Polymer Bulletin 19, 269–274 (1988)

Polymer Bulletin

Spectroscopic characterization of 1,5-diphenyl-3,7-dihydroxy-1,5-diazacyclooctane – (8C ring compound) formed in N,N-diglycidylanaline/aniline curing systems

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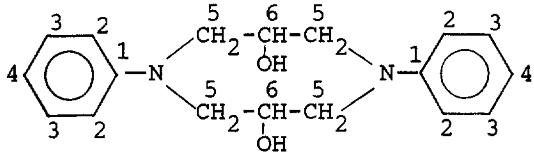
Summary

A NMR and infrared analysis of the cyclic product formed by the reaction of N,N-diglycidylaniline with aniline confirms the structure of an eight-membered ring (I). The conformational structure of this compound is discussed.

Introduction

Epoxy resins based on N,N-diglycidylamine derivatives, e.g., tetraglycidyldiaminodiphenylmethane (TGDDM), are used for preparation of high-performance epoxy composites. Polyamines are the usual curing agents. The mechanism of the reaction of N,N-diglycidylamines with amines is complicated by dependent reactivities of glycidyl groups and relatively strong cyclization, not encountered in epoxy systems based on diglycidyl ethers of Bisphenol A (DGEBA) (1-4). Some cyclic compounds were found and isolated in the model system diglycidylaniline-aniline. The main cyclic product was identified (5) as 1,5-diphenyl-3,7-dihydroxy-1,5-diazacyclooctane (I).



(I)

Arrias et al. (6) have found that the crystalline product (I) is formed from the d,l-diastereoisomer of the reaction product of N,N-diglycidylaniline and aniline whereas that from the mixture of l,l and d,d diastereoisomers remains in solution.

In this paper a spectroscopic analysis of this cyclic product is performed by means of NMR and FTIR.

Experimental

Synthesis of the cyclic product (I)

A 20% solution of equimolar mixture of DGA and aniline in toluene or xylene was heated to 135°C for nine days. Upon

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cooling the reaction product crystallized from solution. The product was then filtered off and recrystallized from hot toluene.

Analysis

Purity of the product was 98% according to GPC. Elemental composition found: 72.4% C, 7.4% H, 9.1% N (calculated for (I): 72.48% C, 7.38% H, 9.40% N).

High performance liquid chromatography (HPLC)

HPLC analyses were performed in a Waters liquid chromatograph equipped with a Wisp autoinjection instrument, a system controller solvent delivery system and interfaced with a Hewlett Packard UV diode array detector. Spectrograde CH_3CN and reagent grade H_2O were used. The experimental reversed bonded - phase HPLC conditions were as follows: concentration 2 mg/4 ml CH_3CN, injection volume 10 µl, mobile phase H_2O/CH_3CN, flow rate 1 ml/min, column 250 mm × 4.6 mm Zorbax C_8 at room temperature; UV detection at 254 nm.

Results and Discussion

Identification of 8C ring (I)

The 50 MHz ^{13}C NMR spectrum given in Fig.1 shows only six resonances: four in the aromatic region and two signals in the aliphatic region around 60 ppm. ^{13}C NMR shifts were compared with those available and predicted from literature data and are listed in Table 1. Satisfactory agreement between experimental and calculated values was obtained except for C_1 where the deviation exceeded 2 ppm.

This result definitely supports the existence of structure (I).

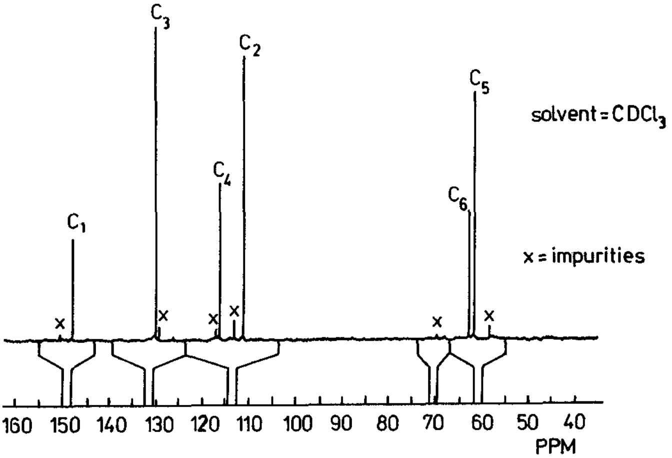


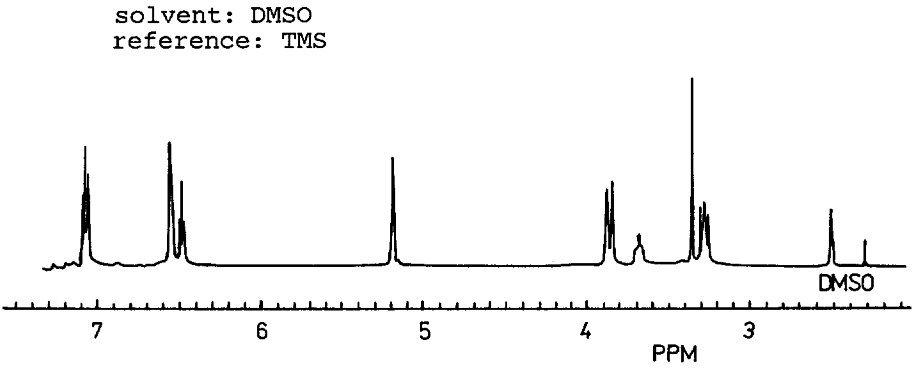
Fig. 1 ^{13}C NMR spectrum of (I) (50 MHz)

TABLE I

Comparison Between Experimental and Calculated NMR ^{13}C Chemical Shifts for (I)

	C_1	C_2	C_3	C_4	C_5	C_6
Observed ppm/TMS	147.68	111.1	129.9	116.2	61.5	62.6
Predicted ppm/TMS (7)	150.4	112.1	129.1	115.9	40-60	60-75

3 Determination of the coupling constants ^2J H_a,H_m, ^3J H_m, H_x, ^3J H_a, H_x in CH_2-CHOH systems from a first order analysis of the 500 MHz ^1H NMR AMX spectrum allows us to suggest a particularly symmetrical conformation for the product in DMSO (Fig. 2, Table 2). Only one coupling constant^{3} ^3J H_m, H_x/$^3J H'_a$,H_x could be detected (Table 2), which indicates either a value for the dihedral $H_{m,a}$-C-C-H_x angle close to 90° according to the KARPLUS theory (7) or the existence of equienergetic forms which leads to the same values of interaction constants.



irradiated spectrum

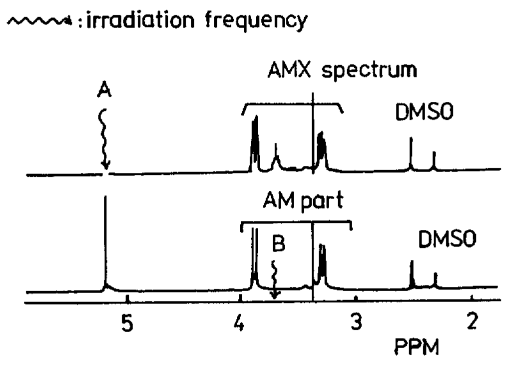


Fig. 2 500 MHz ^1H NMR spectrum of (I)

TABLE II

500 MHz ^1H NMR Chemical Shift Assignments (δ ppm/TMS)

	δppm	Nbr ^1H	Assignment
1	3.260	8	- quadruplet part of AMX type spectrum
2	3.281		
3	3.289		
4	3.310		- $\underline{CH_2}$-$\underline{CH}$- ^3J H_x, H_m = (4)-(3)=10.2 Hz
5	3.367		- singlet HOH/DMSO
6	3.667	2	
7	3.681		- triplet -$\underline{CH}$-OH
8	3.701		
9	3.853	8	- doublet - $\underline{CH_2}$-CH part of AMX type spectrum
10	3.881		
11	5.181	2	$^2JH_m,H_a \sim (9)-(10) \approx -14,6$ Hz
12	5.188		- doublet - CH-$\underline{OH}$ $^3J \approx 3.8$ Hz
13	6.470	10	Aromatic protons
14	6.484		
15	6.498		
16	6.545		
17	6.562		
18	7.056		
19	7.0705		
20	7.073		
21	7.087		

Therefore, delocalization of unpaired electrons on nitrogen may only occur if a partial combination of p/π orbitals of both nitrogen and benzene is allowed; this may arise from an sp^2 hybridization tendency of nitrogen and justifies a co-planar position of nitrogen and benzene likages. The molecule can be schematized as follows:

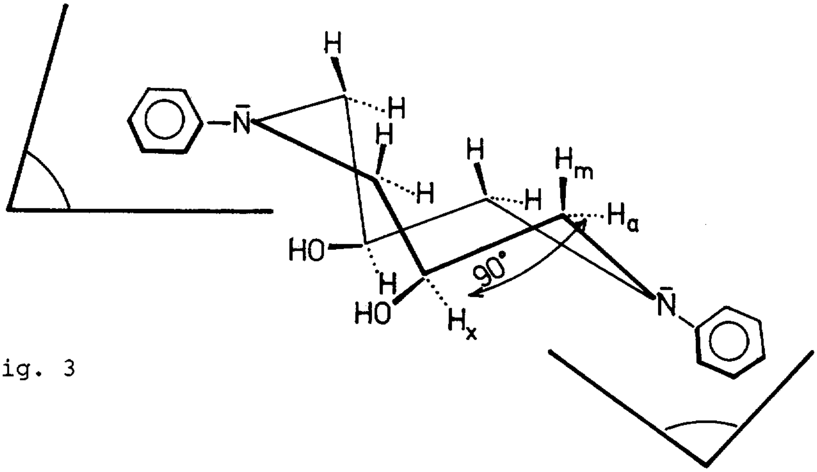


Fig. 3

The FTIR analysis was made by comparing major frequencies of (I) with those occurring in similar methylaniline compounds (8-10)(Fig.4, Table 3). While typical bands could be assigned easily, bands between 1400 and 1000 cm^{-1} are difficult to assign because of combination bands that could occur in this region.

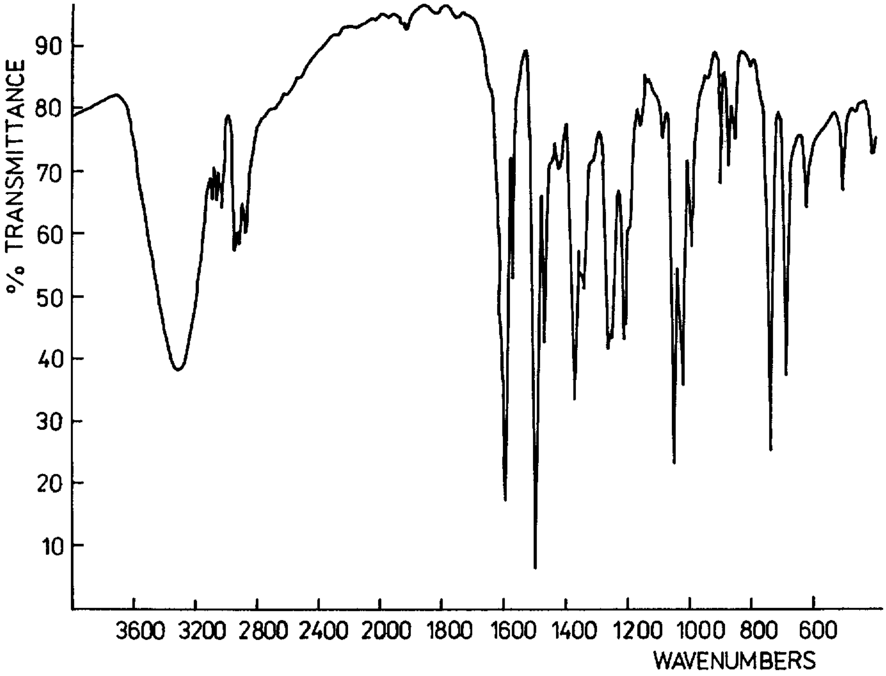


Fig. 4 FTIR spectrum of (I)

TABLE III

Major Frequencies of (I) in IR Region and Possible Assignments

cm^{-1}	Assignments
3322	νOH stretching
3094-3062 3039-3027	ν CH aromatic stretching
2950-2933 2912-2873	ν CH + CH_2 aliphatic stretching
1598-1574 1505-1473	ν C = C aromatic stretching
1450-1429	δ CH_2 aromatic bending deformation
1375	νaromatic C-N stretching
1347	δ OH in plane deformation
1266	ν CH_2-N stretching
1160-1022	δ CH in plane aromatic deformation
1054	ν C-OH alicyclic stretching
996	δ CH in plane aromatic deformation
903-877-857	δ CH_2 skeleton ring deformation
739	δ CH out of plane aromatic deformation

Such ring structures may occur in the products of reaction between tetrafunctional TGDDM and diamines and lower their crosslinking density.

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Accepted December 4, 1987 C