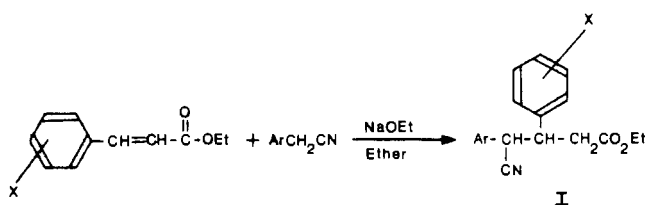


banion ArCHCN to the ethyl cinnamates as shown in the following scheme.



X	Ar
a. H	<i>p</i> -Cl-C ₆ H ₄ -
b. H	<i>p</i> -Br-C ₆ H ₄ -
c. H	<i>o</i> -F-C ₆ H ₄ -
d. H	α -naphthyl
e. <i>o,p</i> -dichloro	<i>p</i> -Cl-C ₆ H ₄ -
f. <i>o,p</i> -dichloro	α -naphthyl
g. <i>p</i> -Br	α -naphthyl
h. <i>p</i> -CH ₃	<i>p</i> -Br-C ₆ H ₄ -
i. <i>p</i> -CH ₃	<i>o</i> -F-C ₆ H ₄ -
j. <i>p</i> -CH ₃	α -naphthyl

Although a priori two diastereomers are possible, the condensation under these conditions proceeded with the formation of only one single isomer. The structure of the reaction products was deduced from their spectral data as well as their elemental analysis. The infrared spectral data showed an absorption band at 2240 cm⁻¹ which corresponds to the cyano group, and the band at 1730 cm⁻¹ was characteristic of the ester carbonyl stretching frequency (5). The proton nuclear magnetic resonance spectral data (Table I) gave evidence for the structure of the ethyl β,γ -diaryl- γ -cyanobutyrate. The carboxy group appeared as triplet and quartet δ 1.15 and 4.08 integrating for three and two protons, respectively. A

doublet at 4.36 integrating for one proton was attributed to the γ -methine proton. The β -methine proton appeared as multiplet at 3.45. This high degree of spin-spin splitting is expected due to the presence of the two diastereomeric protons at the α -carbon (δ). Another doublet at 2.82 integrating for two protons corresponding to the α -methylene protons was observed. The aromatic protons appeared as multiplet at 7.20. The mass spectroscopy of these compounds showed exact molecular ion peaks M⁺ and the elemental analysis of these compounds was in good agreement with the theoretical values.

Registry No. Ia, 100899-37-4; Ib, 100899-38-5; Ic, 100899-39-6; Id, 17532-78-4; Ie, 100899-40-9; If, 100909-01-1; Ig, 100899-41-0; Ih, 100899-42-1; Ii, 100899-43-2; Ij, 100899-44-3; *p*-ClC₆H₄CH₂CN, 623-03-0; *p*-BrC₆H₄CH₂CN, 623-00-7; *o*-FC₆H₄CH₂CN, 394-47-8; PhCH=CHCOOEt, 103-36-6; *p*-BrC₆H₄CH=CHCOOEt, 15795-20-7; *p*-MeC₆H₄CH=CHCOOEt, 20511-20-0; 2,4-Cl₂C₆H₃CH=CHCOOEt, 1504-68-3; α -naphthylacetonitrile, 132-75-2.

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Synthesis and Spectroscopic Data of 3,3',5,5'-Tetrabromo-4,4'-diaminodiphenyldibromomethane

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3,3',5,5'-Tetrabromo-4,4'-diaminodiphenyldibromomethane has been synthesized and its spectral and thermal characteristics have been examined.

Diaminodiphenylmethane (DADPM) is widely used in the synthesis of polyamides (1) and polyurethanes (2) and as a cross-linking agent for epoxy resins (3, 4) and polyurethane elastomers (5, 6). Since bromine compounds are used to promote flame retardancy in polymers (7, 8), the bromo derivative of DADPM can act as a cross-linking agent-cum-fire retardant. Recently, tetrabromobisphenol-A has been used as such an additive in COCl-terminated polybutadiene (9).

Bromination of DADPM gives 3,3'-dibromo-4,4'-diaminodiphenylmethane (10, 11) and 3,3',5,5'-tetrabromo-4,4'-diaminodiphenylmethane (TB-DADPM) (10-13); the latter has been used as a flame retardant additive in polyamides (14) and polyurethanes (12). The synthesis of a hexabromo derivative of DADPM, which will be a more effective flame retardant because of its high bromine content, is not reported so far. In

the present communication, the synthesis, characterization, and thermal stability of 3,3',5,5'-tetrabromo-4,4'-diaminodiphenyldibromomethane (HB-DADPM) are discussed.

Experimental Section

DADPM was synthesized according to the procedure of Scalan (15). HB-DADPM was prepared as follows. To a dilute HCl solution of DADPM (500 mg) bromine entrained in N₂ at room temperature was passed until the reaction mixture begins to show charring. The solid thus obtained was thoroughly washed with water and recrystallized from benzene (yield 800 mg).

IR spectra were recorded as Nujol mull on a Perkin-Elmer 597 spectrophotometer. ¹H NMR spectra were recorded on a 60-MHz Varian T-60 spectrometer at ambient temperature in Me₂SO-*d*₆ containing Me₄Si as internal standard; ¹³C NMR spectra were recorded on a Bruker WH-270 FT spectrometer at room temperature. The solvent Me₂SO-*d*₆ provided the required deuterium lock. The solutions (ca. 10% w/v) contained

Table I. Spectral and DTA Data of DADPM and HB-DADPM

compd	IR freq, cm^{-1}	^1H NMR, δ	^{13}C NMR		DTA		
			broad band, δ	off-reson, split. pattern	heating rate, $^{\circ}\text{C}/\text{min}$	melting temp, $^{\circ}\text{C}$	endotherm decomp temp, $^{\circ}\text{C}$
DADPM ^a	3450 (m)						
	3338 (m)	3.6 (s, 2 H)	40.20	t	5	88	248
	1630 (s)	4.6 (broad s, 4 H)	114.86	d	10	88	258
	1510 (s)		129.27	d	15	88	268
	1290 (s)	6.4–6.4 (m, $J = 8$ Hz, 8 H)	130.67	s	20	88	297
	1180 (m)		145.74	s			
	830 (m)						
HB-DADPM	3420 (m)						
	3320 (m)				5	119	202
	1630 (s)	4.6 (broad s, 4 H)	106.64	s	10	119	210
	1510 (s)	7.4 (s, 4 H)	108.0	s	15	119	216
	1290 (s)		133.42	d	20	119	222
	1180 (m)		140.76	s			
	630 (m)		142.48	s			

^aLiterature (18) IR; Literature (19) H NMR; Literature (20) ^{13}C NMR.

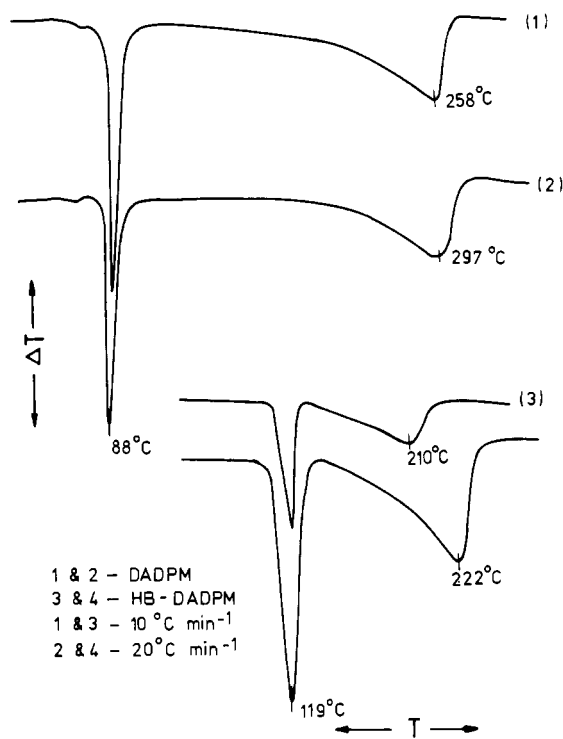


Figure 1. DTA traces of DADPM and HB-DADPM.

Me_4Si (1%) as the internal standard. Instrumental parameters are as follows: frequency of irradiation, 67.89 MHz; spectral width, 17271 Hz; pulse width, 15 μs ; pulse delay, 3 s; number of scans, 100; and number of data points, 16 K.

Differential thermal analysis (DTA) studies were carried out on a Stanton Red Croft Instrument Model 671 at various heating rates in N_2 atmosphere.

Results and Discussion

The IR, ^1H NMR, ^{13}C NMR, and DTA data are summarized in Table I. IR spectrum of DADPM shows two medium bands at 3450 and 3340 cm^{-1} for $\nu_{\text{N-H}}$ and a strong band at 1630 cm^{-1} for $\delta_{\text{N-H}}$. A strong band at 1290 cm^{-1} corresponds to $\nu_{\text{C-N}}$. A medium band at 830 cm^{-1} corresponds to the absorption of two adjacent hydrogens in the phenyl ring. There is no evidence for $-\text{OH}$ or secondary amino groups. The IR spectrum of HB-DADPM also gives a similar pattern except that the band at 830 cm^{-1} disappears and a new band around 630 cm^{-1} appears for $\nu_{\text{C-Br}}$.

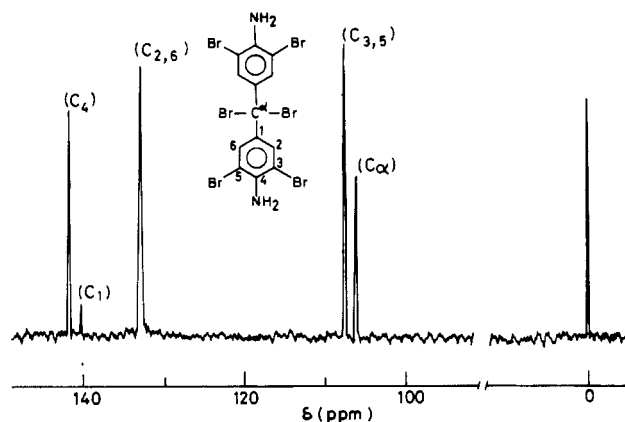


Figure 2. Broad band ^1H decoupled ^{13}C spectrum of 3,3',5,5'-tetrabromo-4,4'-diaminodiphenylmethane in $\text{Me}_2\text{SO}-d_6$.

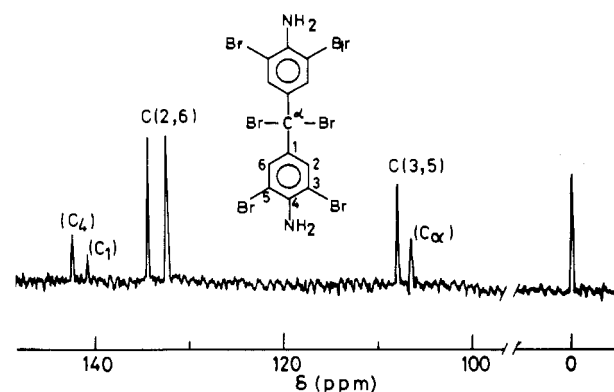


Figure 3. Off-resonance ^1H decoupled ^{13}C spectrum of 3,3',5,5'-tetrabromo-4,4'-diaminodiphenylmethane in $\text{Me}_2\text{SO}-d_6$.

^1H NMR of HB-DADPM shows a broad singlet at δ 4.5, which corresponds to the amino group. A singlet at δ 7.4 appears for aromatic protons in HB-DADPM whereas they appear as symmetrical multiplets at δ 6.7–7.1 for DADPM. Had the bromine atoms been at the 2,2' and 6,6' positions in the brominated derivative, the signal for the protons would have been slightly higher field because of the presence of the amino groups (mesomerically electron donating substituent) at 4,4' positions.

Broad band and off-resonance ^1H decoupled ^{13}C NMR spectra are given in Figures 2 and 3, respectively. The assignments were carried out by using the normal additivity parameters for the substituents into benzene and considerations of the off-resonance spectrum in conjunction with the difference

in intensity of the signal among the quaternary carbons and methine carbons.

Typical DTA traces of DADPM and HB-DADPM are shown in Figure 1. Scalan has reported the melting point (mp) of DADPM as 90–91 °C. From DTA the melting points of DADPM and HB-DADPM were found to be 88 and 119 °C, respectively. It may be seen that HB-DADPM starts degrading soon after the melting is over, while DADPM starts much later; the comparatively lower stability of HB-DADPM may be due to the production of HBr which catalyzes the degradation. TB-DADPM is also reported to decompose at its melting point (12). HBr is known to be an effective agent for the cleavage of C–C and C–H bonds in many polymers (16, 17).

Registry No. DADPM, 101-77-9; HB-DADPM, 100683-14-5.

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Correction

Low-Volatility Polar Organic Solvents for Sulfur Dioxide, Hydrogen Sulfide, and Carbonyl Sulfide. Georg H. Härtel, *J. Chem. Eng. Data* **1985**, 30, 57–61.

The following footnote should appear with the heading of the top section of Table III:

Poly(ethylene glycols) 200 and 400/SO₂ (15): $\ln S = -5.2954 + 3371.8/T$, S being milligrams of SO₂ per gram of solvent bar.

Table VII should be as follows:

Table VII. Henry Coefficient H (mbar/Mole Fraction) as a Function of Temperature and Calculated Enthalpy of Solution for the Systems Poly(ethylene glycol)/Hydrogen Sulfide

H			C	D	-ΔH _s , kJ/mol	
60 °C	80 °C	100 °C				
Poly(ethylene glycol) 200/H ₂ S						
23 958	32 904	43 728	1870	15.7	15.5	(15) ^a
21 989	33 121	44 812	2218	16.7	18.4	(this work)
Poly(ethylene glycol) 400/H ₂ S						
11 378	15 451	20 383	1811	14.7	15.1	(15) ^b
9 998	15 032	20 598	2412	16.4	20.1	(this work)

^a $\ln S = -3.7573 + 1915.0/T$. ^b $\ln S = -3.6376 + 1904.0/T$; S is the milligrams of H₂S per gram of solvent bar.