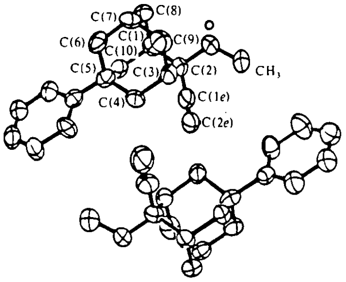

Fig. 2. An *ORTEP* drawing of a pseudo-centrosymmetric pair.

$C_{10}H_{13}.C_6H_5.(C\equiv CH).OH$, (Okaya, Chiou & le Noble, 1979). In this molecule the dihedral angles are quite different from each other (10·5 and 44·5°).

The observed bond distances and angles are all normal for this type of compound. The C(2*p*)—C(1*p*)—C(6*p*) angles of 115·7 (3) and 118·0 (3)° are smaller than the normal angles of 120°. The appearance of smaller angles is common to all the phenyladamantanes studied by us (le Noble, Chiou, Małuszyńska & Okaya, 1977), and the structure serves as another example of the non-bonded steric-hindrance effect as discussed by Domenicano, Vaciago & Coulson (1975). The steric effect around the methoxy bond is such that it is almost parallel to the O(1)—C(2)—C(1)—C(10) plane.

The molecules are arranged in the structure by the usual van der Waals interactions. No unusual intermolecular contacts were observed.

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Structure of 2-Ethynyl-2-adamantanol*†

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Abstract. $C_{12}H_{16}O$, monoclinic, $P2_1/c$, $a = 6{\cdot}820$ (2), $b = 22{\cdot}644$ (3), $c = 12{\cdot}708$ (2) Å, $\beta = 94{\cdot}5$ (2)°, $V = 1956{\cdot}5$ Å^3, $Z = 8$, $\rho_o \simeq \rho_c = 1{\cdot}19$ g cm^{-3}. $R = 5{\cdot}0\%$ for 2200 observed reflections measured on a diffractometer using Cu $K\alpha$ radiation. The two crystallographically independent molecules in the asymmetric unit exhibit almost identical shapes and sizes. The hydroxyl group of one of the molecules forms a hydrogen bond of 2·839 (2) Å with the hydroxyl O of the other molecule, which in turn is involved in an intramolecular O—H···π hydrogen bond with the ethynyl group.

Introduction. An extensive study has been made in our Department on 2-substituted-5-phenyladamantanes as probes to determine the stereochemical course of various reactions. In this connection, the configurations of a number of 2-substituted-5-phenyladamantanes, especially those with a 2-ethynyl group, have been determined. The present paper reports the structure of the parent alcohol, 2-ethynyl-2-adamantanol.

The diffraction data were obtained on an Enraf–Nonius CAD-4A diffractometer. The data collection range was up to 65° in θ, and the θ–2θ scan technique

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[*] IUPAC name: 2-ethynyltricyclo[3.3.1.1^{3,7}]decan-2-ol.

[†] Crystallographic Studies on Adamantanes. V.

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 the PDP-11/45 computer (Frenz, 1978). The function minimized was $\sum w(kF_c - F_o)^2$ with $w^{-1} = \sigma F_o^2 + (0{\cdot}04F_o^2)^2$ where σ is the standard deviation depending on the counting statistics. Those reflections with $I/\sigma(I) < 3$ were removed from refinements. All the H atoms were located in difference-Fourier maps and refined with isotropic temperature factors. The atomic scattering factors used for the calculations are those derived from results of Cromer & Waber (1974). The positional parameters are given in Table 1.* The two crystallographically independent molecules are labelled *A* and *B*.

Table 1. *Fractional atomic coordinates and isotropic thermal parameters*

For non-H atoms $B_{eq} = \frac{1}{3}\sum_i\sum_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}/B (Å^2)
Molecule *A*				
O(*A*)	−0·0434 (3)	0·03150 (8)	0·3506 (2)	3·42 (1)
C(1*A*)	0·1655 (4)	0·0394 (1)	0·7766 (2)	2·82 (2)
C(2*A*)	0·0719 (3)	0·0316 (1)	0·6642 (2)	2·60 (2)
C(3*A*)	−0·1259 (4)	0·0648 (1)	0·6538 (2)	3·16 (2)
C(4*A*)	−0·0872 (5)	0·1299 (1)	0·6765 (3)	4·46 (3)
C(5*A*)	0·0058 (5)	0·1381 (1)	0·7881 (3)	4·24 (2)
C(6*A*)	−0·1305 (5)	0·1136 (2)	0·8672 (3)	4·90 (3)
C(7*A*)	−0·1683 (4)	0·0481 (1)	0·8445 (2)	3·98 (2)
C(8*A*)	0·0266 (4)	0·0151 (1)	0·6557 (2)	3·76 (2)
C(9*A*)	−0·2625 (4)	0·0400 (1)	0·7326 (3)	3·72 (2)
C(10*A*)	0·2003 (4)	0·1052 (1)	0·7990 (2)	4·00 (2)
C(1*eA*)	0·2049 (4)	0·0515 (1)	0·5859 (2)	3·13 (2)
C(2*eA*)	0·3156 (4)	0·0654 (2)	0·5235 (2)	4·25 (2)
H(1*A*)	0·291 (3)	0·0198 (9)	0·781 (2)	1·9 (5)
H(3*A*)	0·822 (4)	0·0617 (12)	0·579 (2)	4·1 (6)
H(4*A*)	0·788 (4)	0·1451 (12)	0·668 (2)	4·9 (7)
H(4*A*′)	0·992 (4)	0·1465 (14)	0·627 (3)	6·1 (8)
H(5*A*)	0·047 (3)	0·1767 (12)	0·803 (2)	3·9 (6)
H(6*A*)	0·757 (4)	0·1310 (11)	0·858 (2)	4·5 (7)
H(6*A*′)	0·936 (4)	0·1196 (13)	0·951 (3)	5·7 (8)
H(7*A*)	0·736 (4)	0·0289 (14)	0·895 (3)	6·8 (9)
H(8*A*)	0·112 (4)	0·0246 (12)	0·935 (2)	4·8 (7)
H(8*A*′)	−0·001 (3)	0·0277 (10)	0·155 (2)	2·6 (5)
H(10*A*)	0·264 (4)	0·1090 (11)	0·874 (2)	4·1 (6)
H(10*A*′)	0·287 (4)	0·1218 (13)	0·750 (2)	6·0 (8)
H(9*A*)	0·607 (3)	0·0633 (12)	0·721 (2)	4·0 (6)
H(9*A*′)	0·703 (4)	0·9908 (12)	0·711 (2)	4·7 (7)
H(2*eA*)	0·409 (4)	0·0748 (15)	0·476 (3)	7·2 (9)
H(O*A*)	0·062 (4)	0·0345 (13)	0·414 (2)	6·2 (8)
Molecule *B*				
O(*B*)	0·5966 (3)	0·09489 (8)	0·3420 (2)	3·68 (1)
C(1*B*)	0·4288 (4)	0·1844 (1)	0·2942 (2)	3·69 (2)
C(2*B*)	0·6257 (4)	0·1511 (1)	0·2947 (2)	2·84 (2)
C(3*B*)	0·6778 (4)	0·1440 (1)	0·1795 (2)	3·08 (2)
C(4*B*)	0·5183 (5)	0·1098 (1)	0·1170 (2)	4·13 (2)
C(5*B*)	0·3229 (5)	0·1424 (1)	0·1181 (3)	4·63 (3)
C(6*B*)	0·3442 (5)	0·2029 (2)	0·0667 (3)	5·95 (3)
C(7*B*)	0·5040 (5)	0·2384 (1)	0·1293 (3)	4·72 (3)
C(8*B*)	0·4529 (4)	0·2454 (1)	0·2432 (3)	4·72 (3)
C(9*B*)	0·6980 (4)	0·2055 (1)	0·1295 (2)	4·13 (3)
C(10*B*)	0·2692 (4)	0·1500 (1)	0·2309 (3)	4·18 (3)
C(1*eB*)	0·7818 (4)	0·1827 (1)	0·3584 (2)	3·66 (2)
C(2*eB*)	0·9074 (5)	0·2061 (2)	0·4107 (3)	5·54 (3)
H(1*B*)	0·397 (4)	0·187 (1)	0·369 (2)	4·3 (6)
H(3*B*)	0·800 (3)	0·122 (1)	0·180 (2)	3·6 (6)
H(4*B*)	0·546 (4)	0·105 (1)	0·048 (3)	5·8 (8)
H(4*B*′)	0·500 (4)	0·074 (1)	0·148 (2)	4·7 (7)
H(5*B*)	0·232 (4)	0·123 (1)	0·076 (2)	5·5 (8)
H(6*B*)	0·214 (5)	0·222 (1)	0·072 (3)	8·2 (11)
H(6*B*′)	0·260 (9)	0·205 (2)	0·007 (6)	20·7 (23)
H(7*B*)	0·410 (5)	0·198 (2)	0·973 (4)	10·3 (12)
H(8*B*)	0·568 (3)	0·234 (1)	0·784 (2)	4·5 (7)
H(8*B*′)	0·333 (5)	0·235 (2)	0·741 (3)	7·6 (9)
H(10*B*)	0·257 (4)	0·111 (1)	0·259 (3)	6·6 (9)
H(10*B*′)	0·143 (4)	0·170 (1)	0·232 (2)	4·2 (6)
H(9*B*)	0·799 (4)	0·231 (1)	0·173 (2)	4·8 (7)
H(9*B*′)	0·731 (4)	0·208 (1)	0·060 (3)	5·8 (8)
H(2*eB*)	0·001 (5)	0·222 (2)	0·459 (3)	8·1 (10)
H(O*B*)	0·728 (5)	0·090 (1)	0·359 (3)	7·5 (10)

Discussion. A schematic drawing of the molecule with the numbering system is illustrated in Fig. 1. The bond distances and angles are tabulated in Tables 2 and 3, respectively. It is quite clear from these tables that the two molecules in the asymmetric unit exhibit similar bond distances and angles which are in normal ranges. There is an approximate mirror plane through the adamantane skeleton and, as expected, the ethynyl group and the hydroxyl O lie in this plane with the latter showing a slightly large deviation from the plane. The planarity data are tabulated in Table 4.

The molecules are connected in the structure by weak O(*B*)—H···O(*A*) hydrogen bonds of 2·839 Å (O—H···O of 144°). The hydroxyl portion of the molecule *A* is involved in an intramolecular O—H···π hydrogen bond with the ethynyl group. The distances between this proton and C(1*e*) and C(2*e*) are 2·35 and 2·25 Å, respectively, and the two O—H···C angles are about 161°. The hydrogen bond observed here may be compared with the results of the recent structure of 2,6-diphenylphenol where H···C distances of 2·40 and 2·43 Å are observed (Nakatsu, Yoshioka, Kunimoto, Kinugasa & Ueji, 1978). The observed large differences in the C—O distances (8σ) in the two molecules may be

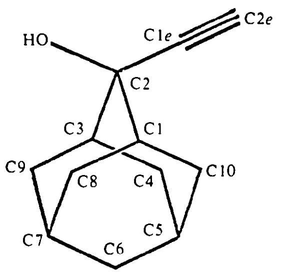

Fig. 1. The numbering of atoms used in the *Discussion*.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36640 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond distances in* Å

	Molecule *A*	Molecule *B*
C(1)–C(2)	1·528 (3)	1·539 (2)
C(1)–C(8)	1·536 (3)	1·540 (3)
C(1)–C(10)	1·532 (3)	1·517 (3)
C(2)–C(3)	1·541 (2)	1·541 (3)
C(2)–C(1*e*)	1·468 (2)	1·472 (3)
C(2)–O	1·452 (2)	1·428 (2)
C(3)–C(4)	1·521 (3)	1·510 (3)
C(3)–C(9)	1·527 (3)	1·541 (3)
C(4)–C(5)	1·519 (3)	1·525 (3)
C(5)–C(6)	1·526 (3)	1·528 (3)
C(5)–C(10)	1·519 (3)	1·516 (3)
C(6)–C(7)	1·529 (3)	1·528 (3)
C(7)–C(8)	1·522 (3)	1·523 (4)
C(7)–C(9)	1·525 (3)	1·518 (3)
C(1*e*)–C(2*e*)	1·180 (3)	1·170 (3)

Table 3. *Bond angles in degrees*

	Molecule *A*	Molecule *B*
C(2)–C(1)–C(8)	109·6 (1)	108·6 (2)
C(2)–C(1)–C(10)	109·5 (2)	109·9 (2)
C(8)–C(1)–C(10)	108·8 (2)	109·5 (2)
C(1)–C(2)–C(3)	108·8 (1)	108·2 (2)
C(1)–C(2)–C(1*e*)	111·3 (1)	111·0 (2)
C(1)–C(2)–O	106·1 (1)	106·7 (1)
C(3)–C(2)–C(1*e*)	112·0 (2)	111·3 (2)
C(3)–C(2)–O	111·2 (1)	111·0 (2)
C(1*e*)–C(2)–O	107·3 (1)	108·7 (2)
C(2)–C(3)–C(4)	108·6 (2)	110·0 (2)
C(2)–C(3)–C(9)	109·8 (2)	109·4 (2)
C(4)–C(3)–C(9)	109·7 (2)	109·4 (2)
C(3)–C(4)–C(5)	110·5 (2)	109·9 (2)
C(4)–C(5)–C(6)	109·8 (2)	108·5 (2)
C(4)–C(5)–C(10)	108·8 (2)	109·8 (2)
C(6)–C(5)–C(10)	109·5 (2)	110·0 (2)
C(5)–C(6)–C(7)	109·3 (2)	109·7 (2)
C(6)–C(7)–C(8)	109·0 (2)	110·0 (2)
C(6)–C(7)–C(9)	110·2 (2)	109·2 (2)
C(8)–C(7)–C(9)	109·2 (2)	108·3 (2)
C(1)–C(8)–C(7)	110·0 (2)	110·3 (2)
C(3)–C(9)–C(7)	109·5 (2)	109·8 (2)
C(1)–C(10)–C(5)	109·8 (2)	110·0 (2)
C(2)–C(1*e*)–C(2*e*)	177·4 (2)	177·9 (2)

Table 4. *Deviations* (Å) *of atoms from the adamantane mirror plane* C(2)–C(5)–C(6)–C(7)

Mean e.s.d.'s are about 0·005 Å.

Molecule *A*

C(2)	C(5)	C(6)	C(7)
–0·002	0·004	–0·005	0·004
O*	C(1*e*)*	C(2*e*)*	
–0·084	–0·006	–0·043	

Molecule *B*

C(2)	C(5)	C(6)	C(7)
0·002	–0·005	0·007	–0·004
O*	C(1*e*)*	C(2*e*)*	
–0·050	–0·003	–0·003	

* Atoms not included in the evaluation of the planes.

attributed to the difference in hydrogen-bond formations. No unusually short intermolecular distance is observed.

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