

NMR Behaviour and Crystal Structure of Tri-ter-butylphosphineallylchloroplatinum(II)

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The NMR behaviour of the title compound in $CDCl_3$ solution is reported and discussed in terms of the allyl asymmetry induced by the difference in bonding modes between $P(t\text{-butyl})_3$ and Cl^- . The X-ray structure determination shows the presence of four possible orientations of the allyl group in the molecule.

Introduction

The PMR features of Pd(II) and Pt(II) allyl complexes depend markedly on both the ancillary ligands and – to a minor extent – on the allyl group itself. Generally, species of type $[(allyl)PdLCl]$ display a dynamic PMR spectrum at temperatures much lower than their $[(allyl)PdCl]_2$ analogs [1]. Further, both $[(allyl)MLX]$ ($M = Pd, Pt$; $L =$ phosphines or arsines; $X =$ halide or acetate) and $[(allyl)Pd(PMe_2Ph)(X_2CY)]$ ($X_2CY =$ xanthate, carbamate, oxinate) [2–7] show *syn-anti* proton exchange, whereas $[(allyl)PdCl]_2$ displays a static PMR behaviour under the same experimental conditions [1, 8]. Thus, the magnetic non-equivalence of allyl protons appears to decrease, along with the allyl group dynamism, with decreasing difference in the σ donor ability between L and X in complexes $[(allyl)MLX]$. Examples of this trend are provided by complexes in which either $L = X$ or the difference in bonding modes between L and X tends to vanish, such as $[(C_3H_5)Pt(PCy_3)_2]^+$ [9], $[(2,Me-C_3H_4)Pt(L-L)]^+$ ($L-L = o$ -phenylene-bis(dimethylarsine) and bis(diphenylphosphino)ethane) [10], $[(allyl)Pd(X-Y)]$ ($X-Y =$ bidentate Schiff base [11], and $[(allyl)MLR]$ ($M = Pd, Pt$; $R = C_6H_5$ and C_6HCl_4 [12, 13]) which show a static PMR spectrum at ambient temperature. These facts might be interpreted in terms of a perturbation of the allyl symmetry caused by the ligands L and X . As a matter of fact, the *syn-anti* proton exchange via $\eta^1-\eta^3$ interconversion – which was invoked to account for

the allyl group mobility [14–17] – is likely to be enhanced by asymmetry in the allyl group. For instance, $[(2,Me-allyl)Pd(PPh_3)Cl]$ was shown by X-ray analysis to contain an asymmetric allyl moiety [18] and it displays a static PMR spectrum only at low temperature [1], whereas $[(2-Me-allyl)Pd(X-Y)]$ ($X-Y =$ bidentate Schiff base) has a symmetric allyl group [19] and a static PMR spectrum at room temperature [11, 19].

However, there is a number of other factors liable to induce fluxionality of the allyl moiety, such as (i) the presence in solution of potentially coordinating ligands (e.g., $[(\eta^3-allyl)PtL_2]^+$ is fluxional in the presence of halides [20, 21], and (ii) the strength of the metal–allyl bond, *viz.* dynamic behaviour sets in when the metal–allyl bond is lengthened, as in the case of $[(\eta^3-C_3H_5)Pd(PPh_3)(SnCl_3)]$ [22] and, possibly, of $[(allyl)Pt(diene)]^+$ [23] and $[(allyl)ML(SnCl_3)]$ [24, 25].

Which connection exists, if any, between asymmetry and fluxionality of the allyl group is an open question requiring a wealth of evidence from structural investigations.

We have determined the crystal structure of the new complex $\{(\eta^3-allyl)Pt[P(t\text{-butyl})_3]Cl\}$, and studied the PMR behaviour in $CDCl_3$ solution which allows the measurement of J_{Pt-P} , J_{P-H} , and J_{Pt-H} as clues to the nature of the Pt–allyl bond in solution. Also, the $P(t\text{-butyl})_3$ was expected to induce significant asymmetry on the allyl group owing to its steric hindrance and basicity [26].

Results and Discussion

NMR Behaviour

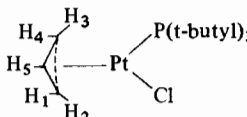
The PMR spectrum of $\{(\eta^3-C_3H_5)Pt[P(t\text{-butyl})_3]Cl\}$ varies appreciably with temperature. At low temperature the spectrum is consistent with an approximate first order pattern for the allylic protons. The values of chemical shifts and coupling constants are quoted in Table I. The values of J_P and

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TABLE I. PMR and ^{31}P NMR Spectrum of $\{(\eta^3\text{-allyl})\text{Pt}[\text{P}(\text{t-butyl})_3]\text{Cl}\}^{\text{a}}$.

τ_5	τ_1 <i>syn</i>	τ_2 <i>anti</i>	τ_3 <i>anti</i>	τ_4 <i>syn</i>	Phosphine Resonance
5.25	5.71	6.62	7.85	6.22	8.41
—	$J_5 = 8.2$	$J_5 = 12.6$	$J_5 = 12.1$	$J_5 = 8.2$	$^3J_{\text{P-H}} = 12.8$
b	$J_{\text{P}} = 4.0$	$J_{\text{P}} = 8.1$	—	—	
$J_{\text{Pt}} = 67.5$	$J_{\text{Pt}} < 0.3$	$J_{\text{Pt}} = 32.3$	$J_{\text{Pt}} = 85.5$	$J_{\text{Pt}} = 24.1$	

^1H NMR: (1) at -40°C



^1H NMR: (2) at 60°C : coalescence of protons 3 and 4 was observed.^c

^{31}P NMR: $+80.5\text{ ppm}^{\text{d}}$, $J_{\text{Pt-P}} = 4,453\text{ Hz}$.

^a J values are in Hz, solvent CDCl_3 . ^b $J_{\text{Pt-P}}$ not assigned. ^cUsing a 90 MHz instrument. ^dSign convention recommended by IUPAC [27].

J_5 give rise to the assignments for protons 1, 2, 3, 4 and 5 [6, 28] and therefore the two *syn* protons 1 and 4 are both at lower field with respect to the *anti* protons 2 and 3. Thus, the two high field signals which were assigned, on the basis of chemical shifts, to one *syn* and one *anti* proton in the case of $[(\text{allyl})\text{Pt}(\text{AsPh}_3)\text{Cl}]$ [7] and $[(\text{allyl})\text{Pt}(\text{isocyanide})\text{Cl}]$ [29] may be reassigned (in analogy to the present case) to two *anti* protons. On the other hand, the high quality of the PMR spectra of $\{(\eta^3\text{-allyl})\text{Pt}[\text{P}(\text{t-butyl})_3]\text{Cl}\}$ supported also by decoupling experiments on all allyl protons, provides full confidence on the assignments made.

The peculiarity of the PMR spectrum of this new compound arises from the values of $J_{\text{Pt-H}}$ which deserve some comments. The very high value of $J_{\text{Pt-H}}$ of proton 3 (85.5 Hz) is closer to the $^2J_{\text{Pt-H}}$ values for η^1 -allyl Pt(II) complexes [7, 12, 29] than to the $J_{\text{Pt-3}}$ observed for η^3 -allyl derivatives (which usually fall in the range 40–70 Hz [9, 10, 12]) and parallels the $J_{\text{Pt-3}}$ values for strongly asymmetric η^3 -allyl Pt(II) derivatives [7]. The $J_{\text{Pt-4}}$ is also the largest value reported so far.

These results and the large difference observed between $J_{\text{Pt-3}}$ and $J_{\text{Pt-2}}$ or between $J_{\text{Pt-4}}$ and $J_{\text{Pt-1}}$ suggest a strong asymmetry of the allyl group [30]. The possibility of binuclear species in solution as in the case of $[(\text{allyl})\text{Pt}(\text{acac})_2]$ [7, 31] was ruled out by molecular weight measurements in CDCl_3 (found 475; $\text{PtClC}_{15}\text{H}_{32}$ requires 474). The observed dynamism of the NMR spectrum with increasing temperature can be interpreted as with other η^3 -allyl-Pt(II) complexes [3, 4, 14], in terms of η^3 - η^1 allyl conversion. The process does not involve intermolecular phosphine exchange: in fact the ^{31}P NMR spectrum is

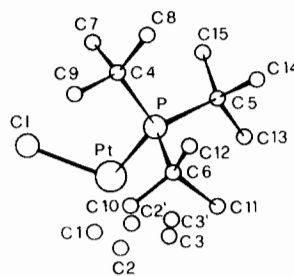


Figure 1. Stereochemistry of $\{(\eta^3\text{-C}_3\text{H}_5)\text{Pt}[\text{P}(\text{t-butyl})_3]\text{Cl}\}$, as viewed along the a axis.

not affected by temperature and ^{31}P is coupled with ^{195}Pt even at 90°C (D_8 -toluene and CDCl_3 solution).

These facts appear to support the hypothesis that the allyl group fluxionality may be related to the difference in bonding modes with the metal between L and X in $[(\eta^3\text{-allyl})\text{MLCl}]$ complexes and prompted us to undertake the X-ray structure determination of $\{(\eta^3\text{-allyl})\text{Pt}[\text{P}(\text{t-butyl})_3]\text{Cl}\}$.

Crystal Structure

The stereochemistry of the complex, as viewed along the a -axis, is shown in Figure 1, which shows the atom numbering used. The final structural parameters with their e.s.d.'s of the non-hydrogen and H atoms are reported in Tables II and III, respectively; in Table IV bond lengths and valence angles for all non-hydrogen atoms, not corrected for changes due to thermal vibrations, are given. Some least-squares planes and dihedral angles are shown in Table V.

The structure described by the cell constants, the symmetry operations of the space group, and the atomic parameters consists of the packing of

TABLE II. Final Structural Parameters and Their e.s.d's in Parentheses for Non-hydrogen Atoms. Anisotropic thermal parameters ($\times 10^3$) are in the form $\exp[-2\pi^2(\sum_{ij} U_{ij} a_i^* a_j^* h_i h_j)]$ and the isotropic thermal parameters are listed as U_{11} .

	x	y	z	p	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pt	0.14401(2)	0.08805(5)	0.45741(5)	1	30.5(2)	52.4(2)	36.7(2)	16.4(1)	0.4(1)	1.5(1)
Cl	0.1692(2)	-0.2035(3)	0.4333(4)	1	88(2)	43(1)	72(2)	9(1)	-4(1)	-4(1)
P	0.2653(1)	0.2480(3)	0.6845(3)	1	32(1)	35(1)	35(1)	16(1)	0(1)	2(1)
Cl	0.0266(9)	-0.024(1)	0.235(2)	1	80(3)					
C2	0.061(2)	0.118(3)	0.238(3)	0.55	75(5)					
C3	0.095(2)	0.274(4)	0.345(5)	0.55	79(6)					
C2'	0.019(2)	0.163(3)	0.335(3)	0.45	65.(6)					
C3'	0.064(2)	0.292(4)	0.400(5)	0.45	70(8)					
C4	0.3323(6)	0.115(1)	0.806(1)	1	47(2)					
C5	0.2256(7)	0.145(1)	0.869(1)	1	53(2)					
C6	0.3511(7)	0.309(1)	0.567(1)	1	52(2)					
C7	0.2615(7)	0.024(1)	0.866(1)	1	61(3)					
C8	0.4033(8)	0.220(1)	0.974(1)	1	71(3)					
C9	0.3846(8)	-0.035(1)	0.673(1)	1	67(3)					
C10	0.3590(8)	0.145(1)	0.389(1)	1	85(3)					
C11	0.3124(8)	0.456(1)	0.517(1)	1	71(3)					
C12	0.4517(8)	0.361(1)	0.673(1)	1	74(3)					
C13	0.1507(9)	0.553(2)	0.785(2)	1	78(3)					
C14	0.3048(9)	0.596(2)	0.983(2)	1	78(3)					
C15	0.1778(8)	0.411(2)	0.993(2)	1	74(3)					

TABLE III. Fractional Coordinates for the Hydrogen Atoms.

	x	y	z
H' (C7)	0.227	0.120	0.970
H'' (C7)	0.306	-0.055	0.919
H''' (C7)	0.210	-0.061	0.756
H' (C8)	0.374	0.321	1.084
H'' (C8)	0.457	0.278	0.939
H''' (C8)	0.433	0.118	1.013
H' (C9)	0.440	0.019	0.639
H'' (C9)	0.344	-0.132	0.552
H''' (C9)	0.414	-0.098	0.759
H' (C10)	0.288	0.111	0.320
H'' (C10)	0.390	0.034	0.411
H''' (C10)	0.399	0.177	0.308
H' (C11)	0.243	0.416	0.442
H'' (C11)	0.356	0.478	0.435
H''' (C11)	0.309	0.578	0.636
H' (C12)	0.446	0.478	0.795
H'' (C12)	0.489	0.394	0.589
H''' (C12)	0.489	0.261	0.706
H' (C13)	0.175	0.590	0.690
H'' (C13)	0.132	0.670	0.896
H''' (C13)	0.090	0.466	0.719
H' (C14)	0.358	0.548	1.057
H'' (C14)	0.268	0.702	1.076
H''' (C14)	0.337	0.646	0.904
H' (C15)	0.223	0.355	1.072
H'' (C15)	0.118	0.323	0.918
H''' (C15)	0.154	0.538	1.081

TABLE IV. Bond Distances Å and Angles ($^\circ$).

Pt-Cl	2.367(2)	Cl-Pt-P	102.2(1)
Pt-P	2.333(2)	Cl-Pt-C(1)	86.9(3)
Pt-C(1)	2.20(1)	Cl-Pt-C(3')	154.0(7)
Pt-C(2)	2.12(2)	Cl-Pt-C(3)	151.9(7)
Pt-C(3)	2.17(3)	C(1)-Pt-C(3)	68.2(7)
Pt-C(2')	2.13(2)	C(1)-Pt-C(3')	67.6(8)
Pt-C(3')	2.18(3)	P-Pt-C(3)	102.4(7)
P-C(4)	1.924(8)	P-Pt-C(3')	103.4(7)
P-C(5)	1.922(9)	C(6)-P-Pt	105.6(3)
P-C(6)	1.910(8)	C(5)-P-Pt	113.9(3)
C(4)-C(7)	1.57(1)	C(4)-P-Pt	114.0(3)
C(4)-C(8)	1.53(1)	C(4)-P-C(5)	105.9(4)
C(4)-C(9)	1.54(1)	C(5)-P-C(6)	109.7(4)
C(5)-C(13)	1.55(1)	C(4)-P-C(6)	107.6(4)
C(5)-C(14)	1.54(1)	C(8)-C(4)-C(7)	107.0(7)
C(5)-C(15)	1.52(1)	C(8)-C(4)-C(9)	107.9(8)
C(6)-C(10)	1.55(1)	C(7)-C(4)-C(9)	106.3(7)
C(6)-C(11)	1.51(1)	C(13)-C(5)-C(14)	107.2(8)
C(6)-C(12)	1.55(1)	C(13)-C(5)-C(15)	105.7(8)
C(1)-C(2)	1.30(2)	C(15)-C(5)-C(14)	109.3(8)
C(2)-C(3)	1.29(3)	C(10)-C(6)-C(11)	106.7(8)
C(1)-C(2')	1.43(3)	C(10)-C(6)-C(12)	107.2(8)
C(2')-C(3')	1.16(3)	C(11)-C(6)-C(12)	109.0(8)
C(2)-C(3')	1.50(4)	C(1)-C(2)-C(3)	143(3)
C(2')-C(3)	1.44(4)	C(1)-C(2)-C(3')	141(3)
		C(1)-C(2)-C(3)	121(3)
		C(1)-C(2')-C(3)	117(3)
		P-Pt-C(1)	170.6(3)

TABLE V. Equations of Some Planes in the Molecule with Their Dihedral Angles.

<i>Plane 1</i>	$0.7156X - 0.1665Y - 0.6784Z = -1.3786$		
Pt	0.000	P	0.000
Cl	0.000	C(1)*	0.065
C(2)*	0.622	C(2)*	-0.481
C(3)*	0.505	C(3)*	-0.154
<i>Plane 2</i> (C(1)-C(2)-C(3)) $0.9101X - 0.3805Y + 0.1641Z = 0.4413$			
<i>Plane 3</i> (C(1)-C(2')-C(3')) $0.1150X - 0.1217Y + 0.9859Z = 2.0232$			
<i>Plane 4</i> (C(1)-C(2)-C(3')) $0.8588X - 0.2185Y + 0.4633Z = 1.0124$			
<i>Plane 5</i> (C(1)-C(2')-C(3')) $0.3398X - 0.0809Y + 0.9370Z = 1.9243$			
<i>Dihedral Angles</i> (°)			
Plane 1-Plane 2	127.1		
Plane 1-Plane 3	124.5		
Plane 1-Plane 4	109.7		
Plane 1-Plane 5	112.3		

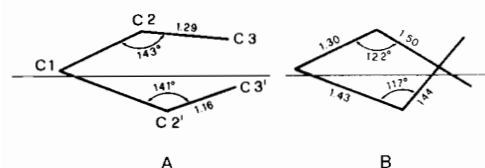


Figure 2. The two possible allylic patterns named A and B.

discrete molecules of $\{(\eta^3\text{-C}_3\text{H}_5)\text{Pt}[\text{P}(\text{t-butyl})_3]\text{Cl}\}$ separated by van der Waals contacts.

The η^3 -allyl derivative under investigation shows a grossly approximated planar geometry about the platinum atom: the deviations from the planar arrangement are related to the geometry and bonding mode of the allyl group. Moreover, there are also significant deviations of angles between the platinum atom and its coordinated neighbors from their idealized values of 90° and 180° .

The average bonding parameters of the phosphine ligand compare favorably with those found in similar structures and with predictions from covalent radii sums [32]. In particular the P-C distances range from 1.910 to 1.924 Å and average 1.919(9) Å; the C-P-C angles range from 105.9° to 109.7° and average $107.7(4)^\circ$; the C-C distances range from 1.51 to 1.57 Å and average 1.54(1) Å; finally the C-C-C angles range from 105.7° to 109.3° and average $107.4(8)^\circ$.

The Pt-P bond length (2.333(2) Å) found here falls within the range found for Pt-P distances in several square-planar Pt(II) complexes [33-34].

The Pt-Cl distance of 2.367(2) Å in the present complex is greater than that predicted from available covalent radii (2.30 Å). It is not, however, as long as the Pt-Cl bond in *trans*-[PtCl(CH₂CN)(PPh₃)₂] (2.390(4) Å [35]), in *trans*[PtCl(Me₃SiCH₂)(PMe₂

Ph)₂] (2.415(5) Å [36]) and in *trans*-[Pt($\eta^1\text{-C}_3\text{H}_5$)-Cl(PPh₃)₂] (2.425(2) Å [33]).

In the allyl moiety region there are five carbon atoms C(1), C(2), C(3), C(2') and C(3'), whose population parameter is 1 for C(1) and about 0.5 for the others.

The central carbons C(2) and C(2') are 0.622 Å above and 0.481 Å below the plane P-Pt-Cl respectively; the terminal carbons C(1) and C(3) are 0.065 and 0.505 Å above the same plane, while C(3') is 0.154 Å below.

The distances of the platinum from the three terminal carbons C(1), C(3) and C(3') are 2.20(1), 2.17(3) and 2.18(3) Å respectively; the average Pt-C distance of 2.19 Å is somewhat larger than the distance of 2.12(2) and 2.13(2) Å of the platinum from the central carbon atoms C(2) and C(2').

Based on the interatomic distances among the five carbons C(1), C(2), C(3), and C(3'), we assumed that two allylic patterns are extant, (A) and (B), each one having two possible orientations (Figure 2). It is sound practice not to place much trust on carbon-carbon bond lengths of disordered structures of Pt complexes; in this case the e.s.d.'s have to be multiplied by at least a factor of 2 to provide an idea of the true e.s.d.'s. Assuming a difference in the C-C bond length as being surely significant if larger than about 5 e.s.d.'s, the two allyl configurations C(1)-C(2')-C(3'), and the C(1)-C(2)-C(3'), are definitely asymmetric and hence in line with the spectroscopy evidence. This would also agree with the hypothesis that the asymmetry of the allyl group can be directly associated with the fluxional behaviour in solution.

As the other possible orientations of Figure 2, their apparent symmetry may be related to the position of the C(3) atom. The difference in *trans*-influence between PBu₃^t and chloride is likely to be

more effective in distorting the symmetry of the allyl configuration as the terminal allyl carbons are closer to the Pt–Cl plane. As a matter of fact, the effect of *trans*-influence should be fully operative only when a square-planar geometry is achieved. In the apparently symmetric configurations C(1)–C(2)–C(3) and C(1)–C(2)–C(3) the C(3) carbon occupies a space position rather away from the Pt–Cl plane.

Experimental

¹H NMR spectra were recorded in CDCl₃ solution with Varian 90 MHz and Bruker 270 MHz Spectrometers. ³¹P NMR spectra were registered in CDCl₃ and d₈-toluene with a Bruker WP-60 Spectrometer operating at 24.28 MHz with ¹H complete decoupling. Molecular weight was determined in CHCl₃ solution with a Knauer Dampfdruck-Osmometer. IR spectra were recorded with a Perkin-Elmer 457 spectrophotometer.

[Pt(allyl)Cl]₄ was prepared as previously described [37] and P(t-butyl)₃ was synthesized according to the literature method [38]. The preparation of {(η³-allyl)Pt[P(t-butyl)₃]Cl} has been performed according to the method described by Mann *et al.* [7] for the preparation of the PPh₃ analog. *Anal.* Found: C = 37.7, H = 7.0, Cl = 7.2%. PtClC₁₅H₃₂ requires: C = 38.00, H = 6.80, Cl = 7.48%. $\nu_{\text{Pt-Cl}} = 288 \text{ cm}^{-1}$. P.M. = 170–180 °C (dec.).

Single crystals were obtained as transparent prisms on cooling at –20 °C a solution in toluene. Procession photographs and single-crystal diffractometry showed that the crystals belong to the triclinic system, space group P $\bar{1}$ (after structure determination), with $a = 14.505(5)$, $b = 8.338(3)$, $c = 8.321(3)$ Å, $\alpha = 115.1(1)$, $\beta = 99.6(1)$, $\gamma = 87.0(1)^\circ$, $V = 898.4$ Å³; $D_o = 1.60$, $D_c = 1.62 \text{ g cm}^{-3}$ for $Z = 2$; $\mu(\text{MoK}\alpha) = 62.82 \text{ cm}^{-1}$.

Intensity data were collected from a crystal of approximate dimensions 0.31 × 0.23 × 0.20 mm, on a Philips PW1100 four-circle diffractometer operating in the $\theta/2\theta$ scan mode (scan width = 0.8°, scan speed = 0.03° s⁻¹). 3120 independent reflections up to $\theta = 25^\circ$ were measured, of which 2779 had $I \geq 2.5\sigma(I)$, $\sigma(I)$ being calculated from counting statistics. During the data collection two standard reflections were measured every 180 min to check the stability of the crystal and electronics. Intensities were corrected for Lorentz and polarization effects and converted to the absolute scale by Wilson's method. Experimental absorption correction was applied following the method proposed by North, Phillips and Mathews [39].

The structure was determined by the heavy-atom technique. A Patterson synthesis revealed the position of the Pt atom; the conventional R value was 0.22. The positions of the remaining non-hydrogen

atoms were derived from subsequent difference Fourier maps.

The structure was refined by full-matrix least-squares procedure. The function minimized was $\sum w [|F_o| - |F_c|]^2$, in which $w = 1$.

The scattering factors were those of the International Tables for X-ray Crystallography [40]. The correction for the real and imaginary parts of the anomalous dispersion was applied to Pt, Cl and P [41]. The refinement was carried out allowing the Pt, Cl and P atoms to vibrate anisotropically, while isotropic thermal parameters were applied to the C atoms of the t-butyl groups. At this stage a difference Fourier synthesis, phased with these atoms, was calculated. Inspection of this map in the allyl moiety region showed five maxima (instead of three), named C(1), C(2), C(3), C(2') and C(3'), whose weights are about 1 for C(1) and about 0.5 for the remaining ones. This reveals disorder in this part of the complex and a model was chosen, on the basis of the weights, in which the allyl group was allowed to take up the different orientations of Figure 2. Probably the maximum C(1) represents the overlap between two carbon atoms with a weight of 0.5 for each. Nevertheless, no evidence of this situation arises from an accurate inspection of the difference Fourier map. Therefore we assume a model in which C(1) is the same for any orientation. The molecular arrangement shows that C(2), C(3) and C(2'), C(3') are approximately related by a mirror plane passing through Pt, Cl and P. A further refinement cycle was carried out in which the population parameters of C(2), C(3), C(2') and C(3') were introduced. The R value fell to 0.038. At this stage a difference Fourier map yielded the coordinates of the H atoms of the methyl groups. The refinement was carried on with the H atoms of the methyl groups constrained to their normal geometry (C–H = 1.08 Å) using the group-refinement procedure [42]. The final R value for the 2779 observed reflections with $I \geq 2.5 \sigma(I)$ was 0.033.

The calculations were carried out on the CYBER 76 computer of the "Centro di Calcolo Interuniversitario Italia Nord Orientale" with the SHELX-76 system of crystallographic programs [43].

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