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Structure of (*E*)-2-Chlorovinylidene-5-phenyladamantane*

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Abstract. $C_{18}H_{19}Cl$, monoclinic, $C2/c$, $a = 26{\cdot}672\ (5)$, $b = 6{\cdot}933\ (2)$, $c = 23{\cdot}947\ (5)$ Å, $\beta = 137{\cdot}2°$, $V = 2971{\cdot}0$ Å^3. The number of molecules in the unit cell is eight ($\rho_{\rm calc} = \rho_{\rm obs} = 1{\cdot}21$ g cm^{-3}). $R = 0{\cdot}050$ for 2935 reflections measured on a diffractometer using Cu $K\alpha$ radiation. The C—C distances in the adamtane moiety fall into two groups: the six nearest or next-nearest neighbors of the phenyl group with an average of 1·533 Å, and others with an average of 1·517 Å (omitting one longer than 1·53 Å). The Cl atom is in the *anti* configuration with respect to the phenyl group. Effects of overcrowding on the shape of the phenyl group are observed in the structure.

Table 1. *Positional parameters and their e.s.d.'s*

	x	*y*	*z*
Cl	0·38348 (3)	−0·4554 (1)	0·19615 (4)
C(1)	0·38564 (9)	−0·1460 (3)	0·02057 (9)
C(2)	0·38853 (9)	−0·0805 (4)	0·08330 (9)
C(3)	0·42902 (10)	0·1097 (4)	0·12341 (9)
C(4)	0·38814 (9)	0·2636 (4)	0·05484 (9)
C(5)	0·38556 (8)	0·2055 (3)	−0·00923 (9)
C(6)	0·46637 (9)	0·1761 (4)	0·03720 (10)
C(7)	0·50628 (10)	0·0214 (4)	0·10462 (11)
C(8)	0·46535 (9)	−0·1698 (4)	0·06563 (10)
C(9)	0·34555 (8)	0·0097 (3)	−0·04725 (9)
C(10)	0·50913 (12)	0·0834 (4)	0·16786 (12)
C(1*v*)	0·36111 (9)	−0·1818 (4)	0·10142 (10)
C(2*v*)	0·33289 (10)	−0·2822 (5)	0·11791 (11)
C(1*p*)	0·34332 (8)	0·3551 (3)	−0·07857 (9)
C(2*p*)	0·37458 (9)	0·4478 (4)	−0·09865 (10)
C(3*p*)	0·33423 (11)	0·5803 (4)	−0·16345 (11)
C(4*p*)	0·26220 (12)	0·6234 (4)	−0·20895 (12)
C(5*p*)	0·23001 (11)	0·5355 (4)	−0·19002 (12)
C(6*p*)	0·26986 (9)	0·4024 (4)	−0·12581 (10)
H(1)	0·3569 (9)	−0·270 (4)	−0·0053 (10)
H(3)	0·4302 (9)	0·148 (4)	0·1621 (11)
H(4)	0·3373 (7)	0·278 (3)	0·0279 (8)
H(4′)	0·4120 (9)	0·386 (4)	0·0795 (10)
H(6)	0·4907 (8)	0·300 (4)	0·0610 (9)
H(6′)	0·4655 (9)	0·141 (4)	−0·0047 (10)
H(7)	0·5564 (9)	0·008 (4)	0·1306 (10)
H(8)	0·4644 (8)	−0·216 (3)	0·0252 (9)
H(8′)	0·4909 (9)	−0·262 (4)	0·1107 (10)
H(9)	0·2931 (9)	0·022 (3)	−0·0732 (10)
H(9′)	0·3438 (8)	−0·030 (3)	−0·0872 (9)
H(10)	0·5369(10)	−0·019 (4)	0·2164 (11)
H(10′)	0·5378 (10)	0·205 (4)	0·1938 (11)
H(2*v*)	0·2857 (10)	−0·270 (4)	0·0919 (11)
H(2*p*)	0·4227 (9)	0·415 (4)	−0·0707 (10)
H(3*p*)	0·3576 (10)	0·644 (4)	−0·1762 (12)
H(4*p*)	0·2355 (10)	0·713 (4)	−0·2520 (12)
H(5*p*)	0·1786 (10)	0·552 (4)	−0·2211 (11)
H(6*p*)	0·2437 (9)	0·343 (4)	−0·1160 (10)

Introduction. This study is part of our systematic investigations on 2-substituted 5-phenyladamantanes. The present compound has been studied to confirm the stereospecificity of the reaction between thionyl chloride and (*E*)-2-ethynyl-5-phenyladamantan-2-ol.

The diffraction data were obtained on an Enraf–Nonius CAD-4 diffractometer using Cu $K\alpha$ radiation up to 65° in θ. The θ–2θ scan method was used. The structure was solved by *MULTAN* (Germain, Main & Woolfson, 1971) and refined by a full-matrix least-squares program using the Enraf–Nonius structure determination package on a PDP-11/45 computer. The function minimized was $\sum w(F_o - kF_c)^2$ with $w^{-1} = [\sigma_c F_o^2 + (0{\cdot}05F_o^2)^2]$ where σ_c is the deviation depending on the counting statistics. All the H atoms were located in a difference Fourier map and refined with isotropic temperature factors. The final disagreement factor $R = 0{\cdot}050$. The atomic scattering factors used for Cl and C atoms are those of Doyle & Turner (1968) and for H those of Stewart, Davidson & Simpson (1965). Because of the small absorption coefficient of the specimen, no absorption correction was made. The positional parameters of all the atoms are given in Table 1.§

Discussion. A schematic drawing of the molecule with the numbering system used is shown in Fig. 1. The bond distances and angles are in Tables 2 and 3 respectively. There is a trend in the C—C bond distances of the adamantane part of the molecule. Those bonds which are either nearest or next-nearest neighbors (average 1·533 Å) to the C(5)—C(1*p*) bond are systematically longer than the others [average 1·517 Å,

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§ Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33682 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

excluding C(3)–C(10)]. The latter bonds constitute a cyclohexane ring with a double-bonded substituent. No such trend is observed in those phenyladamantanes with substituents which are only single-bonded to the adamantane cages. C(2*p*)–C(1*p*)–C(6*p*) is 117·0 (2)° – smaller than the normal angle of 120°. This situation is common to all the phenyladamantanes studied by us (le Noble, Chiou, Małuszyńska & Okaya, 1977) and suggests interference between the H atom halo made by the adamantane H atoms and the *ortho* H atoms, H(2*p*) and H(6*p*), of the phenyl group. This is another example of the effects of intramolecular non-bonded interactions on the shapes of aromatic rings (Domenicano, Vaciago & Coulson, 1975). The bond distances and angles involving the H atoms are normal and are listed in Table 4 as their averaged values.

The adamantane moiety possesses an approximate mirror plane through C(2), C(5), C(6) and C(7). The equation of this plane and deviations of relevant atoms from it are shown in Table 5(*a*). The slight asymmetry shown by the deviations of C(8) and C(10) from the plane may be due to the tilt of the chlorovinylidene group from the mirror towards C(8). In fact, the difference in the magnitudes of the two deviations is quite close to twice the deviation of the Cl atom of the chlorovinylidene group, indicating close contact between the Cl and the methylene groups of these two C atoms. The planarity data for the phenyl group are listed in Table 5(*b*). The dihedral angle between these two planes is 3·5°. The chlorovinylidene group [Table 5(*c*)] is also parallel to the adamantane mirror with a dihedral angle of only 1·6°.

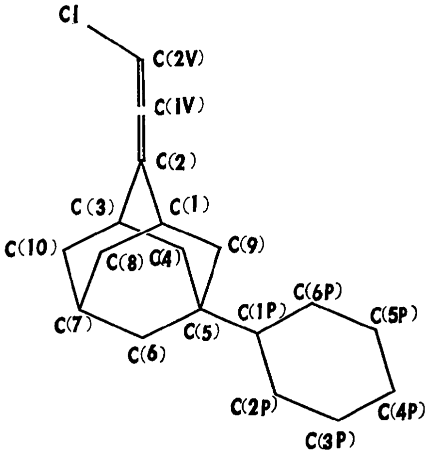

Fig. 1. The atom-numbering scheme.

Table 2. *Bond distances* (Å)

C(1)–C(2)	1·516 (2)	C(6)–C(7)	1·529 (2)
C(1)–C(8)	1·519 (2)	C(7)–C(8)	1·519 (2)
C(1)–C(9)	1·539 (2)	C(7)–C(10)	1·521 (2)
C(2)–C(3)	1·513 (2)	C(1*p*)–C(2*p*)	1·391 (2)
C(2)–C(1*v*)	1·299 (2)	C(2*p*)–C(3*p*)	1·389 (2)
C(3)–C(4)	1·538 (2)	C(3*p*)–C(4*p*)	1·364 (3)
C(3)–C(10)	1·535 (3)	C(4*p*)–C(5*p*)	1·375 (3)
C(4)–C(5)	1·537 (2)	C(5*p*)–C(6*p*)	1·385 (3)
C(5)–C(6)	1·538 (2)	C(6*p*)–C(1*p*)	1·392 (2)
C(5)–C(9)	1·539 (2)	C(1*v*)–C(2*v*)	1·284 (2)
C(5)–C(1*p*)	1·525 (2)	C(2*v*)–Cl	1·738 (2)

Table 3. *Bond angles* (°)

C(2)–C(1)–C(8)	108·3 (1)	C(6)–C(7)–C(8)	110·1 (1)
C(2)–C(1)–C(9)	108·7 (1)	C(6)–C(7)–C(10)	109·5 (2)
C(8)–C(1)–C(9)	109·6 (1)	C(8)–C(7)–C(10)	109·9 (2)
C(1)–C(2)–C(3)	112·2 (2)	C(1)–C(8)–C(7)	109·3 (1)
C(1)–C(2)–C(1*v*)	122·8 (2)	C(1)–C(9)–C(5)	111·2 (1)
C(3)–C(2)–C(1*v*)	125·0 (1)	C(3)–C(10)–C(7)	109·2 (1)
C(2)–C(3)–C(4)	108·7 (1)	C(5)–C(1*p*)–C(2*p*)	122·9 (1)
C(2)–C(3)–C(10)	107·9 (1)	C(5)–C(1*p*)–C(6*p*)	120·2 (1)
C(4)–C(3)–C(10)	110·0 (2)	C(2*p*)–C(1*p*)–C(6*p*)	117·0 (2)
C(3)–C(4)–C(5)	110·8 (1)	C(1*p*)–C(2*p*)–C(3*p*)	121·7 (2)
C(4)–C(5)–C(6)	108·2 (1)	C(2*p*)–C(3*p*)–C(4*p*)	120·1 (2)
C(4)–C(5)–C(9)	108·6 (1)	C(3*p*)–C(4*p*)–C(5*p*)	119·6 (2)
C(6)–C(5)–C(9)	107·2 (1)	C(4*p*)–C(5*p*)–C(6*p*)	120·6 (2)
C(4)–C(5)–C(1*p*)	111·0 (1)	C(5*p*)–C(6*p*)–C(1*p*)	121·1 (2)
C(6)–C(5)–C(1*p*)	112·6 (1)	C(2)–C(1*v*)–C(2*v*)	179·0 (2)
C(9)–C(5)–C(1*p*)	109·2 (1)	C(1*v*)–C(2*v*)–Cl	122·9 (2)
C(5)–C(6)–C(7)	111·1 (1)		

Table 4. *Average bond distances* (Å) *and angles* (°) *involving* H *atoms*

C(sp^3)–H	0·99	H–C(sp^3)–H	109·0
C(ar.)–H	0·96	C(sp^3)–C(sp^3)–H	109·5
C(2*v*)–H(2*v*)	0·90	C(ar.)–C(ar.)–H	119·7

Table 5. *Equations of the planes and deviations* (Å) *of atoms from them*

(*a*) The C(2)–C(5)–C(6)–C(7) adamantane mirror plane

$$0{\cdot}2620X - 0{\cdot}7022Y - 0{\cdot}6621Z = 1{\cdot}8345$$

(i)	C(2)	C(5)	C(6)	C(7)
	0·000	0·001	−0·001	0·000
(ii)	C(1)	C(8)	C(9)	
	1·257	1·373	1·255	
	C(3)	C(10)	C(4)	
	−1·256	−1·248	−1·243	
(iii)	C(2*v*)	C(2*v*)	Cl	
	0·024	0·064	0·065	

(*b*) The phenyl group [C(1 *p*) through C(6 *p*)]

$$0{\cdot}2192X - 0{\cdot}7371Y - 0{\cdot}6392Z = 1{\cdot}3014$$

C(1*p*)	C(2*p*)	C(3*p*)	C(4*p*)	C(5*p*)	C(6*p*)
0·003	−0·004	0·001	0·003	−0·004	0·001
C(5)					
0·033					

(*c*) The chlorovinylidene group

$$0{\cdot}2894X - 0{\cdot}6956Y - 0{\cdot}6576Z = 2{\cdot}0767$$

C(2)	C(1*v*)	C(2*v*)	Cl
0·003	−0·005	0·002	0·000

The Cl atom in the chlorovinylidene group is *anti* [or (*E*)] to the phenyl group on C(5), confirming the result of the stereospecific reaction discussed previously.

The molecules are arranged in the structure by normal van der Waals contacts. No anomaly was found in intermolecular distances.

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The Structure of the Free Acid of Antibiotic A204A

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Abstract. $C_{49}H_{84}O_{17}.H_2O.C_3H_6O$, monoclinic, $C2$, $a = 27{\cdot}576\ (2)$, $b = 14{\cdot}711\ (1)$, $c = 14{\cdot}348\ (1)$ Å, $\beta = 92{\cdot}573\ (4)°$, $Z = 4$ and $\rho_c = 1{\cdot}167$ g cm^{-3}. The compound crystallizes in a 1:1:1 ratio with water and acetone. While the overall conformation of the solvated ionophore resembles that of the Na and Ag ion complexes, changes in the hydrogen-bonding scheme are observed.

Introduction. Single crystals of uncomplexed A204A (Fig. 1) were grown from a water/acetone solution. A total of 4513 independent data ($\sin\theta_{\max}/\lambda = 0{\cdot}562$ Å^{-1}) were collected on an Enraf–Nonius CAD-4 diffractometer using Ni-filtered Cu radiation from a single crystal of dimensions 0·12 × 0·22 × 0·80 mm. Intensities were corrected for Lorentz and polarization factors but not for extinction or absorption [μ(Cu $K\alpha$) = 7·32 cm^{-1}]. On the basis of a $2\sigma(I)$ test, 3735 intensities were considered observed. The variance of each F was calculated according to the method of Stout & Jensen (1968) $\{\sigma^2(F) = k/4(\mathrm{Lp})I[\sigma^2(I) + (0{\cdot}06I)^2];\ w(F) = 1/\sigma^2(F)\}$. Unobserved data were assigned weights of zero.

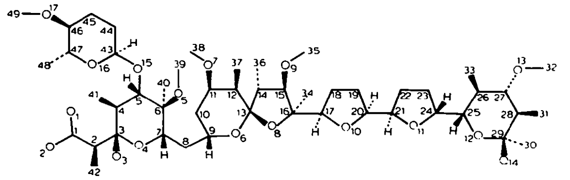

Fig. 1. Chemical structure of A204A and numbering scheme.

The structure was solved through the use of the direct-methods program *QTAN* (Langs & De Titta, 1975). Although the residual and negative quartet figures of merit would have ultimately allowed the selection of the correct solution, an unambiguous choice of the solution was made possible by eliminating triples identified as unreliable through estimates of the triple invariants based on the ten-magnitude second neighborhood (Kruger, Green & Hauptman, 1977). A total of 48 atoms were correctly identified from the initial E map. Subsequent Fourier refinement revealed the positions of the remaining atoms; the acetone molecule was located with considerable difficulty because of its high thermal motion. The structure was

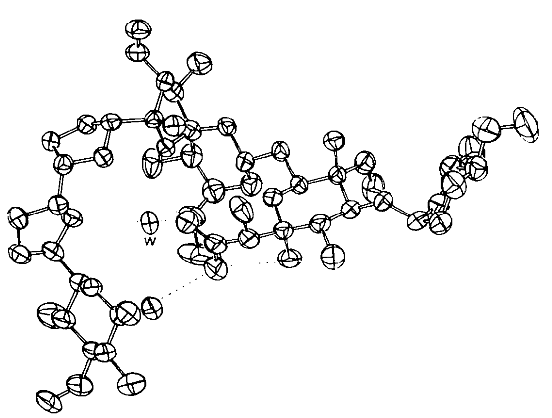

Fig. 2. Observed conformation of A204A with ellipsoids plotted at 50% probability.