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Cyclic Compounds from the Reaction of Bisphenol A Diglycidyl Ether with Amines

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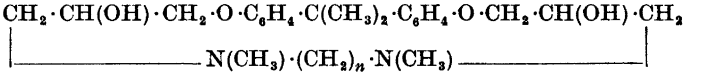
The possibility of obtaining cyclic compounds directly from the reaction of one molecule of 2,2-bis[4-(2,3-epoxypropoxy)-phenyl]-propane (=Bisphenol A diglycidyl ether) with one molecule of amine was studied.

By carrying out the reaction in highly diluted systems such cyclic compounds were obtained with the following secondary diamines: (a) 1,2-bis(methylamino)-ethane, (b) 1,3-bis(methylamino)-propane, (c) 1,4-bis(ethylamino)-butane, (d) 1,6-bis(methylamino)-hexane, (e) *trans*-1,4-bis(methylamino)-2-butene, and (f) piperazine.

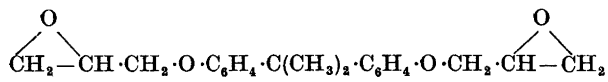
Primary monoamines and 1,2-dimethylhydrazine seemed incapable of closing the ring and even (a) gave only a relatively small yield. As the distance between the amino groups increased from the dimethylene chain in (a) to the hexamethylene chain in (d) the yield increased rapidly:



where $n \geq 2$. The cyclic compounds from (b) and from (d) were isolated in crystalline form (possibly as a mixture of the two diastereomers), the others as amorphous products.

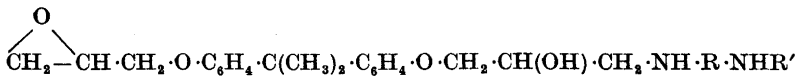
Sodium sulphide, like the primary monoamines, did not yield the simple cyclic product. However, the "dimeric" cyclic sulphide of the diglycidyl ether containing 36 ring atoms was readily obtained.

Bisphenol A diglycidyl ether (DGEBA) or 2,2-bis[4-(2,3-epoxypropoxy)-phenyl]-propane



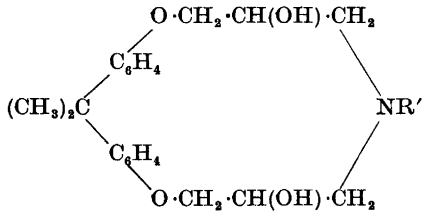
forms the lower molecular weight fraction of the commercial epoxy resins in most widespread use today. Room temperature curing of these resins is usually carried out by adding primary and secondary di- or polyamines. The

primary reaction of an amine, such as $NH_2 \cdot R \cdot NHR'$, is normally a nucleophilic attack on the terminal carbon atom of the oxiran ring giving the primary adduct

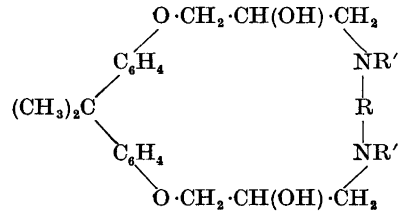


This reaction is favoured by the electron attracting effect of the phenoxy group and perhaps assisted to some extent by a neighbouring group effect of the nucleophilic ether oxygen.[1,2] Steric hindrance and a certain preference for conformations positioning the terminal carbon atom near the negative *ortho*-position of the benzene ring may reduce this activation.[3] The curing reaction then proceeds to completion with the ultimate formation of a highly cross-linked network. Surprisingly, the secondary amino groups of the main chain react at almost the same rate in this process as the primary amino groups from which they were formed.[4,5]

In the practical applications of epoxy resins the concentration of one or both reactants is normally too high to give the primary adduct much chance to cyclize before it reacts with other molecules. However, if the reactions are allowed to take place at high dilution and provided steric- and conformationally unfavourable conditions are absent one would expect a considerable fraction of cyclic product to be formed. Primary monoamines and secondary diamines would appear most promising since the corresponding cyclic products (A and B below, with two diastereomers of each), once formed, have little tendency to react further:



A



B

Molecular models indicate the presence of a certain amount of strain in a ring of type A, although it may be difficult to decide how the strain is divided on angular and torsional strain and on non-bonded interactions (overcrowding). Rings of type B appear to be strain-free. Even in the latter case, however, structural conditions may reduce the chance of a successful ring closure reaction. The purpose of the present investigation has been to establish the relative ring-closure ability of the various types of amines in this system and, more specifically, its dependence upon the distance between the nitrogen atoms in diamine, *i.e.*, the size of the group R in formula B.

The following amines have been included in this investigation: *Primary monoamines:* aniline, *p*-toluidine, 1-aminobutane, *tert*-butylamine, and 1-

aminopentane. *Primary diamines:* 1,2-diaminoethane, 1,5-diaminopentane, 1,6-diaminohexane, 1,8-diaminooctane, 1,2-diaminobenzene, 1,4-diaminobenzene, and 1,8-diaminonaphthalene. *Secondary diamines:* 1,2-dimethylhydrazine, 1,2-bis(methylamino)-ethane, 1,3-bis(methylamino)propane, 1,4-bis(ethylamino)-butane, 1,6-bis(methylamino)-hexane, *trans*-1,4-bis(methylamino)-2-butene, 1,4-bis(ethylamino)-2-butyne, and piperazine.

The DGEBA was optically inactive and no attempts were made to isolate possible diastereomers of this diepoxide or of the resulting cyclic products. Some separation of the diastereomers of DGEBA may have taken place during its purification (see Experimental part), since the least volatile fraction (about half of the total) was discarded. However, the relative amounts of the corresponding isomers of the cyclic products may still differ from those of the DGEBA since the ease with which ring-closure takes place may be different for the two DGEBA isomers.

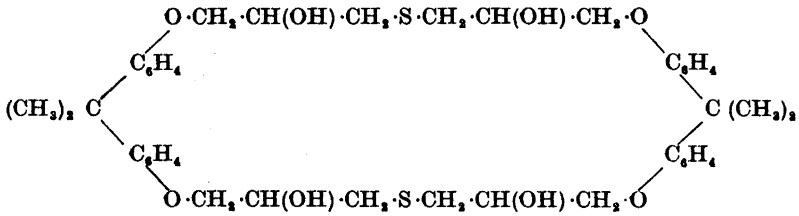
ATTEMPTS TO CYCLIZE DGEBA WITH PRIMARY AMINES AND WITH SODIUM SULPHIDE

In order to carry out the reaction with primary amines under conditions most favourable for cyclization, a high-dilution apparatus as described by Adams and Kornblum [6] was used. This was modified in order to introduce two reactants in equimolar quantities and the concentrations used were in the $0.001-0.01$ molar range.

All attempts to isolate well defined products from the reaction between DGEBA and primary aliphatic and aromatic monoamines in a series of solvents and at different temperatures (from 66°C in boiling methanol to 210°C in nitrobenzene) were negative. Thin layer chromatography revealed the presence of a large number of products which seemed to react further when isolation was attempted. Since the cyclic compound would be rather unreactive it is concluded that the tendency for cyclization is very small compared to intermolecular reactions. It was stated in the introduction that the secondary amino group of the primary adduct is quite reactive towards epoxy groups. Hence, the reasons for the reluctance to cyclization with primary monoamines are probably steric hindrance lowering the chance of a successful reaction and the insufficiency of one nitrogen atom to bridge the two epoxy groups in DGEBA to form a strain-free ring.

It was of interest in this connection to investigate the possibility of using sodium sulphide instead of the primary monoamine. Sulphides react even faster with epoxide groups than do amines [7] and cyclization should be favoured. Equivalent amounts of DGEBA and sulphide were dissolved in methanol and the solutions slowly combined in the high-dilution apparatus at 50°C. Subsequent removal of the solvent *in vacuo* gave an amorphous product from which a small fraction (about 10 %) could be extracted with ether. However, this lower molecular fraction had a molecular weight, as measured in a vapour pressure osmometer, which was very nearly twice the value expected for the simple cyclic sulphide. This was confirmed by the mass spectrum (GEC/AEI MS 902) showing the molecular ion to be $M^+ = 748$. Since the IR spectrum showed no sign of epoxide, there is little doubt that

the isolated compound is the cyclic bissulphide (one or a mixture of some of the five possible diastereomers) of formula C containing 36 ring atoms.



C

Hence, a single sulphur atom seems incapable of bridging between the DGEBA epoxy groups to form a cyclic monosulphide.

Similarly to monoamines all the primary diamines yielded mixtures of reaction products which could not be isolated because they reacted further and became partly insoluble.

CYCLIC COMPOUNDS FROM DGEBA AND SECONDARY DIAMINES

By the use of secondary diamines it should be possible to obtain the necessary bridge length and to isolate cyclic products of type B without the interference of other reactions.

In these experiments it was found quite satisfactory to simply mix the two highly diluted (0.006 molar) solutions at room temperature and then heat to 65°C under reflux in methanol for 5 – 7 days. Methanol was used as a solvent in order to take advantage of its acceleratory effect on the epoxide-amine reaction. A certain amount of methanol addition to the epoxide groups could hardly be avoided. Thus, a product in which both epoxy groups of DGEBA had reacted with methanol was readily isolated, amounting, however, to only a few percent of the total reaction product.

At the end of the reaction period the solvent was removed *in vacuo* and a small amount of the viscous mixture of products was dissolved in chloroform and used for a gas-chromatographic determination of the primary yield of the cyclic compound. The remainder was used for a chromatographic separation and isolation of the cyclic product on a silica gel column, as described in the Experimental part. The final yields of pure cyclic compound were naturally much lower than the primary yields presented in Table 1. This table also shows the experimental and theoretical molecular weights and also the melting points of two of the cyclic compounds (III and V) which were obtained in crystalline form. The elementary analyses of III and V gave carbon contents within 0.3 % and hydrogen and nitrogen contents within 2 % of the theoretical values.

The primary yields of cyclic compounds as obtained from the gas chromatogram (using flame ionization detector) of the raw reaction mixture were calculated from the area of the corresponding product peaks, compound V being

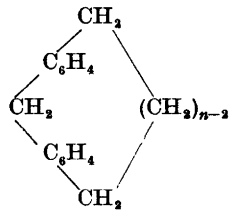
Table 1.

Cyclic product	Secondary diamine	Primary yield	Molecular weight			M.p. °C
			Vapour pressure osmometric	Mass spectroscopic	Theoretical	
I	1,2-Dimethylhydrazine	0	—	—	400	—
II	1,2-Bis(methylamino)-ethane	3	—	—	428	—
III	1,3-Bis(methylamino)-propane	10	440	442	442	135
IV	1,4-Bis(ethylamino)-butane	13	490	484	484	—
V	1,6-Bis(methylamino)-hexane	28	480	484	484	115
VI	*trans*-1,4-Bis(methylamino)-2-butene	5	463	454	454	—
VII	1,4-Bis(ethylamino)-2-butyne	<0.5	—	—	480	—
VIII	Piperazine	<1.0	—	426	426	—

used as a standard. These values should give a satisfactory measure of the relative cyclization tendencies with the different amines, and they will be discussed later in this paper.

SPECTROSCOPIC INVESTIGATIONS OF THE CYCLIC COMPOUNDS III AND V

(i) *Ultraviolet spectra.* The ultraviolet spectra (Perkin-Elmer Spectrophotometer Model 137 UV) of DGEBA and the two cyclic compounds III and V in methanol solution are shown in Fig. 1. As might have been expected, the three spectra are very similar and display also many features in common with the spectra of the corresponding [1,*n*]-paracyclophanes of Cram *et al.*[8] (formula D).



D

The spectra of [1,9]- and [1,12]-paracyclophane and of the open chain bis(4-propylphenyl)-methane for comparison are also shown in Fig. 1. The general shift towards lower frequencies as the bridge length (*n*) becomes smaller may, according to a suggestion by Cram *et al.*, be caused by an increasing trans-

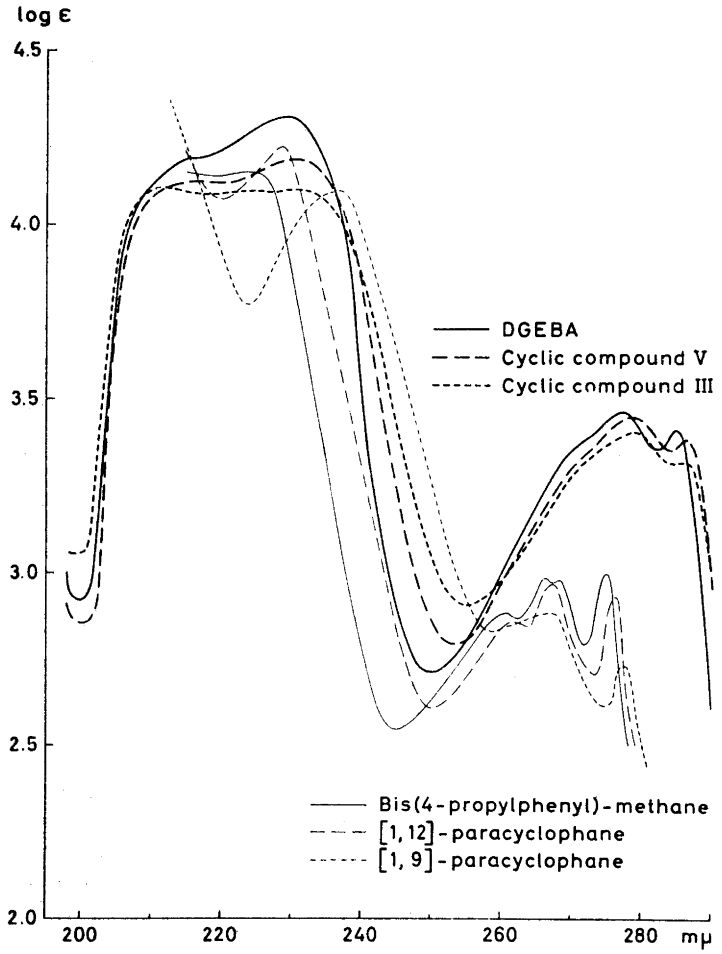


Fig. 1. Ultraviolet spectra of DGEBA and the cyclic compounds III and V and of paracyclophanes for comparison.[8]

annular coupling between the two benzene rings as they are bent closer together. The paracyclophanes were not prepared by a direct cyclization reaction but through the corresponding cyclohexane derivatives as intermediates.

The spectra of our cyclic compounds III and V also show a general shift relative to that of DGEBA, although in this case the shift is almost the same for both. This supports our previous belief that these rings are fairly strain-free.

The shift of the small, sharp peak near 280 mμ of the [1,n]-paracyclophane spectra seems to give a good indication of the amount of ring-strain present. As the length of the methylene chain increases from $n=7$, λ_{max} decreases

from 282 mμ and reaches a limiting value of $\lambda_{max} = 275$ mμ at a chain length in the $n = 10 - 12$ carbon atom range. The minimum value of n which molecular models predict for an almost strain-free ring is $n = 10$.

In our smallest cyclic compound II the number of chain atoms is 12, including the ether oxygen atoms, and no strain would be expected. The shift observed on going from our cyclic compounds to the open-chain DGEBA must therefore have a different cause. It may perhaps be due to a much greater freedom of rotation of the two benzene rings relative to each other when they are no longer locked into a cyclic structure. The different constitution may make this effect more pronounced here than with the paracyclophanes. However, a slight shift of a similar nature seems to be observable in the spectra of Cram *et al.*'s compounds also.

(ii) *Infrared spectra.* The infrared spectra (Beckman Infrared Spectrophotometer Model 5 A) of DGEBA, III, and V (all crystalline in KBr discs) served mainly to confirm the analytical finding that no remaining epoxide could be detected in the cyclic compounds. Likewise, there was no carbonyl band from a possible isomerization product of the epoxide nor any secondary amine.

(iii) *Nuclear magnetic resonance spectra.* The proton magnetic resonance spectra (60 Mc, Varian Spectrometer, Model A-60 A) of III and V and of the two amines used in their syntheses were first run in deutero-chloroform solution using TMS as internal standard.

One feature of these spectra which seems directly related to the ring structure of III and V is the 0.2 ppm upfield shift of the signals from the diamine methylene protons as they become part of the cyclic compound. This is illustrated in Fig. 2 showing the NMR spectra at 37°C in the $\delta = 0 - 5.5$ ppm range. The shift may be interpreted as a transannular shielding effect of the two benzene rings, both directing their shielding cones on the opposite ring atoms. The somewhat diffuse character of the signal from III may be a result of the presence of two diastereomers as well as a more rigid conformation in this smaller ring, leading to a difference in chemical shift of the two methylene protons and a more complex coupling pattern.

The corresponding signal from the protons of the four inner methylene groups in compound V has also become broader. This may partly be due to a difference in the transannular shielding of the various methylene protons. The main peak remains quite sharp and is probably the signal from the four protons of the two nearly identical methylene groups in the middle of the chain. The fact that it remains sharp may indicate that a high degree of flexibility is retained in the methylene chain of this larger ring structure. There is a similar shift of the *N*-methyl and *N*-methylene protons and the anisotropic shielding from the benzene rings is a plausible explanation in this case also.

The hydroxyl protons of III and V give a singlet at $\delta = 2.73$ and 3.06 ppm, respectively. Rapid exchange normally prevents these protons from coupling. However, in deuterated dimethyl sulphoxide (DMSO-d_6), hydrogen bonding reduces this exchange sufficiently to permit observation of hydroxyl proton splitting. This effect may therefore be used to decide whether the alcohol is primary or secondary,[9] *i.e.*, whether the nucleophilic attack on the epoxide group has taken place at the terminal carbon ("normal" addition) or at the

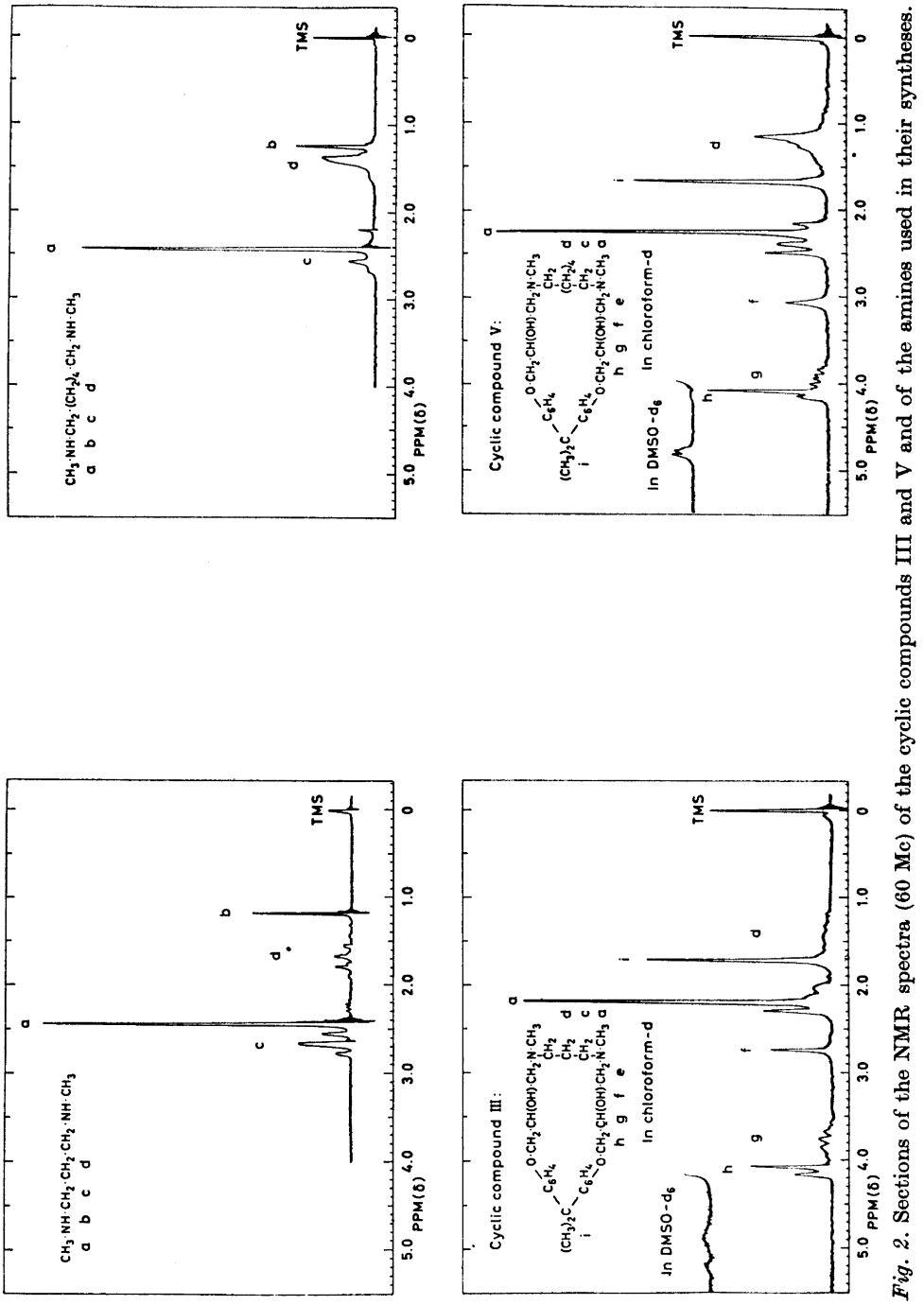


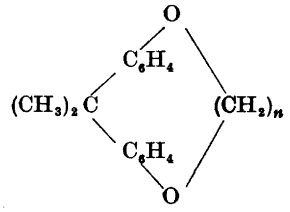
Fig. 2. Sections of the NMR spectra (60 Mc) of the cyclic compounds III and V and of the amines used in their syntheses.

other oxiran carbon atom. The spectra of III and V in DMSO-d_6 at 15°C in the $\delta = 4.0 - 5.5$ ppm region are also shown in Fig. 2. Strong hydrogen bonding has moved the hydroxyl proton signals downfield to this region. V shows a doublet at about $\delta = 4.8$ ppm with a reasonable value for the coupling constant ($J = 4$ cps) corresponding to a secondary alcohol and a "normal" addition in this case. With III the situation is not so clear. The two broad peaks at $\delta = 4.8$ and 5.2 ppm are too far apart to be a doublet. Again, stiff conformations and the presence of diastereomers leading to at least two types of hydroxyl groups may possibly explain these signals.

AMINE STRUCTURE AND THE YIELD OF CYCLIC COMPOUND

Our results illustrate clearly the effect of chain length of the amine with regard to its ability to form simple cyclic compounds with DGEBA: Monoamines (and sulphides) as well as 1,2-dimethyl hydrazine do not appear large enough to overcome the strain and/or steric hindrance involved in the formation of rings. Not until the amino groups are separated by a dimethylene chain does a small yield of cyclic product (II, Table 1) appear in the reaction mixture. The yield then increases rapidly with the length of the methylene chain within the range of compounds studied.

It is interesting to compare these results with the work of Lüttringhaus *et al.*[10] on the cyclization of Bisphenol A by means of α,ω-dihalogenated alkanes to the corresponding cyclic ethers (formula E).



E

These workers found the minimum length of the methylene chain needed to bridge the two phenolic oxygen atoms to be 7 – 8 carbon atoms. This is 2 – 3 atoms less than the minimum of 8 carbon and two nitrogen atoms needed in our compounds. A number of effects may conceivably contribute to this difference in critical chain length. One might suggest as some of the more important factors the distinctive bond angles at the epoxide group, the ability of the charged oxygen atom of the phenoxide ion to capture the electrophilic carbon atom from a somewhat larger distance, and the reduced flexibility due to the *N*-alkyl groups. Other factors may also favour the intermolecular reaction in our system, such as the neighbouring effect of the phenoxy ether oxygen and the attraction of the electrophilic epoxide carbon to the negative *ortho* position of the benzene ring. One might also speculate on the consequences of the fact that in our cyclization reaction the ends of two more or less randomly

wriggling chains must collide with each other, whereas in the other system the end of one chain must collide with the relatively fixed phenoxide oxygen atom.

Increasing chain stiffness, with its steric consequences, may be the main reason for the rapid decrease in yield on going from the tetramethylene chain of cyclic compound IV (Table 1) to the *trans*-2-butenylene chain of VI and the 2-butynylene chain of VII. The same is probably true for the differing yields of the ethylene diamine product II and the piperazine product VIII.

CALORIMETRIC MEASUREMENTS ON THE CYCLIC COMPOUNDS III AND V

The crystalline cyclic compounds III and V were run on a differential scanning calorimeter (Perkin-Elmer, Model DSC-1B) from -90 to $+150$°C. No sharp solid-solid transitions could be observed, but with compound III there were indications of a gradual transition 10–15° below the melting point overlapping the final enthalpy peak. The measured total molar heats of fusion, ΔH_f, were 4 and 9.7 kcal/mole corresponding to entropies of fusion, ΔS_f, of 10 and 25.0 cal/mole deg for III and V, respectively.

Due to the small yield of cyclic compound III in crystalline from, the corresponding values of ΔH_f and ΔS_f are not quite as accurate as those found for the cyclic compound V. However, the order of magnitude is a strong indication that the former has a fairly rigid molecular structure, while the structure of the latter is quite flexible, yielding a considerable conformational contribution to the entropy of fusion. This supports our previous conclusions.

EXPERIMENTAL

DGEBA. The DGEBA was obtained, crystalline and pure (at least constitutionally), from the commercial epoxy resin Epikote 827 (Shell Chemical Co.) by first distilling the resin twice at 0.05 mmHg (boiling range 210–240°C), discarding the first 10 % and the last 20 % in each distillation. Then the product was recrystallized from absolute alcohol by cooling to 5°C, washed and ground to a fine powder. This was washed again in ethanol, methanol, and finally in a low boiling petroleum ether fraction.

It was of particular importance to have a pure *p*-phenylene derivative in this case, since the other isomers would have a shorter distance between the glycidyl groups and presumably be more readily cyclized.

The purified DGEBA had m.p. 42–44°C and $n_D^{20}=1.5707$ in accordance with published data [11] and elemental analysis revealed 74.09 % C (theor. 74.20) and 6.97 % H (7.05). The epoxy-equivalent was determined by direct titration with HBr in glacial acetic acid using the method of Durbetaki [12] and a value of 171.6 (theor. 170.2) was found. Lassaigne test for halogen was negative. Both thin-layer chromatography on silica gel using various eluents and gas chromatography on a silicone column indicated only one single product as compared to at least seven in the raw resin. The same result was obtained by gel permeation chromatography on a poly(ethylene glycol monomethacrylate) gel prepared (K. Dragsnes and S. Ore) by pearl polymerization using *paraffinum liquidum* as the dispersion medium.

The molecular weight as measured in chloroform solution on a vapour pressure osmometer was 343 ± 4 (theor. 340) and the mass spectrometer gave no lines higher than the theoretical corresponding to the molecular ion $M^+=340$.

Secondary amines. The 1,2-dimethylhydrazine was distilled from the hydrochloride with alkali, and 1,2-bis(methylamino)-ethane (pract.), 1,3-bis(methylamino)-propane (*puriss.*), 1,4-bis(ethylamino)-butane, 1,6-bis(methylamino)-hexane (*puriss.*), *trans*-1,4-

bis(methylamino)-2-butene (*purum*), and 1,4-bis(ethylamino)-2-butyne (*purum*) were all distilled before use.

Isolation of the cyclic products. The viscous reaction product of DGEBA and the secondary diamines was treated with petroleum ether to which 20—30 % by volume of benzene had been added. The crude extract obtained was then fractionated on a silica gel column using a mixture of chloroform and methanol as eluent in a 2:1 volume ratio. The fractions were then studied by gas-chromatography using a silicone column (5 % SE30). The first fractions were always dominated by a compound shown by mass spectrometry, IR and NMR spectroscopy to be the methanol adduct in which both epoxy groups of DGEBA had reacted with methanol. The following fractions gave only one single peak in the gas-chromatogram and a preliminary determination of the molecular weight (vapour pressure osmometer) gave values corresponding to those of the cyclic compounds. In the later fractions the average molecular weight increased rapidly and they were therefore discarded.

Two of the cyclic compounds were obtained in crystalline form, *i.e.*, compounds III and V and also a trace amount of IV, by a rapid and only partial extraction of the dried fractions of the cyclic product with boiling petroleum ether (50/70°C) to which a little benzene had been added. From this solution crystalline clusters developed locally on the glass surface during 48 h at room temperature. They were further purified by crystallization from a petroleum ether (40/50°C)-methylene chloride mixture.

Neither by thin layer or paper chromatography using a number of different eluents, nor by gel permeation chromatography on the poly(ethyleneglycolmonomethacrylate) gel mentioned earlier, could any of the final products be resolved any further.

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