Table 2. *Deviations of the atoms from the least-squares planes*

		Free molecule	Hydrobromide molecule
Ring *A*	C(1)	0·012 Å	0·001 Å
	C(2)	−0·014	−0·009
	C(3)	0·003	0·008
	C(4)	0·010	0·002
	C(10)	−0·013	−0·010
	N(1)	0·002	0·009
	N(2)*	0·091	0·008
Ring *B*	N(3)	0·001	−0·001
	C(4)	−0·004	0·001
	C(10)	0·006	−0·001
	N(4)	−0·005	0·000
	N(5)	0·003	0·000
Ring *C*	N(4)	0·018	−0·003
	C(5)	−0·009	0·002
	C(6)	−0·007	−0·002
	C(7)	0·014	0·003
	C(8)	−0·005	0·003
	C(9)	−0·011	0·003
	C(11)*	−0·029	0·020

* Atoms not included in the least-squares calculation.

pyrimidines and purines (Sundaralingam & Jensen, 1965; Singh, 1965; Rao & Sundaralingam, 1970; Prusiner, Brennan & Sundaralingam, 1973; Koyama, Nakamura, Umezawa & Iitaka, 1976).

Comparison of the corresponding bond lengths and angles in the hydrobromide with those in Trp-P-1 acetic acid solvate (Itai & Iitaka, 1978) indicates that the most significant deviations are found in the five-membered ring. This may be the effect of the substitution of the C atom by N(4). As can be seen in Fig. 3(*b*), the protonated N(3) forms a strong hydrogen bond to the water O(1) with an N(3)···O(1) distance of 2·700 Å.

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The Structure of (*Z*)-2-Ethynyl-5-phenyl-2-adamantanol*

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(*Received* 22 *January* 1979; *accepted* 4 *May* 1979)

Abstract. $C_{18}H_{20}O$, orthorhombic, $P2_12_12$, a = 20·743 (6), b = 13·286 (3), c = 10·243 (3) Å, Z = 8. R = 0·050 for 2700 reflections collected on a diffractometer using Cu $K\alpha$ radiation. There are two crystallographically independent molecules in the asymmetric unit which have the same Z configuration, but their phenyl groups are oriented differently with respect to the mirror planes of the adamantane moieties. The dihedral angles between these planes are 44·5 and 10·4°, the latter being the normal contact angle. The molecule with the larger angle exhibits strong thermal motion by fitting loosely in the structure. Effects of overcrowding on the shape of the phenyl groups are observed. A network of O—H···O hydrogen bonds holds the polar parts of the molecules with a disordered arrangement of the hydroxyl H atoms.

Introduction. This report is the second in our series of investigations on 2-substituted adamantanes (for the previous report see Okaya, Małuszyńska, Chiou & le Noble, 1978). The present structure has been chosen in order to establish its configuration; it is expected that

* Crystallographic Studies on Adamantanes. II.

0567-7408/79/092268-04$01.00

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

	Molecule *A*			Molecule *B*			
	x	*y*	*z*		*x*	*y*	*z*
O*A*	0·0633 (1)	0·0377 (2)	0·2760 (3)	O*B*	0·4355 (1)	0·4717 (2)	0·4662 (2)
C(1*A*)	0·1744 (2)	0·0856 (3)	0·2350 (4)	C(1*B*)	0·4238 (2)	0·3724 (3)	0·2663 (3)
C(2*A*)	0·1140 (2)	0·0314 (3)	0·1805 (3)	C(2*B*)	0·4000 (2)	0·3909 (3)	0·4058 (4)
C(3*A*)	0·0930 (2)	0·0860 (3)	0·0551 (3)	C(3*B*)	0·4080 (2)	0·2931 (3)	0·4844 (4)
C(4*A*)	0·0774 (2)	0·1964 (3)	0·0864 (4)	C(4*B*)	0·4796 (2)	0·2632 (3)	0·4872 (3)
C(5*A*)	0·1371 (2)	0·2510 (3)	0·1397 (3)	C(5*B*)	0·5051 (2)	0·2450 (2)	0·3473 (3)
C(6*A*)	0·1006 (2)	0·2439 (3)	0·0374 (4)	C(6*B*)	0·4640 (2)	0·1614 (3)	0·2857 (5)
C(7*A*)	0·2071 (2)	0·1340 (3)	0·0088 (4)	C(7*B*)	0·3934 (2)	0·1921 (3)	0·2819 (5)
C(8*A*)	0·2286 (2)	0·0780 (4)	0·1324 (5)	C(8*B*)	0·3853 (2)	0·2872 (4)	0·2020 (4)
C(9*A*)	0·1580 (2)	0·1948 (3)	0·2637 (4)	C(9*B*)	0·4949 (2)	0·3426 (2)	0·2684 (3)
C(10*A*)	0·1471 (2)	0·0808 (3)	−0·0460 (4)	C(10*B*)	0·3689 (2)	0·2096 (3)	0·4183 (6)
C(1*EA*)	0·1281 (2)	−0·0771 (3)	0·1569 (4)	C(1*EB*)	0·3315 (2)	0·4242 (3)	0·4021 (4)
C(2*EA*)	0·1401 (3)	−0·1630 (3)	0·1429 (5)	C(2*EB*)	0·2782 (2)	0·4517 (4)	0·3942 (6)
C(1*pA*)	0·1193 (2)	0·3608 (3)	0·1673 (4)	C(1*pB*)	0·5770 (2)	0·2181 (2)	0·3501 (3)
C(2*pA*)	0·1069 (2)	0·3951 (3)	0·2938 (4)	C(2*pB*)	0·6226 (2)	0·2893 (3)	0·3827 (4)
C(3*pA*)	0·0875 (3)	0·4954 (4)	0·3153 (5)	C(3*pB*)	0·6878 (2)	0·2686 (3)	0·3826 (4)
C(4*pA*)	0·0813 (3)	0·5617 (4)	0·2159 (7)	C(4*pB*)	0·7090 (2)	0·1727 (3)	0·3504 (5)
C(5*pA*)	0·0922 (4)	0·5282 (4)	0·0907 (7)	C(5*pB*)	0·6654 (2)	0·1019 (3)	0·3196 (6)
C(6*pA*)	0·1110 (3)	0·4294 (4)	0·0669 (6)	C(6*pB*)	0·5990 (2)	0·1217 (3)	0·3192 (5)
H(1*A*)	0·191 (2)	0·042 (3)	0·324 (4)	H(1*B*)	0·420 (2)	0·434 (2)	0·218 (3)
H(3*A*)	0·049 (2)	0·045 (3)	0·022 (4)	H(3*B*)	0·397 (2)	0·309 (3)	0·578 (4)
H(4*A*)	0·042 (2)	0·199 (3)	0·146 (4)	H(4*B*)	0·987 (2)	0·827 (2)	0·475 (3)
H(4*A*′)	0·067 (2)	0·226 (3)	0·010 (4)	H(4*B*′)	0·483 (2)	0·191 (3)	0·534 (4)
H(6*A*)	0·218 (2)	0·280 (3)	0·076 (5)	H(6*B*)	0·480 (2)	0·135 (3)	0·195 (4)
H(6*A*′)	0·172 (2)	0·277 (3)	−0·050 (4)	H(6*B*′)	0·471 (2)	0·100 (3)	0·330 (4)
H(7*A*)	0·241 (2)	0·115 (3)	−0·054 (4)	H(7*B*)	0·368 (2)	0·144 (3)	0·227 (4)
H(8*A*)	0·265 (2)	0·098 (3)	0·150 (5)	H(8*B*)	0·342 (2)	0·308 (3)	0·202 (4)
H(8*A*′)	0·244 (2)	0·003 (3)	0·116 (4)	H(8*B*′)	0·396 (2)	0·274 (3)	0·113 (5)
H(9*A*)	0·194 (2)	0·231 (3)	0·332 (3)	H(9*B*)	0·521 (1)	0·402 (2)	0·305 (3)
H(9*A*′)	0·125 (1)	0·203 (2)	0·330 (3)	H(9*B*′)	0·504 (2)	0·331 (3)	0·180 (3)
H(10*A*)	0·134 (2)	0·142 (3)	−0·122 (3)	H(10*B*)	0·375 (2)	0·153 (3)	0·469 (5)
H(10*A*′)	0·165 (2)	0·011 (3)	−0·063 (3)	H(10*B*′)	0·331 (2)	0·230 (2)	0·416 (4)
H(O*A*)	0·027 (3)	0·031 (4)	0·253 (7)	H(O*B*)	0·475 (2)	0·466 (3)	0·447 (5)
H(2*EA*)	0·147 (2)	−0·237 (3)	0·127 (4)	H(2*EB*)	0·235 (2)	0·483 (4)	0·381 (5)
H(2*pA*)	0·108 (3)	0·343 (4)	0·385 (7)	H(2*pB*)	0·612 (1)	0·352 (2)	0·409 (3)
H(3*pA*)	0·035 (3)	0·506 (8)	0·428 (9)	H(3*pB*)	0·718 (2)	0·328 (3)	0·403 (4)
H(4*pA*)	0·057 (4)	0·648 (5)	0·214 (9)	H(4*pB*)	0·757 (2)	0·148 (3)	0·346 (5)
H(5*pA*)	0·094 (3)	0·583 (5)	0·014 (6)	H(5*pB*)	0·685 (2)	0·031 (3)	0·309 (5)
H(6*pA*)	0·125 (3)	0·387 (6)	−0·027 (9)	H(6*pB*)	0·553 (2)	0·065 (3)	0·294 (4)

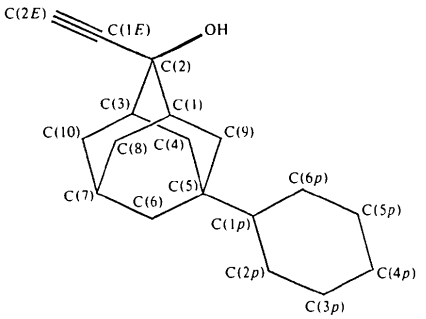

Fig. 1. The atom-numbering scheme.

this knowledge will facilitate investigations concerning the stereospecificity of a number of reactions (le Noble, Chiou, Małuszyńska & Okaya, 1977). 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 $w^{-1} = \sigma_c F_o^2 + (0{\cdot}05\ F_o)^2$ where σ_c is the standard deviation depending on counting statistics. All the H atoms have been located in a difference Fourier map and refined with isotropic thermal factors. The final disagreement factor, $R = \sum||F_o| - |F_c||/\sum|F_o|$, is 0·050. The atomic scattering factors used in the calculations are those derived from the data of Cromer & Waber (1974). A drawing of the molecule with the atomic numbering used is shown in Fig. 1. The atomic parameters of all atoms are given in Table 1.* The two molecules in the asymmetric unit have been designated

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34445 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond distances* (Å)

	Molecule *A*	Molecule *B*		Molecule *A*	Molecule *B*		Molecule *A*	Molecule *B*
C(1)–C(2)	1·549 (4)	1·528 (4)	C(5)–C(9)	1·536 (4)	1·542 (4)	C(2)–O(1)	1·439 (4)	1·441 (4)
C(1)–C(8)	1·542 (5)	1·552 (5)	C(5)–C(1*p*)	1·531 (5)	1·534 (4)	C(1*p*)–C(2*p*)	1·395 (5)	1·378 (5)
C(1)–C(9)	1·519 (5)	1·534 (4)	C(6)–C(7)	1·528 (6)	1·521 (6)	C(2*p*)–C(3*p*)	1·409 (6)	1·380 (5)
C(2)–C(3)	1·538 (4)	1·538 (4)	C(7)–C(8)	1·535 (6)	1·515 (6)	C(3*p*)–C(4*p*)	1·352 (7)	1·388 (5)
C(3)–C(4)	1·536 (5)	1·538 (4)	C(7)–C(10)	1·537 (5)	1·505 (7)	C(4*p*)–C(5*p*)	1·376 (9)	1·342 (6)
C(3)–C(10)	1·528 (5)	1·532 (5)	C(sp^3)–C(sp^3)(av.)	1·534	1·532	C(5*p*)–C(6*p*)	1·391 (8)	1·402 (6)
C(4)–C(5)	1·536 (4)	1·546 (4)	C(2)–C(1*E*)	1·491 (5)	1·489 (4)	C(6*p*)–C(1*p*)	1·385 (6)	1·396 (5)
C(5)–C(6)	1·529 (5)	1·536 (4)	C(1*E*)–C(2*E*)	1·177 (5)	1·167 (5)	C(ar)–C(ar)(av.)	1·385	1·381

Table 3. *Bond angles* (°) *with e.s.d.'s in parentheses*

	Molecule *A*	Molecule *B*		Molecule *A*	Molecule *B*		Molecule *A*	Molecule *B*
C(2)–C(1)–C(8)	108·3 (3)	110·6 (3)	C(4)–C(5)–C(6)	108·2 (3)	107·7 (3)	C(3)–C(10)–C(7)	109·1 (3)	110·1 (3)
C(2)–C(1)–C(9)	109·4 (3)	109·9 (3)	C(4)–C(5)–C(9)	106·9 (3)	107·8 (2)	C(sp^3)–C(sp^3)–C(sp^3)(av.)	109·45	109·45
C(8)–C(1)–C(9)	110·9 (3)	108·5 (3)	C(4)–C(5)–C(1*p*)	108·7 (3)	110·6 (2)	C(2)–C(1*E*)–C(2*E*)	177·5 (4)	177·2 (4)
C(1)–C(2)–C(3)	108·1 (3)	108·6 (3)	C(6)–C(5)–C(9)	109·4 (3)	108·5 (3)	C(5)–C(1*p*)–C(2*p*)	121·8 (3)	120·8 (2)
C(1)–C(2)–C(1*E*)	110·4 (3)	109·4 (3)	C(6)–C(5)–C(1*p*)	111·2 (3)	112·3 (2)	C(5)–C(1*p*)–C(6*p*)	121·3 (4)	121·8 (3)
C(1)–C(2)–O	108·7 (3)	110·8 (2)	C(9)–C(5)–C(1*p*)	112·3 (3)	109·8 (2)	C(2*p*)–C(1*p*)–C(6*p*)*	116·7 (4)	117·4 (3)
C(3)–C(2)–C(1*E*)	112·1 (3)	111·5 (2)	C(5)–C(6)–C(7)	110·7 (3)	110·5 (3)	C(1*p*)–C(2*p*)–C(3*p*)	120·4 (4)	122·3 (3)
C(3)–C(2)–O	109·4 (3)	110·5 (2)	C(6)–C(7)–C(8)	111·7 (4)	110·2 (4)	C(2*p*)–C(3*p*)–C(4*p*)	121·7 (5)	119·7 (4)
C(1*E*)–C(2)–O	108·1 (3)	106·1 (3)	C(6)–C(7)–C(10)	109·1 (3)	110·1 (4)	C(3*p*)–C(4*p*)–C(5*p*)	118·4 (5)	119·0 (4)
C(2)–C(3)–C(4)	109·6 (3)	109·4 (3)	C(8)–C(7)–C(10)	108·3 (3)	109·6 (4)	C(4*p*)–C(5*p*)–C(6*p*)	120·9 (6)	122·1 (4)
C(2)–C(3)–C(10)	109·7 (3)	108·9 (3)	C(1)–C(8)–C(7)	108·6 (3)	109·0 (3)	C(5*p*)–C(6*p*)–C(1*p*)	121·7 (5)	119·5 (4)
C(4)–C(3)–C(10)	109·8 (3)	109·4 (3)	C(1)–C(9)–C(5)	111·6 (3)	110·9 (2)	C(ar)–C(ar)–C(ar)(a.v.)	120·00	120·00
C(3)–C(4)–C(5)	110·8 (3)	110·7 (3)						

* See text.

arbitrarily as molecules *A* and *B*. Each H atom carries the number of the atom to which it is attached. When there are two H atoms on a C atom, the second H, which is chosen arbitrarily, is distinguished by a prime.

Discussion. Bond distances and angles calculated from the parameters in Table 1 are listed in Tables 2 and 3.

Aside from a difference in the orientations of the phenyl groups which is to be discussed further below, no substantial differences have been observed in the sizes and shapes of the two molecules. All the bond distances and angles are well within the normal values for such compounds. The phenyl groups are planar within the standard deviations of the positions of the atoms forming them. The configurations of both molecules are such that the hydroxyl groups are *syn* (or *Z*) to the phenyl groups on C(5).

The C(2*p*)–C(1*p*)–C(6*p*) angles [116·7 (4) for molecule *A* and 117·4 (3)° for *B*] are smaller than the normal angle of 120°. This situation is common to all the 5-phenyladamantanes studied in this series and suggests steric hindrance among the H atoms near the C(1*p*)–C(5) bonds (le Noble *et al.*, 1977). This structure is a further example showing the type of effect discussed by Domenicano, Vaciago & Coulson (1975) in which the shapes of the phenyl groups are affected by intramolecular interactions.

An interesting feature of the present structure is that the asymmetric unit contains two molecules and their conformations are different. The dihedral angle between the phenyl plane and the mirror plane through the adamantane moiety [C(5)–C(6)–C(7)–C(2)] is 44·5° for molecule *A*, whereas the corresponding angle for molecule *B* is 10·4°. From the dihedral angles observed in other 5-phenyladamantanes, it can be assumed that the dihedral angle for molecule *B* is in the normal range. Table 4 lists examples of such dihedral angles. *ORTEP* drawings (Johnson, 1965) in Fig. 2 illustrate the above difference between the dihedral angles for *A* and *B*. It is also of interest to note that molecule *B* is in closer contact with other molecules in the structure than molecule *A*. The aromatic C atoms of molecule *A* have relatively few non-hydrogen neighbors within 3·8 Å. Thus, the phenyl group of molecule *A*, avoiding a close intramolecular contact with the OH group, sits loosely in the structure.

The hydroxyl groups of the molecules form a network of hydrogen bonds. First, each molecule forms an O–H···O bond around the twofold axis with its equivalent molecule. Their distances are 2·810 (5) and 2·781 (4) Å for molecules *A* and *B*, respectively. In addition, there exists a short O(*A*)–O(*B*) approach of 2·782 (3) Å along the twofold screw axis parallel to *b*. The hydrogen bonds around the twofold axes are too

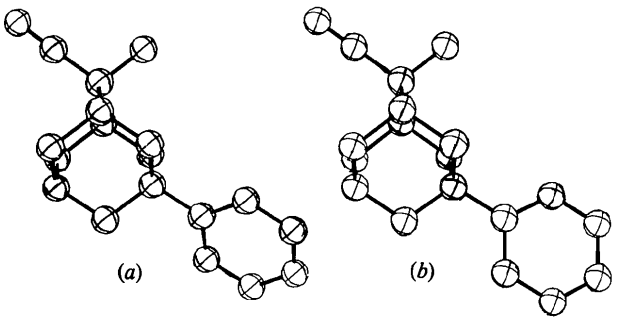

Fig. 2. *ORTEP* drawings of (*a*) molecule *A* and (*b*) molecule *B*. The mirror plane through the adamantane moiety lies parallel to the plane of the paper. Note the difference in the projections of the phenyl rings.

long to be symmetric, and the existence of the third approach suggests disordered arrangements of the two active H atoms. The relatively high thermal motions of these H atoms indicate such a tendency, but no detailed analysis has been made. The difference electron-density map did not reveal a reasonable H atom position for the third approach.

The diffraction data used in this study were collected at the Brookhaven National Laboratory. One of the authors (W. J. le Noble) wishes to acknowledge support by the National Science Foundation (NSF-CHE-7512847).

Table 4. *5-Phenyladamantanes: dihedral angles between the phenyl plane and the mirror through the adamantane cage*

Substituents on C(2)			
anti to phenyl	*syn* to phenyl	Angles (°)	Reference
−Cl	−C≡CH	62·5	*a*
−C≡CH	Cl	65·5	*a*
−C≡CH	OH	10·4 44·5	*b*
=C=CHCl (Cl *anti* to phenyl)		3·6	*c*

References: (*a*) Lin *et al.* (1979). (*b*) This work. (*c*) Okaya *et al.* (1978).

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Acta Cryst. (1979). B**35**, 2271–2273

Bis(*p*-méthoxyphényl)-3,3 Phényl-2 Acrylonitrile

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(*Reçu le* 2 *septembre* 1978, *accepté le* 3 *mai* 1979)

Abstract. $C_{23}H_{19}NO_2$, monoclinic, $P2_1/c$, a = 8·595 (1), b = 9·379 (1), c = 22·602 (2) Å, β = 92·85°, V = 1819·4 Å^3, Z = 4, d_c = 1·224 Mg m^{-3}. The structure was solved by direct methods and refined by least-squares procedures to a final R of 0·035 using 2740 independent observed reflexions. The angles between the three aromatic rings are nearly the same as those found in other triphenylethylenes.

0567-7408/79/092271-03$01.00

Introduction. Certains dérivés du triphényléthylène (tamoxifène, broparestrol) sont utilisés en thérapeutique et possèdent des affinités biochimiques intéressantes pour le récepteur cytoplasmique des oestrogènes. Il nous a semblé possible d'envisager l'utilisation de cette propriété biochimique pour la mise au point d'un substrat synthétique de chromatographie d'affinité pour purifier le récepteur. Par ailleurs, l'analyse radio-