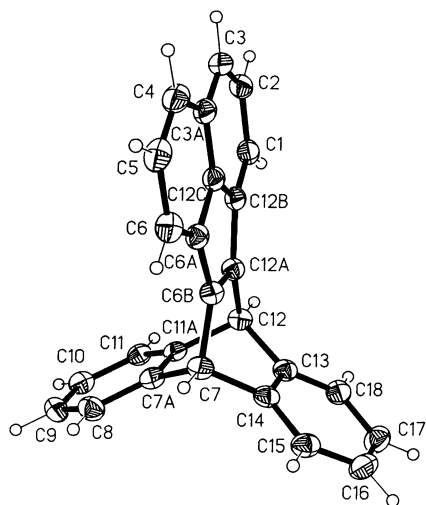
## Results and discussion

The Diels–Alder product **6** is formed in 76% yield by heating a 1:2 mixture of acenaphthylene **4** and anthracene **5**, both constituents of coal tar,<sup>12</sup> at 215 °C for 4 h<sup>13</sup> (Scheme 1). Pre-



**Scheme 1** Synthesis of the annelated barrelene **8**. Reaction conditions: i, 215 °C, 4 h, N<sub>2</sub>; ii, NBS (2 equiv.), CCl<sub>4</sub>, AIBN, 5 h, reflux; iii, excess Zn, DMF, 150 °C, 3 h.

sumably, **6** itself is a hitherto undetected component of coal tar. Bromination of **6** with *N*-bromosuccinimide (2 equiv.) in CCl<sub>4</sub> takes place regioselectively at the benzylic positions of the acenaphthene moiety to give the dibromide **7** (64%). The bridgehead position adjacent to the benzene rings is not brominated, since a radical intermediate at this position is not stabil-



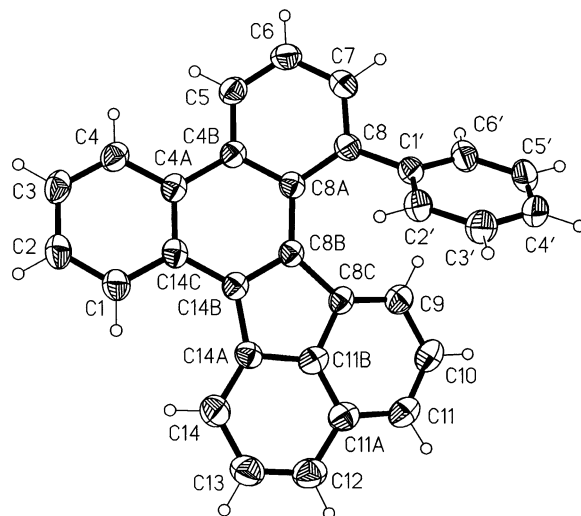
**Fig. 1** Perspective views of the X-ray structure of barrelene **8**, atomic radii are arbitrary

ized by conjugation due to geometric constraints. The final step is the dehalogenation of **7**, which can be efficiently achieved by refluxing a solution of the dibromide **7** with an excess of powdered zinc in DMF for 3 h.<sup>14</sup> Barrelene **8** was obtained as orange crystals in excellent yield (97%).

In the <sup>1</sup>H NMR spectrum of **8** the signal of the bridgehead hydrogen atoms ( $\delta$  5.64) is shifted downfield compared to that of the methine protons in triphenylmethane ( $\delta$  5.54)<sup>8a</sup> and triptycene ( $\delta$  5.44).<sup>8a</sup> The AA'BB' spin system of the former anthracene and the ABC spin system of the acenaphthylene moiety can be easily identified in the aromatic range of the spectrum.

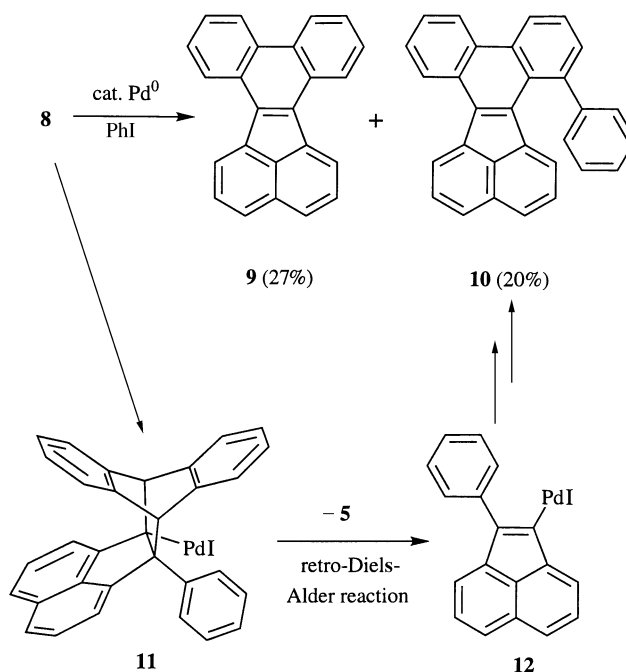
The molecular structure of barrelene **8**, as determined by an X-ray crystallographic analysis, is shown in Fig. 1. In the side view it becomes clear that the double bond is slightly pyramidalized with a hinge angle  $\psi$  of 8.9°.<sup>15</sup> This observation is presumably due to effects of the crystal packing. The C(6B)–C(12A) bond of **8** [135.8(3) pm] is almost 4 pm shorter than the corresponding bond in acenaphthylene<sup>16</sup> and, therefore, is to be regarded as a localized double bond.

We tested **8** as a coupling component in a palladium-catalysed process. In general, the reactivity of tetrasubstituted C=C double bonds towards arylpalladium complexes<sup>17</sup> is sufficient only for intramolecular cases.<sup>18</sup> The intermolecular palladium-catalysed arylation of tetrasubstituted alkenes was



**Fig. 2** X-Ray structure of hydrocarbon **10**, atomic radii are arbitrary

observed exclusively with acenaphtho[1,2-*a*]acenaphthylene and fullerene C<sub>60</sub>,<sup>19</sup> where the double bonds are especially strained and steric hindrance is minimized. The palladium-catalysed arylation of **8** with an excess of iodobenzene under typical conditions<sup>19</sup> (Scheme 2) leads to a complex product



**Scheme 2** Palladium-catalysed arylation of **8**. Reaction conditions: Pd(OAc)<sub>2</sub> (5 mol%), iodobenzene (30 equiv.), K<sub>2</sub>CO<sub>3</sub>, Bu<sub>4</sub>NBr, DMF, N<sub>2</sub>, 100 °C, 7 d.

mixture of hydrocarbons: besides anthracene **5** (almost quantitatively), dibenzo[*j,k*]fluoranthene **9**<sup>20</sup> (27%) was obtained as the main product. The phenylated derivative **10** was isolated (20%) and identified by an X-ray structure analysis (Fig. 2). Obviously, a retro-Diels–Alder reaction takes place under the conditions, presumably at the stage of the intermediate palladium complex **11**. The vinylpalladium complex **12** should then undergo domino coupling reactions in analogy to the known annelation reactions of norbornene,<sup>21</sup> forming the phenanthrene moiety of the hydrocarbons **9** and **10**.

A perspective view of the structure of molecule **10** is pictured in Fig. 2, showing the displacement of atoms from the plane and indicating a helical structure.

The molecule **10** (except for the substituted phenyl ring) is only approximately planar with a mean deviation of 22.7 pm,

although most atoms show a significant deviation from the plane. The torsion angles involving the atoms C(8), C(8a) and C(8b) [C(7)–C(8)–C(8a)–C(8b): 169.4(2)°; C(8)–C(8a)–C(8b)–C(8c): –21.1(3)°; C(8a)–C(8b)–C(8c)–C(9): –9.0(3)°] are associated with the greatest distortion.

Further studies of the reactivity of barrelene **8** are in progress. Reaction sequences of cycloaddition at the reactive double bond and subsequent retro-Diels–Alder reaction should open a valuable route to strained annelated ring systems.

## Experimental

General experimental techniques and analytical measurements were applied as previously described.<sup>22</sup>

### 6b, 7, 12, 12a-Tetrahydro-7,12-benzenobenzo[*k*]fluoranthene **6**

A mixture of acenaphthylene **4** (70%; 2.04 g, 9.38 mmol) and anthracene **5** (3.75 g, 21.0 mmol) was stirred under N<sub>2</sub> at 215 °C for 4 h after which it was cooled and fractionally sublimed in a Kugelrohr apparatus; from the first fraction (160 °C/0.1 mbar) unchanged anthracene and acenaphthylene were isolated. The second fraction (160–180 °C/0.1 mbar) was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>–pentane (2:1) and dried *in vacuo* to give colourless crystals of **6** (2.34 g, 76%), mp 242 °C (lit.,<sup>13</sup> 242–244 °C); λ<sub>max</sub>(CH<sub>3</sub>CN)/nm (log ε) 208 (4.78), 228 (4.69), 274 (3.78), 282 (3.85), 294 (3.92), 302 (3.74), 308 (3.64), 316 (3.03) and 322 (3.05); ν<sub>max</sub>(KBr)/cm<sup>-1</sup> 3068w, 3033w, 3021w, 2947w, 2939w, 2916m, 1605w, 1482w, 1463m, 1372w, 1166w, 795m, 772s, 753s, 739m, 689w, 618s, 553m and 525m; δ<sub>H</sub>(400 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>) 4.13 (2 H, br s), 4.65 (2 H, br s), 6.62 (2 H, m), 6.79 (2 H, m), 7.18 (2 H, m), 7.32–7.40 (6 H, m) and 7.43 (2 H, m); δ<sub>C</sub>(100 MHz, CDCl<sub>3</sub>) 49.89 (d), 50.92 (d), 118.79 (d), 122.66 (d), 123.96 (d), 124.77 (d), 125.18 (d), 126.03 (d), 127.61 (d), 131.10 (s), 140.09 (s), 140.67 (s), 143.94 (s) and 145.49 (s); *m/z* (%) 330 (1.1; M<sup>+</sup>), 326 (1), 324 (0.8), 286 (0.4), 179 (19), 178 (100), 176 (8), 152 (10) and 73 (12).

### 6b, 12a-Dibromo-7,12-dihydro-7,12-benzenobenzo[*k*]fluoranthene **7**

A solution of **6** (500 mg, 1.52 mmol), *N*-bromosuccinimide (565 mg, 3.17 mmol) and AIBN (10 mg, 0.06 mmol) in dry CCl<sub>4</sub> (50 ml) was refluxed for 5 h after which it was filtered; the residue was washed several times with CCl<sub>4</sub>. The combined filtrate and washings containing the crude product were filtered through a pad of silica, and then evaporated *in vacuo*. The residue was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>–pentane to give colourless crystals of **7** which were dried *in vacuo* (472 mg, 64%), mp 265–267 °C (Found: C, 63.91; H, 3.25. C<sub>26</sub>H<sub>16</sub>Br<sub>2</sub> requires C, 63.96; H, 3.30); λ<sub>max</sub>(CH<sub>3</sub>CN)/nm (log ε) 210 (4.89), 228 (4.74), 290 (3.93, sh), 302 (4.01), 310 (3.90, sh); ν<sub>max</sub>(KBr)/cm<sup>-1</sup> 3068w, 3042w, 3024w, 2954w, 1498w, 1467m, 1459m, 1224w, 1162w, 1026w, 866m, 811s, 796m, 774s, 754s, 720w, 681w, 645w, 631s, 611m, 557s, 544m and 440w; δ<sub>H</sub>(400 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>) 5.08 (2 H, s), 6.59 (2 H, m), 6.72 (2 H, m), 7.31 (2 H, m), 7.47–7.52 (4 H, m), 7.53 (2 H, m) and 7.60 (2 H, m); δ<sub>C</sub>(100 MHz, CDCl<sub>3</sub>) 60.40 (d), 120.53 (d), 124.77 (d), 125.06 (d), 126.21 (d), 126.50 (d), 126.78 (d), 128.24 (d), 130.23 (s), 134.92 (s), 138.46 (s), 140.09 (s) and 144.62 (s); *m/z* (%) 490 (0.14), 488 (0.29; M<sup>+</sup>), 486 (0.16), 409 (0.34), 407 (0.34), 328 (22), 327 (31), 326 (21), 178 (100) and 163 (19).

### 7,12-Dihydro-7,12-benzenobenzo[*k*]fluoranthene **8**

A mixture of the dibromide **7** (150 mg, 0.30 mmol) and powdered zinc (300 mg, 4.60 mmol) in dry DMF (30 ml) was heated for 3 h at 150 °C. The orange-coloured reaction mixture was filtered and the residue washed twice with diethyl ether. The combined filtrate and washings were diluted with water (100 ml), and the layers were separated; the aqueous layer was then extracted with diethyl ether (3 × 50 ml). The combined extracts were washed twice with water, dried (MgSO<sub>4</sub>) and filtered. The filtrate was concentrated by removal of solvent in a rotary

evaporator (500 mbar) and the crude product was purified by flash chromatography (silica, hexanes–diethyl ether, 100:1) to give orange plates of barrelene **8** (96 mg, 97%), mp 281–282 °C (Found: C, 94.91; H, 4.78. C<sub>26</sub>H<sub>16</sub> requires C, 95.09; H, 4.91%); λ<sub>max</sub>(CH<sub>3</sub>CN)/nm (log ε) 200 (4.86, sh), 230 (4.72), 288 (3.92), 320 (3.90, sh), 330 (4.00) and 338 (3.68, sh); ν<sub>max</sub>(KBr)/cm<sup>-1</sup> 3065w, 3038w, 3017w, 2964m, 2924s, 2853m, 1465m, 1455s, 1429m, 1218w, 1193w, 1178w, 1146w, 1133w, 1020w, 819s, 780m, 766s, 761s, 744m, 681m, 635s, 624s, 561m, 480w and 467w; δ<sub>H</sub>(400 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>) 5.64 (2 H, s), 6.94 (4 H, m), 7.39 (4 H, m), 7.45 (2 H, dd, *J* 8.3, 6.9), 7.64 (2 H, d, *J* 8.3) and 7.71 (2 H, d, *J* 6.9); δ<sub>C</sub>(100 MHz, CDCl<sub>3</sub>) 49.33 (d), 121.49 (d), 123.44 (d), 124.76 (d), 127.18 (d), 127.31 (d), 128.30 (s), 128.58 (s), 135.50 (s), 146.62 (s) and 151.87 (s); *m/z* (%) 329 (26), 328 (100; M<sup>+</sup>), 327 (94), 326 (52), 324 (16), 250 (8), 178 (21), 163 (20), 162 (12) and 157 (6).

### Crystal structure determination<sup>23</sup>

Crystals were grown from CH<sub>2</sub>Cl<sub>2</sub>–pentane.

**Crystal data.** C<sub>26</sub>H<sub>16</sub>, orthorhombic, *Pbca*, *a* = 831.22(8), *b* = 1611.2(2), *c* = 2508.5(3) pm, *V* = 3.3596 nm<sup>3</sup>, *Z* = 8, λ(Mo-Kα) = 71.073 pm, *T* = –130 °C.

**Data collection.** Orange prism *ca.* 0.6 × 0.5 × 0.3 mm, Stoe STADI-4 diffractometer, 2θ<sub>max</sub> = 50°, 2966 reflections, 2961 unique.

**Structure solution and refinement.** Direct methods, refined on *F*<sup>2</sup> using SHELXL-93 (G. M. Sheldrick, Univ. of Göttingen). Hydrogen atoms: riding model. Final *wR*(*F*<sup>2</sup>) = 0.120, *R*(*F*) = 0.045 for 235 parameters; max. Δρ = 173 e nm<sup>-3</sup>, *S* = 1.14.

### Palladium-catalysed arylation of **8** with iodobenzene

A mixture of **8** (130 mg, 0.39 mmol), iodobenzene (2.47 g, 12 mmol), K<sub>2</sub>CO<sub>3</sub> (475 mg, 3.44 mmol), Bu<sub>4</sub>NBr (266 mg, 0.83 mmol) and Pd(OAc)<sub>2</sub> (5.6 mg, 25 μmol) in dry DMF (4 ml) was stirred under N<sub>2</sub> in a sealed tube (for convenience) for 7 d at 100 °C. After dilution with water (100 ml), the reaction mixture was extracted thrice with diethyl ether (75 ml). The combined extracts were filtered through a pad of silica and evaporated *in vacuo* (500 mbar). Volatile starting materials and by-products such as biphenyl were removed in a Kugelrohr apparatus at 50 °C/0.1 mbar. Flash chromatography of the residue with hexanes–diethyl ether (100:1) as solvent gave two main fractions: yellow needles of dibenzo[*j*,*l*]fluoranthene (**9**) (*R*<sub>F</sub> 0.18) (31 mg, 27%), mp 267–268 °C [lit.,<sup>20</sup> 253–254 °C (toluene)] and orange crystals of 1-phenyldibenzo[*j*,*l*]fluoranthene (**10**) (*R*<sub>F</sub> 0.15) (29 mg, 20%), mp 197 °C (Found: C, 95.13; H, 4.86. C<sub>30</sub>H<sub>18</sub> requires C, 95.21; H, 4.79%).

**Compound 9.** δ<sub>H</sub>(400 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>) 7.69 (2 H, m), 7.75 (2 H, m), 7.71 (2 H, dd, *J* 8.3, 7.1), 7.90 (2 H, d, *J* 8.2), 8.57 (2 H, d, *J* 7.1), 8.80 (2 H, d, *J* 7.7), 8.92 (2 H, d, *J* 8.1); δ<sub>C</sub>(100 MHz, CDCl<sub>3</sub>) 123.51 (d), 124.84 (d), 126.08 (d), 127.07 (d), 127.43 (d), 127.81 (d), 129.23 (s), 129.70 (s), 130.76 (s), 131.81 (s), 133.66 (s) and 137.68 (s); *m/z* (%) 305 (14), 304 (57), 302 (100; M<sup>+</sup>), 300 (34), 298 (11), 152 (9), 151 (21) and 150 (27).

**Compound 10.** δ<sub>H</sub>(400 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>) 6.65 (1 H, d, *J* 7.3), 6.99 (1 H, 'dd', *J* ≈ 8.0), 7.28–7.32 (3 H, m), 7.53–7.79 (9 H, m), 8.52 (1 H, 'd', *J* ≈ 7.3), 8.76 (2 H, m) and 8.92 (1 H, 'd', *J* ≈ 8.0); δ<sub>C</sub>(100 MHz, CDCl<sub>3</sub>) 122.44 (d), 123.93 (d), 124.55 (d), 124.88 (d), 125.82 (d), 126.25 (d), 126.40 (d), 127.20 (d), 127.22 (d), 127.30 (d), 127.35 (d), 127.61 (d), 127.82 (d), 128.64 (d), 128.92 (s), 129.72 (s), 130.35 (d), 130.85 (d), 131.21 (s), 132.77 (s), 134.45 (s), 135.02 (s), 137.71 (s), 137.79 (s), 139.65 (s) and 144.23 (s); *m/z* (%) 380 (21), 379 (37), 378 (100; M<sup>+</sup>), 376 (36), 374 (20), 363 (10), 349 (9), 302 (6), 188 (9), 187 (15), 181 (12), 180 (7) and 178 (6).

### Crystal structure determination<sup>23</sup>

Crystals were grown from CH<sub>2</sub>Cl<sub>2</sub>–pentane.

**Crystal data.** C<sub>30</sub>H<sub>18</sub>, monoclinic, *P2*<sub>1</sub>/*c*, *a* = 1083.87(10),

$b = 1586.1(2)$ ,  $c = 1123.7(2)$  pm,  $\beta = 102.813(10)^\circ$ ,  $V = 1.8836$  nm<sup>3</sup>,  $Z = 4$ ,  $\lambda(\text{Mo-K}\alpha) = 71.073$  pm,  $T = -100$  °C.

**Data collection.** Pale orange prism ca.  $0.9 \times 0.5 \times 0.25$  mm, Siemens P4 diffractometer,  $2\theta_{\text{max}} = 50^\circ$ , 3482 reflections, 3301 unique ( $R_{\text{int}} = 0.025$ ).

**Structure solution and refinement.** Direct methods, refined on  $F^2$  using SHELXL-93 (G. M. Sheldrick, Univ. of Göttingen). Hydrogen atoms: riding model. Final  $wR(F^2) = 0.097$ ,  $R(F) = 0.041$  for 271 parameters and 306 restraints (to  $U$  components); max.  $\Delta\rho = 146$  e nm<sup>-3</sup>,  $S = 0.86$ .

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- Further details of the crystal structure investigation are available on request from the Cambridge Crystallographic Data Centre;† such a request should be accompanied by a full bibliographic citation together with the reference number CCDC 207/95.

† For details of the Scheme, see Instructions for Authors (1997), *J. Chem. Soc., Perkin Trans. 1*, 1997, Issue 1.

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