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Higher Aliphatic Aldehyde Polymers. V. Cyclic Trimers of C_9 to C_{12}, Normal Aliphatic Aldehydes

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Higher Aliphatic Aldehyde Polymers. V.* Cyclic Trimers of C_9 to C_{12} Normal Aliphatic Aldehydes

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ABSTRACT

Cyclic trimers of n-nonaldehyde (NA), n-decaldehyde (DA), n-undecaldehyde, (UA) and n-dodecaldehyde (DDA) were prepared by reacting the individual aldehydes with protic or Lewis acids. Higher aliphatic aldehydes whose long paraffinic chains dominate the general properties of these compounds do not trimerize readily the trimers, when formed, are purified with difficulty. The cyclic trimers, characterized by IR and NMR spectroscopy, are exclusively the cis isomers and commonly exist in all equatorial conformations. The melting behavior of the cyclic trimers was studied by DSC. The melting endotherms and the enthalpies of fusion increase with increasing chain length. Although the melting temperatures of the cyclic trimers are similar to the melting range of the side-chain crystallization of the corresponding crystalline isotactic polyaldehydes, the transition peaks of the trimers are single peaks and much sharper than the corresponding polymer peaks.

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*For Part IV, see Negulescu and Vogl, J. Polym. Sci. Polym. Chem. Ed., 14, 2995 (1976).

INTRODUCTION

It is well known that aliphatic aldehydes when treated with acids at room temperature form cyclic trimers [1]. This cyclization of acetaldehyde to paraldehyde has been particularly well studied [2]. The normally obtained paraldehyde is the cis isomer which exists in the equatorial conformation (eee) [3]. The trans isomer [eea] has also been synthesized, but by an indirect method [4]. The cyclic tetramer of acetaldehyde, metaldehyde, is also known and exists in the cis (eeee) form [5]; another isomer of metaldehyde with one or two trans linkages has also been reported [6].

Formaldehyde also forms a cyclic trimer and a cyclic tetramer when treated with specific acids under the proper reaction conditions. This cyclic trimer, trioxane, is used on a large scale for the preparation of polyoxymethylene. Tetraoxane, the cyclic tetramer, is more difficult to prepare, but when prepared is more reactive [7]. Trioxane is always prepared together with polyoxymethylene of low molecular weight. The ΔH value for the ring opening polymerization of trioxane is -4 kcal/mole [8], which means that it can be readily polymerized to POM. Paraldehyde is generally prepared above the ceiling temperature of acetaldehyde polymerization [9], and the polymerization of paraldehyde or any other cyclic aldehyde trimer or tetramer, other than those of formaldehyde, has never been reported, and it was assumed that the free energy of polymerization of cyclic trimers of higher aldehydes was positive [10]. Comparative data for the heat of polymerization and for the trimerization of aliphatic aldehydes, although reported, are not sufficiently reliable to draw any final conclusions on the basis of thermodynamic data [11].

As the chain length of the aldehyde increases, the trimerization becomes more difficult and, although most trimers of high aliphatic aldehydes have been prepared, few specific data are available.

During the course of our investigations on the preparation of crystalline polyaldehydes it was early recognized that acetaldehyde polymerization can only be used as a typical example of an aldehyde polymerization for aldehydes with very short chains [12]. The polymerizations of aliphatic aldehydes with slightly longer n-alkyl chains [but lower than n-octaldehyde (OA)] show a less usual behavior and were recently more critically investigated [13]. It was noted that as the alkyl chain length of the aliphatic aldehyde is increased, the polymerization of acetaldehyde becomes unsuitable as a model for the polymerization of higher aliphatic aldehydes, and more importantly, for the characteristics of the higher aliphatic aldehyde polymers [14]. As one increases the paraffinic chain length of the aldehyde, the aldehydic group becomes less important, and the side chain influences the polymerization [12].

In acetaldehyde polymerization initiated with cationic initiators, the cyclic trimer, paraldehyde, is always present. It has never been observed as an impurity in anionic aldehyde polymerization [15]. Cyclic aldehyde trimers can always be present when the polymerizations of higher aliphatic aldehydes are conducted under cationic conditions or under conditions whose anionic mechanism is not beyond question, and which may possibly go by a cationic mechanism. Trimers formed along with polymer during polymerization could cocrystallize with the polymer but might be very difficult to detect if the polymer is of low molecular weight and, in fact, could be very difficult to differentiate from the polyaldehyde, particularly when the alkyl group increases in length.

It was the purpose of this investigation to prepare the cyclic trimers of NA, DA, UA, and DDA, to characterize them spectroscopically, and most importantly to investigate the melting behavior of these compounds by careful DSC studies in order to see if the side-chain crystallization behavior, which was found earlier with polyaldehydes of shorter side-chain lengths, is indeed specific for polymers, or whether this crystallization behavior can also be observed with the cyclic trimers.

EXPERIMENTAL

Materials

The aliphatic aldehydes n-nonaldehyde (NA), n-decaldehyde (DA), n-undecaldehyde (UA), and n-dodecaldehyde (DDA) were purchased from the Aldrich Chemical Company and purified as described below.

n-Pentane, n-hexane, methanol, and sulfuric acid were obtained from the Fisher Scientific Company. n-Hexane and n-heptane were dried over molecular sieves (3 Å) prior to their use.

Antimony pentachloride ($SbCl_5$) was obtained from Matheson, Coleman and Bell and was distilled under reduced pressure (bp 82-85°C/85 Torr).

Prepurified nitrogen (99.995% minimum, Airco, Riverton, N. J.) was used in all procedures requiring N_2. Copper, glass, or butyl rubber tubing was used as a conduit for the N_2.

For the DSC investigation of the aliphatic aldehyde monomers the monomers were handled and sealed in the gold sample pans in a glove bag filled with argon (grade 5, 99.9995% minimum, Airco, Riverton, N. J.).

Purifications

All glassware, syringes, and syringe needles used for the purification or used in subsequent handling of the aldehyde were soaked for several hours in warm (ca. 60°C) 2% Micro cleaning solution (International Products Corporation, Trenton, N. J.), rinsed well with distilled water, and dried for at least 3 hr in an oven maintained at 110°C. The glassware was assembled hot and cooled under a blanket of dry N_2 or, alternatively, in a desiccator over granular P_2O_5.

When the aliphatic aldehydes were distilled, a small amount (0.1%) of N,N'-di-β-naphthyl-p-phenylenediamine was routinely added to the still pot. In all reduced-pressure distillations of aliphatic aldehydes, a magnetic stirrer was used to maintain vigorous agitation of the contents in the still pot, and a manostat was normally used to stabilize the pressure. Apiezon grease was exclusively used for the lubrication of ground-glass surfaces.

Purification Procedure

The aldehyde, taken from a freshly opened bottle, was stirred with sodium carbonate monohydrate (ca. 0.05 g/ml of aldehyde) at room temperature for 3-5 hr under a blanket of dry N_2. The stirrer was stopped and the suspension was pressure-filtered (N_2 pressure) through a coarse fritted funnel directly into a flask which was maintained under an atmosphere of N_2.

When the filtration was complete, a magnetic stirring bar and CaH_2 (ca. 0.02 g/ml of aldehyde) were placed into the flask containing the aldehyde. The flask was then closed with an adapter with stopcock, connected to a N_2 source and a mineral oil bubbler, and stirred for 1-3 hr at 0°C. The slurry was pressure-filtered, CaH_2 (ca. 0.005 g/ml of aldehyde) was added to the filtrate and the flask was mounted on a distillation apparatus which was connected to a vacuum pump. The aldehyde was distilled at reduced pressure through an 18-cm microglass Vigreux column which was wrapped well with glass fiber insulation. A multiple fraction collector was employed. Normally, a forecut amounting to 10-15% of the pot charge and a main cut of 40-60% of the pot charge were collected.

In order to minimize possible reactions of the aldehydes in the still pot and, perhaps, on the glass surfaces of the distillation apparatus, heating of the contents of the still pot was kept to a minimum practical distillation rate.

At the termination of the distillation N_2 was admitted into the still (Hg-filled check valve). The flask containing the main fraction was removed from the fraction cutter under a positive pressure of N_2 and rapidly closed with a serum stopper. The aldehyde could be stored over molecular sieves for up to 48 hr prior to its use at room temperature in the dark. Storage of the higher aliphatic aldehydes in contact with molecular sieves for a longer period of time (> 1 week) was found to cause marked visible deterioration of the aldehyde. For accurate work the aldehyde should be used immediately after distillation.

The water content of the thus purified aldehydes was estimated by GC to be less than 0.04%. The gas chromatograms of NA and DA exhibited a small peak on the generally broad tail on the high retention time side of the major aldehyde peak. This peak could have contained the acids corresponding to the aldehydes. The acid content of the NA and DA was determined to be on the order of 0.05%. The gas chromatographic analysis of UA and DDA gave a poor resolution in the higher boiling region, and no accurate estimate of this peak and the possible acid contents of the aldehydes could be made. Since the purification procedures were similar, it is expected that the residual acid content of these monomers was not sufficiently different.

Preparation of Cyclic Trimers

2,4,6-Tri-n-octyl-1,3,5-trioxane (NA cyclic trimer)

Preparation in Bulk with H_2SO_4 Catalyst. A 50-ml round-bottomed flask with a magnetic stirring bar was connected to a source of dry N_2, and once-distilled NA (24.8 g, 0.17 mole) was added via syringe under N_2. The stirrer was started and two drops of concentrated H_2SO_4 were added to the aldehyde in the flask. Over a period of 5 min the reaction mixture became warm; it was allowed to cool gradually to room temperature over a period of 40 min. The reaction mixture was then stirred at room temperature for a period of 1.5 hr, the stirrer was stopped, and the mixture was added to 65 ml of a diethyl ether-ethanol (1:2.5) mixture in a 125-ml Erlenmyer flask.

The flask was cooled in a Dry Ice-methanol mixture, and the resulting precipitate was recovered from the suspension by suction filtration, washed on the filter with the diethyl ether-ethanol mixture (two times, 50 ml), and dried in air overnight; crude yield, 14.2 g (57%). The product was twice recrystallized from a diethyl ether-ethanol mixture (20 ml/g trimer) and dried overnight at room temperature and 0.1 Torr. The recovery after two recrystallizations was 50%.

ANALYSIS. Calcd for $C_{27}H_{54}O_3$: C, 75.99%; H, 12.76%. Found: C, 75.83%; H, 12.71%. The capillary melting point was 36°C.

The infrared spectrum (KBr) showed strong absorptions in the region of 2975 to 2825 cm^{-1} (C–H stretch; CH_2 and CH_3) as well as at 1465 cm^{-1} (scissor CH_2). A moderately strong absorption, having several shoulders, was recorded at 1360 cm^{-1} (twisting, wagging). A moderately strong slightly broadened peak was recorded at 1150 cm^{-1} which was followed by a sharp peak at 1120 cm^{-1} (C–O stretch). A doublet was recorded in the region of 740-720 cm^{-1} (CH_2 rock).

The PMR spectrum ($CDCl_3$) showed a slightly distorted triplet centered at $\delta = 4.80$ (–O–CHR–O–), and a very strong absorption at $\delta = 1.30$ $(C\underline{H}_2)_n$ with a noticeable shoulder on its low frequency side at $\delta = 1.70$ (–CH–CHO). A poorly resolved multiplet near $\delta = 0.95$ ($C\underline{H}_3$–) partially overlapped the strong singlet at $\delta = 1.30$.

2,4,6-Tri-n-nonyl-1,3,5-trioxane (DA Cyclic Trimer)

Preparation in Diethyl Ether-Pentane with $SbCl_5$ Catalyst. A 50-ml three-necked round-bottomed flask containing a magnetic stirring bar and fitted with an addition funnel was assembled hot and cooled under a blanket of dry N_2. Diethyl ether-pentane (1:1) (30 ml) was added, and the flask was immersed in an ice bath, and the stirrer was started. DA (8.5 ml, 0.05 mole), distilled once, was introduced via syringe into the addition funnel. After a period of 30 min, antimony pentachloride (0.5 ml, 0.004 mole) was pipetted into the flask and the charge of decanal was then delivered to the reaction flask over a period of 1 min. Within 5 min after the deliver of the aldehyde was complete, the reaction mixture was transformed into a semisolid mass. It was suction filtered and washed with a diethyl ether-ethanol mixture (1:2.5). The solid product was dried overnight at room temperature and reduced pressure (20 Torr); yield, 6.6 g (95%).

For analysis, the trimer was twice recrystallized from a diethyl ether-ethanol mixture (1:2.5) (30 ml/g trimer), and dried for 24 hr at room temperature and 0.1 Torr. The recovery after two recrystallizations was 50%.

ANALYSIS. Calcd for $C_{30}H_{60}O_3$: C, 76.86%; H, 12.90%. Found: C, 76.79%; H, 12.89%.

The infrared spectrum (KBr) showed a series of strong absorptions in the region of 3000 to 2800 cm^{-1} (C–H stretch; CH_2 and CH_3). A strong absorption was also recorded at 1470 cm^{-1} (scissor; CH_2). A complex series of peaks was also recorded in the region of 1400 to 1200 cm^{-1} with sharp predominant peaks at 1390 and 1370 cm^{-1} (twisting, wagging). Strong absorptions were also recorded at 1160 and 1120 cm^{-1} (C–O stretch). A sharp band was recorded at 720 cm^{-1} which had a pronounced shoulder at 740 cm^{-1} (C–H rock).

The PMR spectrum ($CDCl_3$) showed a triplet at $\delta = 4.85$ (–O–CHR–O–), a strong singlet centered at $\delta = 1.25$ $([-C\underline{H}_2-]_n)$ with a shoulder on its low field side at $\delta = 1.60$ ($-C\underline{H}_2$–CHO), and an unresolved multiplet at $\delta = 0.85$ ($C\underline{H}_3$) which overlapped the strong absorption at $\delta = 1.25$.

2,4,5-Tri-n-decyl-1,3,5-trioxane (UA Cyclic Trimer)

Preparation in Diethyl Ether-pentane with $SbCl_5$ Catalyst. Into a 50-ml three-necked round-bottomed flask containing a magnetic stirring bar and fitted with an addition funnel, was added, under a blanket of dry N_2, diethyl ether (15 ml) and n-pentane (15 ml). The flask was immersed in an ice bath, the stirrer was started, and freshly distilled UA (8 ml, 0.04 mole) was introduced into the addition funnel. After 30 min, $SbCl_5$ (0.5 ml, 0.004 mole) was pipetted into the flask and the aldehyde was slowly delivered. Within 5 min the reaction mixture was transformed into an essentially solid mass which was stored overnight in the freezer (-15°C). The mixture was diluted with 10 ml of pentane (which contained some pyridine to neutralize the acid catalyst) and pressure filtered. The product was washed in the funnel with chilled ethanol (three times, 20 ml), dried on the funnel for 1 hr, and transferred to a 125-ml Erlenmyer flask. The crude yield was 6.3 g (95%). The compound was recrystallized from $CHCl_3$ and acetone and washed with cold acetone, dried overnight at room temperature and reduced pressure (20 Torr); yield, 5.8 g (92%).

For analysis, the trimer was twice recrystallized from a diethyl ether-ethanol mixture (30 ml/g trimer), and was dried overnight at room temperature and 0.1 Torr. The recovery after two recrystallizations was 50%; capillary melting point, 54-57°C; literature melting point [1], 48°C.

ANALYSIS. Calcd for $C_{33}H_{66}O_3$: C, 77.58%; H, 13.02%. Found: C, 77.61%; H, 12.98%.

The infrared spectrum showed a series of strong absorptions in the region of 3000 to 2800 cm^{-1} (C–H stretch). A strong absorption was also found at 1470 cm^{-1} (scissor; CH_2) which had notable shoulders at 1460 and 1440 cm^{-1}. A complex series of absorptions was obtained in the region of 1400 to 1200 cm^{-1}. A moderately sharp band was at 720 cm^{-1}, with a shoulder at 740 cm^{-1} (C–H rock).

The PMR spectrum ($CDCl_3$) showed a triplet centered at $\delta = 4.80$ [$-O-(R)C\underline{H}-O-$]. A strong single absorption was recorded at $\delta = 1.25$ [$-(C\underline{H}_2)_x-$] which had a shoulder on its low field side at $\delta = 1.5$ ($-C\underline{H}_2-CHO-$). An unresolved multiplet was recorded centered at $\delta = 0.85$ ($C\underline{H}_3-$) which overlapped with the tail of the strong absorption at $\delta = 1.25$.

2,4,6-Tri-n-undecyl-1,3,5-trioxane (DDA Cyclic Trimer)

Preparation in Diethyl Ether-pentane with $SbCl_5$ Catalyst. Into a 50-ml three-necked round-bottomed flask containing a magnetic stirring bar, was introduced diethyl ether (15 ml) and n-pentane (15 ml) and the whole apparatus was blanketed with N_2. The flask was immersed into a cool water bath (10°C) and the stirrer was started. Freshly distilled DDA (10 ml, 0.04 mole) was then introduced. After a period of 20 min, $SbCl_5$ (0.8 ml, 0.006 mole) was pipetted into the flask. The contents of the flask became slightly cloudy. After 10 min the water bath was removed and magnetic stirring of the reaction mixture was continued for 1.5 hr. The apparatus was disconnected from the N_2 source and stored in the freezer (-15°C) for 5 days. The cold reaction mixture was suction filtered; the recovered solid was washed with a 9:1 acetone/water mixture (four times, 10 ml) and dried overnight at room temperature and reduced pressured (0.1 Torr) (1.9 g, 23%).

For analysis, the DDA trimer was twice recrystallized from a diethyl ether-ethanol mixture (1:1.5) (30 ml/g trimer), filtered, dried at room temperature overnight (0.1 Torr) and gave a product recovery after two recrystallizations of 50%; capillary mp, 60-63°C; literature melting point [1], 61.5°C.

ANALYSIS. Calcd for $C_{36}H_{72}O_3$: C, 78.19%; H, 13.12%. Found: C, 77.62%; H, 12.95%.

The infrared spectrum (KBr) showed strong absorptions in the region of 3000 to 2800 cm^{-1} (C–H stretch). A moderately strong absorption band, with several shoulders, was found at 1470 cm^{-1} (scissor; CH_2), with a much weaker band at 1360 cm^{-1} and two moderately strong absorptions at 1160 and 1120 cm^{-1} (C–O–C stretching). A band was also observed at 720 cm^{-1} which had a shoulder at 740 cm^{-1} (CH_2 rock).

The PMR spectrum ($CDCl_3$) showed a weak triplet near $\delta = 4.80$ [–O–(R)C$\underline{H}$–O–] and a strong single absorption centered at $\delta = 1.25$ $(-C\underline{H_2}-)_x$ with a small shoulder at $\delta = 1.50$ $(-C\underline{H_2}-\overset{|}{C}HO-)$. An unresolved multiplet, centered at $\delta = 0.85$ $(C\underline{H_3})$, was also present.

The inherent viscosity of a 0.5 g/dl solution of the trimer in tetralin (tetrahydronaphthalene) at 31°C was $\eta_{inh} = 0.03$ dl/g.

Measurements

Infrared spectra were recorded with either a Perkin-Elmer Model 727 or Model 283 spectrophotometer (Perkin-Elmer Corporation, Norwalk, Conn.). Liquid compounds were examined neat between NaCl plates or in solution (3-6%, in $CHCl_3$ or CCl_4). Solid compounds were examined as KBr pellets or in solution (3-6%, in $CHCl_3$ or CCl_4).

PMR spectra were recorded with either a Perkin-Elmer Model R-24 (60 MHz) or Model R-32 (90 MHz) spectrometer (Perkin-Elmer Corporation, Norwalk, Conn.). The latter instrument was equipped with both the field-frequency lock and double resonance accessories. All samples were measured as solutions of 5-20% concentration in $CDCl_3$. Chemical shifts were measured as ppm δ relative to TMS as internal standard.

CMR spectra were recorded with a Bruker Model Fourier transform NMR spectrometer. Samples were measured as solutions of 15-20% concentration in $CHCl_3$, which also served as the internal standard.

Gas chromatographic analyses (GC) were conducted with a Varian Model 1400 gas chromatograph (Varian Associates, Palo Alto, Calif.) equipped with a thermal conductivity detector. For the analysis of aldehyde monomers a 6 ft × 1/8 in. (183 × 0.318 cm) Carbowax 20M (5% on 100/120 Chromosorb W, AW, DMCS) column was employed. The column oven was operated in the temperature programmed mode. The initial and final column oven temperatures and the heating rate were varied according to the aldehyde being analyzed. All other gas chromatographic analyses were conducted isothermally by employing a 3 ft × 1/8 in. (91.4 × 0.318 cm) Porapak Q column. Helium (60 psig inlet pressure) was used as the carrier gas at a flow rate of 30 cc/min.

Thermal transitions in samples were investigated employing either a Perkin-Elmer Model DSC-1B or Model DSC-2 differential scanning calorimeter (Perkin-Elmer Corporation, Norwalk, Conn.). The temperature scale of the instrument was calibrated at the desired heating rate by adjusting the direct dial average temperature readout of the programmer to correspond with the transition temperature of cyclohexane (mp = +6°C) and indium (mp = 156°C). The suitability of the temperature calibration was judged by noting the observed transition temperature of either p-nitrotoluene (mp = 51.5°C) or naphthalene (mp = 80.2°C), or both. The calibration was judged adequate if these transitions were observed within 3°C of their reported values.

Aldehyde samples were contained in sealed volatile sample pans fabricated of gold. Prior to their use, all sample pans were washed with $CHCl_3$ and dried. Samples were placed into tare weighed sample pan assemblies, the pan were sealed and then re-weighed to determine the sample weight. All weighings were made to the nearest 0.002 mg on a Mettler Micro Gram-Atic analytical balance (Mettler Instrument Corporation, Highstown, N. J.).

The sample size, heating rate, ordinate sensitivity (mcal/sec for full scale recorder pen deflection), and recorder chart speed were varied according to the requirement and scope of the individual measurement. A heating rate of 20°C/min was most commonly employed, and the recorder chart speed was usually adjusted so that the numerical value of the chart speed (mm/min) equalled twice the numerical value of the heating rate (°C/min). All measurements were made under a 20-30 cc/min flow of dry N_2.

Peak areas were measured with a planimeter and transition enthalpies were calculated by comparing the area under the sample peak against the area under the fusion peak of a known weight of cyclohexane (7.47 cal/g), or indium (6.79 cal/g).

Elemental analyses were performed by the Microanalysis Laboratory, Office of Research Services, University of Massachusetts.

TABLE 1. Reduced Pressure Boiling Points of Higher Aliphatic Aldehydes and GC Column Conditions

			GC column oven conditions		
Aldehyde	Bp (°C)	Pressure, (Torr)	T_c (initial) (°C)	T_c (final) (°C)	Heating rate (°C/min)
n-Nonaldehyde	68-69	7.0	100	150	12
	62-63	5.0			
	40-45	1.0			
n-Decaldehyde	44-46	0.6	130	170	12
	36-40	0.2			
n-Undecaldehyde	53-55	0.6	145	195	15
	49-51	0.2			
n-Dodecaldehyde	67	0.5	160	205	15

RESULTS AND DISCUSSION

The higher aliphatic aldehydes, NA, DA, UA, and DDA were characterized after suitable conditions for their gas chromatographic analysis were developed. The melting point behavior was studied by DSC and their exact melting temperature and heats of fusion were determined. These four aldehydes were cyclotrimerized with acids; the trimers were identified by infrared and NMR spectroscopy and their melting behavior was studied by DSC.

Aliphatic aldehydes, as a class, are known to be very reactive compounds. For use in polymerization, they must be purified and used immediately because it is difficult to maintain them in pure condition. In preparation for our studies of the polymerization of NA, DA, UA, and DDA, it was found necessary, because of the high boiling points of these materials, to study carefully the purification, crystallization and characterization of these aldehydes. Furthermore, the melting behavior of these higher aliphatic aldehydes was somewhat controversial and had to be carefully determined.

The proper combination of drying agent and distillation conditions

TABLE 2. Melting Points and Heats of Fusion of Higher Aliphatic Aldehydes by DSC[a]

Aldehyde	Peak temperature (°C)	ΔH_f (± 3%)	
		cal/g	cal/mole
n-Nonaldehyde	-17	61.3	8,720
n-Decaldehyde	-3 (-5)[b]	63.8	9,970
n-Undecaldehyde	+2 (-4)[b]	66.1	11,260
n-Dodecaldehyde	+13 (11, 43)[b]	68.5	12,630
Avg. increase per $-CH_2$	-	2.4	1,300

[a] At 20°C/min; at 10°C/min, the peak temperatures were 1°C lower and heats of fusion were 6% higher.

[b] Literature data for melting point [16, 17].

made it possible to obtain higher aliphatic aldehydes of sufficient purity to be used for polymerizations. In Table 1 the boiling temperature-pressure behavior of aliphatic aldehydes is described. As it can be seen, the boiling points increase regularly and the column temperature has to be adjusted appropriately in order to have the appropriate retention time. The retention times were all on the order of 10 min and depended on various column conditions.

Of particular interest were the accurate determination of the melting behavior and the heats of fusion of these aldehydes as shown in Table 2. Some melting points, particularly that of DDA, were in question. It was necessary to use DSC sample pans of gold rather than aluminum since it was found that the aldehydes caused a pronounced darkening of aluminum sample pans. The data (Table 2) indicate that the melting points of the aliphatic aldehydes are near or below room temperature. It was demonstrated that in all cases the enthalpies (endotherms) of fusion were equal to the enthalpies of crystallization (exotherms). In a number of instances different melting points have been reported differently, particularly in the case of DDA [16]. In the early studies, it has been concluded, however, that these aldehydes were compounds which contained unknown amounts of water [17].

The heats of fusion of the aldehydes increased from 61 to 68 cal/gm for an average increase of 2.4 cal/g (or 1300 cal/mole) per CH_2 group. Knowing the position of the exact melting point of these aldehydes and their exact heat of fusion was very important to our studies of the side chain crystallization of higher aliphatic polyaldehydes, because it was believed some could have been contaminated with monomeric aldehyde having been formed by degradation during the DSC investigation. This impurity could falsify the values of transitions or might show transitions in the polymer when these actually do not exist.

Higher Aldehyde Cyclic Trimers

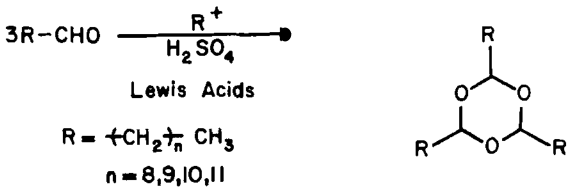
Cyclic trimers (CT) of aliphatic aldehydes from C_9 to C_{12} were prepared and characterized in order to compare their melting points and melting behavior with those of the corresponding linear polymers.

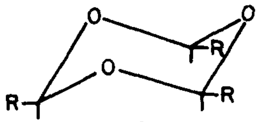
The aliphatic cyclic trimers can exist in two possible geometric isomers, the cis or the trans form. In addition, the cis form can in principle exist in two interconvertible forms; the all-equatorial (eee) form or the all-axial (aaa) form. The all-equatorial form is the form that would normally be expected at or near room temperature. The trans isomer could exist as the normal room temperature (eea) form or in the (eaa) conformation, expected in increasing amounts at higher temperatures. All known aldehyde trimers favor the (eee) form of the cis isomer, except for the trans isomers of acetaldehyde [4] and chloral trimers [18] which are synthesized by a special technique and characterized [19, 20].

Cyclic trimers of higher aliphatic aldehydes can be readily prepared by Lewis acids and particularly $SbCl_5$ but also in the presence of Bronsted acids and other acid catalysts. As the trimers are prepared, they are always in equilibrium with the corresponding monomers as long as acid is present. The monomer-trimer equilibria of some higher aldehydes have been studied recently. Heats of formation of 5-7 kcal/mole, for trimerization of acetaldehyde to paraldehyde, have been previously estimated [21].

As indicated, acids are good catalysts for the preparation of cyclic trimers of higher aliphatic aldehydes. The actual yield not only depends on the position of the monomer-trimer equilibrium which is determined by the temperature and effective catalyst and also by the heat of trimerization, but the actual yield is determined by the ease of isolation and the relative solubility of monomer and cyclic trimer. As a consequence, the yields in this paper of cyclic trimers should not be considered as the equilibrium value but as yields of pure product obtained after workup.

Two procedures were used for the preparation of the cyclic trimers. Trimerization in the presence of $SbCl_5$ gave moderate to excellent yields depending on the aldehyde. In the case of NA, trimerization with sulfuric acid gave also the trimer in good yield. Usually solvent mixtures of diethyl ether-n-pentane were used because the trimers





eee
(cis)
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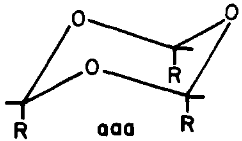
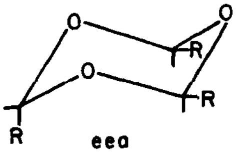
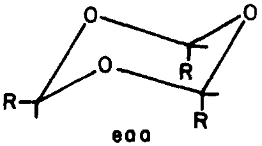


aaa
(cis)
II



eea
(trans)
III



eaa
(trans)
IV

crystallized well from these solvent mixtures. The melting temperature of NA-CT was 36°C; of DA-CT, 46°C; of UA-CT, 55°C; and of DDA, 61°C.

The infrared spectra of the four trimers were consistent with the structure of a 2,4,6-tri-n-alkyl-1,3,5-trioxane. Typical examples of IR spectra for NA-CT and UA-CT are shown in Fig. 1. The spectra of DA-CT and DDA-CT are essentially identical. In Fig. 2 the IR spectra of $CHCl_3$ solutions of aldehyde cyclic trimers are shown as exemplified by NA-CT and DDA-CT where there are strong and most predominant absorptions in the region of 2980-2820 cm^{-1}. These absorptions are invariant from one cyclic trimer to the next and were assigned to the CH absorption of methylene groups of the long aliphatic chains. Moderate to weak absorptions resulting from various CH bending modes were noticed in the region 1480-1340 cm^{-1}, the most predominant band at 1470 cm^{-1}. Moderate to strong absorptions were also found at 1150-1120 cm^{-1} which were assigned to the stretching of skeletal C–O bonds of the trisubstituted trioxane structure.

The PMR and CMR spectra also confirmed the structure of the cyclic trimers of the higher aldehydes. Figure 3 shows the 60 MHz

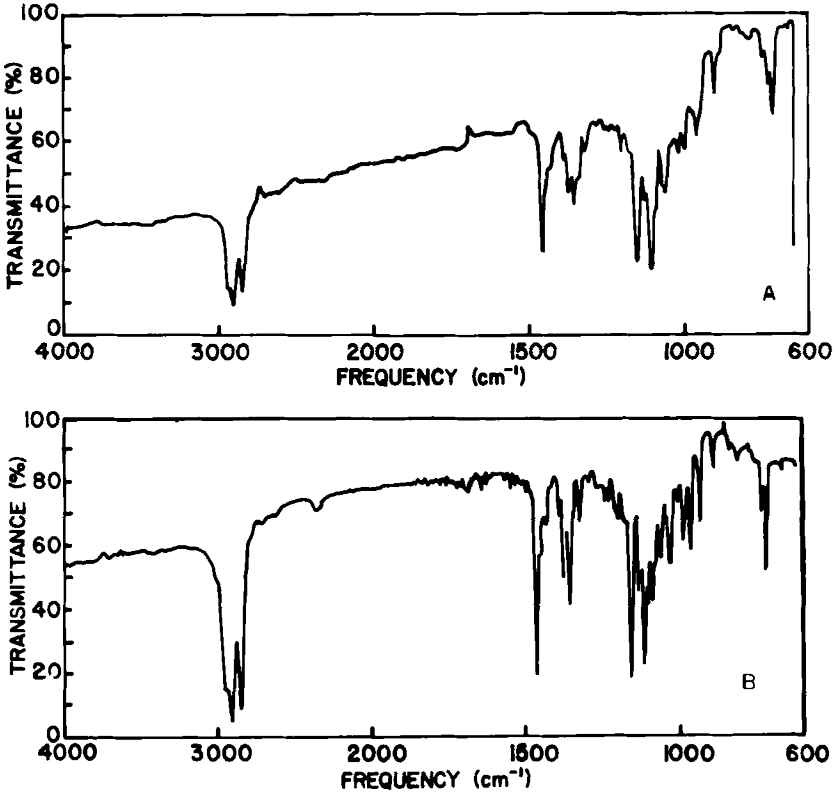


FIG. 1. Infrared spectra (KBr pellets) of aldehyde cyclic trimers: (A) NA-CT; (B) UA-CT.

PMR spectra of NA-CT and DDA-CT. The triplet in the acetal region suggests one single isomer. This becomes clearer in Fig. 4, where 90 MHz PMR spectra of NA-CT and DA-CT are presented.

The PMR spectra (90 MHz) showed as the most important resonance of the spectrum, a triplet, at 4.60-4.80 ppm which represents the acetal protons bound to the carbon atom of the trioxane ring (Fig. 5). As expected, the relative peak height decreases as the length of the alkyl group increases. A single peak was observed near 1.25 ppm assigned to the protons of the interior methylene group. A shoulder (a well separated peak at the 90 MHz spectrum) on the low field side represents the protons of the methylene group directly attached to the acetal carbon atoms of the trioxane ring. The peak

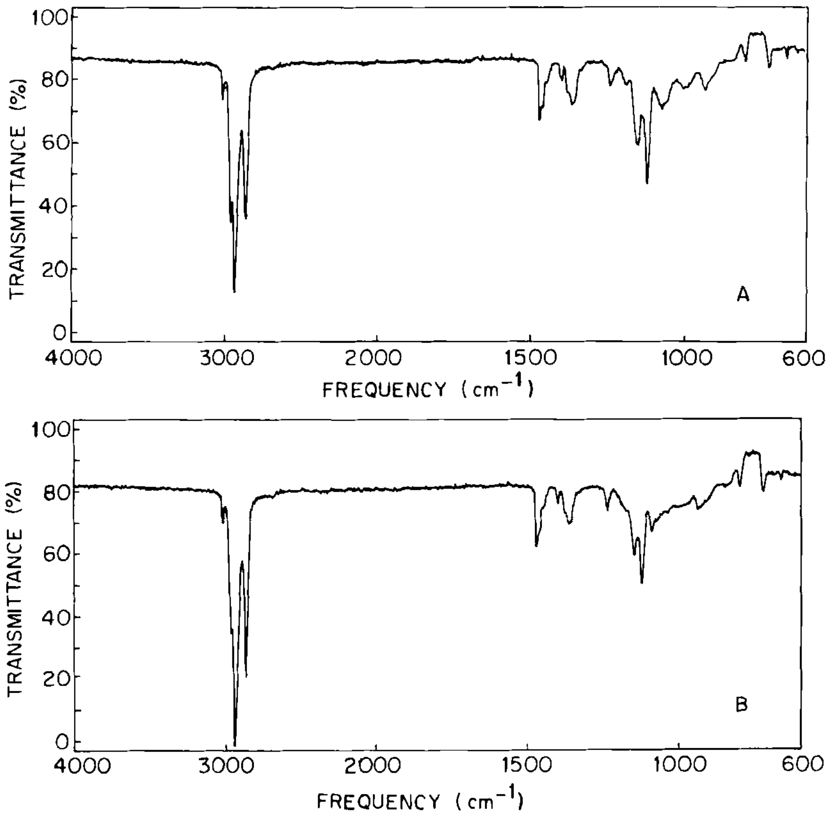


FIG. 2. Infrared spectra ($CHCl_3$ solution, matched) of aldehyde cyclic trimers: (A) NA-CT; (B) DDA-CT.

at 0.90 ppm was assigned to the terminal methyl groups of the n-alkyl group.

It was surprising that simultaneous decoupling of all acetal protons from the proton of adjacent methylene groups should have been possible, although the band width of the decoupling radiation was narrow. It was expected that partial decoupling would produce some changes in the 4.50-4.90 ppm region, if indeed both geometric isomers had been present and in significant proportions.

Results of spin-spin decoupling attempts of the DA-CT show the first-order coupling constant of J = 5.1 Hz. This value agrees well with the value of the coupling constant (J = 5.15 Hz) between the

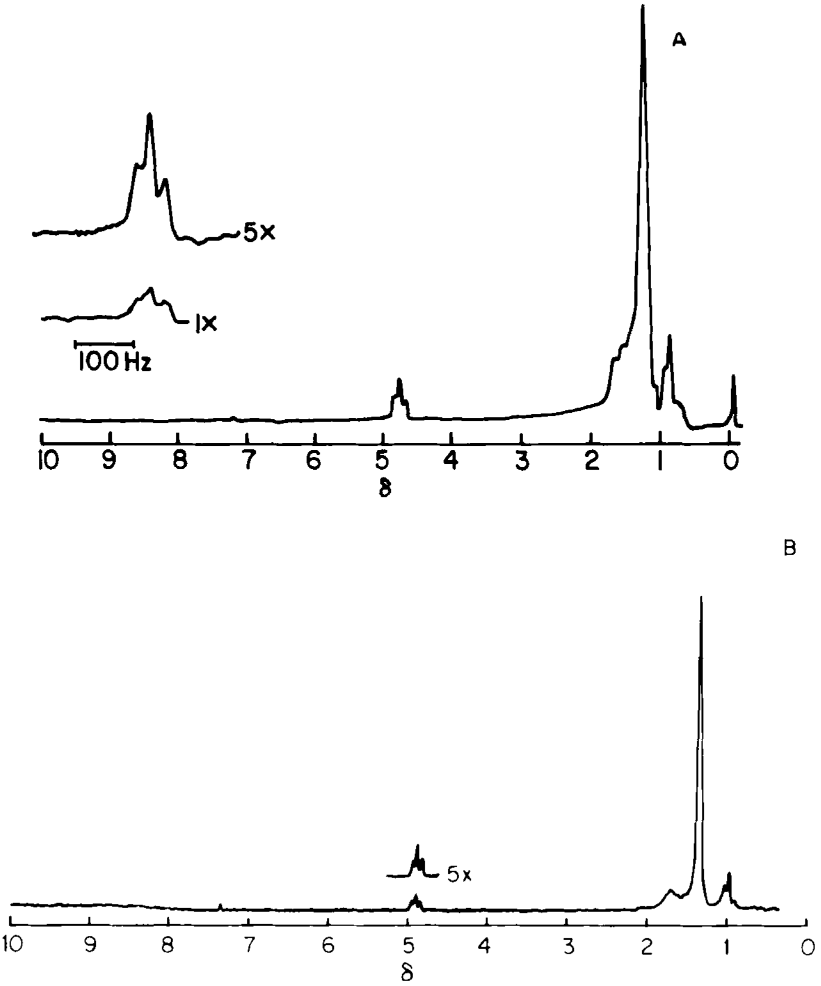


FIG. 3. PMR spectra (60 MHz) of aldehyde cyclic trimers: (A) NA-CT; (B) DDA-CT.

acetal and methylene protons of the cis cyclic trimer of propionaldehyde [2].

The CMR spectra (Fig. 6) of aldehyde cyclic trimers showed that seven carbons can be clearly distinguished with aldehydes of longer side chains. The carbon marked D then becomes the carbons for which the chemical shift values are the same.

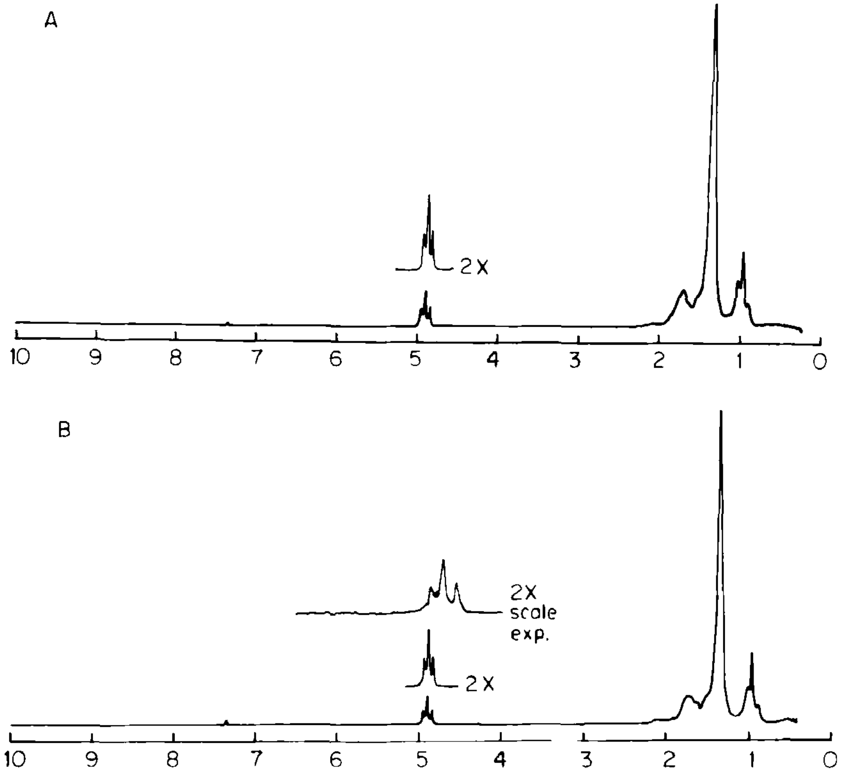


FIG. 4. PMR spectra (90 MHz) of aldehyde cyclic trimers: (A) NA-CT; (B) DA-CT.

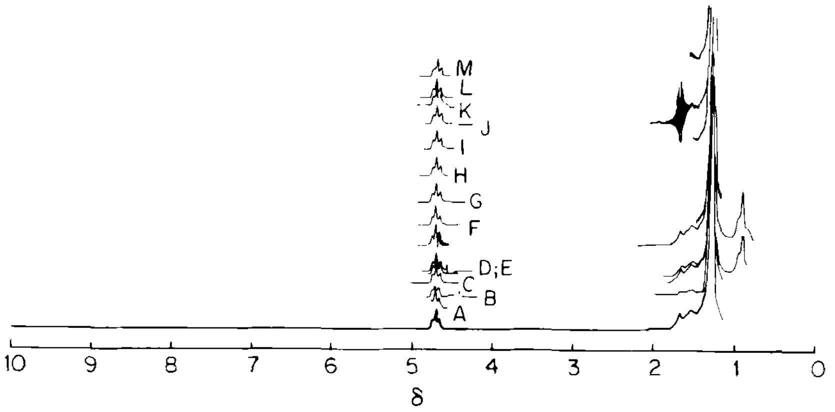


FIG. 5. PMR spectra (90 MHz) of DA cyclic trimer with spin-spin decoupling attempts. Letters indicate slight shifts in decoupling frequency near 1.7 ppm.

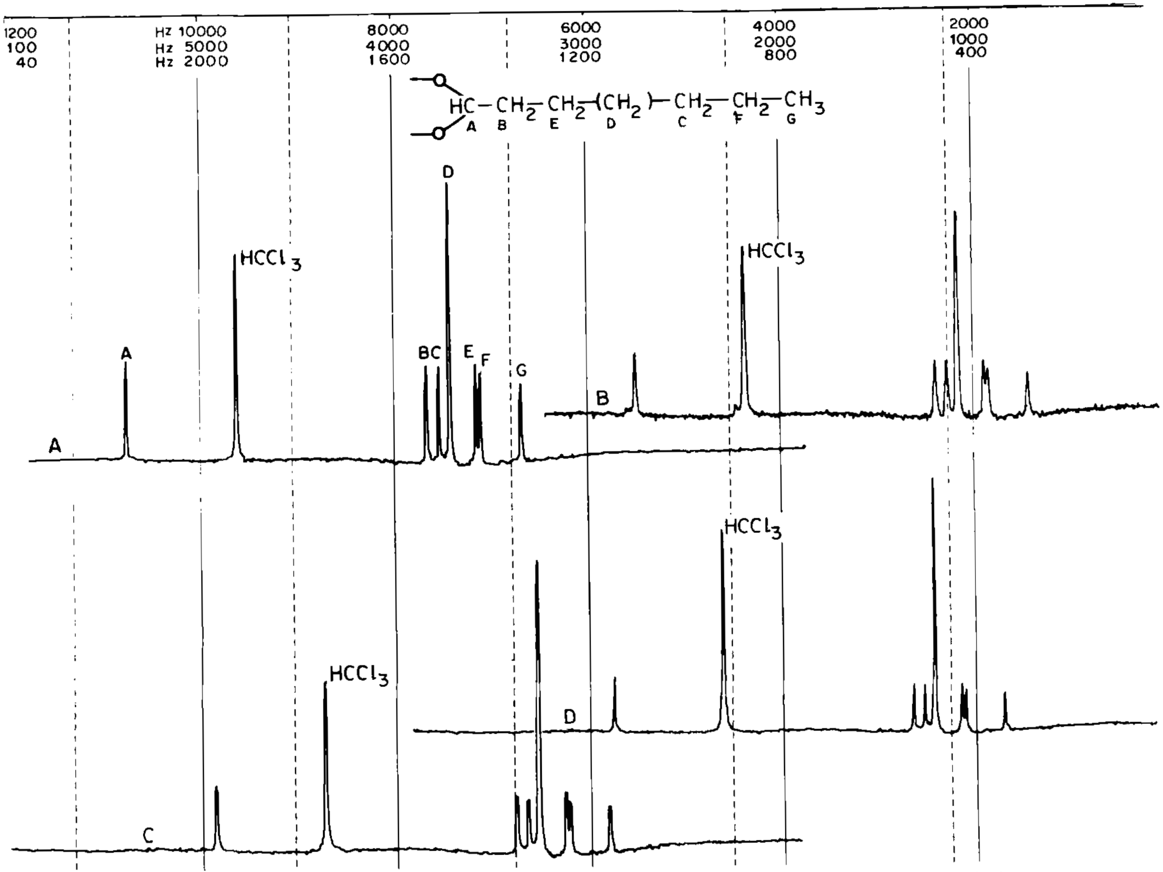


FIG. 6. CMR spectra (22.63 MHz) of aldehyde cyclic trimers: (A) NA-CT; (B) DA-CT; (C) UA-CT; (D) DDA-CT.

TABLE 3. Thermogravimetric Analysis of 2,4,6-Tri-n-alkyl-1,3,5-trioxanes (Aldehyde Cyclic Trimers)[a]

n-Alkyl group	$T_{5\%}$ (°C)[b]	T_{max} (°C)[c]
Octyl	220	276
Nonyl	219	274
Decyl	247	294
Undecyl	182	239

[a] At 20°C/min in N_2. Trimers were twice recrystallized from a diethyl ether-ethanol mixture.

[b] Temperature at which 5% weight loss had occurred.

[c] Maximum degradation temperature (MDT).

Thin-layer chromatography (TLC) on commercially available alumina TLC plates was employed in an attempt to detect the presence of more than one species in the product. A concentrated $CHCl_3$ solution of the cyclic trimer was prepared and spotted onto the TLC plate. Although several solvent mixtures of various compositions were used, only one band was ever observed.

Gas chromatography of the trimers on a Carbowax 20 M column at an injection temperature of 200-250°C and a column temperature of 200-230°C was attempted for a similar purpose. Only two peaks were observed, that of the monomer obtained by thermal degradation and that of one of the cyclic trimers.

The thermal decomposition of the cyclic trimers in N_2 was investigated by TGA with the results given in Table 3. The temperature of maximum degradation and the temperature at which 5% of the weight had been lost show some differences especially in the case of DDA-CT but are generally similar. It should be pointed out that the stability of the cyclic trimers of aldehydes depends not only on their inherent stability but also on the level of impurities, including trace amounts of oxidation products that might have been introduced during the storage of the compounds. For this reason, it is believed that the thermal stability of the aldehyde trimers as presented in Table 3 only partially represents their actual thermal stability and should be taken as only a semiquantitative estimation.

Aldehyde cyclic trimers were also extensively investigated by DSC for their behavior at their melting point under a wide variety of conditions. Results of representative runs are given in Table 4.

The DSC curves of the aldehyde cyclic trimers are presented in

TABLE 4. Melting Temperatures and Heats of Fusion of 2,4,6-Tri-n-alkyl-1,3,5-trioxanes by DSC[a]

n-Alkyl group of aldehyde	Sample treatment	Mp (°C)[b]	Peak temperatures (°C)	ΔH_f (± 3%)	
				cal/g	kcal/mole
Octyl	Virgin trimer	36	36	42.4[c]	17.9[c]
"	Quenched after first melting	-	35	41.2[c]	17.5[c]
"	Annealed at 36°C for 30 min	-	36	43.7	18.3
Nonyl	Virgin trimer	48	46	49.3[c]	22.9[c]
"	Annealed at 44°C for 20 min	-	47	50.1	23.4
Decyl	Virgin trimer	56	55	52.3[c]	26.5[c]
"	Quenched after first melting	-	55	52.6[c]	26.8[c]
"	Annealed at 54°C for 30 min	-	56	52.0	26.5
Undecyl	Virgin trimer	63	61	53.1[c]	29.3[c]
"	Quenched after first melting	-	61	52.5[c]	28.8[c]

[a] At 10°C/min. Trimers twice recrystallized from diethyl ether-ethanol mixture.
[b] Hot stage microscope at 2°C/min.
[c] Average of duplicate determinations.

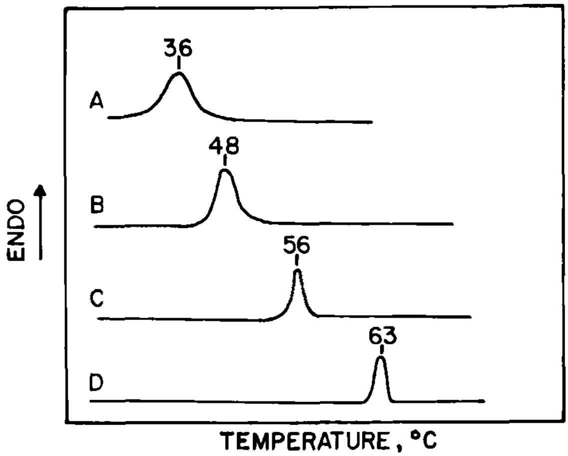


FIG. 7. DSC Curves of aldehyde cyclic trimers: (A) NA-CT; (B) DA-CT; (C) UA-CT; (D) DDA-CT.

Fig. 7. As shown, the melting temperatures of the individual cyclic trimers vary little regardless of their particular thermal history. The heats of fusion increase from 43 cal/g for NA-CT to 53 cal/g for DDA-CT, and the increase in melting points is 25°C from 36°C to 61°C. The increase of the heats of fusion is similar and reflect very clearly the increasing chain lengths.

As seen in Table 3, the largest group increase in melting point (9°C) (hot stage microscope) and peak temperature (DSC) was observed between NA and DA-CT. Similarly the largest step increase in the heat of fusion (8 cal/g) was observed between these two cyclic trimers. The step increase in melting point peak temperatures and transition enthalpies observed between the other trimers were not different. The melting points of the trimers were found in the same general temperature regions in which melting and various transitions are observed for other types of long-chain compounds, particularly glycerides of fatty acids [22]. This observation is perhaps no accident, but reflects the influence of the long groups on the crystallization of the various types of compounds. Polymers of higher aliphatic aldehydes also exhibit thermal transition in the same general temperature region.

A significant influence of thermal history upon the peak temperature and transition enthalpies of aliphatic aldehyde-CT was never observed. Within the limits of experimental error, the enthalpies associated with fusion endotherms always equalize the enthalpies associated with crystallization exotherms. It should be pointed out that the trimers, when crystallized from solution (especially from the melt), exhibit a pronounced tendency to crystallize in a spherulitic morphology.

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