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**PALLADIUM-CATALYZED SYNTHESSES OF CONDENSED
CYCLOPENTANES. THE CRYSTAL AND MOLECULAR STRUCTURE
OF 3-BENZYLIDENPENTACYCLO[9.2.1^{5.8}.1^{1.11}.0^{2.10}.0^{4.9}]-
PENTADECANE**

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Summary

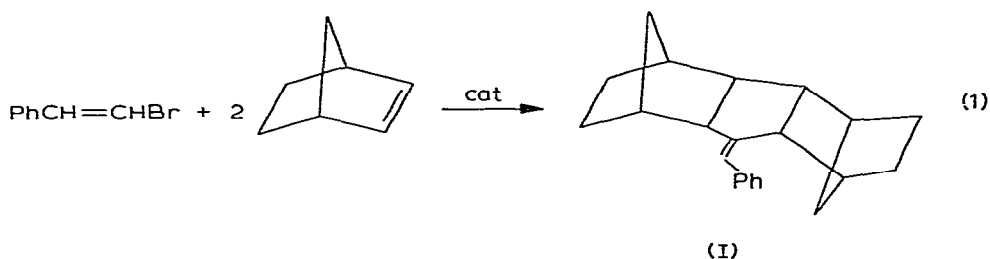
New syntheses of condensed cyclopentanes are described, based on insertion into a sufficiently stable Pd–C bond of molecules able to provide an easy reductive elimination step. These reactions are highly stereoselective. Interesting features are revealed by the X-ray investigation of the title compound, which was obtained in good yield from β -bromostyrene and norbornene. The structural parameters are reported; the molecule adopts the conformation with the bridging carbon atoms of the two norbornanes *trans* with respect to the mean plane of the cyclopentylidene ring. The condensed cyclopentane system is highly symmetric. The phenyl group is twisted out of the plane of the cyclopentylidene ring by 25.3°.

Introduction

We recently showed that when the insertion product of a strained olefin into a C–Pd bond could not easily undergo hydrogen elimination, it was possible to obtain catalytic reactions by transferring hydrogen from an alcohol or another suitable donor to the newly formed C–Pd bond [1] or by some alternative methods allowing hydrogen elimination [2]. We now describe other catalytic reactions involving more complicated behaviour.

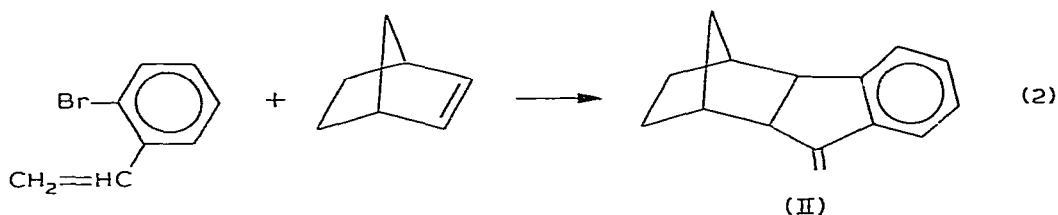
Results

When *E*- β -styryl bromide is treated with norbornene in presence of Pd(Ph₃)₄ and potassium acetate, product I is formed in good yield, according to eq. 1:



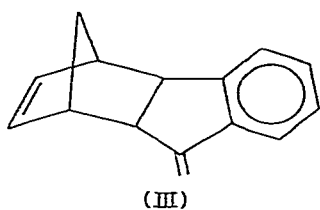
The reaction is highly stereoselective although many stereoisomers are possible. The X-ray crystal structure of I has shown that the phenyl group is exclusively located in the position shown.

Extension of this procedure to aromatic compounds has led us to obtain another type of condensed cyclopentane ring. *o*-Bromostyrene was caused to react with norbornene under similar conditions and product II was isolated (eq. 2).



This reaction also is stereoselective, product II being the *cis,exo* isomer.

Analogous results can be obtained with other strained olefins. Norbornadiene in particular gives almost exclusively compound III, corresponding to the reaction of only one of the two double bonds:



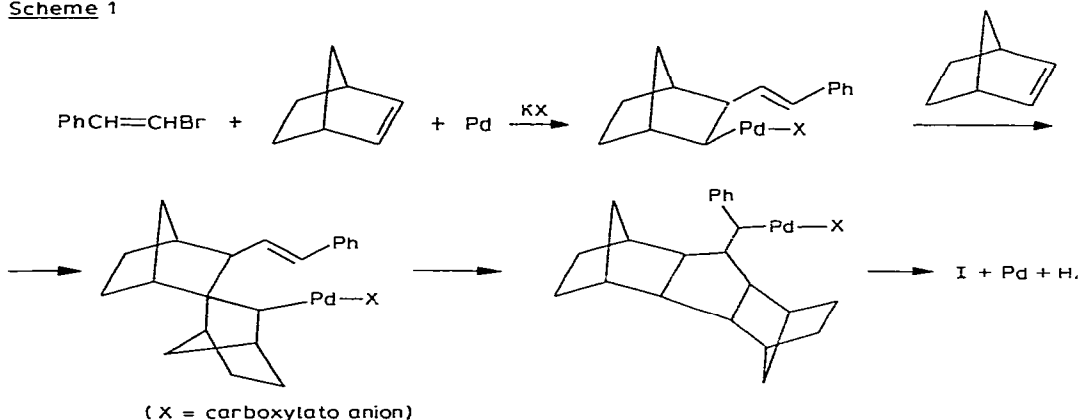
This adds to the synthetic potential of the method because of the many reactions which are possible with cyclopentadiene adducts.

The mechanisms of these reactions appear to involve similar intermediates. In the case of compound I an oxidative addition of β -bromostyrene to palladium(0) first occurs, followed by *cis,exo* norbornene insertion. As previously shown [1], the Pd-bonded organic group resulting from this insertion can be cleaved catalytically by hydrogen transfer. In the absence of hydrogen transfer agents an *anti* elimination of H and Pd-X does not occur easily and other routes are followed.

With certain organic halides we even observed C-H activation of the norbornane skeleton [2] with formation of nortricyclene derivatives. However, when another molecule of norbornene is available a further norbornene insertion readily takes place. The situation, as far as elimination is concerned, is not changed at this stage, but a further attack on the styryl double bond offers a much more favourable

opportunity for reductive elimination. A benzylidene double bond is formed, thus giving compound I (Scheme 1):

Scheme 1



The behaviour observed in the synthesis of compound I seems to be common to other olefins able to provide a favorable reductive elimination step. Thus *o*-bromostyrene oxidatively adds to palladium, norbornene insertion follows, and a new insertion of the vinyl double bond eventually provides the required geometry for reductive elimination, giving rise to compound II. Norbornadiene behaves similarly, forming compound III.

It can be concluded that when a sufficiently stable Pd-C bond is formed a route to reductive elimination can be easily found by providing other molecules or groups able to insert further until a favorable arrangement for reductive elimination is reached.

Molecular geometry

As shown in Fig. 1, in which a projection of the molecule in the mean plane of cyclopentylidene ring is presented, the skeleton of the pentacyclo[9.2.1^{5,8}.1^{1,11}.0^{2,10}.0^{4,9}]pentadecane can be described in terms of three fused fragments: a cyclopentylidene ring and two norbornanes related by a *pseudo* C₂ axis in the direction of the double bond of the central ring. In fact the molecule adopts the geometry with the bridging carbon atoms of the two norbornanes *trans* with respect to the mean plane of the cyclopentylidene ring.

The two norbornane fragments related by the pseudo C₂ molecular axis do not differ significantly in their internal geometry, as can be deduced from bond distances and angles reported in Table I, and agree with the geometry of other bicyclo [2.2.1] heptyl derivatives [3]. In fact none of the nine pairs of C-C bonds shows differences by more than 0.01 Å, and the eleven pairs of related C-C-C angles show no differences greater than 0.9°.

The angles of the bridging bonds C(1)-C(14)-C(11) 94.7(2)° and C(5)-C(15)-C(8) 94.2(2)° are appreciably smaller than the tetrahedral value, and are characteristic of the norbornane frame [4 and references therein]. All the structural features of the bicycloheptane systems observed in the present molecule are in conformity with those observed in similar compounds [5]. In particular, the bond distances and

TABLE 1

BOND DISTANCES AND ANGLES OF 3-BENZYLIDENPENTACYCLO[9.2.1^{5,8}.1¹¹.0^{2,10}.0^{4,9}]-PENTADECANE*Bond distances (Å)*

C(1)–C(2)	1.546(3)	C(5)–C(6)	1.522(4)	C(11)–C(14)	1.518(3)
C(1)–C(13)	1.525(4)	C(5)–C(15)	1.510(3)	C(12)–C(13)	1.535(3)
C(1)–C(14)	1.517(3)	C(6)–C(7)	1.526(3)	C(16)–C(17)	1.464(3)
C(2)–C(3)	1.499(3)	C(7)–C(8)	1.520(4)	C(17)–C(18)	1.386(3)
C(2)–C(10)	1.551(3)	C(8)–C(9)	1.527(4)	C(17)–C(22)	1.382(3)
C(3)–C(4)	1.505(3)	C(8)–C(15)	1.513(3)	C(18)–C(19)	1.375(3)
C(3)–C(16)	1.334(3)	C(9)–C(10)	1.536(4)	C(19)–C(20)	1.373(3)
C(4)–C(5)	1.536(3)	C(10)–C(11)	1.528(4)	C(20)–C(21)	1.363(4)
C(4)–C(9)	1.547(3)	C(11)–C(12)	1.523(4)	C(21)–C(22)	1.386(4)

Bond angles (°)

C(2)–C(1)–C(13)	108.9(2)	C(4)–C(9)–C(10)	107.4(2)
C(2)–C(1)–C(14)	100.9(3)	C(8)–C(9)–C(10)	114.1(2)
C(13)–C(1)–C(14)	101.2(2)	C(2)–C(10)–C(9)	107.7(2)
C(1)–C(2)–C(3)	114.0(2)	C(2)–C(10)–C(11)	102.7(2)
C(1)–C(2)–C(10)	102.8(2)	C(9)–C(10)–C(11)	115.1(2)
C(3)–C(2)–C(10)	106.9(2)	C(10)–C(11)–C(12)	108.6(3)
C(2)–C(3)–C(4)	110.7(2)	C(10)–C(11)–C(14)	101.9(2)
C(2)–C(3)–C(16)	128.1(2)	C(12)–C(11)–C(14)	101.8(2)
C(4)–C(3)–C(16)	121.2(2)	C(11)–C(12)–C(13)	103.0(2)
C(3)–C(4)–C(5)	114.8(2)	C(1)–C(13)–C(12)	103.5(2)
C(3)–C(4)–C(9)	107.2(2)	C(1)–C(14)–C(11)	94.7(2)
C(5)–C(4)–C(9)	102.5(2)	C(5)–C(15)–C(8)	94.2(2)
C(4)–C(5)–C(6)	108.7(3)	C(3)–C(16)–C(17)	131.1(2)
C(4)–C(5)–C(15)	101.2(3)	C(16)–C(17)–C(18)	124.4(2)
C(6)–C(5)–C(15)	102.1(2)	C(16)–C(17)–C(22)	118.5(2)
C(5)–C(6)–C(7)	103.3(2)	C(18)–C(17)–C(22)	117.0(2)
C(6)–C(7)–C(8)	102.9(2)	C(17)–C(18)–C(19)	121.7(2)
C(7)–C(8)–C(9)	109.3(2)	C(18)–C(19)–C(20)	120.3(2)
C(7)–C(8)–C(15)	101.7(2)	C(19)–C(20)–C(21)	119.2(2)
C(9)–C(8)–C(15)	101.8(2)	C(20)–C(21)–C(22)	120.6(2)
C(4)–C(9)–C(8)	102.7(2)	C(17)–C(22)–C(21)	121.2(2)

Carbon–hydrogen bonds are in the range 0.94(2)–1.08(3) Å

angles indicate a very high C_{2v} symmetry in the bicycloheptane fragments: the plane of the bridging bonds is equally inclined to the two mean planes containing C(1),C(2),C(10),C(11) 57.0°, C(1),C(11),C(12),C(13) 56.1°, C(4),C(5),C(8),C(9), 57.3°, C(5),C(6),C(7),C(8) 56.0°; the latter two planes are inclined to each other at an angle of 113.1 and 113.2°, respectively, as can be observed by the analysis of planarity reported in Table 2.

Confirmation of the very close C_{2v} symmetry of the two norbornane fragments can be derived from the values of torsion angles (Table 3), which agree with those calculated by Altona and Sundaralingam [6]. In the cyclopentylidene fragment, the bond distances and angles are as expected from the hybridisation of the atoms

TABLE 2. ANALYSIS OF THE PLANARITY

Distances ($\text{\AA} \times 10^3$) of relevant atoms from mean planes through the molecule	
Plane I	: C(1), C(14), C(11)
Plane II	: C(1), C(11), C(12), C(13) C(1) 2(4), C(11) -2(4), C(12) 3(4), C(13) -3(4)
Plane III	: C(1), C(2), C(10), C(11) C(1) 3(3), C(2) -4(3), C(10) 4(3), C(11) -3(3)
Plane IV	: C(5), C(8), C(15)
Plane V	: C(5)-C(8) C(5) 7(4), C(6) -10(4), C(7) 11(4), C(8) -7(4)
Plane VI	: C(4), C(5), C(8), C(9) C(4) -6(3), C(5) 5(3), C(8) -5(3), C(9) 6(3)
Plane VII	: C(2), C(3), C(4), C(9), C(10) C(2) 13(3), C(3) -9(3), C(4) 3(3), C(9) 7(4), C(10) -14(4)
Plane VIII	: C(17)-C(22) C(17) -1(4), C(18) 4(4), C(19) -3(4), C(20) -2(4), C(21) 6(4), C(22) -4(4)

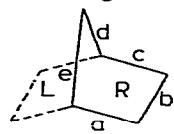
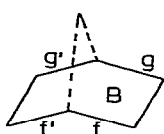
Normal equations of planes in the form $lX + mY + nZ = p$ (X, Y and Z are in \AA , referred to orthogonal axes x, y and z^*)

Plane	l	m	n	p
I	0.9432	0.2229	0.2462	9.2276
II	0.7851	-0.5792	-0.2194	3.7934
III	-0.2520	-0.8325	-0.4934	-6.3845
IV	-0.8898	-0.3538	0.2882	-8.9379
V	0.7682	-0.5760	-0.2783	6.1943
VI	0.2096	0.9774	-0.0270	3.7359
VII	0.6912	-0.6714	-0.2674	3.9203
VIII	-0.8990	0.4363	-0.0378	-9.1617

Dihedral angles ($^\circ$) between planes

I-II	56.1	IV-V	56.0	III-VII	58.9
I-III	57.0	IV-VI	57.3	VI-VII	59.7
II-III	113.1	V-VI	113.2	VII-VIII	25.3

TABLE 3. TORSIONAL ANGLES ($^\circ$) IN THE NORBORNANE SKELETON (the representation is according with ref. [8])

	a	b	c	d	e
ring R 1-2-10-11-14	-35.9	0.7	34.9	-56.6	56.4
5-4-9-8-15	-36.7	1.0	34.9	-56.7	57.2
ring L 1-13-12-11-14	35.4	-0.4	-34.7	55.6	-55.5
5-6-7-8-9	33.8	-1.8	-36.6	56.1	-54.9
	f	g	f'	g'	
ring B 1-2-10-11-12-13	70.1	-72.0	-70.4	72.3	
5-4-9-8-7-6	70.3	-72.1	-72.6	70.4	

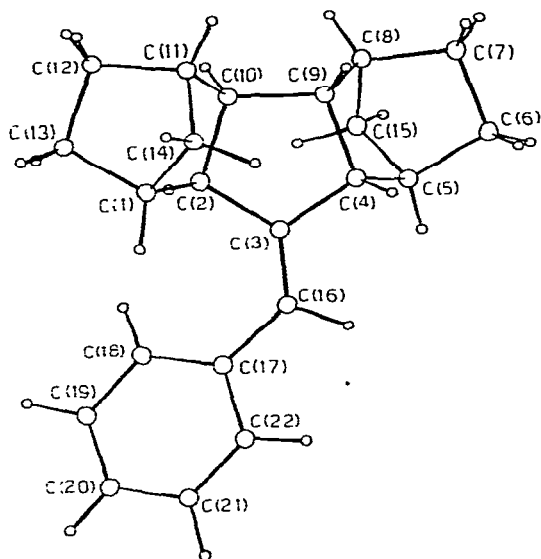


Fig. 1. Projection of the molecule on the mean plane of cyclopentylidene ring.

involved, with the double bond 1.334(3) Å localized in the C(3)–C(16) position. The torsion angle C(3)–C(16)–C(17)–C(18) 21.7° and bond angle C(3)–C(16)–C(17) 131.1(2)°, considerably greater than the sp^2 value, are in agreement with the presence of strain presumably induced by steric hindrance from the phenyl ring. The packing is consistent with Van der Waals interactions.

Experimental

Synthesis and characterization of condensed cyclopentanes

All reagents were commercially products, and were used without further purification. Pd(PPh₃)₄ was prepared according to the literature [7]. All reactions were run under nitrogen. ¹H and ¹³C NMR spectra were recorded on a Varian XL 100 spectrometer in CDCl₃ with TMS as internal standard; multiplicity for ¹³C spectra was derived from off-resonance spectra. The mass spectra were recorded with a Varian Mat Ci15 instrument at 70 eV.

3-Benzylidenepentacyclo[9.2.1^{5.8.1}1.11.0^{2.10.0}4.9]pentadecane (I). A mixture of Pd(PPh₃)₄ (92 mg, 0.08 mmol), norbornene (300 mg, 3.2 mmol), *E*-β-bromostyrene (293 mg, 1.6 mmol) and potassium acetate (156 mg, 1.6 mmol) in degassed anisole (3 ml) was heated at 105–110°C under nitrogen in a capped test tube. Conversion of bromostyrene was 89% in 24 h. After treatment with a dilute solution of H₂SO₄ and ether extraction, the solvent was removed from the extract under reduced pressure and the residue chromatographed on SiO₂ using hexane as eluent. Product I (305 mg, 74% on converted bromostyrene) was obtained as a viscous liquid, from which colourless crystals m.p. 78–79°C, suitable for X-ray analysis separated. Mass spectrum: M^+ 290, m/e 222, 196, 155, 91, 67; ¹H NMR (100 MHz): δ 7.45–7.00 (m, 5H), 6.22 (t, *J* 2 Hz, 1H), 2.89 (br d, *J* 8 Hz, 1H), 2.58 (br d, *J* 8 Hz, 1H), 2.30–2.00 (m, 4H), 1.90–0.80 (m, 14H) ppm; ¹³C NMR (25.2 MHz): δ 156.9, 138.0, 128.1,

125.4, 122.0 (aromatic and vinyl carbons), 58.8, 57.1, 54.2, 54.0, 46.0, 44.2, 44.0, 41.4 (doublets), 34.5, 33.8, 28.6, 28.1, 27.9 (triplets) ppm.

1,2,3,4,4a,9a-Hexahydro-1,4-methano-9-methylen-9H-fluorene (II). Pd(PPh₃)₄ (81 mg, 0.07 mmol), norbornene (300 mg, 3.2 mmol), *o*-bromostyrene (584 mg, 3.2 mmol) and potassium acetate (313 mg, 3.2 mmol) in degassed anisole (3 ml) were heated at 80°C for 6 h under nitrogen in a Schlenk-type flask containing a magnetic stirring bar. After conventional treatment the product was separated by chromatography on a SiO₂ column, using hexane as eluent. A 75% yield of II, determined by GLC, was obtained. Mass spectrum: M^+ 196, m/e 130, 128, 67; ¹H NMR (100 MHz): δ 7.50–7.00 (m, 4H, aromatic protons), 5.45 (d, J 2 Hz, 1H, HC=(aromatic side)), 4.98 (d, J 2 Hz, 1H, HC=(aliphatic side)), 3.00 (d, J 7 Hz, 1H, HC(4a)), 2.76 (br d, J 7 Hz, 1H, HC(9a)), 2.21 (m, 2H, HC(1), HC(4)), 1.74–1.16 (m, 4H, H₂C(2), H₂C(3)), 1.14–0.80 (m, 2H, H₂C(methano)) ppm; ¹³C NMR (25.2 MHz): δ 154.1, 148.6, 142.4 (s, C(9), C(8a), C(4b)), 128.3, 126.4, 124.9, 119.7 (d, C(5), C(6), C(7), C(8)), 102.7 (t, =CH₂), 52.1, 51.9 (d, C(4a), C(9a)), 44.5, 42.4 (d, C(4), C(1)), 32.3 (t, C(methano)), 29.3, 28.6 (t, C(3), C(2)) ppm.

1,4,4a,9a-Tetrahydro-1,4-methano-9-methylen-9H-fluorene (III). Product III was prepared in the same way as II, norbornadiene (294 mg, 3.2 mmol) being used instead of norbornene. A 72% yield of III, as determined by GLC, was obtained, along with a few percent of a peak of M^+ 296 corresponding to the formation of two cyclopentanes on the double bonds of norbornadiene.

Mass spectrum: M^+ 194, m/e 128, 115, 102, 66; ¹H NMR (100 MHz): δ 7.50–7.00 (m, 4H, aromatic protons), 6.20(AB system, 2H, HC(2), HC(3)), 5.48 (d, J 2 Hz, 1H, HC=(aromatic side)), 5.05(d, J 2 Hz, 1H, HC=(aliphatic side)), 3.14(d, J 7 Hz, 1H, HC(4a)), 2.90 (br d, J 7 Hz, 1H, HC(9a)), 2.78(m, 2H, HC(1), HC(4)), 1.26(br d, J 9 Hz, 1H, HC(methano)), 1.14(br d, J 9 Hz, 1H, HC(methano)) ppm; ¹³C NMR (25.2 MHz): δ 151.8, 147.3, 144.1(s, C(9), C(8a), C(4b)), 138.1, 137.3 (d, C(2), C(3)), 128.3, 126.6, 124.5, 120.3(d, C(5), C(6), C(7), C(8)), 103.1 (t, =CH₂), 50.5, 50.1(d, C(4a), C(9a)), 49.6, 47.6 (d, C(4), C(1)), 42.2(t, C(methano)) ppm.

Crystal structure of 3-benzylidenpentacyclo[9.2.1^{5,8}.1^{1,11}.0^{2,10}.0^{4,9}]pentadecane

Crystals were obtained from the liquid isolated by column chromatography. They were colourless prisms elongated on [010]. Lattice constants were determined using the program CTDIF [8] which repeatedly adjusts on the diffractometer the values of (θ, χ, ϕ)_{*hkl*} angles of twenty five reflections to have the maximum of the peak when the angles are moving not more than 0.01°.

Crystal data: C₂₂H₂₆, $M = 290.5$, monoclinic a 13.539(4), b 6.007(2), c 20.038(6) Å, β 94.6(1)°; U 1624.4 Å³; $Z = 4$; Cu- K_{α} radiation, λ 1.5418 Å; μ (Cu- K_{α}) 4.6 cm⁻¹. Space group $P2_1/c$ from systematic absences.

Intensity data were collected on a Siemens AED single-crystal diffractometer up to θ 70°. To collect every reflection the angles were determined on the basis of the orientation matrix and a measuring scan, along the θ circle, was made collecting the outline of the peak. 3506 Independent reflections were measured, of which 1526 were used in the crystal analysis, having intensities $> 2 [\sigma^2(I) + 10^{-4}I^2]^{1/2}$, where I is the relative intensity and $\sigma^2(I)$ its variance. The dimension of the crystal roughly in the x, y, z directions were 0.19, 0.57, 0.19 mm. No absorption correction was applied. The structure was solved by direct methods by use of the system of the Sheldrick computer programs by [9], and refined by a few cycles of full-matrix anisotropic least-squares up to $R = 0.065$.

TABLE 4

FRACTIONAL COORDINATES ($\times 10^4$, $\times 10^3$ for hydrogens) with estimated standard deviations in parentheses

	x/a	y/b	z/c
C(1)	6023(2)	467(4)	4331(1)
C(2)	7101(1)	74(4)	4157(1)
C(3)	7866(1)	1131(3)	4639(1)
C(4)	8417(1)	2925(4)	4299(1)
C(5)	9511(2)	2402(4)	4217(1)
C(6)	9994(2)	4453(4)	3938(1)
C(7)	9563(2)	4522(5)	3211(1)
C(8)	8860(2)	2545(4)	3168(1)
C(9)	7970(2)	3053(4)	3565(1)
C(10)	7139(2)	1311(4)	3480(1)
C(11)	6093(2)	2264(4)	3361(1)
C(12)	5378(2)	362(6)	3179(1)
C(13)	5326(2)	-865(5)	3847(1)
C(14)	5847(2)	2814(4)	4068(1)
C(15)	9423(2)	872(4)	3617(1)
C(16)	8050(2)	715(4)	5291(1)
C(17)	7644(1)	-965(4)	5722(1)
C(18)	7203(2)	-2933(4)	5493(1)
C(19)	6893(2)	-4514(4)	5926(1)
C(20)	7006(2)	-4165(5)	6605(1)
C(21)	7429(2)	-2234(5)	6843(1)
C(22)	7753(2)	-651(5)	6407(1)
H(1)	592(2)	24(4)	484(1)
H(2)	724(2)	-144(4)	410(1)
H(4)	837(1)	429(4)	453(1)
H(5)	987(2)	188(4)	461(1)
H(61)	987(2)	578(5)	417(1)
H(62)	1069(2)	439(4)	399(1)
H(71)	911(2)	598(5)	312(1)
H(72)	1010(2)	427(5)	288(1)
H(8)	867(2)	197(4)	273(1)
H(9)	770(2)	457(4)	345(1)
H(10)	727(2)	31(4)	312(1)
H(11)	605(2)	345(5)	302(1)
H(121)	560(2)	-64(5)	286(1)
H(122)	476(2)	90(4)	298(1)
H(131)	461(2)	-91(5)	401(1)
H(132)	555(2)	-248(5)	382(1)
H(141)	630(2)	397(5)	434(1)
H(142)	514(2)	338(4)	410(1)
H(151)	1007(2)	43(4)	345(1)
H(152)	905(2)	-57(5)	367(1)
H(16)	854(2)	181(4)	554(1)
H(18)	711(2)	-325(4)	504(1)
H(19)	658(2)	-594(4)	571(1)
H(20)	678(2)	-526(4)	691(1)
H(21)	746(2)	-194(5)	737(1)
H(22)	815(2)	69(5)	652(1)

A difference Fourier synthesis computed at this stage revealed the position of all the hydrogen atoms that were refined isotropically. The final conventional R index was 0.042, R_w 0.041 [$w = 1/(\sigma^2(F_o) + 0.005F_o^2)$ where $\sigma^2(F_o)$ were derived from counting statistics]. Positional parameters, together with their standard deviations are given in Table 4. Atomic scattering factors were from ref. [10] for carbon atoms and from ref. [11] for hydrogens. Observed and calculated structure factor amplitudes and thermal parameters can be obtained from the authors on request. All the calculations were carried out on the CDC Cyber 76 computer of the Consorzio per la gestione del Centro di Calcolo Interuniversitario dell'Italia Nord-orientale, Casalecchio, Bologna.

Bibliographic searches were performed using the Cambridge Crystallographic Data Files through the Servizio Italiano di Diffusione dei Dati Cristallografici, Parma (Italy).

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