Two-dimensional n.m.r. characterization of cycloaliphatic epoxy resins

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The cycloaliphatic epoxy resins were studied by various two-dimensional nuclear magnetic resonance (2D n.m.r.) spectroscopies. The [13]C n.m.r. spectra of the epoxy resins were assigned by using DEPT and 2D INADEQUATE techniques and the [1]H n.m.r. spectra were assigned by using 2D ^{1}H–^{1}H and ^{1}H–^{13}C COSY techniques. Complete characterization of the samples synthesized by the oxidation of cyclohexene derivatives not only revealed the existence of the stereochemical isomers resulting from the structural difference of the oxide rings in the samples but also provided the composition ratio of the isomers.

(Keywords: cycloaliphatic epoxy resin; cyclohexene oxide; [1]H n.m.r.; [13]C n.m.r.; two-dimensional n.m.r.)

INTRODUCTION

Epoxy resins are monomers and/or prepolymers which have active epoxy groups in the molecules. They have been used in a wide range of industrial products. The properties of cured epoxy resins largely depend on the structure of the starting resin. Hence both ^{1}H and [13]C n.m.r. spectroscopies have been used to characterize epoxy resins[1–4]. In addition, a variety of two-dimensional nuclear magnetic resonance (2D n.m.r.) techniques have been of considerable use in the spectral assignments[5–7].

Cycloaliphatic epoxy resins are compounds which contain cyclohexene oxide structure and their cured products offer a wide range of properties suitable for electrical and electronic applications. Characterized by a saturated cycloaliphatic ring structure and without any aromatic unsaturation, they have good weathering characteristics and excellent electrical properties, even in use under severe conditions. Cycloaliphatic epoxy resins have higher reactivity than typical bisphenol-A type epoxy resins in photopolymerization[8]. In spite of their use in various industrial products, there have been few studies on the characterization of these epoxy resins.

The molecular structure of cyclohexene oxide has been determined by an electron diffraction investigation of the vapour[9]. Though cyclohexene oxide is the compound in which an oxygen atom is attached to the cyclohexane ring as an epoxy group, the structure is very different from that of cyclohexane itself, which is known to take a chair conformation. The structure is a sort of deformed 'staircase' form[9], and resembles that of cyclohexene. The four carbon atoms nearest to the oxygen atom are coplanar, and the two remaining carbons are placed one above and one below this plane in the cyclohexene oxide molecule.

There has been considerable n.m.r. study of cyclohexane and its derivatives. In particular, the ^{13}C chemical shifts have been investigated in detail, and it is possible to calculate the chemical shift of cyclohexane derivatives

using empirical rules[10,11]. However, there have been few n.m.r. studies of cyclohexene oxide derivatives, including cycloaliphatic epoxy resins[12]. The empirical rules of cyclohexane groups are not valid for the estimation of the ^{13}C chemical shifts of cycloaliphatic epoxy resins because of the distorted ring structure.

In this paper, cycloaliphatic epoxy resins are investigated using 2C n.m.r. spectroscopies. First, the ^{13}C spectra of the epoxy resins were assigned using DEPT (distortionless enhancement by polarization transfer)[13,14] and 2D INADEQUATE (incredible natural abundance double quantum experiment)[15,16] techniques. Then the ^{1}H spectra were assigned using ^{1}H–^{1}H and ^{1}H–^{13}C COSY (correlation spectroscopy)[17,18] techniques on the basis of the ^{13}C assignments. The ^{1}H and [13]C n.m.r. spectral assignments not only revealed the existence of the stereochemical isomers in the epoxy resins used in the present study, but also lead to the determination of the composition and the molecular structures of these isomers.

EXPERIMENTAL

Materials

Cycloaliphatic epoxy resins, 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexane carboxylate (ERL4221) and 3,4-epoxycyclohexyl adipate (ERL4299) were supplied from Union Carbide and were used without further purification. Their structural formulae are given in *Figure 1*. The samples were dissolved in CDCl₃ with a concentration of 20 wt% (50 wt% for 2D INADEQUATE) for the n.m.r. measurements.

N.m.r. measurements

The ^{1}H spectra were recorded at 500 MHz with a Jeol GSX-500 spectrometer using 6 s pulse repetition, 3500 Hz spectral width, 32 000 data points and 16 accumulations. The [1]H-decoupled ^{13}C spectra were recorded at 67.9 MHz with a Jeol GSX-270 spectrometer using 4 s pulse repetition, 16 000 Hz spectral width, 32 000 data points

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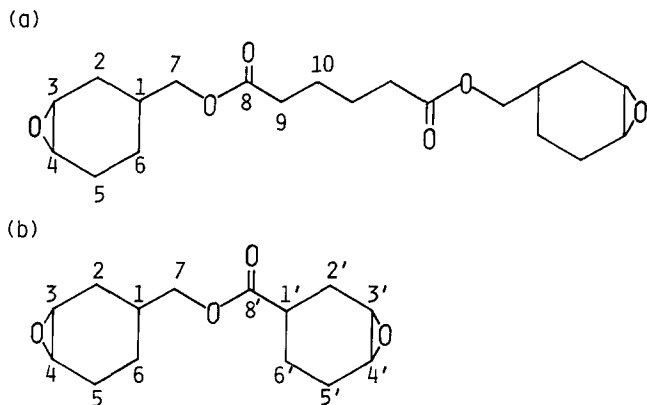
(a)

(b)

Figure 1 Structural formulae of (a) 3,4-epoxycyclohexyl adipate, ERL4299, and (b) 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexane carboxylate, ERL4221

and 1000 accumulations. Chemical shifts are given in parts per million (ppm) from tetramethylsilane with $CDCl_3$ as internal reference (77.0 ppm for ^{13}C and 7.24 ppm for ^1H).

The ^{13}C DEPT, 2D ^1H–^1H and ^1H–^{13}C COSY, and 2D ^{13}C INADEQUATE spectra were observed using standard pulse sequences and procedures. The DEPT experiments were carried out using 90° (^1H)–t_1–180° (^1H)–90° (^{13}C)–t_1–θ(^1H)–180° (^{13}C)–Acq. (acquisition) sequences. The delay time t_1 was set to 3.7 ms, where $t_1 = (2J_{CH})^{-1}$ and $J_{CH} = 140$ Hz. The pulse width of θ was either 90 or 135°. The DEPT spectra were obtained with 2 s repetition, 9000 Hz spectral width, 32 000 data points and 64 accumulations. For the ^1H–^1H COSY experiments, 90°–t_1–90°–Acq. sequences were used. The initial data set consisted of a 1024 × 512 matrix. The spectral width was 3500 Hz and a total of eight transients were accumulated per t_1 value with a pulse delay of 1.3 s. The ^1H–^{13}C COSY experiments were carried out using pulse sequences of 90° (^1H)–$t_{1/2}$–180° (^{13}C)–$t_{1/2}$–D_1–90° (^1H, ^{13}C)–D_2–Acq. The delay times D_1 and D_2 were set to 3.7 and 1.85 ms, respectively, where $D_1 = (2J_{CH})^{-1}$, $D_2 = (4J_{CH})^{-1}$ and $J_{CH} = 140$ Hz. A total of 40 transients were accumulated per t_1 value with a pulse delay of 2 s. The initial data matrix was 1024 (^{13}C, 9000 Hz) × 512 (^1H, 3500 Hz) and was expanded to the final matrix size, 1024 × 1024, by zero filling.

The 2D INADEQUATE experiments were carried out using sequences of 90°–T–180°–T–90°–t_1–Acq. The delay time T was set to 7.14 ms, where $T = (4J_{CC})^{-1}$ and $J_{CC} = 35$ Hz. A total of 256 transients were accumulated per t_1 value with a pulse delay of 2 s. The initial data set consisted of a 2048 × 128 matrix with 18 000 Hz × 9000 Hz spectral widths, and was expanded to the final matrix size, 4096 × 256, by zero filling. The experiments required 20 h of acquisition on the spectrometer.

RESULTS AND DISCUSSION

N.m.r. signal assignments of cycloaliphatic epoxy resins

Figure 2 shows the ^{13}C spectra of ERL4299 and ERL4221. In spite of the similarity in their molecular structures, the ^{13}C n.m.r. spectrum of ERL4299 exhibits fewer peaks than that of ERL4221, clearly reflecting the better symmetry of the molecular structure of the former. There are 10 and 14 chemically inequivalent carbons in ERL4299 and ERL4221, respectively, as seen from

Figure 1. There are 17 and 26 resonances observed in traces (a) and (b) in *Figure 2*, respectively. The extra peaks are not attributed to the impurities in the epoxy resins because of their strong intensities.

Figure 3 shows the DEPT spectra of ERL4299. The DEPT technique can be used to identify clearly the carbon groups[13,14]. Only the methine signals appeared in spectrum (a), while the methine signals appeared as upward peaks and methylene signals appeared as downward peaks in spectrum (b). The signals appearing in spectrum (a) were assigned to either C_1, C_3 or C_4 and, therefore, remaining signals resonating in the chemical shift range 20–70 ppm should arise from the methylene carbons. Using the conventional chemical shift table[10,11], the ^{13}C spectrum of ERL4299 was tentatively assigned. The carbonyl resonance at 172.7 ppm should be assigned to C_8. Two resonances at 68.0 and 67.8 ppm arise from C_7. Four resonances at ≈ 51 ppm were assigned to either C_3 or C_4. The resonance at 37.3 ppm was assigned to C_9. Two resonances at 31.7 and 29.0 ppm were assigned to C_1. Seven resonances at 28–20 ppm originate from C_2, C_5, C_6 and C_{10}. The fact that more than one resonance arises from a carbon suggests that ERL4299 consists of a mixture of isomers. The 2D INADEQUATE spectrum of ERL4299 is shown in *Figure 4*. Starting from the C_7 resonances, ^{13}C–^{13}C connectivities are traced out along
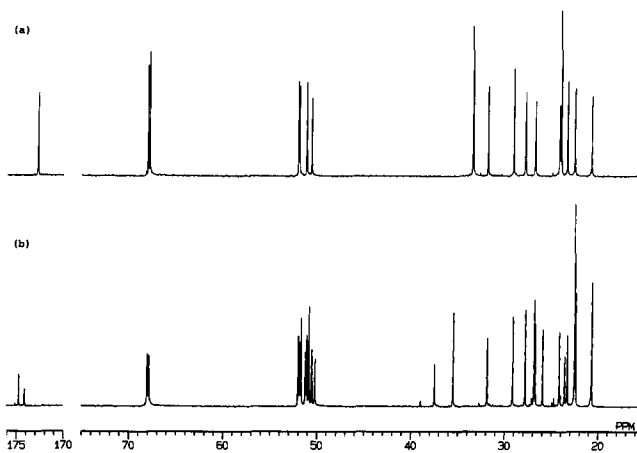
(a)

(b)

Figure 2 ^{13}C n.m.r. spectra of (a) ERL4299 and (b) ERL4221 cycloaliphatic epoxy resins in 20 wt% $CDCl_3$ solution at 27°C
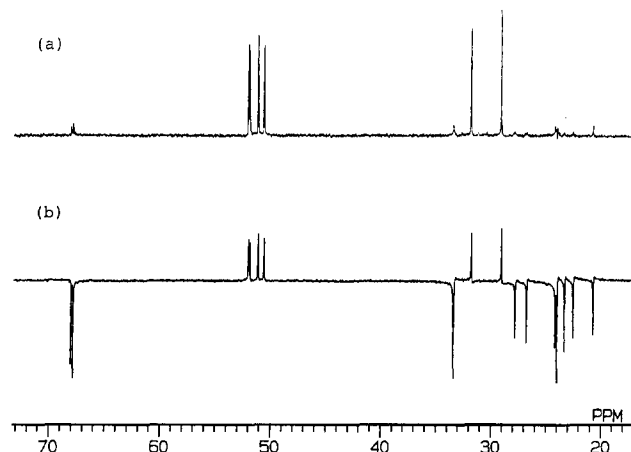
(a)

(b)

Figure 3 ^{13}C DEPT spectra of ERL4299 cycloaliphatic epoxy resin in 20 wt% $CDCl_3$ solution at 27°C. The pulse width of θ is (a) 90° and (b) 135° in the pulse sequence given in the text
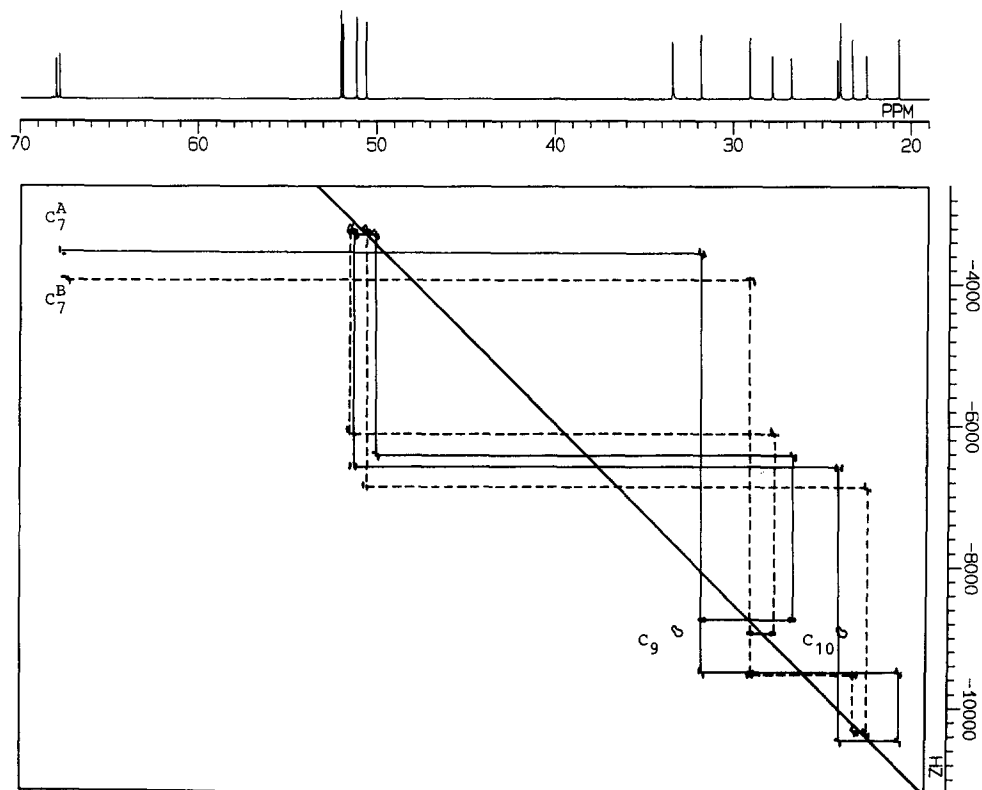
Figure 4 ^{13}C 2D INADEQUATE spectrum of ERL4299 cycloaliphatic epoxy resin in 50 wt% CDCl₃ solution at 40°C. Two independent ^{13}C–^{13}C connectivities of C₁–C₆ arising from two isomers (A and B) are indicated by —— and ---

the carbon skeleton. Two independent ^{13}C–^{13}C connectivities are clearly observed, as shown in the figure, indicating the existence of two isomers, labelled A and B. The C₈–C₁₀ resonances were disconnected from the other resonances, C₁–C₇, in the spectrum because of the interruption of the carbon–carbon connectivity by the ester bond. The final assignments are listed in *Table 1*.

From a comparison of the molecular structures of ERL4221 and ERL4299, it can be assumed that the electronic structure of the cyclohexene oxide ring composed of C₁–C₆ in ERL4221 is almost the same as the ring in ERL4299. Combined analyses on the DEPT and INADEQUATE results, use of the chemical shift table, and the assumption of identical chemical shifts of the C₁–C₆ in ERL4221 and ERL4299, the ^{13}C n.m.r. signals of ERL4221 were completely assigned. *Figure 5* shows the 2D INADEQUATE spectrum of ERL4221. Since the ester bond interrupts the ^{13}C–^{13}C connectivity between two cyclohexene oxide rings, the spin system of each cyclohexene oxide ring was connected separately in the spectrum. A pair of connectivities along the carbon skeleton of the C₁–C₆ ring was the same as that of ERL4299 shown in *Figure 4*. The spin systems of the C₁′–C₆′ ring are indicated by solid and dashed lines in the figure. Two independent ^{13}C–^{13}C connectivities of the C₁–C₆ ring in ERL4221 are labelled A and B, and those of the C₁′–C₆′ ring are labelled C and D. The assignments of the ^{13}C spectrum of ERL4221 are also listed in *Table 1*.

Figure 6 shows ^{1}H spectra of ERL4299 and ERL4221. The spectrum of ERL4221 is more complicated than that of ERL4299, reflecting the asymmetry of the molecular structure for the former. The complexity of the spectra

Table 1 ^{13}C chemical shift assignments of ERL4299 and ERL4221

Carbon number[a]	ERL4299 A	ERL4299 B	ERL4221 A	ERL4221 B	ERL4221 C	ERL4221 D
1	31.7	29.0	31.8	29.1		
2	26.7	27.8	26.7	27.7		
3	50.5	51.9	50.5	51.9		
4	51.8	51.1	51.8	51.0		
5	24.1	22.5	24.1	22.5		
6	20.7	23.3	20.6	23.2		
7	68.0	67.8	68.0	67.8		
8	172.7					
9	33.3					
10	23.9					
1′					37.4	35.4
2′					25.9	26.7
3′					50.1	51.6
4′					51.2	50.8
5′					23.5	22.3
6′					20.6	22.5
8′					174.1	174.7

[a] Carbon numbers are shown in *Figure 1*

is attributed to overlapping of many split peaks by spin–spin couplings. The ^{1}H spectra were assigned by using 2D ^{1}H–^{13}C COSY spectra on the basis of the ^{13}C assignments. The ^{1}H assignments were further confirmed by the ^{1}H–^{1}H COSY spectra. The signal assignments are shown with the spectra in *Figure 6*. The H$_{6b}^{A}$ and H$_{6b}^{B}$ signals in both spectra and the H$_{9}^{D}$ signal in the spectrum of ERL4221 are resolved. The isomer composition was, therefore, determined from their integral intensities.
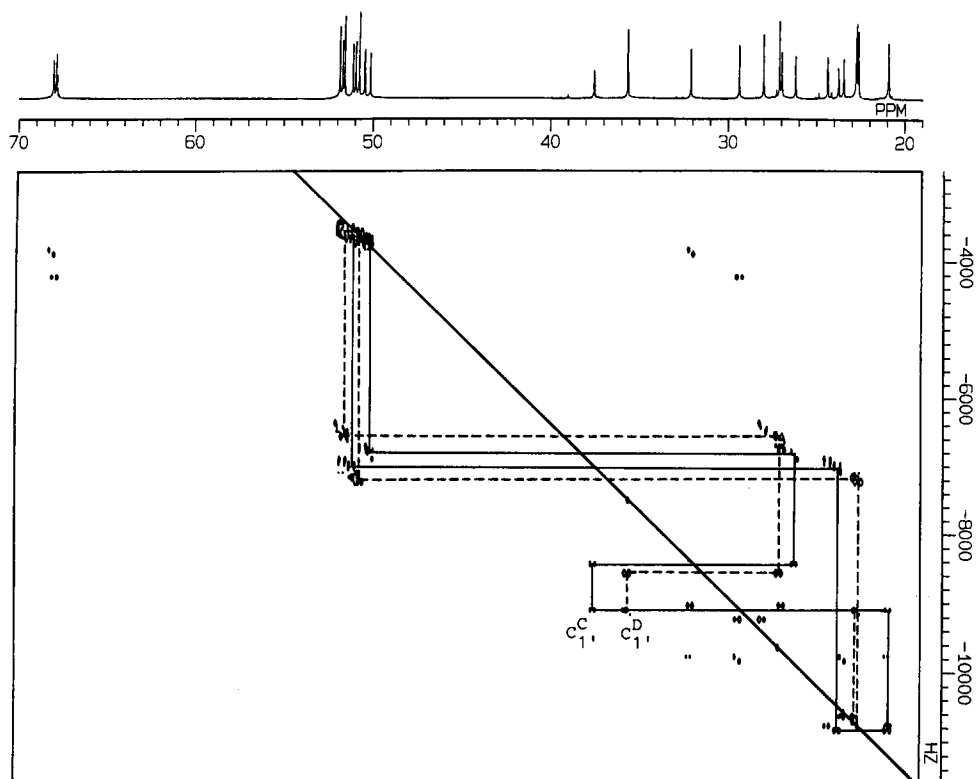
Figure 5 ^{13}C 2D INADEQUATE spectrum of ERL4221 cycloaliphatic epoxy resin in 50 wt% CDCl$_3$ solution at 40°C. Two independent ^{13}C–^{13}C connectivities of C$_1$–C$_6'$ arising from two isomers (C and D) are indicated by —— and – – –. Two ^{13}C–^{13}C connectivities of C$_1$–C$_6$ (A and B) are the same as those indicated in *Figure 4* and are omitted in this figure
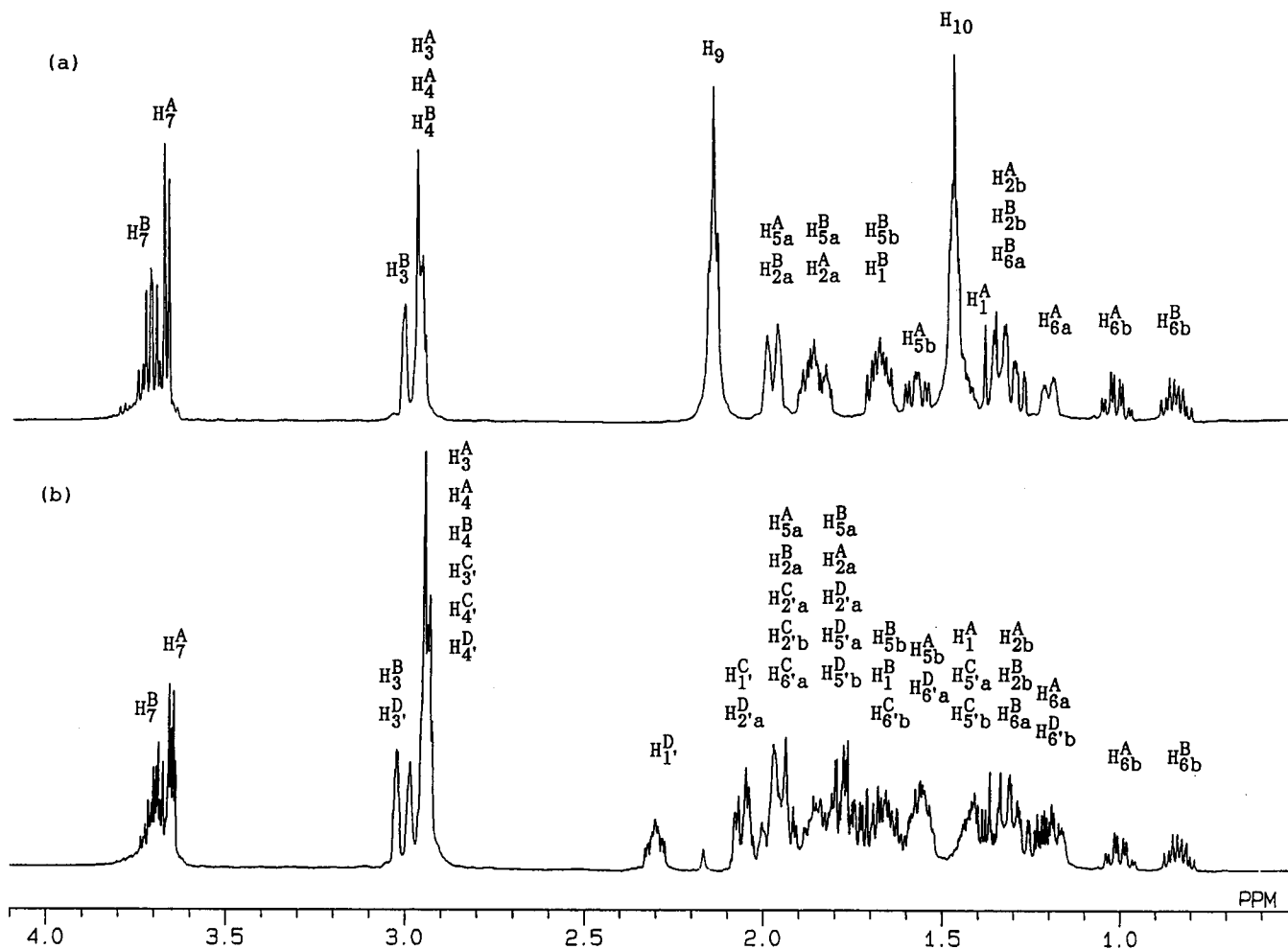

Figure 6 ^{1}H n.m.r. spectra of (a) ERL4299 and (b) ERL4221 cycloaliphatic epoxy resins in 20 wt% CDCl$_3$ solution at 27°C. The assignments are given with the spectra

Structural determination of the isomers

The results of the INADEQUATE analysis revealed that the two isomers are identical in these skeletal configurations. The assignments in *Table 1* indicate that each of C_8, C_9 and C_{10} exhibits only a single corresponding resonance and each of the remaining carbons exhibits two resonances in the spectrum of ERL4299. Thus a pair of resonances may be attributed to the difference of the bonded positions of substituents in the cyclohexene oxide ring. *Figure 7* shows the structural formula of (a) a cyclohexene oxide derivative and (b) its four possible isomers, isomers 1–4. In the model, R_1 and R_4 are in axial positions, while R_2 and R_3 are in equatorial positions. The interatomic distance between the oxygen and C_1 atoms is 3.35 Å* in isomers 1 and 2, and 3.01 Å in isomers 3 and 4. It is well known that the equatorial conformation is more stable than the axial one because of 1,3-diaxial interaction in the cyclohexane derivatives with steric substituents[19]. In cyclohexene oxide derivatives, the axial substituted molecule is also spatially more crowded than the equatorial substituted one. In fact, the quantum chemical calculation, using modified
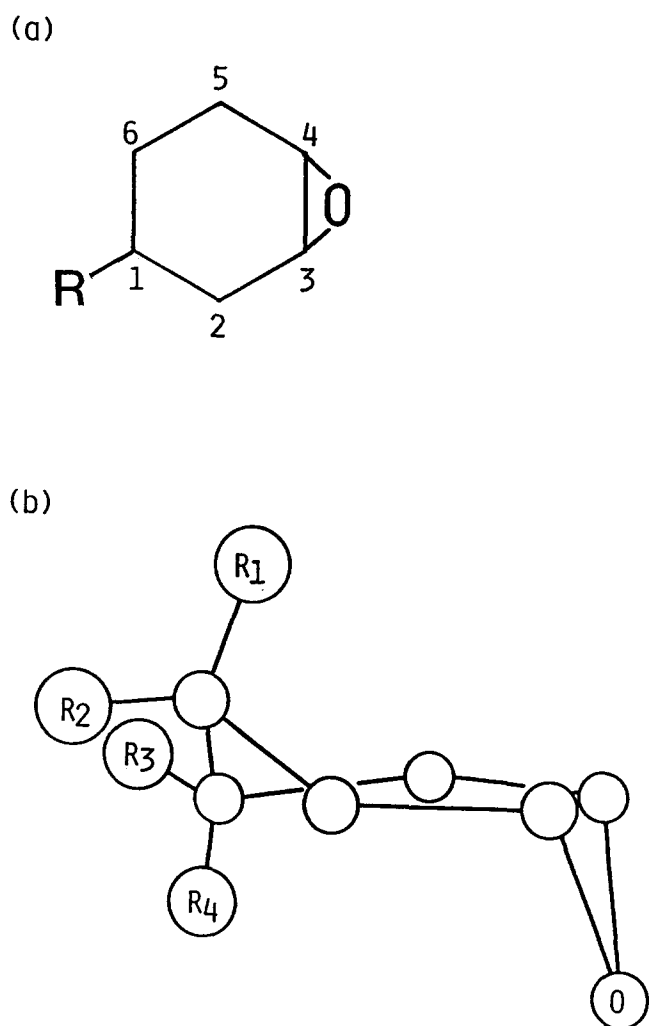
(a)

(b)

Figure 7 (a) Structural formula and (b) molecular model of a cyclohexene oxide derivative. The model represents four possible isomers as follows: isomer 1, $R_1 = R$, $R_2 = R_3 = R_4 = H$; isomer 2, $R_2 = R$, $R_1 = R_3 = R_4 = H$; isomer 3, $R_3 = R$, $R_1 = R_2 = R_4 = H$; isomer 4, $R_4 = R$, $R_1 = R_2 = R_3 = H$, where R is a substituent (a methyl group for the quantum chemical calculation in the text)

* 1 Å = 10^{-10} m

neglect of diatomic overlap method[20], of methyl cyclohexene oxide indicates that the total energy of isomer 1 is 3.23 kJ mol^{-1} higher than that of isomer 2, and that of isomer 4 is 5.48 kJ mol^{-1} higher than that of isomer 3. The energy difference between isomers 2 and 3 is only 0.02 kJ mol^{-1}. Hence the equatorial substitution, either isomer 2 or 3, was supposed to be dominant at room temperatures. Therefore, we conclude that a pair of ^{13}C resonances observed in the n.m.r. spectra reveal the mixture of isomers 2 and 3.

The integral intensities of the ^{1}H spectra were used to quantify the composition ratio of isomers 2 and 3. The composition ratios A:B in ERL4221 and ERL4299 were determined by the relative intensities of the H_{6b}^A and H_{6b}^B resonances in the spectra shown in *Figure 6*. The ratio C:D in ERL4221 was determined from the equation $C:D = (I_A + I_B - I_D):I_D$, where I_A, I_B and I_D are the relative intensities of the H_{6b}^A, H_{6b}^B and H_9^D resonances of ERL4221, respectively. The calculated composition ratio A:B is 52:48 in ERL4299. The ratios of A:B and C:D are 48:52 and 30:70, respectively, in ERL4221.

Cycloaliphatic epoxy resins are synthesized industrially by the oxidation of cyclohexene derivatives[21]. Two directions are possible when an oxygen atom attacks the double bond of a cyclohexene ring: the upper and lower faces of the plane composed of C_2–C_5. This reaction results in the production of the two ring isomers described above. If the reactivities of both directions are approximately equal, the composition ratio of the two structures in the product should be close to 1:1. This is observed for A and B in ERL4221 and ERL4299. For the C_1–$C_{6'}$ ring in ERL4221, the C=O carbon is directly bonded to the ring. The steric hindrance due to the carbonyl group is supposed to lead to a composition ratio C:D of 3:7. Since the interatomic distance between the C=O oxygen and the epoxy oxygen in C is shorter than that in D, we conclude that the structure of C is identical to isomer 3 and hence that of D is identical to isomer 2 in *Figure 7*.

Because of the structural similarity of the C_1–C_6 and C_1–$C_{6'}$ rings, they should exhibit similar n.m.r. spectral patterns. The chemical shifts of the C_1–C_6 resonances were compared with those of the corresponding carbon resonances in the C_1–$C_{6'}$ ring in ERL4221 in order to identify the structure of A and B. In *Figure 8* the ^{13}C chemical shift differences between A and B in the C_1–C_6 ring and between C and D in the C_1–$C_{6'}$ ring are plotted against the corresponding carbon. The similar tendency in the plots indicates that the structure of A is identical to isomer 3 and that of B to isomer 2 in *Figure 7*.

Each cyclohexene oxide ring in ERL4299 has the structure of either A or B. Given the symmetric nature of its molecular structure, three isomers are possible: AA, AB and BB. Because A:B = 52:48, the composition ratio of the three isomers is determined as AA:AB:BB = 27:50:23. The linkage between the two rings is relatively long given that the electronic structure of one ring is ineffective to the structure of the other ring. Hence only one pair of resonances is observed in the ^{13}C n.m.r. spectrum of ERL4299 in spite of the existence of three isomers. Additionally, the degeneracy of the C_8–C_{10} resonances in all three isomers indicates that their chemical shifts are independent of the electronic structures of the two rings. In ERL4221, four isomers are possible: AC, AD, BC and BD. Since A:B = 48:52 and C:D = 30:70, the isomer composition ratio is determined as AC:AD:BC:BD = 14:34:16:36.
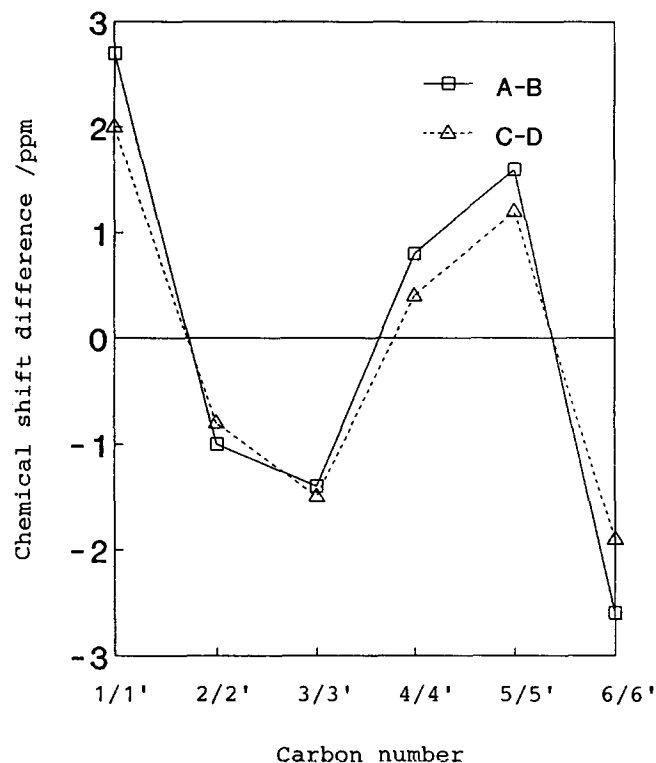
Figure 8 ^{13}C chemical shift difference between A and B in the C_1-C_6 ring (——) and that between C and D in the C_1-C_6, ring (———). The difference was calculated by subtracting either the chemical shift of B from that of A or that of D from that of C

CONCLUSION

The cycloaliphatic epoxy resins ERL4221 and ERL4299 were studied by various 2D n.m.r. spectroscopies. The ^{13}C spectra were completely assigned by using DEPT and 2D INADEQUATE techniques and the ^{1}H spectra were assigned by using 2D ^{1}H–^{1}H and ^{1}H–^{13}C COSY techniques. The assignments reveal the existence of isomers which were found to result from the structural difference of the substituted cyclohexene oxide rings. Though there are four possible isomers in a cyclohexene oxide derivative, the quantum chemical calculation indicates that the equatorial substitutions (isomers 2 and

3 in *Figure 7*) are more stable than the axial substitutions (isomers 1 and 4). The composition of the isomers was determined by using the relative integral intensities of the ^{1}H n.m.r. signals. We conclude that ERL4221 possessed four isomers whose composition ratio is AC:AD:BC:BD = 14:34:16:36, while ERL4299 had three isomers whose composition ratio is AA:AB:BB = 27:50:23.

REFERENCES

1 Fleming, W. W. *J. Appl. Polym. Sci.* 1985, **30**, 2853
2 Sojka, S. A. and Moniz, W. B. *J. Appl. Polym. Sci.* 1976, **20**, 1977
3 Poranski, C. F., Moniz, W. B., Birkle, D. L., Kopfle, J. T. and Sojka, S. A. NRL Report, June 22 1977, Naval Research Laboratory, Washington, D.C., p. 8092
4 Grenier-Loustalot, M.-F. and Grenier, P. *J. Polym. Sci., Polym. Chem. Edn.* 1984, **22**, 4011
5 Herring, F. G. and Jagannathan, N. R. *J. Polym. Sci., Polym. Chem. Edn.* 1985, **23**, 1649
6 Jagannathan, N. R. and Herring, F. G. *Polymer* 1986, **27**, 1493
7 Jagannathan, N. R. and Herring, F. G. *J. Polym. Sci. A Polym. Chem.* 1987, **25**, 897
8 Pappas, S. P. (Ed.) 'US Curing: Science and Technology', Technology Marketing Corp., CT, USA, 1980
9 Ottar, B. *Acta Chem. Scand.* 1947, **1**, 283
10 Breitmaier, E. and Voelter, W. 'Carbon-13 NMR Spectroscopy', VCH Publishers, New York, 1987
11 Kemp, W. 'NMR in Chemistry', Macmillan, London, 1986
12 Onal, A. M., Usanmaz, A., Akbulut, U. and Toppare, L. *Br. Polym. J.* 1983, **15**, 183
13 Doddrell, D. M., Pegg, D. T. and Bendell, M. R. *J. Magn. Reson.* 1982, **48**, 323
14 Doddrell, D. M., Pegg, D. T. and Bendell, M. R. *J. Chem. Phys.* 1982, **77**, 2745
15 Bax, A., Freeman, R. and Kempsell, S. P. *J. Am. Chem. Soc.* 1980, **102**, 4851
16 Bodenhausen, G., Kogler, H. and Ernst, R. R. *J. Magn. Reson.* 1984, **58**, 370
17 Aue, W. P., Bartholdi, E. and Ernst, R. R. *J. Chem. Phys.* 1976, **64**, 2229
18 Bax, A. and Morris, G. *J. Magn. Reson.* 1981, **42**, 501
19 Morrison, R. T. and Boyd, R. N. 'Organic Chemistry', 4th Edn, Allyn and Bacon, Inc., Newton, MA, USA, 1983
20 Dewar, M. J. S. and Thiel, W. *J. Am. Chem. Soc.* 1977, **99**, 4899
21 Batzer, H. *Chem. Ind.* 1964, **2**, 1