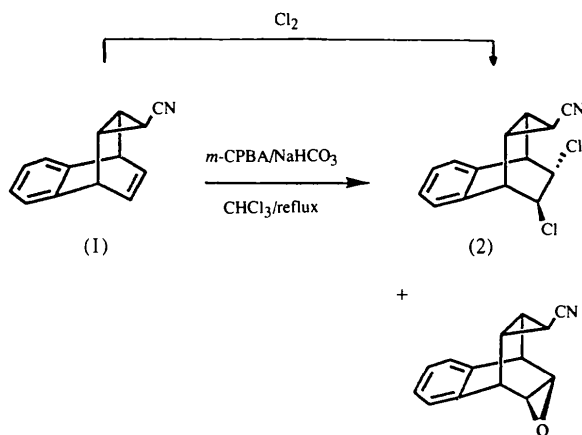Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1193). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Fan, H. F. (1991). *SAPI91. Structure Analysis Programs with Intelligent Control*. Rigaku Corporation, Tokyo, Japan.

Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Molecular Structure Corporation (1992). *TEXSAN. Crystal Structure Analysis Package*. MSC, 3200, Research Forest Drive, The Woodlands, TX 77381, USA.

Ueno, K. (1985). *Acta Cryst.* C41, 1786–1789.

Unusual Chlorination During an Epoxidation Reaction of an Etheno-cyclopropa[b]naphthalene Derivative

Dinçer Ülkü and M. Nawaz Tahir

Department of Engineering Physics, Hacettepe University, 06532 Beytepe, Ankara, Turkey

Abdullah Menzek and Metin Balci

Department of Chemistry, Atatürk University, 24240 Erzurum, Turkey

(*Received* 1 *May* 1995; *accepted* 10 *July* 1995)

Abstract

The structure of (1α,1aα,2β,7aα,8R,9R)-8,9-dichloro-1a,2,7,7a-tetrahydro-2,7-ethano-1H-cyclopropa[b]naphthalene-1-carbonitrile, $C_{14}H_{11}Cl_2N$, consists of two non-planar six-membered carbon rings (constituting a [2.2.2] bicyclic system), one of which shares two C atoms with a benzene ring and has two Cl substituents; the other is fused to a cyclopropane ring carrying a C≡N substituent. The two Cl atoms of the —C—C(Cl)—C(Cl)—C— bridging system have an *anti* arrangement with respect to the plane of the four C atoms.

Comment

In connection with our recently developed high-temperature bromination reactions (Dastan & Balcı, 1994; Dastan, Balcı, Hökelek, Ülkü & Büyükgüngör, 1994), a solution of the *exo*-cyano compound 1a,2,7,7a-

tetrahydro-2,7-etheno-1H-cyclopropa[b]napthalene-1-carbonitrile, (1), in $CHCl_3$ was reacted with *m*-chloro-perbenzoic acid (*m*-CPBA) in order to find out whether electrophiles can attack the double bond from the *endo* face or the *exo* face. Compound (2) was obtained as the major product.

During this reaction we expected only the formation of an epoxide. The formation of a chlorinated compound is unusual. We believe that *m*-chloroperbenzoic acid (as an oxidative reagent) forms chlorine upon oxidation of the chloroform used as solvent, which adds to the double bond. The mechanism of formation of this product is currently under investigation. The same compound was also synthesized by an independent route involving direct chlorination (yield 55%).

The least-squares plane through C1, C2, C3, C4, C5, C6, C11 and C12 indicates that C11 and C12 lie practically in the plane of the benzene ring (Fig. 1), being displaced by 0.032 (7) and −0.008 (8) Å, respectively, from the plane of the benzene ring. The C11—C13 [1.799 (9) Å] and C12—C14 [1.795 (8) Å] bond lengths are not significantly different. The C11—C13—
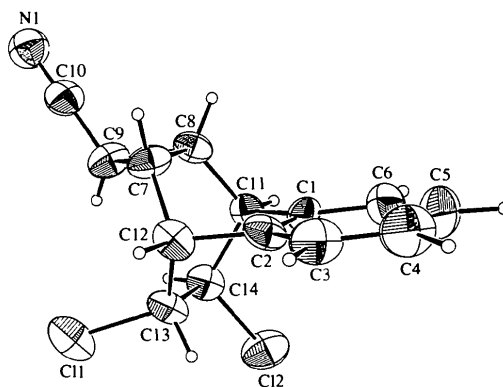

Fig. 1. *ORTEPII* (Johnson, 1976) drawing of $C_{14}H_{11}Cl_2N$ with the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level.

C14 and Cl2—C14—C13 bond angles are 110.7 (6) and 109.7 (5)°, respectively. This results in a symmetrical *anti* arrangement of the Cl atoms with respect to the plane of C11, C12, C13 and C14.

Experimental

To a solution of the *exo*-cyano compound (1) in $CHCl_3$, $NaHCO_3$ and *m*-chloroperbenzoic acid (*m*-CPBA) were added. The resulting mixture was refluxed for 4 h and the resulting precipitate removed by filtration. Colourless crystals of the dichloro compound (2) were isolated. (See *Comment.*)

Crystal data

$C_{14}H_{11}Cl_2N$	Mo $K\alpha$ radiation
$M_r = 264.156$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 16
$C2/c$	reflections
$a = 30.403$ (1) Å	$\theta = 8.25–18.17°$
$b = 8.130$ (1) Å	$\mu = 0.47$ mm^{-1}
$c = 10.354$ (2) Å	$T = 295$ K
$\beta = 101.889$ (1)°	Plate
$V = 2504.2$ (7) Å^3	$0.35 \times 0.25 \times 0.15$ mm
$Z = 8$	Colourless
$D_x = 1.401$ Mg m^{-3}	

Data collection

Enraf–Nonius CAD-4	$R_{int} = 0.029$
diffractometer	$\theta_{max} = 22.79°$
$\omega/2\theta$ scans	$h = -32 \rightarrow 32$
Absorption correction:	$k = -8 \rightarrow 0$
ψ scan (*MolEN*; Fair,	$l = 0 \rightarrow 11$
1990)	3 standard reflections
$T_{min} = 0.85$, $T_{max} = 0.99$	frequency: 120 min
1805 measured reflections	intensity decay: 2.14%
1577 independent reflections	(corrected)
753 observed reflections	
[$I \geq 2\sigma(I)$]	

Refinement

Refinement on F	$(\Delta/\sigma)_{max} = 0.0004$
$R = 0.056$	$\Delta\rho_{max} = 0.164$ e Å^{-3}
$wR = 0.050$	$\Delta\rho_{min} = -0.163$ e Å^{-3}
$S = 1.35$	Extinction correction: none
691 reflections	Atomic scattering factors
187 parameters	from *International Tables*
Only coordinates of H atoms	*for X-ray Crystallography*
refined	(1974, Vol. IV)
$w = 1/\sigma^2(F)$	

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Cl1	0.92496 (9)	0.2206 (3)	0.6539 (2)	5.15 (6)
Cl2	0.81779 (8)	0.0526 (3)	0.7528 (3)	4.94 (6)
N1	1.0378 (2)	0.1942 (9)	1.1310 (7)	4.5 (2)
C1	0.8433 (2)	0.3357 (9)	0.9674 (7)	2.8 (2)
C2	0.8590 (3)	0.4634 (10)	0.8973 (8)	3.3 (2)
C3	0.8353 (3)	0.6109 (11)	0.8839 (9)	4.4 (3)
C4	0.7980 (3)	0.6297 (12)	0.9373 (9)	5.1 (3)
C5	0.7834 (3)	0.5031 (12)	1.0040 (12)	5.4 (3)
C6	0.8059 (3)	0.3559 (12)	1.0196 (8)	4.1 (2)
C7	0.9354 (3)	0.3738 (10)	0.9659 (8)	3.1 (2)
C8	0.9197 (3)	0.2345 (9)	1.0387 (7)	2.9 (2)
C9	0.9599 (3)	0.2116 (10)	0.9753 (8)	3.5 (2)
C10	1.0031 (3)	0.2002 (10)	1.0626 (8)	3.5 (2)
C11	0.8723 (2)	0.1816 (10)	0.9698 (7)	2.9 (2)
C12	0.9007 (3)	0.4204 (10)	0.8468 (7)	3.0 (2)
C13	0.8849 (3)	0.2780 (10)	0.7517 (7)	3.4 (2)
C14	0.8725 (3)	0.1275 (10)	0.8298 (8)	3.2 (2)

Table 2. *Selected geometric parameters* (Å, °)

Cl1—C13	1.799 (9)	C5—C6	1.37 (1)
Cl2—C14	1.795 (8)	C7—C8	1.49 (1)
N1—C10	1.14 (1)	C7—C9	1.51 (1)
C1—C2	1.41 (1)	C7—C12	1.50 (1)
C1—C6	1.37 (1)	C8—C9	1.51 (1)
C1—C11	1.53 (1)	C8—C11	1.53 (1)
C2—C3	1.39 (1)	C9—C10	1.44 (1)
C2—C12	1.51 (1)	C11—C14	1.52 (1)
C3—C4	1.37 (1)	C12—C13	1.53 (1)
C4—C5	1.36 (1)	C13—C14	1.56 (1)
C2—C1—C6	120.9 (8)	C7—C9—C8	59.2 (5)
C2—C1—C11	111.0 (7)	C7—C9—C10	118.2 (7)
C6—C1—C11	128.0 (8)	C8—C9—C10	116.8 (7)
C1—C2—C3	117.7 (8)	N1—C10—C9	178.5 (9)
C1—C2—C12	113.9 (7)	C1—C11—C8	105.2 (6)
C3—C2—C12	128.4 (8)	C1—C11—C14	109.8 (6)
C2—C3—C4	120.8 (9)	C8—C11—C14	109.7 (6)
C3—C4—C5	120.2 (9)	C2—C12—C7	105.8 (6)
C4—C5—C6	120.8 (9)	C2—C12—C13	102.8 (6)
C1—C6—C5	119.6 (9)	C7—C12—C13	114.5 (7)
C8—C7—C9	60.6 (6)	C11—C13—C12	113.4 (6)
C8—C7—C12	111.3 (6)	C11—C13—C14	110.7 (6)
C9—C7—C12	121.9 (7)	C12—C13—C14	109.8 (6)
C7—C8—C9	60.2 (6)	C12—C14—C11	109.7 (6)
C7—C8—C11	110.2 (6)	C12—C14—C13	109.7 (5)
C9—C8—C11	122.0 (6)	C11—C14—C13	108.5 (7)
Cl1—C13—C14—Cl2	−104.2 (5)	Cl1—C13—C14—C11	135.9 (6)
Cl1—C13—C12—C7	−75.4 (8)	Cl1—C13—C12—C2	170.3 (5)
Cl2—C14—C13—C12	129.9 (6)	Cl2—C14—C11—C1	−68.8 (7)
Cl2—C14—C11—C8	176.1 (6)		

Data collection: *CAD-4 Express* (Enraf–Nonius, 1993). Cell refinement: *CAD-4 Express*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *MolEN SIR*. Program(s) used to refine structure: *MolEN LSFM*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *MolEN*.

References

Dastan, A. & Balci, M. (1994). *J. Org. Chem.* **59**, 6534–6538.
Dastan, A., Balci, M., Hökelek, T., Ülkü, D. & Büyükgüngör, O. (1994). *Tetrahedron*, **50**, 10555–10578.
Enraf–Nonius (1993). *CAD-4 Express*. Version 1.1. Enraf–Nonius, Delft, The Netherlands.
Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis.* Enraf–Nonius, Delft, The Netherlands.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.