MICHAELIS, A. & VON SODEN, H. (1885). *Justus Liebigs Ann. Chem.* **229**, 295–334.
MOTHERWELL, S. & CLEGG, W. (1978). *PLUTO.* Univ. of Cambridge, England.
PEDERSEN, B. F. (1969). *Acta Chem. Scand.* **23**, 342.
PEDERSEN, B. F. (1972*a*). *Acta Cryst.* B**28**, 746–754.
PEDERSEN, B. F. (1972*b*). *Acta Cryst.* B**28**, 1014–1016.
PEDERSEN, B. F. & PEDERSEN, B. (1964). *Acta Chem. Scand.* **18**, 1454–1468.
PENNEY, W. G. & SUTHERLAND, G. B. B. M. (1934). *J. Chem. Phys.* **2**, 492–498.
RUDOLPH, H. & REINKING, K. (1967). German Patent 1268619 (13.1.1967/22.5.1968).
SHELDRICK, G. M. (1976). *SHELX.* Program for crystal structure determination. Univ. of Cambridge, England.
SPEAKMAN, J. C. (1967). *Chem. Commun.* pp. 32–33.
TEMPLE, R. D., TSUNO, Y. & LEFFLER, J. E. (1963). *J. Org. Chem.* **28**, 2495.
THIERBACH, D. & HUBER, F. (1979*a*). *Z. Anorg. Allg. Chem.* **451**, 137–142.
THIERBACH, D. & HUBER, F. (1979*b*). *Z. Anorg. Allg. Chem.* **457**, 189–196.

Acta Cryst. (1980). B**36**, 977–979

The Structures of (*E*)- and (*Z*)-2-Chloro-2-ethynyl-5-phenyladamantane*

BY Y. OKAYA, S. Y. LIN, D. M. CHIOU AND W. J. LE NOBLE

Chemistry Department, State University of New York, Stony Brook, NY 11794, *USA*

(*Received* 17 *April* 1979; *accepted* 4 *September* 1979)

Abstract. $C_{18}H_{19}Cl$, *E* isomer: monoclinic, $P2_1/c$, a = 15·308 (2), b = 7·229 (2), c = 14·305 (3) Å, β = 113·5 (3)°, V = 1452 Å^3, Z = 4 (ρ_{obs} = 1·25 Mg m^{-3}). R = 0·038 for 1900 (>3σ) reflections. *Z* isomer: orthorhombic, $P2_12_12_1$, a = 6·773 (1), b = 10·043 (2), c = 21·130 (4) Å, V = 1437 Å^3, Z = 4 (ρ_{obs} = 1·26 Mg m^{-3}). R = 0·050 for 2439 (>3σ) reflections. All the data were measured using Cu $K\alpha$ radiation on a diffractometer. The Cl atom is in the *anti* configuration with respect to the phenyl group in the *E* isomer; for the *Z* isomer the relationship is *syn*. The results confirm the retention of configuration in a stereospecific return reaction during methanolysis, to give (*E*)- and (*Z*)-2-chlorovinylidene-5-phenyladamantane.

Introduction. This report is part of our systematic configurational study of bridge-head phenyl-substituted adamantanes. The present compounds, (*E*)- and (*Z*)-2-ethynyl-2-chloro-5-phenyladamantane, are converted stereospecifically into (*E*)- and (*Z*)-2-chlorovinylidene-5-phenyladamantane, $Cl{-}CH{=}C{=}C_{10}H_{13}.C_6H_5$, respectively, by neutral solvolysis in CH_3OH (le Noble, Chiou & Okaya, 1979). Since the stereochemistry of the chlorovinylidene compound was established by a crystallographic study of its *E* isomer (Okaya, Małuszyńska, Chiou & le Noble, 1978), it seemed worthwhile to determine unambiguously the molecular structures of the *E* and *Z* chloro compounds by the X-ray method. The diffraction data of both compounds were obtained on an Enraf–Nonius CAD-4 diffractometer controlled by a PDP-8 computer which was in turn under the supervision of a PDP-11/45 computer in a resource-sharing mode (Okaya, 1978). Cu $K\alpha$ was used and the data were collected up to 50° (in *E*) and 65° (in *Z*) with the θ–2θ scan method. The structures were solved by using sharpened Patterson functions, and refined by a full-matrix least-squares program using the Enraf–Nonius structure determination package on the PDP-11/45 computer. The function minimized in the refinements was $\sum w(|F_o| - |F_c|)^2$ with $w^{-1} = \sigma c F_o^2 + (pF_o^2)^2$, where σc is the deviation based on counting statistics and p, the adjustment factor, was 0·03 and 0·04 for the *E* and *Z* data, respectively. All H atoms were located in difference Fourier maps and refined with isotropic temperature factors. The final R factors $[= \sum(|F_o| - |F_c|)/\sum|F_o|]$ are 0·038 and 0·050 for the *E* and *Z* structures, respectively. The atomic scattering factors used are derived from data of Cromer & Waber (1974). Because of the relatively small absorption of the specimen, no absorption correction was applied to the diffraction data. The positional parameters of all the atoms are given in Table 1.†

Discussion. The present study has unambiguously assigned the *E* (m.p. = 366 K, acetylenic proton NMR shift = 7·32 τ) and *Z* (m.p. = 364 K, NMR shift 7·30

---

* Crystallographic Studies on Adamantanes. III.

† Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34739 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0567-7408/80/040977-03$01.00

Table 1. *Atomic parameters and e.s.d.'s*

	x	*y*	*z*		*x*	*y*	*z*
(*a*) The *E* isomer				(*b*) The *Z* isomer			
Cl	0·57340 (3)	0·10773 (8)	0·43704 (4)	Cl	0·6382 (2)	0·4976 (1)	−0·03093 (5)
C(1)	0·7528 (1)	0·2330 (3)	0·4539 (1)	C(1)	0·3428 (7)	0·3744 (4)	0·0380 (2)
C(2)	0·6452 (1)	0·2870 (3)	0·4066 (1)	C(2)	0·3892 (6)	0·5052 (4)	0·0036 (2)
C(3)	0·6119 (1)	0·3007 (3)	0·2900 (1)	C(3)	0·3822 (7)	0·6189 (4)	0·0516 (2)
C(4)	0·6703 (1)	0·4554 (3)	0·2678 (1)	C(4)	0·5280 (7)	0·5945 (4)	0·1058 (2)
C(5)	0·7797 (1)	0·4123 (2)	0·3149 (1)	C(5)	0·4816 (6)	0·4632 (4)	0·1402 (2)
C(6)	0·7968 (1)	0·2259 (3)	0·2723 (1)	C(6)	0·2697 (7)	0·4707 (4)	0·1656 (2)
C(7)	0·7389 (1)	0·0712 (3)	0·2949 (1)	C(7)	0·1232 (7)	0·4968 (5)	0·1123 (2)
C(8)	0·7702 (1)	0·0513 (3)	0·4094 (1)	C(8)	0·1341 (7)	0·3841 (5)	0·0656 (2)
C(9)	0·6311 (1)	0·1180 (3)	0·2464 (1)	C(9)	0·1718 (8)	0·6263 (4)	0·0793 (2)
C(10)	0·8103 (1)	0·3884 (3)	0·4306 (1)	C(10)	0·4875 (7)	0·3508 (4)	0·0919 (2)
C(1*p*)	0·8367 (1)	0·5647 (2)	0·2896 (1)	C(1*p*)	0·6251 (7)	0·4431 (4)	0·1956 (2)
C(2*p*)	0·8162 (1)	0·6074 (3)	0·1883 (1)	C(2*p*)	0·7364 (7)	0·3280 (4)	0·2027 (2)
C(3*p*)	0·8681 (1)	0·7407 (3)	0·1622 (1)	C(3*p*)	0·8647 (8)	0·3152 (5)	0·2540 (2)
C(4*p*)	0·9414 (1)	0·8369 (3)	0·2366 (2)	C(4*p*)	0·8857 (8)	0·4146 (5)	0·2975 (2)
C(5*p*)	0·9624 (1)	0·7984 (3)	0·3367 (2)	C(5*p*)	0·7774 (8)	0·5266 (5)	0·2916 (2)
C(6*p*)	0·9110 (1)	0·6642 (3)	0·3633 (1)	C(6*p*)	0·6476 (8)	0·5414 (4)	0·2411 (2)
C(1*E*)	0·6257 (1)	0·4564 (3)	0·4512 (1)	C(1*E*)	0·2568 (8)	0·5259 (5)	−0·0503 (2)
C(2*E*)	0·6095 (2)	0·5905 (3)	0·4872 (2)	C(2*E*)	0·1491 (10)	0·5412 (5)	−0·0936 (2)
H(1)	0·773 (1)	0·224 (3)	0·526 (1)	H(1)	0·342 (5)	0·298 (3)	0·010 (1)
H(3)	0·543 (1)	0·331 (3)	0·259 (1)	H(3)	0·418 (5)	0·697 (3)	0·029 (1)
H(4)	0·648 (1)	0·469 (3)	0·193 (1)	H(4)	0·543 (7)	0·673 (4)	0·134 (2)
H(4′)	0·657 (1)	0·573 (3)	0·294 (1)	H(4′)	0·671 (5)	0·593 (3)	0·088 (1)
H(6)	0·775 (1)	0·234 (3)	0·200 (1)	H(6)	0·240 (5)	0·385 (3)	0·190 (1)
H(6′)	0·869 (1)	0·195 (3)	0·304 (1)	H(6′)	0·266 (5)	0·529 (3)	0·195 (2)
H(7)	0·750 (1)	−0·049 (3)	0·266 (1)	H(7)	0·011 (7)	0·504 (4)	0·134 (2)
H(8)	0·840 (1)	0·026 (3)	0·443 (1)	H(8)	0·137 (6)	0·297 (3)	0·086 (2)
H(8′)	0·735 (1)	−0·047 (3)	0·424 (1)	H(8′)	0·045 (8)	0·397 (5)	0·036 (2)
H(9)	0·594 (1)	0·024 (3)	0·259 (1)	H(9)	0·057 (9)	0·644 (6)	0·052 (3)
H(9′)	0·606 (1)	0·136 (3)	0·172 (2)	H(9′)	0·155 (8)	0·703 (4)	0·113 (2)
H(10)	0·799 (1)	0·506 (3)	0·462 (1)	H(10)	0·447 (6)	0·266 (4)	0·113 (2)
H(10′)	0·878 (1)	0·353 (2)	0·464 (1)	H(10′)	0·596 (5)	0·346 (3)	0·078 (1)
H(2*E*)	0·598 (2)	0·696 (4)	0·516 (2)	H(2*E*)	0·025 (9)	0·551 (5)	−0·125 (2)
H(2*p*)	0·764 (1)	0·543 (3)	0·134 (1)	H(2*p*)	0·711 (6)	0·259 (3)	0·174 (2)
H(3*p*)	0·853 (1)	0·767 (3)	0·095 (2)	H(3*p*)	0·921 (7)	0·239 (3)	0·256 (2)
H(4*p*)	0·973 (2)	0·924 (3)	0·221 (2)	H(4*p*)	0·956 (10)	0·385 (6)	0·330 (3)
H(5*p*)	1·014 (2)	0·871 (3)	0·390 (2)	H(5*p*)	0·774 (8)	0·620 (5)	0·325 (2)
H(6*p*)	0·928 (1)	0·643 (3)	0·430 (1)	H(6*p*)	0·579 (9)	0·621 (5)	0·239 (2)

Table 2. *Bond distances* (Å)

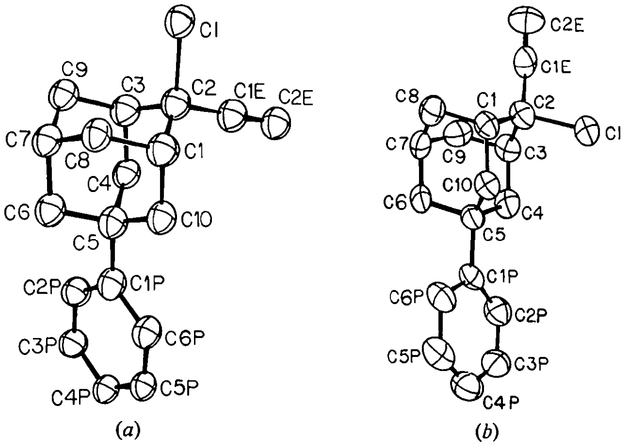
	E isomer	*Z* isomer		*E* isomer	*Z* isomer		*E* isomer	*Z* isomer
C(1)–C(2)	1·560 (2)	1·534 (5)	C(4)–C(5)	1·567 (2)	1·538 (5)	C(1*E*)–C(2*E*)	1·170 (2)	1·181 (7)
C(1)–C(8)	1·529 (2)	1·532 (6)	C(5)–C(6)	1·544 (2)	1·534 (5)	C(1*p*)–C(2*p*)	1·390 (2)	1·387 (6)
C(1)–C(10)	1·543 (2)	1·521 (6)	C(5)–C(10)	1·540 (2)	1·524 (5)	C(1*p*)–C(6*p*)	1·402 (2)	1·386 (6)
C(2)–C(3)	1·540 (2)	1·528 (5)	C(5)–C(1*p*)	1·536 (2)	1·535 (5)	C(2*p*)–C(3*p*)	1·391 (2)	1·395 (6)
C(2)–C(2*E*)	1·465 (2)	1·464 (5)	C(6)–C(7)	1·539 (2)	1·523 (6)	C(3*p*)–C(4*p*)	1·387 (2)	1·365 (6)
C(2)–Cl	1·860 (2)	1·839 (6)	C(7)–C(8)	1·519 (2)	1·504 (6)	C(4*p*)–C(5*p*)	1·365 (2)	1·349 (7)
C(3)–C(4)	1·542 (2)	1·532 (6)	C(7)–C(9)	1·551 (2)	1·512 (6)	C(5*p*)–C(6*p*)	1·394 (2)	1·391 (6)
C(3)–C(9)	1·538 (2)	1·542 (6)						

z) isomers and confirmed the retention of configuration of return during the solvolysis reaction discussed in the *Introduction*. As is evident from a small difference in the chemical shifts of the two isomers, it was impossible to make definite configurational assignments solely on this basis.

ORTEP (Johnson, 1965) drawings of the molecule with the numbering systems used are shown in Fig. 1. The bond distances and angles are tabulated in Tables 2 and 3 and aside from the difference in configuration, both isomers exhibit almost identical shapes and sizes. C(2*p*)–C(1*p*)–C(6*p*) angles (116·6° for *E*; 117·3° for *Z*) are smaller than the normal 120°, suggesting the effects of intramolecular non-bonded interactions between the phenyl groups and nearby aliphatic H atoms on the shape of the aromatic rings (Domenicano,

Table 3. *Bond angles* (°)

	E isomer	*Z* isomer		*E* isomer	*Z* isomer		*E* isomer	*Z* isomer
C(2)–C(1)–C(8)	111·3 (3)	108·4 (3)	C(3)–C(4)–C(5)	112·0 (3)	111·1 (1)	C(3)–C(9)–C(7)	110·3 (3)	109·6 (3)
C(2)–C(1)–C(10)	108·6 (3)	110·9 (3)	C(4)–C(5)–C(6)	108·9 (3)	108·3 (3)	C(1)–C(10)–C(5)	111·0 (3)	111·7 (3)
C(8)–C(1)–C(10)	109·1 (3)	108·6 (3)	C(4)–C(5)–C(10)	107·4 (3)	108·2 (3)	C(2)–C(1*E*)–C(2*E*)	179·3 (4)	179·3 (4)
C(1)–C(2)–C(3)	108·8 (3)	108·7 (3)	C(4)–C(5)–C(1*p*)	111·5 (4)	110·2 (3)	C(5)–C(1*p*)–C(2*p*)	119·5 (3)	122·4 (3)
C(1)–C(2)–C(1*E*)	112·5 (3)	111·3 (3)	C(6)–C(5)–C(10)	107·4 (3)	107·1 (3)	C(5)–C(1*p*)–C(6*p*)	123·9 (4)	120·3 (3)
C(1)–C(2)–Cl	110·1 (3)	110·0 (3)	C(6)–C(5)–C(1*p*)	109·4 (4)	109·4 (3)	C(2*p*)–C(1*p*)–C(6*p*)	116·6 (4)	117·3 (4)
C(3)–C(2)–C(1*E*)	112·5 (3)	113·0 (3)	C(10)–C(5)–C(1*p*)	112·1 (4)	113·4 (3)	C(1*p*)–C(2*p*)–C(3*p*)	121·2 (4)	119·9 (4)
C(3)–C(2)–Cl	109·0 (3)	108·9 (3)	C(5)–C(6)–C(7)	110·4 (3)	111·1 (3)	C(2*p*)–C(3*p*)–C(4*p*)	121·0 (5)	121·4 (4)
C(1*E*)–C(2)–Cl	103·8 (3)	105·0 (3)	C(6)–C(7)–C(8)	109·6 (3)	108·9 (3)	C(3*p*)–C(4*p*)–C(5*p*)	118·9 (5)	119·4 (4)
C(2)–C(3)–C(4)	107·5 (3)	110·7 (3)	C(6)–C(7)–C(9)	110·3 (3)	110·4 (4)	C(4*p*)–C(5*p*)–C(6*p*)	120·4 (5)	120·2 (4)
C(2)–C(3)–C(9)	110·5 (3)	108·4 (3)	C(8)–C(7)–C(9)	109·0 (3)	109·4 (3)	C(5*p*)–C(6*p*)–C(1*p*)	121·9 (5)	121·7 (4)
C(4)–C(3)–C(9)	108·6 (3)	108·7 (3)	C(1)–C(8)–C(7)	109·6 (3)	110·1 (3)			



(*a*) (*b*)

Fig. 1. *ORTEP* drawings, (*a*) *E* isomer, (*b*) *Z* isomer.

Vaciago & Coulson, 1975). The bond distances and angles involving the H atoms are also 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)–C(7). The angles between the approximate plane and the phenyl group are 62·5° (*E*) and 65·5° (*Z*).

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

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

	C(al.)–H	C(ar.)–H	*sp*^{3} angles	*sp*^{2} angles
E	0·95	0·92	109·3	119·6
Z	0·98	0·95	109·2	119·5

One of the authors (WJleN) acknowledges support by the National Science Foundation (Grant No. NSF-CHE-7512847).

References

Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.2B. Birmingham: Kynoch Press.

Domenicano, A., Vaciago, A. & Coulson, C. A. (1975). *Acta Cryst.* **B31**, 221–234.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

Noble, W. J. le, Chiou, D. M. & Okaya, Y. (1979). *Tetrahedron Lett.* p. 1961.

Okaya, Y. (1978). *Computing in Crystallography*, edited by H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld & G. C. Bassi, pp. 153–166. Delft Univ. Press.

Okaya, Y., Małuszyńska, H., Chiou, D. M. & le Noble, W. J. (1978). *Acta Cryst.* **B34**, 3434–3436.