NATIONAL BUREAU OF STANDARDS REPORT

NBS PROJECT		NBS REPORT
311.05-11-3110561	April 28, 1971	10 578

Progress Report

on

CONFIRMATION OF THE STRUCTURE OF PREVIOUSLY REPORTED TERTIARY AROMATIC AMINE ACCELERATORS WITH MOLECULAR WEIGHTS ABOVE 400

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This investigation was supported in part by Research Grant DE02494-03 to the American Dental Association from the National Institute of Dental Research and is part of the dental research program conducted by the National Bureau of Standards in cooperation with the American Dental Association; the Dental Research Division of the United States Army Medical Research and Development Command; the Dental Sciences Division of the School of Aerospace Medicine, USAF; the National Institute of Dental Research; and the Veterans Administration.

U.S. DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS

Confirmation of the Structure of Previously Reported Tertiary Aromatic Amine Accelerators with Molecular Weights Above 400

In a previous report[1], the syntheses and accelerating abilities of a number of novel aromatic amine accelerators (Fig. 1) were presented. In this report, the confirmation of the structure of these compounds by elemental and nuclear magnetic resonance spectroscopic analyses are discussed.

ELEMENTAL ANALYSES.-The results of the elemental analyses are presented in Table 1 and are reasonably consistent with the chemical formulas shown.

In the case of PBX, the predicted elemental analysis depends on the degree of polymerization (i.e., "n"). However, "n" could not be predicted accurately from the ratio of the starting materials used, since the exact epoxy equivalent weight, the extent of fractionation due to the treatment of the product, and other factors (such as epoxide homopolymerization) were not known. Therefore, "n" was estimated from the elemental and NMR spectroscopic analyses. To estimate "n" from CHN data, the following approach was used:

> The calculated C,H,N analyses for 3,5-xylidine are 79.29% C, 9.15% H, and 11.56% N; for the diglycidyl ether of bis-phenol A, 74.09% C, 7.11% H, and 0% N. The found values for these elements were 75.7% C, 8.1% H, and 2.4% N.

These values were arranged into the following simultaneous equations:

$$79.29\,x + 74.09(1-x) = 75.7,\ \%\ C$$
$$9.15\,x + 7.11(1-x) = 8.1,\ \%\ H$$
$$11.56\,x = 2.4,\ \%\ N$$

The first equation is the carbon balance[2]; the second, the hydrogen balance; the third, the nitrogen balance; x is the weight fraction of 3,5-xylidine.

Rearranging, these equations become respectively:

$$1.61 = 5.20\,x$$
$$0.99 = 20.4\,x$$
$$2.4 = 11.56\,x$$

Since the values (Y_i) on the left-hand side of the equations contain all the experimental error and those ($Z_i x$) on the right contain none, these equations are an example of the general case, $Y_i = Z_i x$, where Y_i is the measured value and Z_i the coefficient. The least square solution for x is[3,4]:

$$x = \frac{\Sigma Y_i Z_i}{\Sigma Z_i^2} \quad .$$

Solving, x = 0.2313, the weight fraction of the 3,5-xylidine segments. Based on this value, the difference between calculated and found values for the elemental analysis is 0.5% or less. Converting to mole fractions there are about 1.183 moles bisphenol segment per mole of xylidine segment, indicating a degree of polymerization of about 5.5; i.e., n = 1/(1.183-1).

NMR SPECTROSCOPIC ANALYSES.-To confirm the structures of the synthesized amines, the proton magnetic resonance spectra of the amines in a suitable solvent were obtained using a Varian A-60 spectrometer run at 60 MHz with tetramethylsilane as the external reference*.

With the exception of the high- and low-melting BTX, each amine was analyzed once. After each spectrum was obtained, electronic integration of the spectrum to obtain the intensities of the various peaks was performed at least twice. The heights of the steps of the integration line were measured with a metric rule in centimeters.

The intensities measured from the integration lines were converted to relative intensities by assuming that the area of the benzylic methyl peak is proportional to the number of benzylic hydrogen atoms in the molecule and by multiplying each of the other intensities by the same proportionality factor. Predicted relative intensities were obtained from the structural formulas of the molecule. Assignments were based on published spectra[5].

The results of the NMR analyses are given in Table 4, based on spectra such as the one shown in Figure 2. They are consistent with the depicted structural formulas.

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* The spectra were obtained by R. A. Thompson and Dr. R. B. Johannesen of the National Bureau of Standards.

To obtain an estimate of the degree of polymerization ("n") of PBX by an independent method, calculations, similar to those used with elemental analysis data, were made using the NMR data. Thus, if R is defined as the moles of bisphenol segment per mole of 3,5-xylidine segment, and if I is the intensity for protons of a given δ, then, in theory, $I_{CH_3}* = RI_{CH_3}$, where $_{CH_3}*$ refers to the methyl groups of the bisphenol segment and $_{CH_3}$ refers to the benzylic methyl groups (on the xylidine ring).

$$I_{aliphatic} = \frac{10}{6} RI_{CH_3}$$

and

$$I_{aromatic} = \frac{8}{6} RI_{CH_3} + \frac{3}{6} I_{CH_3}$$

The coefficients were taken to be the ratio of the number of protons of a given type to that of the benzylic protons, assuming a 1:1 addition of the diglycidyl ether of bisphenol A and the amine, and also that no secondary amine was present. For example, in the last equation, $\frac{8}{6}$ is the ratio of the number of aromatic protons in the bisphenol segment to the benzylic protons; $\frac{3}{6}$ is the ratio of aromatic protons in the xylidine ring to benzylic protons. Substituting the experimental values in the above equations and solving as before, R = 1.27 moles bisphenol segment per mole of amine segment. This corresponds to a polymer with "n" about 3.7. The predicted relative intensities were calculated by using the two values of R in the above equation and six for I_{CH_3}.

The foregoing two independent estimates of "n" for the polymeric amine accelerator PBX suggest that its average value is about 4 to 5 with corresponding molecular weights of about 2,200 and 2.600, respectively.

With regard to the elemental analysis of BMX, using a similar approach, namely, the least squares method for determining the weight proportions in a combination of two materials, a good agreement (within 0.1%) between calculated and found values is obtained if the excess glycidyl methacrylate used (and remaining in the product) is assumed to have hydrated to glyceryl methacrylate. Based on the least squares method, it then constitutes 3.7% of the final product. Utilizing NMR data, the glyceryl methacrylate constitutes 2.9% of the product.

References

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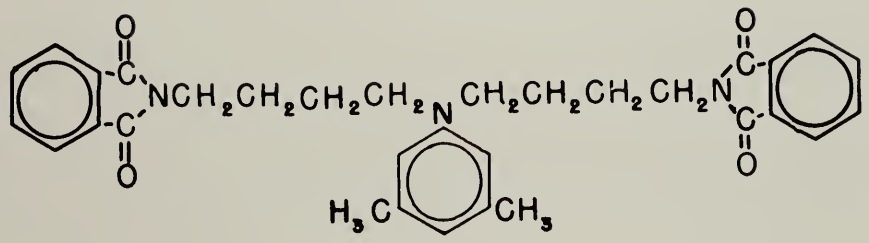
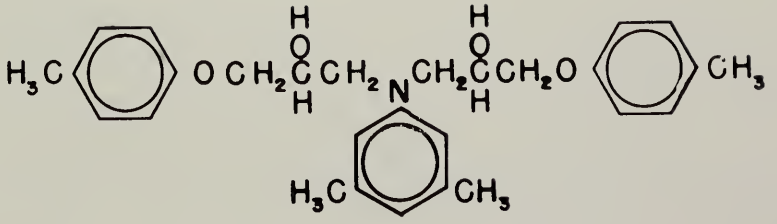
5. Bhacca, N. S., Johnson, L. F. and Shoolery, J. N. (eds): NMR Spectra Catalog, Palo Alto, California, Varian Associates, 1962.



BPX



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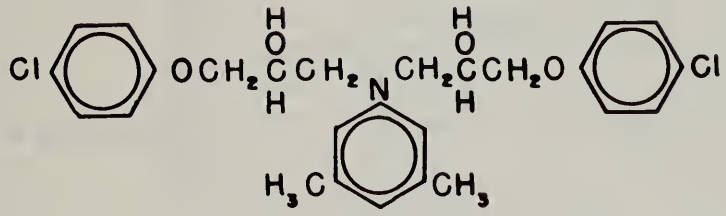

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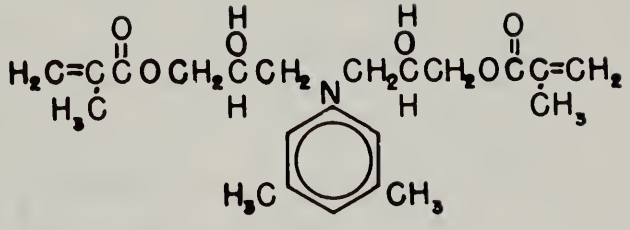
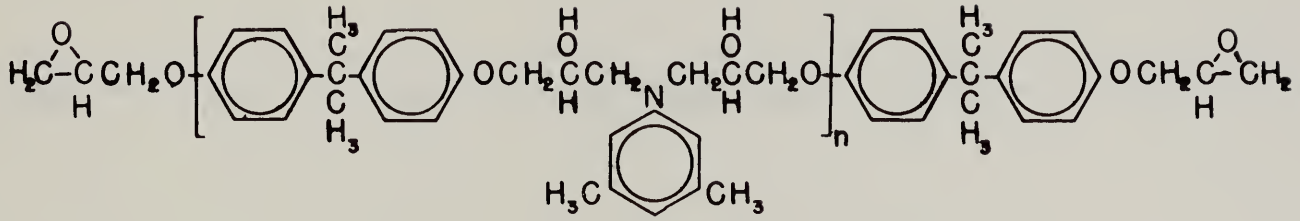


BMX



PBX

Figure 1. Structural formulas of tertiary aromatic amine accelerators synthesized in this investigation. The degree of polymerization, n, for PBX was about 4 to 5.

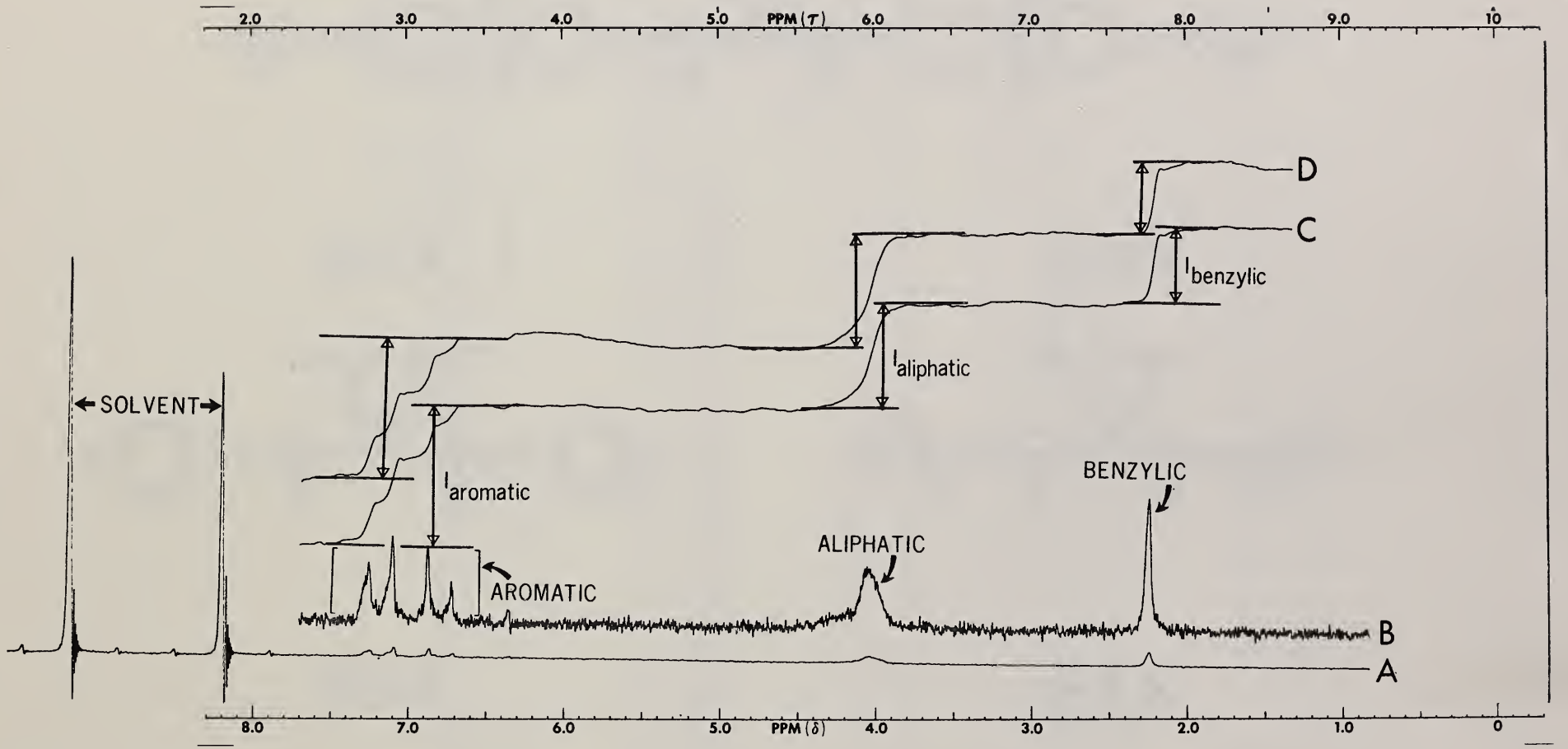

2.0
3.0
4.0
5.0
PPM (τ)
6.0
7.0
8.0
9.0
10
D
C
I benzylic
I aliphatic
SOLVENT
I aromatic
BENZYLIC
ALIPHATIC
AROMATIC
B
A
8.0
7.0
6.0
5.0
PPM (δ)
4.0
3.0
2.0
1.0
0

Figure 2

NMR spectrum of the low-melting fraction of BCX. The PPM(δ) abcissa scale corresponds to differing proton magnetic resonance peak positions. These positions are determined by the electron densities in the vicinity of the protons, and are compared with the peak position of the protons of the external reference compounds, tetramethylsilane. The latter is arbitrarily assigned with a PPM(δ) equal to zero[5] (peak not shown). A is the low-amplification spectrum showing primarily the proton peaks of the solvent (aqueous 90% formic acid). B is the high-amplification spectrum, with benzylic, aliphatic, and four aromatic proton peaks. C and D are integration plots of the spectrum, with the heights (I) proportional to the number of protons of a certain type.

TABLE 1

ELEMENTAL ANALYSIS OF TERTIARY AROMATIC AMINES

Compound	Calculated, %				Found, %			
	C	H	N	Cl	C	H	N	Cl
BPX	73.4	6.4	8.0	--	72.8	6.4	7.9	--
High melting BCX	63.7	6.0	2.9	14.5	63.6	6.0	2.9	14.5
Low-melting BCX	63.7	6.0	2.9	14.5	64.2	6.2	2.9	14.5
High-melting BTX	74.8	7.9	3.1	--	75.2	7.9	3.0	--
Low-melting BTX	74.8	7.9	3.1	--	75.1	7.9	3.2	--
BMX	65.2	7.7	3.5	--	64.7	7.8	3.3	--
PBX (n = 5.5)	75.3	7.6	2.7	--	75.7	8.1	2.4	--

TABLE 2

NMR CHEMICAL SHIFTS,* THE RELATIVE INTENSITIES FOUND AND THOSE PREDICTED†

Compound	Proton Assignment			
	Aromatic	Vinyl	Aliphatic	Methyl‡
BPX§ [5% in $CDCl_3$]	7.76 m* (7.9; 8)†		4.71 m (3.7; 4)	2.20 s (6; 6)
	6.27 s (2.8; 3)	—	3.28 m (3.5; 4)	
			1.67 m (7.5; 8)	
BCX, high melting [20% in aqueous 90% formic acid]	6.67-7.43 m (12.3; 11)	—	4.07 bs (10.1; 10)	2.31 s (6; 6)
BCX, low melting [20% in aqueous 90% formic acid]	6.70-7.40 m (11.8; 11)	—	4.07 bs (9.5; 10)	2.26 s (6; 6)
BTX, high melting [20% in aqueous 90% formic acid	6.58-7.35 m (11.2; 11)	—	3.99 s (9.6; 10)	2.25 s (6; 6)
				2.09 s (6; 6)
BTX, low melting [20% in aqueous 90% formic acid]	6.62-7.18 m (10.9; 11)	—	3.88 bd (10.5; 10)	2.12 s (6; 6)
				1.98 s (6; 6)

TABLE 2 (Continued)

Compound	Proton Assignment			
	Aromatic	Vinyl	Aliphatic	Methyl
BMX [50% in CF_3CO_2H]	7.31 s (2.6; 3)	6.25 s (1.7; 2)	4.09 bs 4.41 bs (10.5; 10)	2.41 s (6; 6)
		5.77 s (2.1; 2)		1.95 s (6.2; 6)
PBX [n = 3.7; 20% in aqueous 90% formic acid]	6.30-7.08 m (12.5; 13.9)	—	3.78 bs (13.4; 12.7)	2.00 s (6; 6)
				1.25 s (7.3; 7.

* In PPM (δ) units relative to external reference compound, tetramethylsilane. The letters after the δ values indicate the following: m, multiplet (a series of several overlapping peaks); s, singlet; bs, broad singlet, and bd, broad doublet.

† The first number in parentheses is the peak intensity found (relative to benzylic methyl protons) and the second is that predicted for a given proton based on the molecular formula.

‡ Methyl protons include aliphatic, benzylic and methacrylate.

§ Internal tetramethylsilane used as standard.