

## Single-crystal structure analysis of a novel aryl phosphinate diglycidyl ether

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### Abstract

The crystal structure of 10-[2,5-bis(2,3-epoxy-1-propoxy)phenyl]-9-oxa-10-phosphaphenanthren-10-one has been studied by single-crystal X-ray diffraction. The unit cell of  $C_{24}H_{21}O_6P$ ,  $M_r = 436.4$ , is triclinic,  $P\bar{1}$ , with  $a = 8.507(3)$ ,  $b = 10.613(4)$ ,  $c = 12.457(3)$  Å,  $\alpha = 80.05(3)$ ,  $\beta = 71.38(2)$ ,  $\gamma = 76.69(3)^\circ$ ,  $V = 1031.1(6)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.406$  Mg m<sup>-3</sup> and  $\mu(\text{Mo } K\alpha) = 0.17$  mm<sup>-1</sup>. The final  $R(wR)$  is 0.063 (0.057)  $\{w = 1/[\sigma^2(F) + 0.0004F^2]\}$  for 3619 unique reflections measured at 295 K. The aryl phosphinate group bonded to the central phenyl ring comes close to one of the two glycidyl ether groups, the epoxide ring of which is ordered. The epoxide ring far from the aryl phosphinate group is disordered. The NMR chemical shifts of the protons of the glycidyl ether group close to the aryl phosphinate group are reduced by the 'ring-current effect'.

### 1. Introduction

Despite their comparatively high cost, epoxy resins have achieved significant importance as industrial materials with applications as surface coatings, adhesives, tooling compounds, matrices in composites and in the encapsulation of electronic components (Lee & Neville, 1972; Lubin, 1982). Epoxy resins can be cured with amines or anhydrides and the cross linking of epoxy resins may be carried out either through the epoxy groups or the hydroxyl groups. Although epoxy resins have many attractive properties, such as low shrinkage on curing, good alkali resistance, and weather resistance, the flammability of epoxy resins is a disadvantage in applications requiring high flame resistance. Thus, modifying the structures of epoxy resins to improve their flame resistance has recently received increasing attention. Introduction of certain phosphorus groups, such as phosphate (Flury *et al.*, 1996), phosphonate (Liu *et al.*, 1996), phosphinate (Welch & Paxton, 1968; Vogt *et al.*, 1968), cyclic phosphine oxide (Shau & Wang, 1996), phosphine oxide and thioxophosphine oxide (Gentzkow *et al.*, 1991), into the backbone of epoxy resins to enhance the flame resistance has been reported. However, reports of the modification of the structures of epoxy resins by introducing phosphorus groups as

pendent groups to improve the flame resistance are scarce.

Recently, a novel aryl phosphinate diglycidyl ether, 10-[2,5-bis(2,3-epoxy-1-propoxy)phenyl]-9-oxa-10-phosphaphenanthren-10-one (DHQEP; Fig. 1), was synthesized in which a cyclic organophosphorus compound was incorporated into the molecular structure of the epoxy ether and grafted onto the main chain. This aryl phosphinate epoxy ether is expected to be highly effective in increasing the flame resistance of the corresponding epoxy resin. During the determination of the structure of DHQEP by <sup>1</sup>H- and <sup>13</sup>C-NMR, it was found that the chemical shifts of the protons of the glycidyl ether group at one end of DHQEP were similar to those observed in the glycidyl ether group of the diglycidyl ether of bisphenol A (DGEBA, Fig. 1). However, the chemical shifts of the protons of the glycidyl ether group at the other end of DHQEP were quite different from those

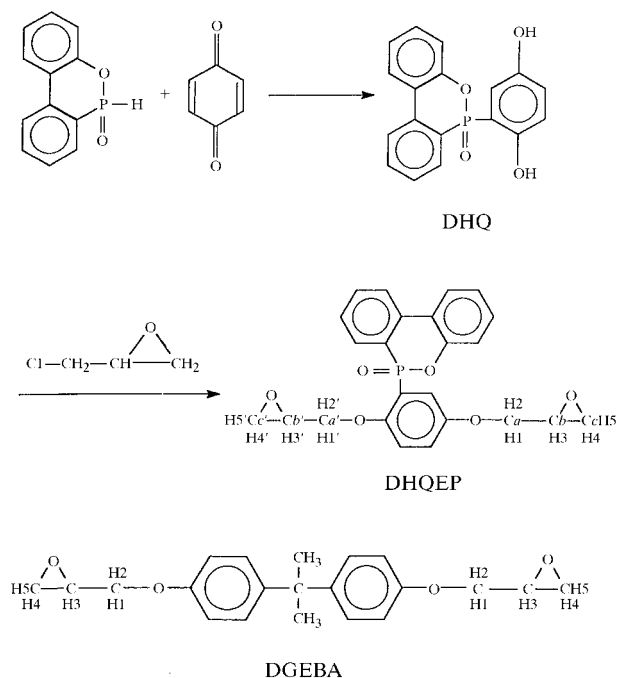


Fig. 1. The synthesis of DHQEP and the schematic structure of DGEBA.

observed in the glycidyl ether group of DGEBA. One possible cause of the unusual chemical shifts is the cyclic organophosphorus group grafted onto the main chain. The relative positions of the glycidyl ether groups and the pendent aryl phosphinate group is the key point. Thus, a single-crystal structure analysis was performed in order to determine the conformation of DHQEP.

## 2. Experimental

DHQEP was synthesized by the reaction of a cyclic organophosphorus compound with 1,4-benzoquinone, followed by glycidyl etherification with excess epichlorohydrin using sodium methoxide as a catalyst (Fig. 1). The chemical structures of the aryl phosphinate diol (DHQ) and DHQEP were confirmed by elemental analysis and mass, FTIR and  $^1\text{H}$ -,  $^{13}\text{C}$ - and  $^{31}\text{P}$ -NMR spectroscopy. The  $^{31}\text{P}$ -NMR spectrum of DHQEP showed only one sharp peak at 19.1286 p.p.m. Differential scanning calorimetry (DSC) thermograms were recorded using a Perkin–Elmer DSC-7 calorimeter at a heating rate of  $10\text{ K min}^{-1}$  under a nitrogen atmosphere. The DSC results showed only one sharp melting peak at 430.6 K for the final product, DHQEP, in the temperature range 323 to 473 K. IR spectra were obtained using a Bio-Rad FTS-40 Fourier transform infrared spectrometer and KBr pellets. The FTIR spectrum of the final product showed the peak of the epoxy group at  $916\text{ cm}^{-1}$ . Elemental analyses were determined by digestion treatment and calorimetry using a Carlo–Erba EA-106 analyzer with the following results for DHQEP:  $\text{C}_{24}\text{H}_{21}\text{O}_6\text{P}$  ( $436.4\text{ g mol}^{-1}$ ) observed: C 65.85, H 4.80, P 6.87. These values are close to the calculated values: C 66.05, H 4.85, P 7.10. The elemental analysis results for DHQ are  $\text{C}_{18}\text{H}_{13}\text{O}_4\text{P}$  ( $234.3\text{ g mol}^{-1}$ ) observed: C 66.60, H 4.02, P 9.54, close to the calculated values: C 66.67, H 4.04, P 9.56. Mass spectra were collected by the electrospray technique using a VG Platform mass spectrometer. The base peak of DHQEP was  $M^+\text{H}^+ = 437.1\text{ m/e}$ .  $^1\text{H}$ -,  $^{13}\text{C}$ -, and  $^{31}\text{P}$ -NMR spectra were recorded using a Bruker Avance-300 spectrometer with  $\text{DMSO-}d_6$  or  $\text{CDCl}_3$  as solvents, working at 300, 75, and 121 MHz, respectively.

The single crystal used for X-ray analysis was prepared by recrystallization from a very dilute DHQEP/acetone solution in a tube exposed in a closed vessel to a saturated vapor of ethyl ether at room temperature for 1 d. Details of the X-ray experiment are given in Table 1.† Atomic scattering factors used for the least-squares refinement were those listed in *International Tables for X-ray Crystallography* (1974). All calculations were performed on a VAX workstation

Table 1. *Experimental details*

Crystal data	
Chemical formula	$\text{C}_{24}\text{H}_{21}\text{O}_6\text{P}$
Chemical formula weight	436.4
Cell setting	Triclinic
Space group	$P\bar{1}$
$a$ (Å)	8.507 (3)
$b$ (Å)	10.613 (4)
$c$ (Å)	12.457 (3)
$\alpha$ (°)	80.05 (3)
$\beta$ (°)	71.38 (2)
$\gamma$ (°)	76.69 (3)
$V$ (Å <sup>3</sup> )	1031.1 (6)
$Z$	2
$D_x$ (Mg m <sup>-3</sup> )	1.406
Radiation type	Mo $K\alpha$
Wavelength (Å)	0.71073
No. of reflections for cell parameters	25
$\theta$ range (°)	7.43–10.94
$\mu$ (mm <sup>-1</sup> )	0.17
Temperature (K)	295
Crystal form	Block
Crystal size (mm)	0.50 × 0.38 × 0.20
Crystal color	Colorless
Data collection	
Diffractometer	Enraf–Nonius CAD-4
Data collection method	$\theta/2\theta$ scans
Absorption correction	Empirical
$T_{\min}$	0.9178
$T_{\max}$	0.9528
No. of measured reflections	3632
No. of independent reflections	3619
No. of observed reflections	2634
Criterion for observed reflections	$I_{\text{net}} > 2\sigma(I_{\text{net}})$
$R_{\text{int}}$	0.010
$\theta_{\text{max}}$ (°)	24.92
Range of $h, k, l$	$-9 \rightarrow h \rightarrow 10$ $0 \rightarrow k \rightarrow 12$ $-14 \rightarrow l \rightarrow 14$
No. of standard reflections	3
Frequency of standard reflections	Every 60 min
Intensity decay (%)	0
Refinement	
Refinement on	$F$
$R$	0.063
$wR$	0.057
$S$	1.48
No. of reflections used in refinement	3619
No. of parameters used	299
Weighting scheme	$1/[\sigma^2(F) + 0.0004F^2]$
$(\Delta/\sigma)_{\text{max}}$	0.010
$\Delta\rho_{\text{max}}$ (e Å <sup>-3</sup> )	4.30
$\Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	-2.50
Extinction method	Larson (1970)
Extinction coefficient	$62(21) \times 10^1$
Computer programs	
Data collection and cell refinement	CAD-4-EXPRESS (Enraf–Nonius, 1994; Gabe <i>et al.</i> , 1989)

using the program *NRCSDP* (Gabe *et al.*, 1989). The refined coordinates and  $U_{\text{eq}}$  values for the heavy atoms are listed in Table 2. The molecular structure of DHQEP is shown in Fig. 2.

† Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA0018). Services for accessing these data are described at the back of the journal.

### 3. Results and discussion

#### 3.1. X-ray diffraction

The X-ray analysis revealed disorder at one end of the molecule (see Fig. 3). Similar disorder of one epoxide ring of DGEBA has been reported (Flippen-Anderson & Gilardi, 1981). The disorder affects the epoxide ring furthest from the pendent aryl phosphinate group and consists of two alternative orientations for the epoxide ring connected to C22. However, both alternatives have one atomic position in common, O6. One possible position of the epoxide group, labeled E, consists of C23—C24—O6 while the other, labeled E', consists of C23'—C24'—O6 (see Fig. 3). The occupancies for the C23 and C24 atomic sites refined to 0.6. The atoms at the common position are different from those reported by Flippen-Anderson & Gilardi (1981). For DGEBA, the common positions for the two alternatives are occupied partially by C and partially by O and are approximately equally favored. Thus, several different possible disordered epoxide-ring structures were tested. However, the refinements converged at larger  $R$  and  $wR$ . Bond lengths and angles are listed in Table 3. Distances and angles in and around the epoxide rings are similar to those observed in DGEBA (Flippen-Anderson & Gilardi, 1981). From a conformation point of view E' is more crowded than E and has shorter bond distances and intramolecular interatomic distances. The ordered epoxide ring below the pendent aryl phosphinate group is more crowded than E and less crowded than E'. However, the difference is not significant.

#### 3.2. NMR chemical shifts

The motivation for the single-crystal X-ray analysis of DHQEP was the observation that the NMR chemical shifts of the protons of the glycidyl ether group at one end of DHQEP are similar to those observed for the glycidyl ether group of DGEBA (Han *et al.*, 1993). However, the chemical shifts of the glycidyl ether group

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

$$U_{\text{eq}} = (1/3)\Sigma_j \Sigma_j U^{ij} a^i a^j$$

	x	y	z	$U_{\text{eq}}$
P	0.91830 (7)	0.72952 (5)	0.42866 (4)	0.0383 (3)
O1	0.9139 (2)	0.88184 (13)	0.41924 (11)	0.0509 (10)
O2	1.01965 (18)	0.65441 (14)	0.50183 (12)	0.0500 (9)
O3	0.62925 (19)	0.88473 (16)	0.34941 (13)	0.0628 (10)
O4	0.4335 (2)	0.50935 (19)	0.70245 (17)	0.0863 (13)
O5	0.6501 (3)	1.0762 (2)	0.13093 (17)	0.0982 (17)
O6	0.3526 (3)	0.3511 (2)	0.93426 (15)	0.0861 (14)
C1	0.9910 (2)	0.69429 (19)	0.28446 (17)	0.0388 (11)
C2	0.9979 (3)	0.5676 (2)	0.26422 (19)	0.0539 (15)
C3	1.0522 (4)	0.5342 (2)	0.1545 (2)	0.0658 (18)
C4	1.0977 (3)	0.6271 (2)	0.0647 (2)	0.0621 (17)
C5	1.0911 (3)	0.7526 (2)	0.08321 (18)	0.0512 (14)
C6	1.0400 (2)	0.78933 (19)	0.19331 (17)	0.0390 (11)
C7	1.0431 (2)	0.92132 (19)	0.21477 (17)	0.0387 (11)
C8	1.1068 (3)	1.0145 (2)	0.12615 (18)	0.0537 (14)
C9	1.1138 (3)	1.1359 (2)	0.1470 (2)	0.0637 (16)
C10	1.0608 (3)	1.1689 (2)	0.2571 (2)	0.0555 (14)
C11	0.9971 (3)	1.0809 (2)	0.34569 (18)	0.0453 (12)
C12	0.9875 (2)	0.96034 (19)	0.32373 (17)	0.0379 (11)
C13	0.7009 (3)	0.7147 (2)	0.48413 (17)	0.0417 (12)
C14	0.5772 (3)	0.7927 (2)	0.43766 (18)	0.0481 (12)
C15	0.4131 (3)	0.7708 (3)	0.4793 (2)	0.0609 (16)
C16	0.3723 (3)	0.6749 (3)	0.5663 (2)	0.0655 (16)
C17	0.4916 (3)	0.5992 (2)	0.6148 (2)	0.0573 (14)
C18	0.6568 (3)	0.6177 (2)	0.57315 (19)	0.0492 (13)
C19	0.5078 (3)	0.9919 (3)	0.3251 (2)	0.0695 (16)
C20	0.5989 (4)	1.0917 (3)	0.2456 (2)	0.0769 (19)
C21	0.5268 (4)	1.1872 (3)	0.1737 (3)	0.097 (23)
C22	0.5480 (4)	0.4195 (3)	0.7485 (3)	0.084 (2)
C23	0.4298 (5)	0.3256 (4)	0.8195 (3)	0.061 (3)
C24	0.4840 (6)	0.2380 (6)	0.9056 (4)	0.092 (4)
C23'	0.4999 (8)	0.3175 (7)	0.8488 (6)	0.072 (4)
C24'	0.3475 (8)	0.2776 (6)	0.8532 (5)	0.063 (4)

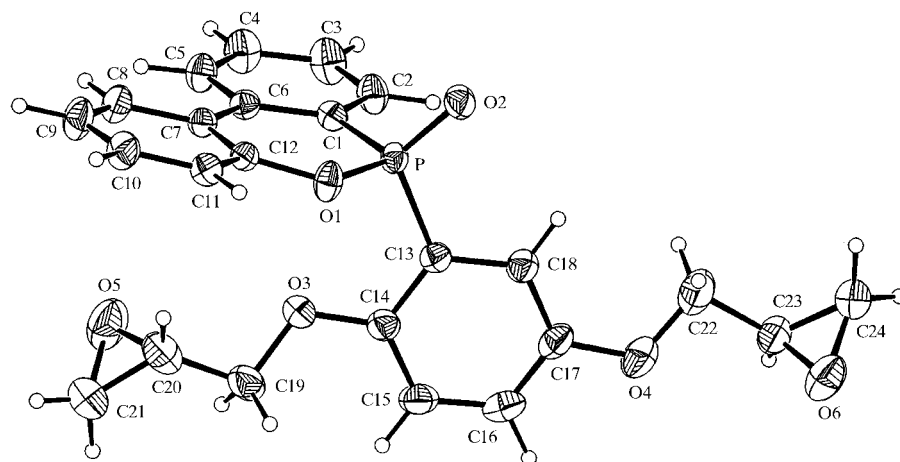


Fig. 2. An ORTEP (Johnson, 1976) drawing of the structure of DHQEP. Displacement ellipsoids are shown at the 30% probability level for non-H atoms.

at the other end of DHQEP are quite different from those observed in the glycidyl ether group of DGEBA (see Table 4). Because of the significant difference in the chemical shifts of the atoms of the two glycidyl ether groups two-dimensional NMR techniques were used to confirm the assignment of the NMR spectra. Figs. 4 and

Table 3. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

P—O1	1.5932 (16)	C7—C8	1.406 (3)
P—O2	1.4641 (15)	C7—C12	1.390 (3)
P—C1	1.779 (2)	C8—C9	1.376 (3)
P—C13	1.790 (2)	C9—C10	1.381 (4)
O1—C12	1.387 (2)	C10—C11	1.371 (3)
O3—C14	1.370 (3)	C11—C12	1.379 (3)
O3—C19	1.412 (3)	C13—C14	1.396 (3)
O4—C17	1.363 (3)	C13—C18	1.396 (3)
O4—C22	1.389 (4)	C14—C15	1.384 (3)
O5—C20	1.381 (3)	C15—C16	1.369 (4)
O5—C21	1.437 (4)	C16—C17	1.375 (4)
O6—C23	1.415 (4)	C17—C18	1.382 (3)
O6—C24	1.447 (6)	C19—C20	1.494 (4)
O6—C23'	1.380 (7)	C20—C21	1.399 (4)
O6—C24'	1.395 (7)	C22—C23	1.541 (5)
C1—C2	1.395 (3)	C22—C23'	1.520 (7)
C1—C6	1.406 (3)	C23—C24	1.415 (6)
C2—C3	1.376 (3)	C23—C23'	0.776 (8)
C3—C4	1.375 (4)	C23—C24'	0.910 (7)
C4—C5	1.377 (3)	C24—C23'	1.008 (8)
C5—C6	1.395 (3)	C24—C24'	1.455 (8)
C6—C7	1.478 (3)	C23'—C24'	1.436 (9)
O1—P—O2	111.96 (9)	O4—C17—C16	115.3 (2)
O1—P—C1	103.87 (9)	O4—C17—C18	125.2 (2)
O1—P—C13	104.14 (9)	C16—C17—C18	119.5 (2)
O2—P—C1	115.46 (9)	C13—C18—C17	120.0 (2)
O2—P—C13	112.41 (9)	O3—C19—C20	108.1 (2)
C1—P—C13	108.07 (10)	O5—C20—C19	116.8 (3)
P—O1—C12	127.02 (13)	O5—C20—C21	62.3 (2)
C14—O3—C19	118.50 (18)	C19—C20—C21	123.4 (3)
C17—O4—C22	119.2 (2)	O5—C21—C20	58.26 (19)
C20—O5—C21	59.49 (19)	O4—C22—C23	98.6 (3)
C23—O6—C24	59.3 (3)	O4—C22—C23'	124.6 (3)
C23—O6—C23'	32.2 (3)	C23—C22—C23'	29.3 (3)
C23—O6—C24'	37.8 (3)	O6—C23—C22	114.2 (3)
C24—O6—C23'	41.7 (3)	O6—C23—C24	61.5 (3)
C24—O6—C24'	61.5 (4)	O6—C23—C23'	71.4 (6)
C23'—O6—C24'	62.3 (4)	O6—C23—C24'	69.9 (5)
P—C1—C2	117.50 (16)	C22—C23—C24	116.7 (4)
P—C1—C6	122.00 (15)	C22—C23—C23'	73.9 (6)
C2—C1—C6	120.51 (19)	C22—C23—C24'	169.4 (6)
C1—C2—C3	120.4 (2)	C24—C23—C23'	43.7 (6)
C2—C3—C4	119.6 (2)	C24—C23—C24'	73.9 (5)
C3—C4—C5	120.8 (2)	C23'—C23—C24'	116.6 (8)
C4—C5—C6	121.2 (2)	O6—C24—C23	59.2 (3)
C1—C6—C5	117.53 (18)	O6—C24—C23'	65.6 (5)
C1—C6—C7	120.62 (18)	O6—C24—C24'	57.5 (3)
C5—C6—C7	121.81 (18)	C23—C24—C23'	32.1 (4)
C6—C7—C8	121.96 (18)	C23—C24—C24'	37.0 (3)
C6—C7—C12	122.35 (17)	C23'—C24—C24'	68.6 (5)
C8—C7—C12	115.67 (18)	O6—C23'—C22	117.7 (5)
C7—C8—C9	121.7 (2)	O6—C23'—C23	76.4 (6)
C8—C9—C10	120.4 (2)	O6—C23'—C24	72.7 (5)
C9—C10—C11	119.6 (2)	O6—C23'—C24'	59.4 (4)
C10—C11—C12	119.6 (2)	C22—C23'—C23	76.8 (6)
O1—C12—C7	122.51 (17)	C22—C23'—C24	169.2 (8)
O1—C12—C11	114.45 (18)	C22—C23'—C24'	111.3 (5)
C7—C12—C11	123.02 (18)	C23—C23'—C24	104.3 (8)
P—C13—C14	122.03 (16)	C23—C23'—C24'	34.5 (5)
P—C13—C18	118.26 (16)	C24—C23'—C24'	70.6 (6)
C14—C13—C18	119.64 (19)	O6—C24'—C23	72.3 (5)
O3—C14—C13	116.71 (19)	O6—C24'—C24	61.0 (4)
O3—C14—C15	123.9 (2)	O6—C24'—C23'	58.3 (4)
C13—C14—C15	119.4 (2)	C23—C24'—C24	69.2 (5)
C14—C15—C16	120.2 (2)	C23—C24'—C23'	28.9 (4)
C15—C16—C17	121.2 (2)	C24—C24'—C23'	40.8 (4)

5 show the two-dimensional NMR spectra of DHQEP from C—H correlation and COSY experiments, respectively, and confirm the assignment of the NMR spectrum of DHQEP. In Table 4 the NMR chemical shifts of the protons in DHQEP and DGEBA are compared. It is obvious that the chemical shifts of H1', H2', H3', H4', and H5' of DHQEP are significantly reduced. A possible reason for this is that these atoms are positioned close to the aryl phosphinate group. An aromatic molecule can be visualized as a current loop in which the  $\pi$  electrons are free to move on a circle formed by the  $\sigma$  framework. A diamagnetic ring current is induced when these compounds are subjected to an external magnetic field  $B_0$  and a dipole opposed to  $B_0$  and centered in the middle of the ring is induced by the diamagnetic ring current. Therefore, protons in the molecular plane and outside the ring are deshielded. Conversely, protons in the region above or below the plane of the ring are strongly shielded (Günther, 1980). Thus, the chemical shifts of H1', H2', H3', H4', and H5' (the atomic labels of the protons are show in Fig. 1) of DHQEP are significantly reduced by the 'ring-current effect' of the pendent aryl phosphinate group.

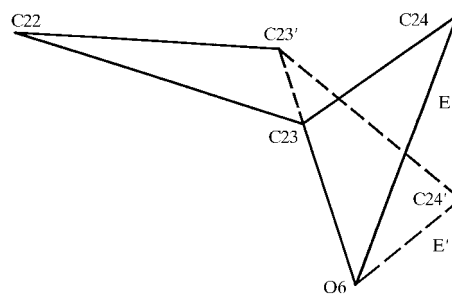


Fig. 3. The two alternative structures of the epoxide ring (solid line: E; dashed line: E').

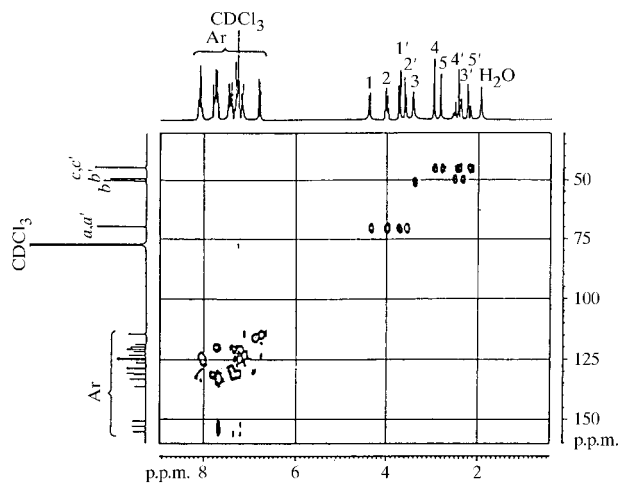


Fig. 4. The two-dimensional NMR spectrum of DHQEP (C—H).

Table 4. Chemical shifts (p.p.m.) of the glycidyl ether groups in the  $^1\text{H-NMR}$  spectra of DHQEP and DGEBA in  $\text{CDCl}_3$ 

	H1	H2	H3	H4	H5	H1'	H2'	H3'	H4'	H5'
DHQEP	4.40	4.02	3.43	2.99	2.84	3.73	3.63	2.43	2.45	2.19
DGEBA	4.16	4.02	3.31	2.87	2.73					

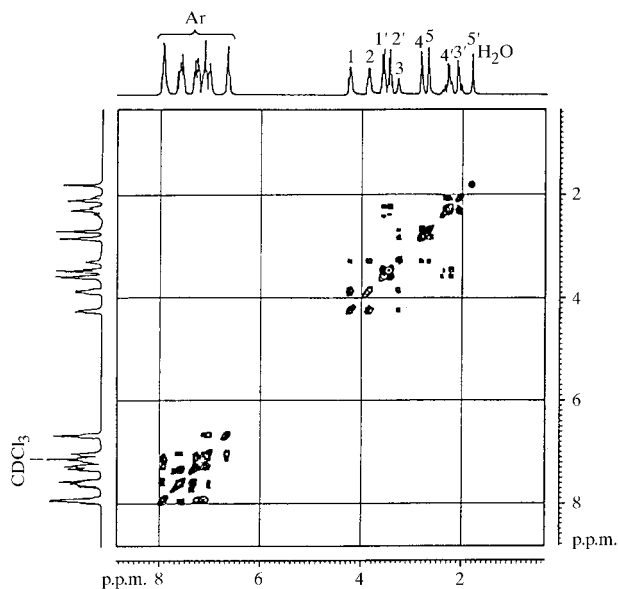


Fig. 5. The two-dimensional NMR spectrum of DHQEP (H-H).

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University, Taiwan) for collecting the single-crystal X-ray diffraction data.

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