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The Synthesis and Polymerization of 1,3-Disubstituted Cyclohexanes.
I. The Isomeric 1,3-Diisocyanatocyclohexanes*

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SUMMARY

The synthesis of cis- and trans-1,3-diisocyanatocyclohexane is described. With water the cis-diisocyanate gave a bicyclic urea and a polyurea, which decomposed on heating to the bicyclic urea, and the trans-diisocyanate formed a polyurea. cis-1,3-Diisocyanatocyclohexane was polymerized using sodium cyanide as initiator to give soluble polymers which contained little or no residual isocyanato groups and hence cyclopolymerization had occurred. The polymers were thermally unstable and depolymerized quantitatively to monomer in the temperature range 270-370°. Two different structural units are possible for the cyclopolymer and the proportions of each unit were estimated by a quantitative aminolysis using di-n-butylamine. trans-1,3-Diisocyanatocyclohexane did not polymerize under similar conditions.

INTRODUCTION

Organic isocyanates are converted to their dimers (1,3-disubstituted uretidinediones) and their trimers (1,3,5-trisubstituted isocyanurates) in the presence of basic catalysts [1, 2]. Shashoua [3] found that basic catalysts

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such as sodium cyanide in N,N-dimethylformamide are also effective for the polymerization of both aliphatic and aromatic isocyanates to yield linear, high molecular-weight polymers which, structurally, are "1-nylons." Although other methods of isocyanate polymerization have since been reported [4-9], anionic polymerization is most commonly used.

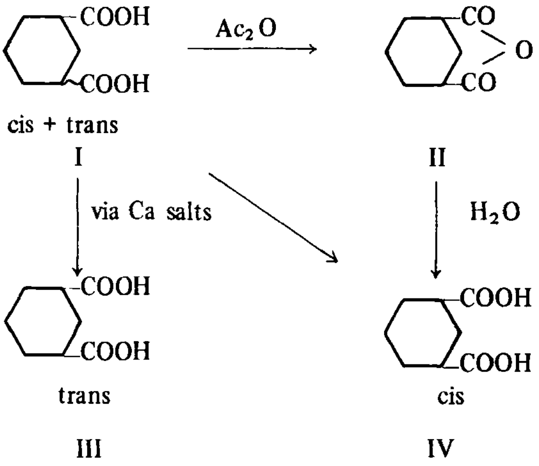
Shashoua [3] found that if the isocyanato group was attached to a primary aliphatic carbon atom, polymerization occurred readily, whereas an isocyanato group attached to a secondary carbon atom did not polymerize under the same conditions. Examples quoted included isocyanatocyclohexane and 2-isocyanatopropane. There are also apparent steric limitations to the trimerization of isocyanates since Brauner [10] has reported that 2-isocyanato-2-methylpropane did not trimerize. Although Iwakura et al. [11] later succeeded in polymerizing isocyanatocyclohexane in low conversion using sodium cyanide as a catalyst, attempts to prepare its trimer, 1,3,5-tricyclohexyl isocyanurate, were unsuccessful. Thus an isocyanato group in a cyclohexane system does not readily polymerize.

However, since 1,2-diisocyanatocyclohexane and 1,2-diisocyanatopropane readily polymerized to produce linear cyclopolymers [12], it appears that formation of a cyclopolymer constitutes a powerful driving force to effect polymerization through an otherwise poorly polymerizable structure.

cis-1,3-Diisocyanatocyclohexane, because of the diaxial conformation which the molecule can assume, is functionally and configurationally capable of polymerizing by the cyclopolymerization mechanism to give linear polymers containing bicyclic units. The trans-isomer, if polymerization occurred, might be expected to yield cross-linked polymers eventually because the isocyanato groups would be too far apart, in equatorial and axial positions, respectively, for the intramolecular step to occur.

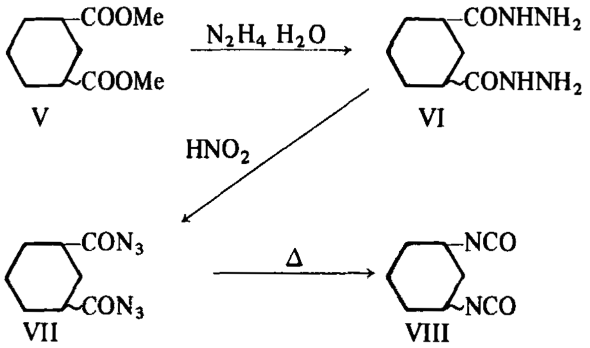
RESULTS AND DISCUSSION

Suitable starting materials for the preparation of the 1,3-disubstituted cyclohexanes under discussion were the isomeric cyclohexane-1,3-dicarboxylic acids. An aqueous solution of sodium isophthalate was hydrogenated at high temperature and pressure in the presence of freshly prepared Raney nickel catalyst. After acidification the product of the hydrogenation was a mixture of cis- and trans-cyclohexane-1,3-dicarboxylic acid. The acids were separated into the cis- and trans-isomers, via their calcium salts, by the method of Haggis and Owen [13]. The cis-acid was also obtained through the cyclic cis-anhydride using Komppa's method [14] (I-IV). The product of the hydrogenation was predominantly the cis-acid. Further amounts of trans-acid were obtained by partial isomerization of the cis-acid at 180°, alone [15] or with hydrochloric acid [16]; unchanged cis-acid being removed as calcium salt.

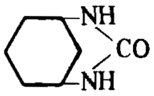


The isomeric 1,3-diisocyanatocyclohexanes were obtained from the dimethyl esters of the cyclohexane-1,3-dicarboxylic acids by converting them to the dihydrazides and hence to the diazides in the usual way for the Curtius reaction (V-VIII). The diazides were decomposed by refluxing in dilute benzene-carbon tetrachloride solution to afford the diisocyanates as colorless lachrymatory liquids giving single peaks in a vapor phase chromatogram and confirmatory analytical and spectral data. The IR spectrum of the two compounds showed the expected very strong absorption band due to the N=C=O antisymmetric stretch at approximately 2250 cm^{-1}.

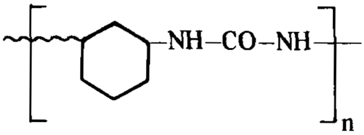
On standing in the atmosphere cis-1,3-diisocyanatocyclohexane was converted to a white solid, vacuum sublimation of which yielded 2,4-diazabicyclo [3,3,1] nonan-3-one (IX). The small residue from the sublimation had an IR spectrum different from that of IX but identical to the product obtained after refluxing the cis-diisocyanate with water. The IR spectrum is consistent with a poly(cis-1,3-cyclohexylidene)urea structure (Xa) for this product. Hall and Zbinden [17] have found that there is a difference between the IR absorption frequencies of n-membered rings



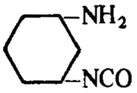
and their acyclic analogs. The difference between the carbonyl absorption frequency of the bicyclic urea (IX) and N,N′-dicyclohexylurea is 50 cm^{-1}, the bicyclic urea showing a band at 1678 cm^{-1} and N,N′-dicyclohexylurea at 1628 cm^{-1}. The product of the reaction between the cis-diisocyanate and water has a strong absorption at 1628 cm^{-1}, providing evidence of the acyclic nature of the carbonyl group in this product. There is further support for this structure in an NH band (3300 cm^{-1}) and an amide II band (1548 cm^{-1}) in the spectrum (Fig. 1a).



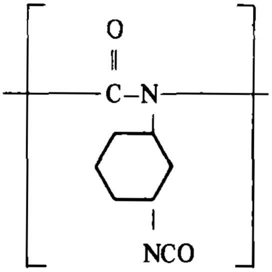
IX



Xa; cis
Xb; trans



XI



XVI

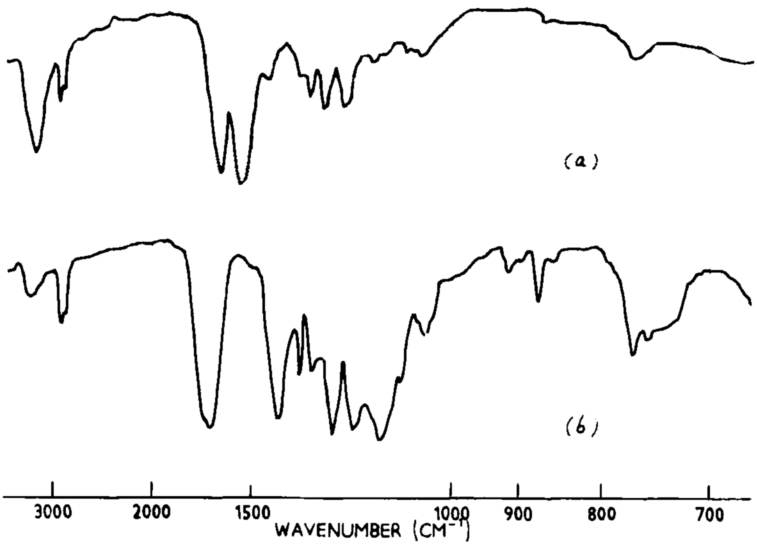


Fig. 1. Infrared spectrum of (a) poly(cis-1,3-cyclohexylidene)urea and (b) poly(cis-1,3-diisocyanatocyclohexane).

The polymer depolymerized to a large extent on vacuum sublimation to give a sublimate of the bicyclic urea (IX), the residue being identical, from its IR spectrum, to the starting polymer. It seems likely that the polymer breaks down on heating to give $-NH_2$ and $-NCO$ groupings and some amino-isocyanate molecules (XI). These can either cyclize to produce the bicyclic urea (IX) or can recombine to give the polymer (Xa).

Because of the axial-equatorial conformation of the isocyanato groups, trans-1,3-diisocyanatocyclohexane cannot react intramolecularly with water. Intermolecular reaction with water would be expected to give the polyurea (Xb). On heating the trans-diisocyanate with water, carbon dioxide is evolved and a white polymeric solid, readily soluble in N,N-dimethylformamide, is deposited. The IR spectrum was similar to that of the polymer from the cis-diisocyanate; a band for the carbonyl stretching absorption appearing at 1630 cm^{-1}, for the –NH– stretching frequency at 3300 cm^{-1} and an amide II band at 1540 cm^{-1}.

cis-1,3-Diisocyanatocyclohexane polymerized readily in dry N,N-dimethylformamide, under nitrogen, using sodium cyanide as initiator. The polymers were obtained as white powders (after precipitation and extraction) with melting points varying from 224 to 265°, and having an intrinsic viscosity of about 0.1 dl/g. The polymers, from their IR spectra, contained little or no residual isocyanato groups and were soluble in, for example, benzene, m-cresol, and formic acid (98-100%), being recovered unchanged from such solutions.

Representative polymerization conditions and results are shown (Table 1). Several factors were found to influence the polymer formation. In particular, the initial polymerization temperature, the concentration of the monomer, and the concentration of the catalyst. Comparison of Experiments A and B shows an increase in yield with an increase in the initial polymerization temperature. However, as suggested by the increase in solubility of the polymer prepared in Experiment B, this appears to be accompanied by a decrease in molecular weight. The effect of an increase in monomer concentration (compare Experiments A and C) and catalyst concentration (Experiments A and D) is to increase the yield of polymer.

A pure sample of cis-1,3-diisocyanatocyclohexane spontaneously polymerized on storage over a long period at room temperature and in anhydrous conditions. The polymer formed in this manner was very hard, transparent, and soluble in formic acid (98-100%). Clearly, cyclopolymerization is so favored in this system that it is the predominant, or sole, mechanism even in bulk polymerization.

Consideration of the mechanism of this cyclopolymerization (Fig. 2) suggests that two different structural units (XIV and XV) are possible. The initiation step occurs by attack of the cyanide ion on the carbon atom of one of the isocyanato groups, leading to a hybrid anion (XII). The intramolecular step would then presumably occur via the nitrogen in the hybrid anion, leading to the six-membered bicyclic anion (XIII), again having the negative charge delocalized over the nitrogen and oxygen atoms. If the succeeding intermolecular step, involving attack on another monomer molecule, occurs through the negative nitrogen in this hybrid anion, then Structure XIV would be formed. Conversely, reaction through the negative oxygen would lead to the unit Structure XV.

The IR spectra of the polymers do not allow a differentiation between these two possible unit structures. The absence of strong absorption at approximately 3300 or 1545 cm^{-1} shows the absence of –NH– and –CO.NH– groups. The very strong absorption band of the isocyanato group, at 2250 cm^{-1}, was either absent or present to only a very small extent, so the degree of cyclization appears to be nearly 100%. In those polymers containing a few residual isocyanato groups, the recurring unit XVI must be present to a small extent in the linear chain. The polymers gave a broad absorption band centered at 1675 cm^{-1}. Two absorption bands might be expected in this

Table 1. Polymerization of cis-1,3-Diisocyanatocyclohexane

						Concentration						
	Monomer		Solvent[a]	Catalyst[b]		Monomer in solvent	Catalyst to monomer		Time	Yield[c]		Soluble
Experiment	g	moles	(ml)	ml	mmoles	(mole/vol. %)	(mole %)	Temp (°C)	(hr)	(%)	mp[d]	in
A	1.66	0.01	9	1	0.1	0.1	1	-55	2	87	240	Formic acid
B	1.66	0.01	9	1	0.1	0.1	1	+25	2	100	260	Benzene
C	1.66	0.01	99	1	0.1	0.01	1	-55	2	51	230	Formic acid
D	1.66	0.01	9.9	0.1	0.01	0.1	0.1	-55	2	49	232	Formic acid

[a] N,N-Dimethylformamide.

[b] Prepared by dissolving 0.49 g sodium cyanide in 100 ml N,N-dimethylformamide.

[c] Polymer precipitated by the addition of ether.

[d] Melting accompanied by decomposition.

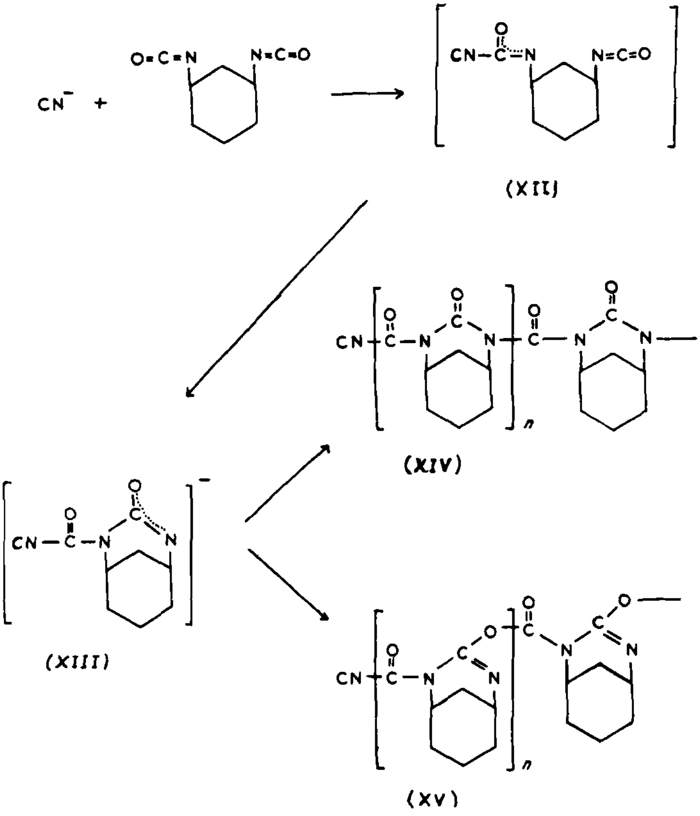


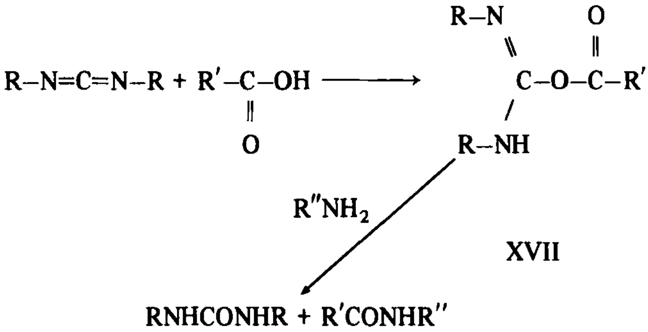
Fig. 2. Cyclopolymerization of cis-1,3-diisocyanatocyclohexane.

region, corresponding either to the stretching vibrations of the C=O group in the ring and the C=O group between the rings, or to the C=O and C=N stretching vibrations, respectively. Thus Polymer B, Table 1, for example showed absorption at 1675 cm^{-1} with a shoulder at 1705 cm^{-1} (Fig. 1b). The NMR spectrum of this polymer provided further evidence that would support the proposed structures. The spectrum shows two broad regions of absorption; a large signal at high field (7.3-8.9 τ) and a smaller signal at low field (5.2-6.0 τ) of relative area 8:2. The signal at low field is due to the protons in the 1,3-positions on the cyclohexane ring which are deshielded by the "polyisocyanato" grouping.

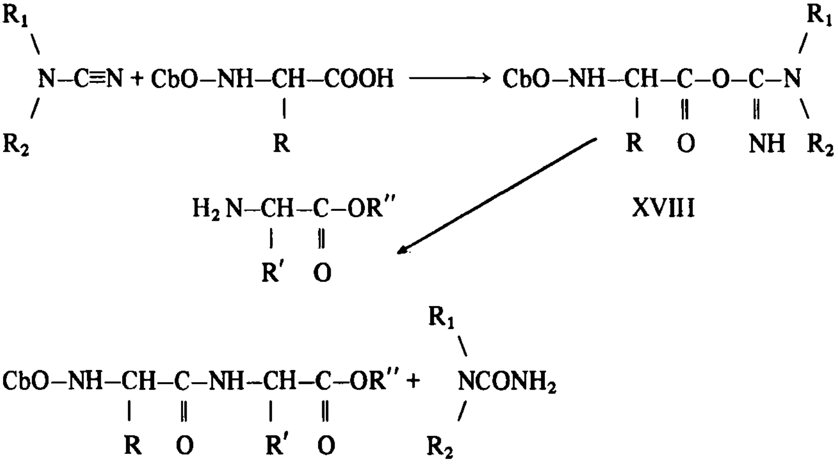
Melting was accompanied by decomposition to monomer, as is the case for the N-alkyl "1-nylons" [3]. A thermogravimetric analysis on the polymers indicated a quantitative weight loss and the characteristic odor of the monomer was noted. When the products of the pyrolysis were drawn, in a current of air, through a solution of di-n-butylamine in petroleum ether, a white precipitate of the bis-di-n-butylurea derivative of the monomer was formed. Further evidence was provided by the deposition of the bicyclic urea (IX) in the apparatus, formed by reaction of the monomer from the depolymerization with moisture in the current of air. The temperature at which maximum depolymerization occurs is 370° for the polymers prepared at low temperature and 275° for the polymer prepared at 25°. This increased thermal stability supports the view, expressed earlier, that the low temperature polymerization gave polymers of higher molecular weight.

It has been reported that N,N′-disubstituted carbodiimides [18] and N,N-dialkylcyanamides [19] react with carboxylic acids and amines to give amides and ureas. The intermediates XVII and XVIII have the same structural group, –N=C–O–CO–, as the polymer Structure XV. Iwakura et al. [20] found that cleavage of the single carbon-oxygen bond of the urethane linkage in the repeating units having this structure could be effected by reaction of the polymer with amines. Aminolysis of the polymer was investigated using di-n-butylamine, similar to the method developed by Iwakura et al. [20]. Di-n-butylamine was consumed when the polymer was treated at 25° with an excess of di-n-butylamine in N,N-dimethylformamide containing a catalytic amount of sodium cyanide. The amount of amine consumed was measured by titration with hydrochloric acid. Figure 3 shows the curve obtained on plotting the percentage of polymer reacted against the reaction time, it being assumed that the amine reacts with equivalent moles of the polymer.

It can be seen that two kinds of reaction are involved in aminolysis of the polymer. A relatively fast reaction over the first 10 hr, followed by an extremely slow reaction continuing up to and beyond 100 hr. By analogy with the high reactivity of the intermediates XVII and XVIII, the rapid uptake of amine is believed to correspond with the reaction of the repeating unit XV with 1 mole of the amine. The cleavage of the single carbon-oxygen bond in the urethane linkage produces a pseudourea type intermediate (XIX) which is tautomeric with 2-(N,N-di-n-butylcarbamoyl)-2,4-diazabicyclo [3,3,1] nonan-3-one (XX). The slow uptake of the amine is believed to be due to the reaction of the urea grouping, with fission of the nitrogen-carbonyl bond (XX → XXI and XIV → XXII). For the slow reaction a linear relationship is observed between the amount of polymer reacted and time. By extrapolation of this straight line to the vertical axis the approximate amount of each



XVII



XVIII

CbO = $C_6H_5CH_2OCO$–, carbobenzyloxy-

structure in the polymer was determined. The results show that Structures XIV and XV are present in the approximate ratio 65:35.

According to the above mechanism the aminolysis reaction should produce 2-(N,N-di-n-butylcarbamoyl)-2,4-diazabicyclo [3,3,1] nonan-3-one (XX) and the bis-di-n-butylurea (XXI). A small amount of white solid was isolated from the reaction. The IR spectrum of this material showed absorption bands at 1735 and 1690 cm^{-1}, which are believed to be due to the two carbonyl groups of XX, and at 1630 cm^{-1}, which corresponds with the carbonyl stretching absorption of an authentic sample of XXI. A further sample of material, after recrystallization from methylcyclohexane, gave an almost correct analysis for XX and a mass spectrum which showed

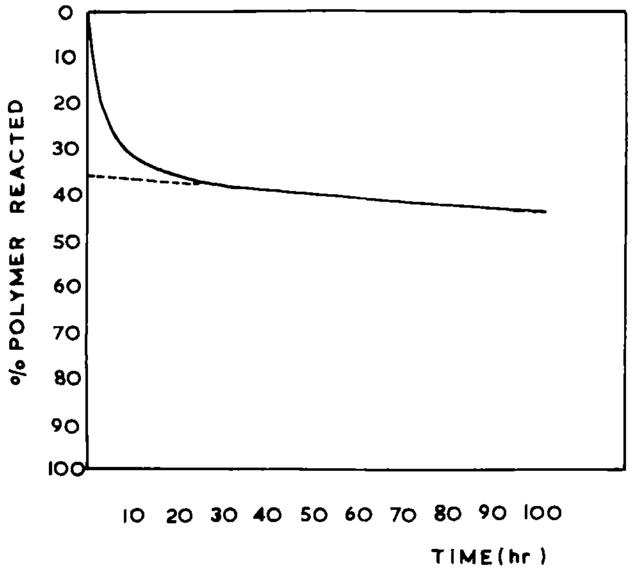


Fig. 3. Aminolysis of poly(cis-1,3-diisocyanatocyclohexane).

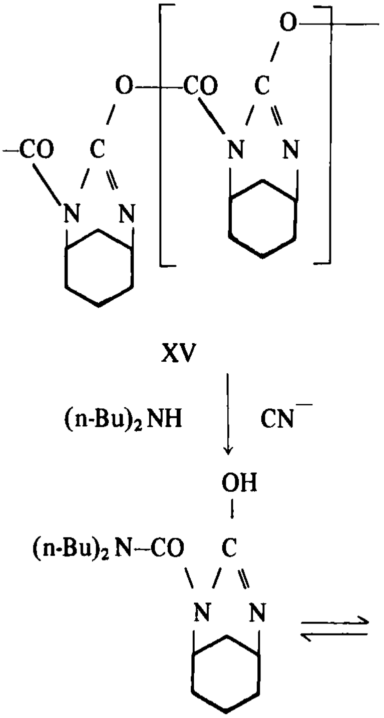
a prominent molecular peak at m/e 295 in agreement with the calculated value for $C_{16}H_{29}N_3O_2$ (XX).

The polymerization of trans-1,3-diisocyanatocyclohexane was attempted using sodium cyanide in N,N-dimethylformamide as initiator under a variety of conditions, but no polymerization occurred. Since Shashoua [3] found that monoisocyanates in which the isocyanato group is attached to a secondary carbon atom are not polymerized under these conditions, and because the axial-equatorial arrangement of the isocyanato groups in trans-1,3-diisocyanatocyclohexane will not allow the formation of a cyclopolymer to act as a driving force, this result was perhaps to be expected.

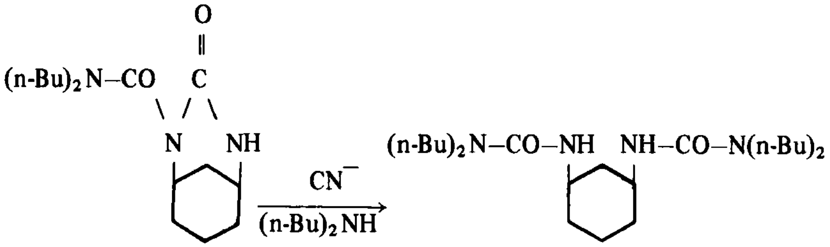
The results of a study by high resolution NMR spectroscopy of the conformational equilibrium in cis-1,3-diisocyanatocyclohexane, and their consequences in relation to the ability of this monomer to undergo cyclopolymerization, have been discussed in an earlier publication [21].

EXPERIMENTAL

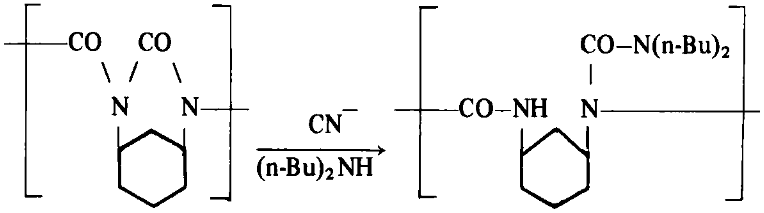
Melting points, determined on a Gallenkamp apparatus (design no. 889, 339), are uncorrected. Refractive indices were determined on a Bellingham



XIX XX



XX XXI



XIV XXII

and Stanley Abbe 60 refractometer. Vapor phase chromatograms were recorded on a Pye Argon Chromatograph with 20% silicone elastomer E301 on a 30/80 mesh celite column 1.2 m long. IR spectra were recorded as liquid films or as potassium bromide disks on a Perkin-Elmer Infracord.

Cyclohexane-1,3-dicarboxylic Acids. Isophthalic acid (300 g) was dissolved in the minimum amount (approx 700 ml) of 20% sodium hydroxide solution. The solution was neutralized to litmus with dilute hydrochloric acid, boiled with 50 g of activated charcoal, and filtered. After repeating the charcoal treatment, 30 g of sodium hydroxide was added and the solution warmed at 100° for 2½ hr with fresh Raney nickel catalyst W5 [22] from 120 g of nickel-aluminum alloy (1:1). After filtration a fresh portion of Raney nickel catalyst, as above, was added and the solution hydrogenated at 180°/110 atm of hydrogen in a 3-liter rocking autoclave. The catalyst was filtered off and the solution strongly acidified with concentrated hydrochloric acid. The precipitated acids were removed, dissolved in aqueous ammonia, and treated with calcium chloride solution, and, after filtration, the precipitate was acidified with concentrated hydrochloric acid and crystallized from hot water to yield cyclohexane-cis-1,3-dicarboxylic acid (160 g), mp 165-167° (Ref. 13, 161-162°).

The filtrate from the calcium chloride treatment was acidified and extracted with ether. The acid obtained was dissolved in aqueous ammonia and treated with calcium chloride solution to yield a further small amount of the cis-acid after filtration and acidification of the precipitate. The filtrate was acidified and extracted with ether and the acid obtained crystallized from hot water to yield cyclohexane-trans-1,3-dicarboxylic acid (5 g), mp 146-148° (Ref. 13, 147-148°).

Anhydride of Cyclohexane-cis-1,3-dicarboxylic Acid. Cyclohexane-1,3-dicarboxylic acid (20 g, mixture of isomers) was refluxed for 30 min with acetic anhydride and evaporated to dryness under reduced pressure. This procedure was repeated twice and the resulting white powder sublimed in vacuo to yield white crystals of the cis-anhydride (15 g), mp 192-193°. (Found: C, 62.24; H, 6.36. Calc for $C_8H_{10}O_3$: C, 62.32; H, 6.54%.)

Isomerization of Cyclohexane-1,3-dicarboxylic Acid. (a) Cyclohexane-1,3-dicarboxylic acid (product of hydrogenation, 95% cis- 5% trans- by VPC after esterification using diazomethane in ether) was heated in a sealed tube at 180° for 20 hr. The product was dissolved in water and ether extracted. Vpc analysis indicated 74% cis- and 26% trans-isomer.

(b) Cyclohexane-1,3-dicarboxylic acid (30 g) and concentrated hydrochloric acid (45 ml) were heated together for 20 hr at 180° (sealed tube). The product contained 26% trans-isomer.

The acids were separated via their calcium salts.

Dimethyl-cis-hexahydroisophthalate. Cyclohexane-cis-1,3-dicarboxylic acid (60 g) was refluxed with methanol (300 ml) and concentrated sulfuric acid (6 ml) for 12 hr. The mixture was poured into water, ether extracted, and the extract washed with sodium bicarbonate solution and water and dried over anhydrous sodium sulfate. After filtration and removal of the ether under reduced pressure, the residue was distilled under reduced pressure to yield dimethyl cis-hexahydroisophthalate (68 g), bp 134°/9 mm, n_D^{20} 1.4562. Dimethyl trans-hexahydroisophthalate, bp 128°/9 mm, n_D^{20} 1.4580 was similarly prepared.

Cyclohexane-cis-1,3-dicarboxylic Dihydrazide. Hydrazine hydrate (25 g) dissolved in 300 ml of 95% ethanol was refluxed overnight with dimethyl cis-hexahydroisophthalate (25 g). The mixture was filtered to yield cyclohexane-cis-1,3-dicarboxylic dihydrazide (25 g), mp 272-274° (Ref. 23, 265°; Ref. 24, 270-272°).

Cyclohexane-trans-1,3-dicarboxylic Dihydrazide. Dimethyl trans-hexahydroisophthalate (25 g) was added, dropwise with stirring, over 4 hr, to hydrazine hydrate (25 g) at 80°. The addition was at a rate such that all the previous amount had reacted before a further addition was made. After concentration of the mixture under high vacuum, a sticky semi-solid material remained, which was treated with petroleum-ether (80-100°) to yield cyclohexane-trans-1,3-dicarboxylic dihydrazide (24 g), mp 128-130° (Ref. 23, 130°; Ref. 24, 125-126°).

cis-1,3-Diisocyanatocyclohexane. A 400-ml beaker, equipped with a thermometer and a mechanical stirrer and externally cooled in an ice bath, was charged with crushed ice (100 g), carbon tetrachloride (20 ml), concentrated hydrochloric acid (12 ml), and cyclohexane-cis-1,3-dicarboxylic dihydrazide (12 g). A solution of sodium nitrite (8.5 g in 20 ml water), pre-cooled to 0°, was added dropwise to the stirred mixture over a period of 20 min. The temperature of the reaction mixture was maintained below 8° by addition of pieces of ice, 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-di-isocyanatocyclohexane (6.8 g), bp 83.5°/0.9 mm, n_D^{20} 1.4787, characterized as the bis-di-n-butylurea (by treatment with di-n-butylamine), mp 185.5-186° (from ethyl acetate) (found: C, 67.66; H, 11.26; N, 13.05; $C_{24}H_{48}N_4O_2$ requires C, 67.88; H, 11.40; N, 13.19%), and the bisphenylurea (by treatment with aniline), mp 255-256° (from glacial acetic acid) (found: N, 15.72; $C_{20}H_{24}N_4O_2$ requires N, 15.90%).

trans-1,3-Diisocyanatocyclohexane was similarly prepared bp 82°/1.6 mm, n_D^{20} 1.4809, characterized as the bis-di-n-butylurea, mp 93-94° (from petroleum ether, 40-60°) (found: C, 68.08; H, 11.36; N, 13.19; $C_{24}H_{48}N_4O_2$ requires C, 67.88; H, 11.40; N, 13.19%).

Polymerization of cis-1,3-Diisocyanatocyclohexane. 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 2 hr, ether was added to precipitate the poly(cis-1,3-diisocyanatocyclohexane) which was filtered off, washed with ether, and dried at room temperature under vacuum.

Aminolysis of Poly(cis-1,3-diisocyanatocyclohexane). A mixture of the polymer (1.216 g), N,N-dimethylformamide (100 ml), the initiator solution (5 ml), and di-n-butylamine (10 ml) was maintained at 25°. At intervals, 5 ml of the reaction mixture, after dilution with 10 ml of dioxan, was titrated with 0.1 N hydrochloric acid, using methyl orange indicator. The extent of the reaction was calculated from the titre on the assumption that the amine reacts with equivalent moles of the polymer (Table 2).

Table 2

Time (hr)	2	3	4.5	6.5	8.5	24	74	96
Amine reacted (g)	0.168	0.193	0.234	0.274	0.291	0.340	0.382	0.406
Polymer reacted (g)	0.216	0.248	0.307	0.353	0.374	0.437	0.491	0.522
% Reacted	17.8	20.4	24.8	29.0	30.8	36.0	40.4	43.0

After filtration, the filtrate was distilled at 40-50° under reduced pressure, leaving a light yellow viscous oil which was treated with ether to precipitate a white solid, presumably an oligomer. The ethereal filtrate was washed with water, dried over calcium chloride, and the ether removed at room temperature to leave a small amount of white solid.

IR absorption bands were at 1630, 1690, and 1735 cm^{-1} (shoulder). An authentic sample of XXI showed IR absorption at 1630 cm^{-1} (C=O). The peaks at 1690 and 1735 cm^{-1} are believed to be due to the two carbonyl groups of XX.

A further sample of the aminolysis product, mp 176-177° (from methylcyclohexane), gave m/e 295 (A.E.I./M.S.2) in agreement with the calculated value for XX. (Found: C, 64.76; H, 10.77; $C_{16}H_{29}N_3O_2$ requires C, 65.05; H, 9.89%.)

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