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## The Preparation and Cyclopolymerization of cis- and trans-1,3,5-Triisocyanatocyclohexane\*

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### SUMMARY

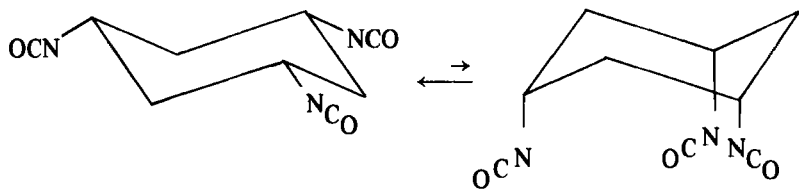
The preparation of cis- and trans-1,3,5-triisocyanatocyclohexane is described. The coupling constants  $J_{AB}$ ,  $J_{AX}$ , and  $J_{BX}$  were obtained from the NMR spectrum of the cis-isomer. Both isomers were polymerized using sodium cyanide in N,N-dimethylformamide as initiator. The evidence indicated that cyclopolymerization had occurred and, in both cases, predominantly bicyclic structures obtained.

### INTRODUCTION

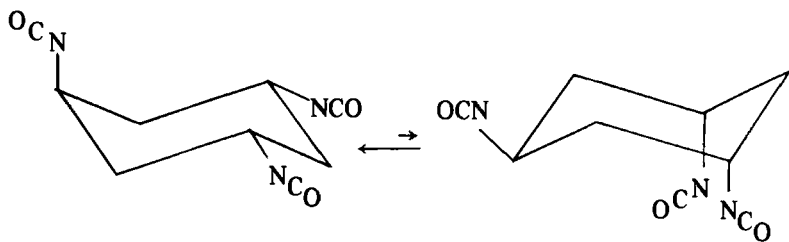
The cis- and trans-isomers of 1,3,5-triisocyanatocyclohexane (I and II, respectively), because of the cis-triaxial and trans-diaxial-equatorial conformations which can be achieved, are structurally capable of cyclopolymerizing to linear polymers containing tricyclic and bicyclic units, respectively. The cis-isomer is also capable of forming 1,3,9-triazatetracyclo[4,4,0,1<sup>3,9</sup>,1<sup>4,8</sup>] dodecan-2,10,11-trione (III) by an intramolecular trimerization of the isocyanato groups.

\*Presented at the 5th IUPAC Microsymposium of Cyclopolymers and Cyclopolymerization, Prague, Czechoslovakia, September, 1969.

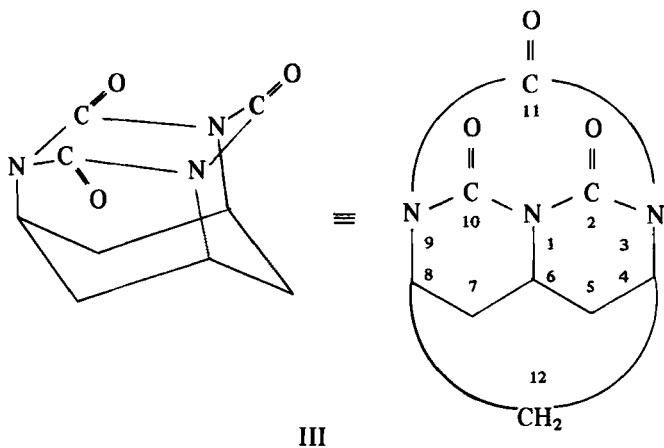
†Present address: Department of Chemistry, Sheffield Polytechnic, Sheffield S1 1WB, England.



I



II



III

## RESULTS AND DISCUSSION

## Preparation

Trimethyl trimesate in glacial acetic acid was hydrogenated at ambient temperature and 40 psi pressure in the presence of rhodium-on-alumina catalyst. The product of the hydrogenation was mainly the cis-triester. The trans-isomer was obtained by a method similar to the one used by Steitz [1]. The cis-triester was converted to the cis-triacid which was epimerized by heating a solution of the acid in acetic anhydride containing sodium acetate. The basic epimerization catalyst was neutralized by refluxing with acetyl chloride, and after concentration, the product esterified. The isomeric 1,3,5-triisocyanatocyclohexanes were obtained from the trimethyl esters of cyclohexane-1,3,5-tricarboxylic acid via the trihydrazides and triazides.

The NMR spectrum of the cis-isomer (Fig. 1) showed three main regions of absorption of relative areas 1:1:1. The signal at lowest field is due to the tertiary protons bonded to the same carbon atom as the isocyanato groups ( $\alpha$ -protons) which have a lower diamagnetic shielding than the other protons. The axial and equatorial protons adjacent to the  $\alpha$ -protons are not identical and the signal of the  $\alpha$ -protons is the X part of an  $A_2B_2X$  system. The observed signals of the cis-isomer were assigned as shown. The coupling constants  $J_{AB}$ ,  $J_{AX}$ , and  $J_{BX}$  were obtained from the spectrum. The X signal showed a fine structure in agreement with expectations. The signal should be a triplet, separations  $J_{BX}$ , each component itself a triplet, separations  $J_{AX}$ . Direct measurement on the nonet gave  $J_{AX}$  and  $J_{BX}$ . Calculation from the band width of the A signal quartet ( $= 2J_{AX} + J_{AB}$ ) gave  $J_{AB}$ . The values obtained are shown in Table 1. Spectral measurements were carried out in deuteriochloroform and carbon disulfide. The solvent had no influence on the spin-coupling constants but a little on the chemical shift.

The NMR spectrum of trans-1,3,5-triisocyanatocyclohexane showed two main regions of absorption of relative areas 2:1 (Fig. 2). The signal at low field, due to the two axial and one equatorial  $\alpha$ -protons, consisted of two overlapping multiplets centres at 6.17 and 5.78  $\tau$ , respectively. The signal due to the axial protons is broader and appears at higher field than the signal due to the equatorial proton. The equatorial proton signal is largely unresolved but the axial protons signal, because of the larger value of the spin-spin interactions, is almost completely resolved into the expected nonet.

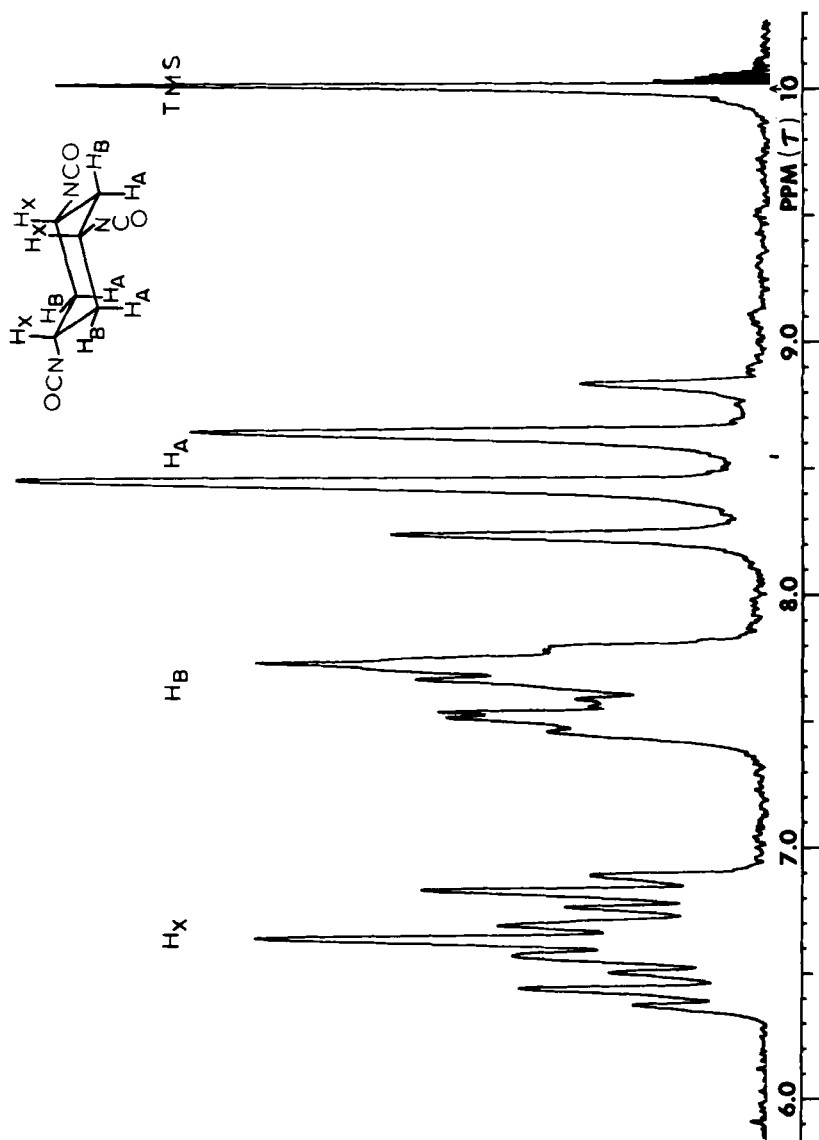


Fig. 1. NMR spectrum of cis-1,3,5-triisocyanatocyclohexane.

**Table 1.** Chemical Shifts and Coupling Constants of cis-1,3,5-Triisocyanatocyclohexane<sup>a</sup>

Solvent	Chemical shift <sup>b</sup>			Spin-coupling constants <sup>c</sup>		
	A	B	X	J <sub>AB</sub> <sup>d</sup>	J <sub>BX</sub>	J <sub>AX</sub>
CDCl <sub>3</sub>	8.53	7.62	6.63	13.0	3.9	11.5
CS <sub>2</sub>	8.56	7.66	6.68	13.0	3.9	11.5

<sup>a</sup>Recorded at 40° and 60 Hz.

<sup>b</sup> $\tau$  value with respect to TMS.

<sup>c</sup>In Hz; signs are neglected.

<sup>d</sup>Calculated from separation between the outermost peaks of the H<sub>A</sub> signal ( $J_{AB} + 2 J_{AX} = 36.0$  Hz).

### Polymerization

Attempts to form III by intramolecular trimerization of the isocyanato groups of I, using triethylamine, triphenylphosphine, aluminum trichloride, and sodium cyanide in N,N-dimethylformamide catalysts, were unsuccessful.

When sodium cyanide in N,N-dimethylformamide was added to I at ambient temperature under nitrogen, an exothermic reaction occurred with immediate precipitation of polymer. Extraction with benzene yielded a soluble fraction which from its IR spectrum (Fig. 3) contained a considerable amount of residual isocyanato groups. The spectrum showed no strong absorption bands at approximately 3300 or 1545 cm<sup>-1</sup> (-NH- or -CONH- groups) but gave a broad split absorption (1710 and 1680 cm<sup>-1</sup>) in the carbonyl region. The spectrum of the fraction of the polymer insoluble in benzene was very similar to that of the soluble fraction. However, in addition, it contained bands attributable to -NH- and -CO.NH- groups. Thus it would appear that they are of similar structure but that in the latter case some cross-linking has occurred by reaction of the pendent isocyanato groups with adventitious water. The polymer was thermally unstable and degraded when Soxhlet extracted with N,N-dimethylformamide.

The polymerization of I in N,N-dimethylformamide using sodium cyanide initiator was investigated. Table 2 shows representative conditions and results. High yields of polymer were obtained under a variety of conditions and the polymers exhibited similar properties and IR spectra.

The polymer is clearly a linear cyclopolymer in which, by analogy with

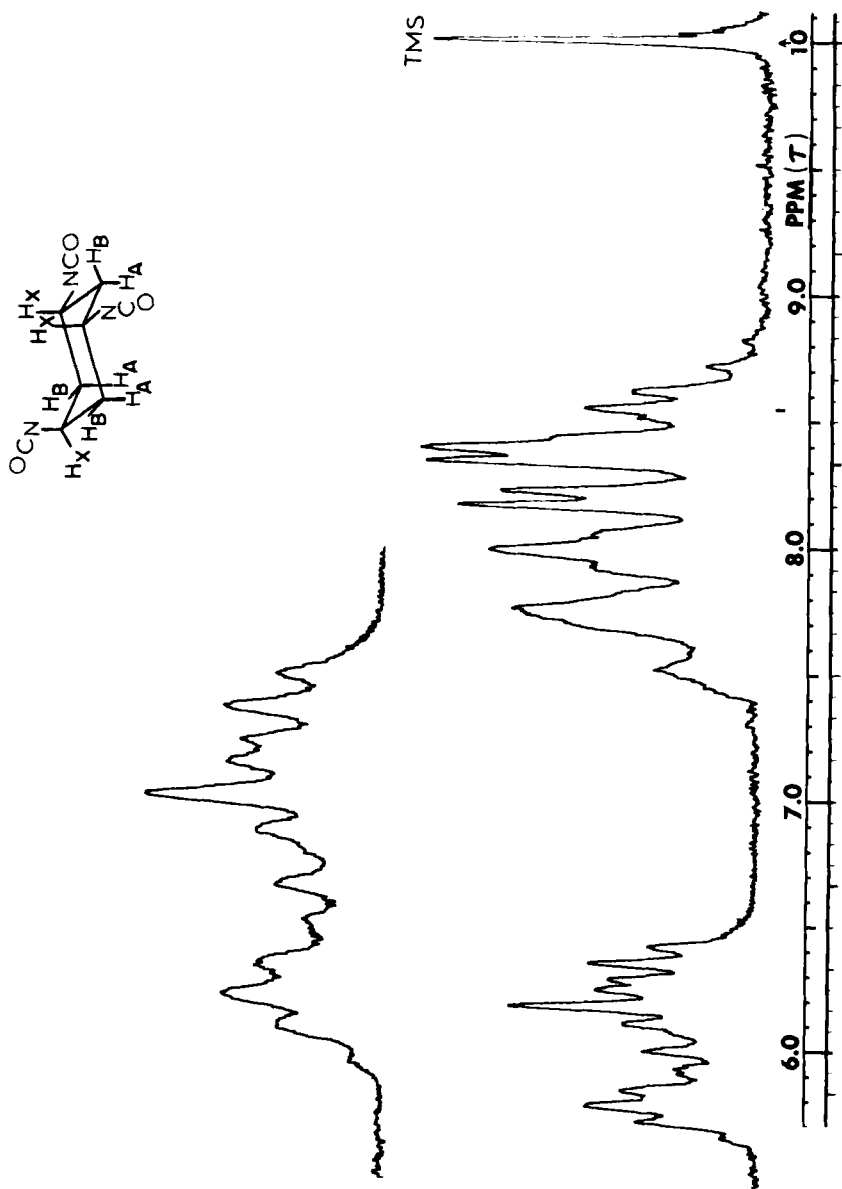
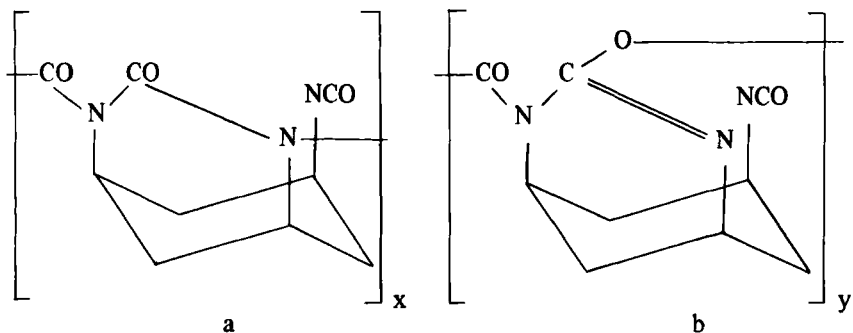
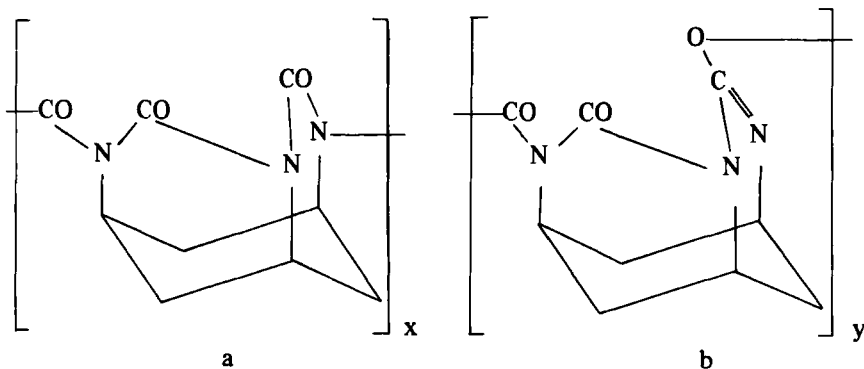
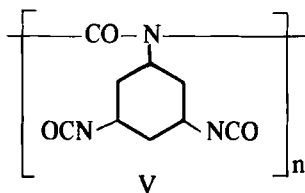


Fig. 2. NMR spectrum of trans-1,3,5-triisocyanatocyclohexane.



IV



VI

poly(*cis*-1,3-diisocyanatocyclohexane) [2], the main structural units are IV although the units V and VI may be involved in the linear chain to a small extent.

The thermal behavior of poly(*cis*-1,3,5-triisocyanatocyclohexane) is very different from that of common aliphatic isocyanates but similar to poly(isocyanatocyclohexane) [3]. The polymer exhibited a broad endotherm commencing at its melting point, 312°. When the polymer was



Table 2. Polymerization of cis-1,3,5-Triisocyanatocyclohexane

Experiment	Monomer g moles	Solvent <sup>a</sup> (ml)	Catalyst <sup>b</sup> ml mmoles	Concentration		Temp (°C)	Time (hr)	Yield (%)	
				Monomer in solvent (mole/vol %)	Catalyst to monomer (mole %)				
A	1.03	0.005	—	Et <sub>3</sub> N (Trace)	—	—	25	60	No reaction
							40	24	No reaction
							60	60	No reaction
							80	12	No reaction
B	0.52	0.0025	—	Ph <sub>3</sub> P (Trace)	—	—	150	60	Polymer
C	0.52	0.0025	—	AlCl <sub>3</sub> (Trace)	—	—	25	24	No reaction
							60	12	No reaction

D	1.03	0.005	—	0.5	0.05	—	1	25	Immediate ppt	100
E	2.07	0.01	9	1.0	0.1	0.1	1	-45	½	82 <sup>c</sup>
F	1.03	0.005	24.75	0.25	0.025	0.02	0.5	25	2	100 <sup>c</sup>
G	1.03	0.005	49.75	0.25	0.025	0.01	0.5	-50	2	No reaction
H	1.03	0.005	49.75	0.25	0.025	0.01	0.5	25	4	100 <sup>c</sup>
I	2.07	0.01	9.9	0.1	0.01	0.1	0.1	-45	½	40 <sup>c</sup>
J	1.03	0.005	49.75	0.25	0.025	0.01	0.5	25	2	78 <sup>d</sup>

<sup>a</sup>N,N-Dimethylformamide.

<sup>b</sup>Prepared by dissolving 0.147 g sodium cyanide in 25 ml N,N-dimethylformamide unless otherwise stated.

<sup>c</sup>Polymer precipitated by addition of ether.

<sup>d</sup>Polymer precipitated by addition of methanol.

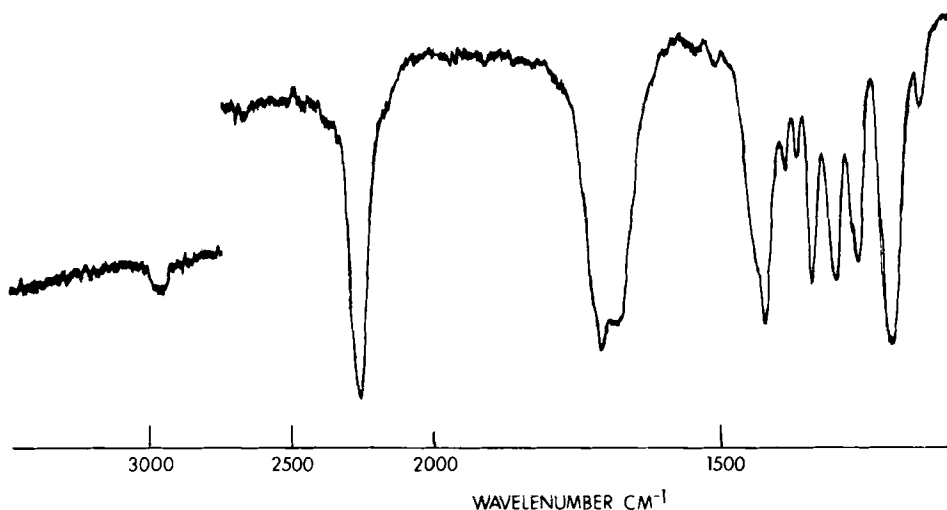


Fig. 3. Infrared spectrum of poly(cis-1,3,5-triisocyanatocyclohexane).

heated at 350° for 10 min, it degraded completely to monomer. The main product from most aliphatic polyisocyanates was trimer and the net reaction exothermic. This anomolous behavior of the polymer of I can be attributed to steric factors which prevent formation of a trimer.

trans-1,3,5-Triisocyanatocyclohexane (II) was also successfully polymerized (Table 3). The polymers were obtained in high yield as white powders with properties and IR spectra similar to those obtained from the cis-isomer. Clearly, cyclopolymerization has occurred and two different structural units (VIIa and b) are possible for the polymers. It was apparent that the pendant isocyanato groups in the polymers of II were more reactive towards adventitious water than those from I. The axial isocyanato group in I is more sterically hindered and therefore reacts more slowly than the equatorial position in II.

I and II are further examples of systems where the formation of a six-membered ring via a cyclopolymerization mechanism is the driving force for polymerization of isocyanato groups attached to secondary carbon atoms which, otherwise, do not polymerize [2, 4].

## EXPERIMENTAL

Melting points, determined on a Thomas Hoover apparatus, are uncorrected.

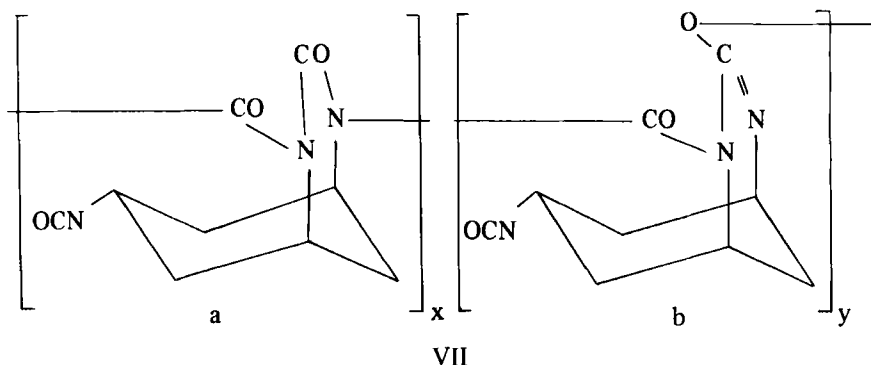
**Table 3.** Polymerization of *trans-1,3,5-Triisocyanatocyclohexane*

Experiment	Monomer g	Solvent <sup>a</sup> (ml)	Concentration			Temp(°C)	Time(hr)	Yield <sup>c</sup> (%)	
			Monomer in solvent (mole/vol %)	Catalyst <sup>b</sup> ml	Catalyst to monomer (mole %)				
A	0.52	—	0.25	0.025	—	1	25	Immediate ppt	81
B	1.03	9.75	0.25	0.025	0.05	0.5	25	2	100
C	0.52	24.75	0.25	0.025	0.01	1	25	2	100

<sup>a</sup>*N,N*-Dimethylformamide.

<sup>b</sup>Prepared by dissolving 0.147 g sodium cyanide in 25 ml *N,N*-dimethylformamide.

<sup>c</sup>Polymer precipitated by addition of ether.



Refractive indices were determined on a Bausch and Lomb Abbe refractometer. Vapor phase chromatograms were recorded on a Wilkins Aerograph chromatograph with 20% silicone elastomer on a celite column 9 ft long. IR spectra were recorded as liquid films or as potassium bromide disks on a Beckman IR8. NMR spectra were determined for deuteriochloroform or carbon disulfide solutions, at normal temperature, with tetramethylsilane as internal standard, on a Varian Associates A60 spectrometer.

**Triethyl cis-Hexahydrotrimesate.** A slurry of triethyl trimesate (29.4 g) in glacial acetic acid (200 ml) was hydrogenated at 50° and 40 psi pressure using as catalyst 5% rhodium on alumina (1 g). Hydrogen uptake (26 psi) ceased in 24 hr. Catalyst was filtered from the otherwise homogeneous product, solvent removed by evaporation under reduced pressure, and the residue distilled to yield triethyl cis-hexahydrotrimesate (28 g), bp 150°/0.5 mm.

**Triethyl trans-Hexahydrotrimesate.** Triethyl cis-hexahydrotrimesate (6 g), concentrated hydrochloric acid (50 ml), and water (100 ml) were refluxed overnight and the solution then evaporated to dryness under reduced pressure. The solid residue, presumably the triacid, was refluxed for 1 hr with acetic anhydride (50 ml) and sodium acetate (1 g). After evaporating to dryness the residue was refluxed for 1 hr with a further 50 ml of acetic anhydride. The base was removed by refluxing for 1 hr with acetyl chloride (20 ml) and the mixture evaporated to dryness. Benzene (100 ml) and absolute ethanol (25 ml) were added and the solution refluxed overnight, filtered, solvent removed under reduced pressure, and the residue fractionally distilled to yield triethyl trans-hexahydrotrimesate (3.5 g), bp 145°/1 mm.

**Cyclohexane-cis-1,3,5-Tricarboxylic Trihydrazide.** Triethyl cis-hexahydrotrimesate (15 g) and hydrazine hydrate (20 ml) were heated together at 80°

for 30 min. Sufficient absolute ethanol was added to just cover the white solid which had formed, the mixture refluxed overnight, and then filtered to yield cyclohexane-*cis*-1,3,5-tricarboxylic trihydrazide (13 g), mp  $>300^{\circ}$  (from water-ethanol), (found: C, 41.65; H, 7.11; N, 32.81;  $C_9H_{18}N_6O_3$  requires C, 41.85; H, 7.02; N, 32.54%).

**Cyclohexane-*trans*-1,3,5-tricarboxylic Trihydrazide**, mp  $208-209^{\circ}$ , was similarly obtained in high yield but was not purified by crystallization since it was found that this caused isomerization (found: N, 32.01;  $C_9H_{18}N_6O_3$  requires N, 32.54%).

***cis*-1,3,5-Triisocyanatocyclohexane.** A 600-ml beaker equipped with a thermometer and a mechanical stirrer and externally cooled in an ice-bath, was charged with crushed ice (50 g), water (100 ml), concentrated hydrochloric acid (12.5 ml), and cyclohexane-*cis*-1,3,5-tricarboxylic trihydrazide (13 g). A solution of sodium nitrite (10.5 g in 21 ml water), pre-cooled to  $0^{\circ}$ , was added dropwise to the stirred mixture over a period of 25 min. The temperature of the reaction mixture was maintained below  $8^{\circ}$  by addition of pieces of ice. Halfway through the addition benzene (50 ml) was added and stirring was continued for 30 min after completion of the addition. After separation of the layers the azide solution was combined with two benzene extractions of the aqueous layer, dried overnight over anhydrous calcium chloride, filtered, and then refluxed for 2 hr to complete the decomposition of the azide. Solvent was removed and the residue distilled under reduced pressure to yield *cis*-1,3,5-triisocyanatocyclohexane (4.8 g), bp  $135^{\circ}/1.0$  mm,  $n_D^{20}$  1.4992, characterized as the tris-di-*n*-propylurea (by treatment with di-*n*-propylamine), mp  $196^{\circ}$  d (from ethyl acetate) (found: C, 63.18; H, 10.38; N, 16.31;  $C_{27}H_{54}N_6O_3$  requires C, 63.49; H, 10.66; N, 16.46%).

***trans*-1,3,5-Triisocyanatocyclohexane** was similarly obtained; although a comparison of vpc with an authentic sample of the *cis*-isomer indicated that isomerization had occurred to a small extent, fractional distillation yielded the pure *trans*-isomer, bp  $131^{\circ}/1.0$  mm,  $n_D^{20}$  1.5030, characterized as the tris-*d*-*n*-propylurea, mp  $203^{\circ}$  d (from ethyl acetate) (found: C, 63.66; H, 10.78; N, 16.20;  $C_{27}H_{54}N_6O_3$  requires C, 63.49; H, 10.66; N, 16.46%).

**Polymerization of *cis*-1,3,5-Triisocyanatocyclohexane.** Table 1 shows representative reaction conditions; the following is a typical polymerization procedure. *N,N*-Dimethylformamide was stood over potassium hydroxide

overnight, distilled, and stored over sodium hydride. Before use in polymerizations the solvent was redistilled. The initiator solution was prepared by distilling N,N-dimethylformamide (100 ml) directly into a flask containing previously dried sodium cyanide (0.49 g) and the solution stored under nitrogen. A three-necked flask was equipped with a magnetic stirrer, thermometer, dropping funnel, nitrogen inlet tube, and calcium chloride tube. The monomer and solvent were added to the flask and the contents brought to the indicated temperature (Dry Ice-acetone bath for low temperatures). The initiator solution was added all at once from the dropping funnel with vigorous stirring. Usually the reaction proceeded exothermically. After stirring for the required time ether was added to precipitate the poly(cis-1,3,5-triisocyanatocyclohexane) which was filtered off, washed with ether, and dried at room temperature under vacuum.

**Poly(trans-1,3,5-triisocyanatocyclohexane)** (Table 3) was similarly prepared.

#### ACKNOWLEDGMENT

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