Conformational analysis of amine-cured epoxy resins

R. Lovell* and A. H. Windle
Department of Materials Science and Metallurgy, University of Cambridge, Pembroke Street, Cambridge CB2 3QZ, UK

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Analysis using molecular mechanics has been performed on the six-bond aliphatic link segment formed when diglycidyl ether of bisphenol-A (DGEBA) is cured with aromatic amines. It is found to have restricted conformational freedom owing to coulombic repulsion between oxygen and nitrogen atoms. Hence the segment can be approximated by a virtual bond about 9.5 Å long. The study of the local network structure is therefore simplified.

(Keywords: molecular mechanics; conformation; epoxy resin; conformational analysis)

INTRODUCTION

The local structure of highly crosslinked networks such as cured epoxies is still poorly characterized. In contrast, the chemical reactions of network formation are quite well understood[1,2] so that the predominant chemical structures are not in doubt. We report conformational analysis using molecular mechanics for a typical chemical structure found in aromatic amine cured epoxy resins.

Figure 1 shows the chemical reactions between an aromatic primary amine and an epoxy resin, such as diglycidyl ether of bisphenol-A (DGEBA). An etherification reaction can also occur (particularly at temperatures above 100°C) between unreacted epoxy and the hydroxyls formed earlier, but this is not important for stoichiometric mixtures[3].

Conformational analysis has already been reported for the diphenyl linkages found in DGEBA and in curing agents such as diaminodiphenylmethane (DDM) and diamino diphenyl sulphone (DDS) (for a review see ref. 4). The present work concerns the link segment shown in *Figures 1* and *2* which is an important component of all aromatic amine cured DGEBA.

EARLIER CONFORMATIONAL ANALYSIS

The most important conformational variables in the link segment are the rotations about the chain bonds (ϕ_1 to ϕ_5) and the rotation of the phenyl (ϕ_6) as shown in *Figure 2*. Note that the rotations are defined as 180° for *trans* and that ϕ_5 is defined as the angle C–C–N–CH_3 for consistency in describing the fully reacted polymer.

Banks and Ellis[5] have published work on the conformation of the epoxy link segment. They proposed that the chain takes on an all-*trans* conformation (ϕ_2 to $\phi_4 = 180°$) although they did not take account of electrostatic interactions between oxygen and nitrogen atoms which can increase the relative stability of *gauche* conformations.

Infra-red measurements by Salamatina *et al.*[6] on epoxy networks and model compounds led to the conclusion that the link segment has high flexibility which is unaffected by the formation of chemical crosslinks.

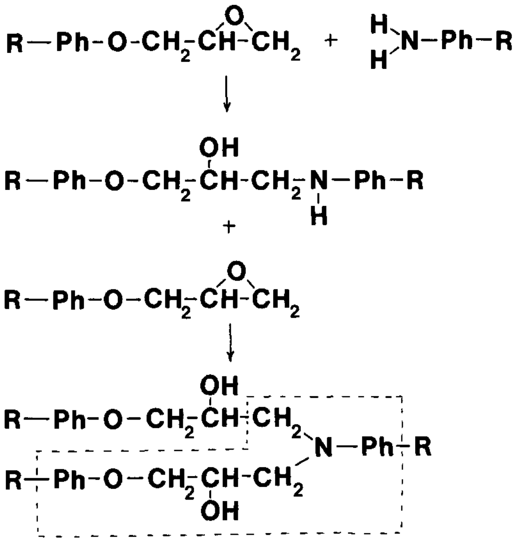

Figure 1 Chemical reactions between an aromatic primary amine and an epoxy resin such as DGEBA. These lead to chain and network formation via the link segment outlined

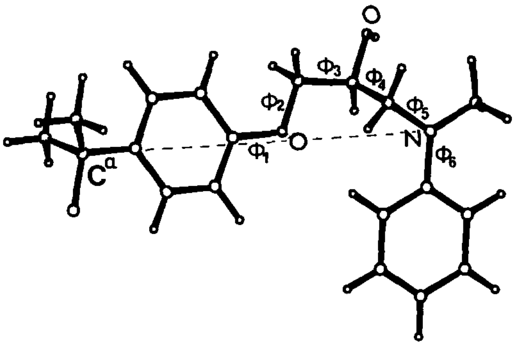

Figure 2 Minimum-energy conformation for the link segment, showing the proposed virtual bond

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* Present address: Cambridge Molecular Design, St John's Innovation Centre, Cowley Road, Cambridge CB4 4WS, UK

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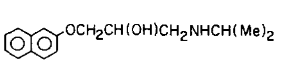
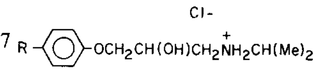
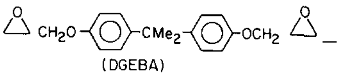
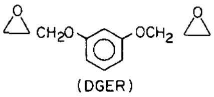
Bellenger *et al.*[7] have presented infra-red evidence for the occurrence of intrasegmental hydrogen bonding (between the -OH and the N). Such bonding would have a marked effect on the segment conformation but would be highly strained as it involves a five-membered ring. However, most evidence[1,8] is that almost all hydrogen bonds in cured epoxies are intermolecular $(\underset{|}{\mathrm{O}}\mathrm{H}\text{---}\underset{|}{\mathrm{O}}\mathrm{H})$.

RELEVANT CRYSTAL DATA

The Cambridge Structural Database* was searched for structures containing fragments of the link segment. No structure was found to contain the whole of the segment.

Tables 1 and *2* show relevant data for the six torsional angles, the ether oxygen bond angle and the shape of the tertiary aromatic amino group. The most consistent results are for the angles ϕ_1, ϕ_2 and ϕ_6.

Table 1 Torsion angles and ether oxygen bond angle (θ_{ether}) (in degrees) for crystal structures containing the ether portion of the link segment

Ref.	Structure	ϕ_1	ϕ_2	ϕ_3	θ_{ether}
26		0	178	174	118
27		13	177	−60	118
23	 (DGEBA)	−2 4	175 177	– –	117 118
24	 (DGER)	20 8	148 175	– –	119 118

For crystal structures containing Ph–O–C, the torsional angle for the Ph–O bond (ϕ_1) is generally near 0° (or 180°) so that the O–C bond is approximately co-planar with the phenyl ring. This is the conformation which gives the maximum conjugation between the π lone pair of the oxygen and the π-electrons of the phenyl[9]. Since bond 2 is consistently near *trans* (180°), the fragment Ph–O–C–C is always approximately planar. The bond angle (θ_{ether}) for the ether oxygen is always very close to 118°.

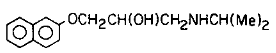
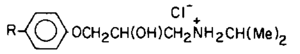
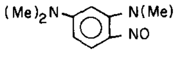
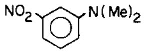
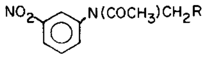
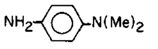
The crystal evidence for bond 3 is inconclusive, with one structure giving *trans* and the other *gauche*$^-$ (−60°) (such that the hydroxyl oxygen is *trans* to the ether oxygen). Bond 4 is usually *trans*, although in one structure it is near *gauche*, whereas bond 5 shows a wide variation in torsional angle.

For most structures containing Ph–NR_1R_2, the three bonds of the nitrogen are close to a trigonal planar arrangement (sp^2). This is shown by the angular deficit being close to zero (for the pyramidal sp^3 nitrogen found in ammonia, the angular deficit is ~40°). However, Nakai *et al.*[10] have found angular deficits of 18.6° and 19.0° in *N*,*N*-dimethyl-1,4-phenylenediamine, which they suggest may be due to hydrogen bonding. The modelling presented here adopts a planar configuration for the bonds, which is the default structure in Chem-X† for a nitrogen bonded to an sp^2 carbon. Since the torsional angle for the Ph–N bond (ϕ_6) is generally near 0°, the N–C bonds are approximately co-planar with the phenyl ring. This is the conformation which gives the maximum conjugation between the lone pair of the nitrogen and the π-electrons of the phenyl.

MODELLING METHODS

Conformational modelling of the link segment was performed using the Chem-X molecular modelling and

Table 2 Torsion angles and angular deficit at nitrogen (Δ) (in degrees) for crystal structures containing amino portion of link segment. The angular deficit is calculated by subtracting the sum of the three bond angles at the nitrogen from 360°

Ref.	Structure	ϕ_4	ϕ_5	ϕ_6	Δ
26		−173	−169	–	0
27		179	172	–	–
28		–	–	−6 14	0.2 0.6
29	$RCH_2CH_2N(C_2H_5)C_6H_5$	−68 –	131 71	10 −23	6.6
30		– –	– –	−4 7	0.7
31		– –	−11 12	−102 −93	0.8
32	$C_6H_5N(Me)CH_2CH(OH)R$	−178	−72	−20 5	4.0
10		– –	– –	2 54	18.6 19.0

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* The Cambridge Structural Database is accessed via SERC Daresbury Laboratory, Warrington WA4 4AD, UK

† Chem-X is developed and distributed by Chemical Design Ltd, Oxford, UK

graphics routines. Bond lengths and bond angles were usually assigned the fixed values shown in *Tables 3* and *4*, the main conformational variables being rotations about the six bonds shown in *Figure 2*.

Molecular mechanics energy calculations used parameters based on Allinger's MM2 force-field[11]. For rotation about bonds, there are two contributions to the energy:

1. a torsional potential of the form:
   $0.15(1+\cos 3\phi)$ for non-conjugated bonds (one or both atoms sp^3 carbons) or
   $3.5(1-\cos 2\phi)$ for conjugated bonds;
2. non-bonded interactions of the form:
   $$\frac{A}{r^{12}}-\frac{B}{r^6}+\frac{Kq_1q_2}{\varepsilon r}$$
   where $A=e_1e_2(r_1+r_2)^{12}$ and $B=2e_1e_2(r_1+r_2)^6$. Values for e and r (van der Waals radii) are shown in *Table 5*.

The first two terms of the non-bonded interaction are the Lennard–Jones 6–12 potential for the van der Waals energy and the third term is the electrostatic (coulomb) interaction. Partial charges (q_1, q_2) were assigned by the Chem-X default method which is due to Skorczyk[12]. Values for the partial charges are shown in *Table 6*. No truncation or smoothing was applied to the non-bonded potentials.

Refinement of low energy structures was performed using an optimization procedure in which all the atoms are moved until a local energy minimum is found. In this case, a further three contributions to the energy are having an effect:

1. bond stretching, $a(l-l_0)^2$;
2. bond bending, $b(\cos\theta-\cos\theta_0)^2$; and
3. out-of-plane bending for planar atoms, $1000(\cos(\gamma-90°))^2$

The parameters for these are given in *Tables 3* and *4*. The angle γ is the improper torsion angle, defined for each of three atoms bonded to a central atom as 90° minus the angle between the plane of the three atoms and the bond between each atom and the central one. No cross terms were included. The equilibrium bond lengths (l_0) tended to be smaller than the fixed values (l) used initially (particularly for C_{ar} bonded to N and O) and led to more realistic bond lengths on optimization. The equilibrium bond angle (θ_0) for the ether oxygen was unrealistic and so θ_{ether} was fixed at 118°.

The optimization used the Chem-X default method which is a quadratic gradient method.

Table 3 Fixed bond lengths (l) used in initial conformational modelling, together with bond-stretching parameters (l_0 and a) used in optimization

	C_{al}	C_{ar}	N	O	
l (Å)	1.080	1.050		0.950	H
l_0 (Å)	1.080	1.050		0.950	
a (kcal mol^{-1})	330.9	330.9		330.9	
l (Å)	1.530		1.450	1.420	C_{al}
l_0 (Å)	1.523		1.420	1.407	
a (kcal mol^{-1})	316.5		395.7	383.9	
l (Å)		1.390	1.430	1.420	C_{ar}
l_0 (Å)		1.384	1.355	1.355	
a (kcal mol^{-1})		696.6	395.7	431.6	

Table 4 Fixed bond angles (θ) used in initial conformational modelling, together with bond-bending parameters (θ_0 and b) used in optimization

	θ (°)	θ_0 (°)	b (kcal mol^{-1})
C_{al}	110	109.9	60
C_{ar}	120	120	90
N	120	120	90
O_{ether}	118	107.5	80
$O_{hydroxyl}$	108	107.5	80

Table 5 Parameters for van der Waals interactions

	e (kcal mol^{-1})	r (Å)
H	0.09	1.468
C	0.30	1.800
N	0.28	1.600
O	0.32	1.340

Table 6 Partial changes assigned to atoms by Chem-X default method (ref. 12)

H		C		N	O	
Hydroxyl	+0.63	C_{ar}–O	+0.39	−0.35	Hydroxyl	−1.02
Other	+0.08	C_{ar}–N	+0.12		Ether	−0.78
		Other C_{ar}	−0.08			
		Methyl	−0.12			
		C_{al}–O	+0.24			
		C_{al}–N	−0.04			
		C–OH	+0.31			

MODELLING RESULTS

The crystal data were used to limit the number of conformations considered by allowing only a small number of rotation states for each bond. Thus ϕ_1 and ϕ_6 were initially fixed at 0°, whereas ϕ_2, ϕ_3 and ϕ_4 were each allowed the three staggered-bond values (*trans*, *gauche*$^-$ or *gauche*$^+$). There are therefore still 27 different conformations for the three-bond unit (ϕ_2, ϕ_3, ϕ_4). Because of the chiral carbon atom between bonds 3 and 4, 'mirror image' conformations for the backbone (all ϕ_i changed to $-\phi_i$) will have slightly different energies.

As no conclusions for ϕ_5 could be drawn from the crystal data, it was decided to allow four rotation states for bond 5 (−90°, 0°, 90°, 180°). The initial study therefore calculated energies for 108 ($=1\times3\times3\times3\times4\times1$) conformations. Of these, the conformation (0°, 180°, −60°, 180°, 90°, 0°) had the lowest energy. The *gauche*$^-$ conformation found for ϕ_3 is that which gives a maximum separation between the two oxygen atoms (–O– and –OH), thus minimizing the repulsive energy between the negative charges on the atoms. No evidence was found for intrasegmental hydrogen bonding due to electrostatic interaction between the OH and either the nitrogen or the ether oxygen.

Further optimization of bond lengths, angles and torsions for the low-energy structure gave a minimum energy conformation (6°, 178°, −63°, 142°, 93°, 2°). The main change here is ϕ_4 which moves 38° away from *trans*. This is caused by a similar repulsion between negative charges on the –OH and the nitrogen. All the other torsion angles stay within 6° of the values initially set. This minimum-energy conformation is shown in *Figure 2*.

Using these results as a starting point, energy maps were then calculated for rotations about pairs of adjacent bonds. All other variables were maintained fixed in an idealized low energy conformation (0°, 180°, –60°, 150°, 90°, 0°). The maps are shown in *Figures 3* to *5* and may be thought of as two-dimensional sections through the six-dimensional energy surface about the minimum. These show that the minima occupy a very small part of conformational space and hence the link segment has low static flexibility. Bonds 2, 3 and 4 have a single minimum energy conformation (180°, –60° and 150° respectively) whereas bonds 1 and 6 each have two equivalent minima (0° and 180°). Bond 5 has two nearly equivalent minima at ±90° in both of which the plane of the nitrogen bonds is perpendicular to the plane of bonds 4 and 5.

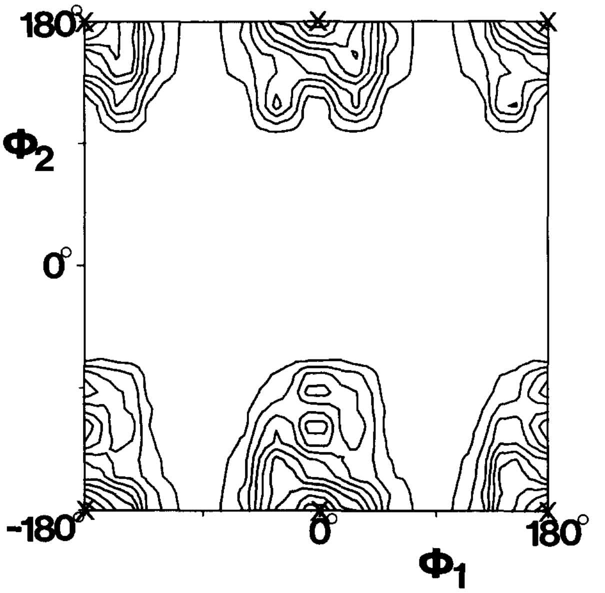

Figure 3 Conformational energy map for rotations about bonds 1 and 2. Minima are marked by crosses and contours are at 1 kcal mol^{-1} intervals above the minima

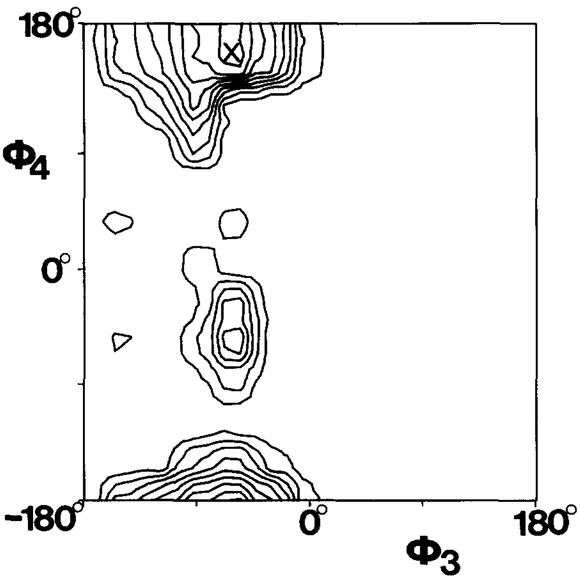

Figure 4 Conformational energy map for rotations about bonds 3 and 4

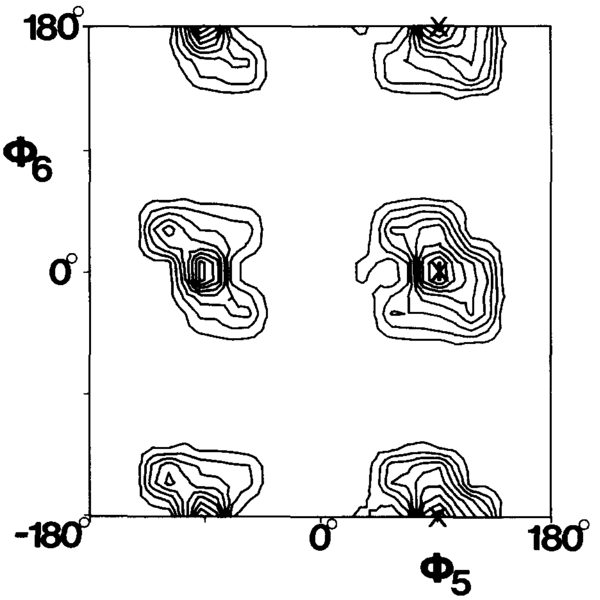

Figure 5 Conformational energy map for rotations about bonds 5 and 6

Since, in the lowest energy conformation, the rotations are all near to the minima of the torsional potentials, the sensitivity to other parameters should be low. The forms of the maps show that most features are parallel to the axes so that rotations about adjacent bonds are almost independent.

Crankshaft conformation

A *trans–cis–trans* (180°, 0°, 180°) conformation for bonds 2, 3 and 4 gives a 'crankshaft' with bonds 1 and 5 approximately co-linear (the bonds are not exactly co-linear since the bond angle at –O– is greater than at $-CH_2-$). Although this conformation is quite close to the low energy conformations, its energy is in fact about 8 kcal mol^{-1} higher than the minimum energy.

The strong β relaxation peak in cured epoxies is thought to be due to motion in the hydroxy-ether group ($-O-CH_2-CH(OH)-$)[13–16] and Pogany[17] has proposed a crankshaft mechanism involving a conformation of the *trans–cis–trans* form. However, its high energy means it is unlikely to be a common feature of the structure. Moreover, the crankshaft mechanism for chain motion in polymers has been criticized by a number of workers[18,19] who propose that a rotation about one bond is more easily relieved by small rotations about many neighbouring bonds rather than by a compensating rotation about a second bond[19].

Perhaps the main implication of the presence of the strong β peak is that an all-*trans* conformation does not predominate for the link segment, since such a conformation restricts the motion of the hydroxy-ether group, because any motion about all-*trans* would require a shortening of the chain.

Virtual bonds

The length of the segment from C^α to N depends purely on rotations about bonds 2, 3 and 4. Since these three bonds have a single minimum, this length takes on a fixed value of ~9.5 Å. Moreover, the line of C^α to N is nearly co-linear with the phenylene bonds at the DGEBA end of the segment so that even changes in ϕ_1 have quite a small effect on the relative positions of C^α and N. Hence

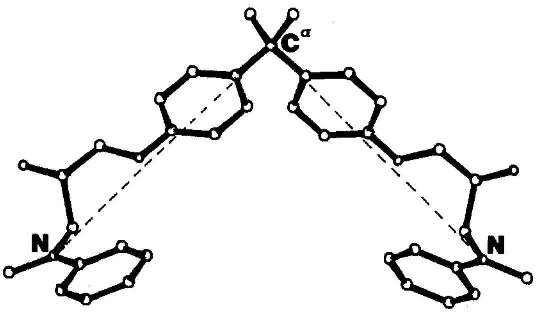

Figure 6 Structure consisting of diphenyl propane plus 2 link segments in the lowest energy conformation (hydrogen atoms omitted for clarity)

the link segment can be approximated by a virtual bond 9.5 Å long (*Figure 2*). This structurally-based proposal verifies the suggestion[20] of rigid virtual bonds to explain results of light-scattering experiments on anhydride-cured DGEBA.

Conformation in polymers

So far, we have only considered the link segment in isolation. In amine-cured DGEBA, however, the main structural repeat unit consists of two link segments (bonds 1 to 5) and one diphenyl propane (DPP) unit. This structure forms a V-shaped chain (*Figure 6*) between the nitrogen atoms which are the branch points in the network.

With the link segments acting as virtual bonds at a fixed angle of 110°, this repeat unit has an almost rigid conformation with the spacing between the branch points (nitrogens) being almost constant at ~15 Å. There is, however, some freedom of rotation about the virtual bonds. This has contributions from both components of the chain. First, the conformational energy map for the DPP unit shows an elongated minimum centred on ($\Psi = \Omega \approx 50°$) which leads to the possibility of coordinated rotation of the phenylenes with $\Psi + \Omega$ staying approximately constant ($\approx$90–100°)[21,22]. The conformation of the DPP unit can change to its mirror image by this process. Second, the two equivalent minima for each ϕ_1, (0° or 180°) lead to three distinct conformational states for the repeat unit, with rotations about the virtual bonds of: (0°, 0°), (0°, 180°) and (180°, 180°). As the link segments almost certainly act independently, about 50% of the repeat units will be in the asymmetric form (0°, 180°) with about 25% in each of the symmetric ones. (Asymmetric conformations have been found for crystalline DGEBA[23] and diglycidyl ether of resorcinol (DGER)[24].)

Once two or more link segments are being studied, the chirality of the links must be considered. Since the DPP unit can have rotation symmetry (but not mirror symmetry), the chain segment between nitrogen atoms can only be truly symmetric when both arms have the same chirality. Surprisingly, Flippen-Anderson and Gilardi[23] found that in crystalline DGEBA both arms of the molecule did have the same chirality. Although an opposite chirality gives a mirror image conformation for the link segment, the position of the nitrogen is little changed and (since the planes of the two phenyls at the ends of the link are nearly parallel in the lowest energy conformation) the relative positions of the phenyls are also little changed. The shape and dimensions of the chain segment between nitrogen atoms (branch points) is thus insensitive to differences in chirality as well as to changes in conformation.

When an amino group has reacted fully, two chain segments will meet at each nitrogen (*Figure 1*). Such close interaction means that the conformations of the two link segments (one either side of the nitrogen) will not be independent. Modelling shows that the lowest energies are when $\phi_5 = \phi'_5$, which gives local C_2 symmetry at the nitrogen (ignoring chirality).

For an isolated link segment, $\phi_5 = +90°$ gave slightly lower energy than $\phi_5 = -90°$ (about 1 kcal mol^{-1} difference). However, for two links meeting at a nitrogen, $\phi_5 = \phi'_5 = -90°$ gives slightly lower energy than $\phi_5 = \phi'_5 = +90°$.

In contrast to the chain segment centred on the DPP unit, the two low energy conformations for the chain segment centred on the nitrogen are markedly different. For $\phi_5 = +90°$ there is an angle of about 180° between virtual bonds (i.e. there is approximately a linear chain between α-carbons), whereas for $\phi_5 = -90°$ there is an angle of about 50° between virtual bonds (*Figure 7*).

SIMPLIFIED CHAINS AND NETWORKS

The results obtained so far are applicable equally to the linear polymers formed when DGEBA is cured with an aromatic monoamine such as aniline, and to the network polymers formed when it is cured with an aromatic diamine such as *m*-phenylene diamine (mPDA) or DDM.

Aromatic amine cured DGER will contain the same link segments as cured DGEBA (DGER has a *meta*-phenylene instead of a DPP unit), and infra-red measurements on cured DGER have, in fact, shown that the conformation of the link segment in the linear polymer is very similar to that in the network polymer[6].

Wide-angle X-ray scattering results[25] also provide evidence that the conformational characteristics of monoamine and diamine cured DGEBA are very similar.

Linear epoxy polymers

The basic repeat unit of these chains is the rigid V-shaped structure shown in *Figure 6*. The different conformations possible at the junction points (nitrogen atoms) impart considerable flexibility to the chain so that it might reasonably be approximated by a freely-jointed chain of such units. This implies that the distribution of distances between neighbouring DPP units would be uniform between 0 and 19 Å. In fact, the distance has only two values (19 Å or 8 Å) depending on whether ϕ_5 is +90° or −90° at the intermediate nitrogen atom

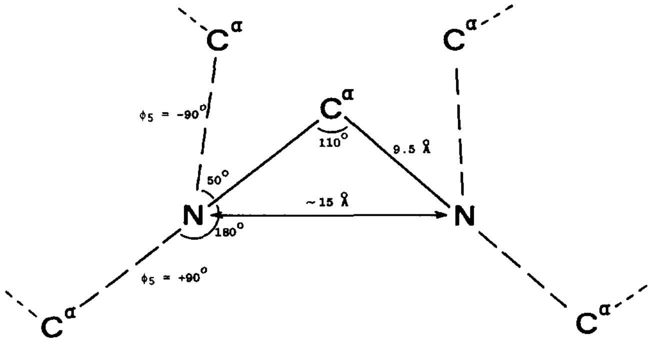

Figure 7 Structural unit of a chain of virtual bonds

(*Figure* 7). The precise nature of the aromatic monoamine should have little effect on the chain conformation.

Epoxy networks

Although epoxy networks are formed by random branching and crosslinking, the fully-cured structure formed from stoichiometric mixtures of DGEBA and diamine can be considered as a system of crosslinked linear chains[25]. These chains are chemically identical to the linear polymers and so it is not surprising if they have very similar conformations.

The links between the chains are formed by the diamine molecules, most of whose conformations have already been studied. For example, DDM and DDS (which contain Ph–CH_2–Ph and Ph–SO_2–Ph respectively) are both likely to adopt a butterfly conformation[4], although DDM should be more flexible.

The simplified virtual-bond structure for the chains means that the network structure of the fully crosslinked materials can be simplified to a network of jointed rods. However, the length of the virtual bonds implies that the mesh size of the network will be quite large and so the densely packed structure of the real materials could only be achieved by a large degree of interpenetration. Thus most neighbouring chains would not be directly bonded and would be physical neighbours rather than topological ones.

CONCLUSIONS

The aliphatic link-segment formed in aromatic amine cured DGEBA has a single minimum energy conformation where the six torsion angles take values close to 0°, 180°, −60°, 150°, 90°, 0°. This conformation is stabilized by coulombic repulsion between oxygen and nitrogen atoms.

The distance between the C^α of the DGEBA unit and the nitrogen of the amine is nearly fixed at about 9.5 Å, so that the link segment can be approximated by a virtual bond 9.5 Å long. Since these virtual bonds meet at a fixed angle of about 110° at C^α, the nitrogen-to-nitrogen distance will be almost constant at about 15 Å.

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