(3) T. Alfrey, Jr., J. J. Bohrer, and H. Mark, "Copolymerization," Vol. VIII, Interscience, New York, N.Y., 1952, p 59.
(4) F. M. Lewis and F. R. Mayo, *J. Amer. Chem. Soc.*, **70**, 1533 (1948).
(5) C. H. Bamford and W. G. Barb, *Discuss. Faraday Soc.*, **14**, 208 (1953).
(6) T. Wagner-Jauregg, *Chem. Ber.*, **63**, 3213 (1930).
(7) K. W. Doak, *J. Amer. Chem. Soc.*, **70**, 1525 (1948).
(8) T. Alfrey, Jr., and S. Greenberg, *J. Polym. Sci.* **3**, 297 (1948).
(9) C. Walling, "Free Radicals in Solution," Wiley, New York, N.Y., 1957, p 127.
(10) E. T. Burrows, R. N. Haward, J. Proges, and J. Street, *J. Appl. Chem.*, **5**, 379 (1955).
(11) S. H. Ronel and D. H. Kohn, *J. Polym. Sci., Part A-1*, **7**, 2209, 2221 (1969).
(12) A. Liebersohn and D. H. Kohn, *J. Polym. Sci., Polym. Chem. Ed.*, **12**, 945 (1974).
(13) G. Noren and H. K. Hall, Jr., *J. Polym. Sci.*, **10**, 3183 (1972).
(14) H. Nomori, M. Hatano, and S. Kambara, *J. Polym. Sci., Part B*, **4**, 261 (1966).
(15) Y. Shirota, M. Yoshimura, A. Matsumoto, and H. Mikawa, *Macromolecules*, **7**, 4 (1974).
(16) L. P. Ellinger *Chem. Ind. (London)* 1982 (1963).
(17) L. P. Ellinger, *Polymer*, **5**, 559 (1964).
(18) W. A. Lee and G. J. Knight, "Polymer Handbook," J. Brandrup and E. H. Immergut, Ed., Interscience, New York, N.Y., 1968, pp III and 61.
(19) C. L. Dickinson, D. W. Wiley, and B. C. McKusick, *J. Amer. Chem. Soc.*, **82**, 6132 (1960).
(20) P. Ykman, and H. K. Hall, Jr., submitted for publication.
(21) L. M. Jackman and R. H. Wiley, *J. Chem. Soc.*, 2881, 2886 (1960).
(22) C. Pascual, J. Meier, and W. Simon, *Helv. Chim. Acta*, **49**, 164 (1966).
(23) S. W. Tobey, *J. Org. Chem.*, **34**, 1281 (1969).
(24) B. B. Corson, and W. L. Benson "Organic Syntheses," Collect. Vol. II, Wiley, New York, N.Y., 1943, p 273.

Synthesis and Optical Properties of Asymmetric Polyamides Derived from Optically Active Dicarboxylic Acids and Spirodiamine

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ABSTRACT: Optically active polyamides derived from either (+)-(*S*)-*trans*-1,2-cyclopropanedicarboxylic acid [(+)-C3] or (+)- and (−)-*trans*-1,2-cyclohexanedicarboxylic acids [(+)- and (−)-C6] with 2,6-diazaspiro[3.3]heptane (DSH) were prepared by interfacial polycondensation reactions. Several model compounds, (±)-*trans*-2-methylcyclopropanecarboxylic acid azetidide (I), (+)-*trans*-cyclopropanedicarboxylic acid diazetidide (II), 2,6-di[(±)-*trans*-2-methylcyclopropanecarbonyl]-2,6-diazaspiro[3.3]heptane (III), IV, V, and (+)-*trans*-1,2-cyclohexanedicarboxylic acid dipiperidide (VI), were also made for studying the conformation of the polymers. The optical rotatory dispersion (ORD) and circular dichroism (CD) of these compounds indicated that the polyamide [(+)-C3 · DSH] and the model compounds, II, IV, and V, derived from (+)-C3 did not change their conformations in various solvents. Solvents used were 2,2,2-trifluoroethanol (TFE), water, methanesulfonic acid (MSA), and sulfuric acid. The conformation of the carbonyl groups of a cyclopropane ring in all compounds may be the same. Model compound VI may have a different conformation in strong acids and nonacidic solvents (water and TFE), whereas the polyamide (C6-DSH) derived from C6 showed no variance in conformation in the above solvent systems. Optically active and racemic polyamides derived from C6 and C6 had the same solution viscosities in TFE and in sulfuric acid. All polymers had melting points higher than 300°.

Poly(L-proline) is known to exist in two different regular forms in solution without hydrogen bonds, and extensive studies on this polymer have been done.[1] Theoretical calculations have attributed the cause of the regularity of poly(L-proline) mainly to steric hindrance to rotation around the peptide bond and to the geometric restriction on the polymer backbone.[2] A regular conformation may exist in a synthetic asymmetric polyamide derived from a rigid monomer as well. We have been studying this problem by making various optically active polyamides with rigid structures.[3–5]

In the present study, we prepared optically active polyamides derived from either (+)-(*S*)-*trans*-1,2-cyclopropanedicarboxylic acid [(+)-C3] or (+)- and (−)-*trans*-1,2-cyclohexanedicarboxylic acid [(+)- and (−)-C6] with rigid spirodiamine, 2,6-diazaspiro[3.3]heptane (DSH). We also prepared several model compounds, I–VI, as shown below.

The conformations of the polymers and the model compounds were investigated by means of ORD, CD, and hydrodynamic methods.

Experimental Section

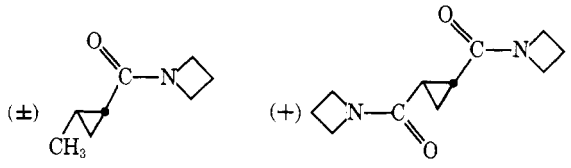
(+)-(*S*)-*trans*-1,2-Cyclopropanedicarboxylic Acid. The synthesis of optically pure (+)-(*S*)-*trans*-1,2-cyclopropanedicarboxylic acid was reported previously.[4] The dicarboxylic acid was prepared by ozonolysis of optically active (+)-(*S*)-*trans*-2-phenylcyclopropanecarboxylic acid:[6] mp 172.5–173.5° (lit.[4] mp 172–173°); $[\alpha]^{20}D$ +258° (water, *c* 1.0 g/dl); $[\alpha]^{20}D$ +250° (water, *c* 1.0 g/dl).

(+)- and (−)-*trans*-1,2-Cyclohexanedicarboxylic Acids. *trans*-1,2-Cyclohexanedicarboxylic acid (Aldrich Chemical Co.) was recrystallized twice from methanol–water (1:1). Activated charcoal was used in the recrystallizations. Optical resolution was carried out according to the procedure of Nishimura[7] and Applequist and Werner.[8] The quinine salt of the diacid was recrystallized from 95% ethanol. Free (+)-diacid liberated from the quinine salt was recrystallized from water again using charcoal: mp 181.5–182.5° (lit.[7] mp 179.5–181.5°); $[\alpha]^{20}D$ +19.4° (acetone, *c* 1.0 g/dl); $[\alpha]^{25}D$ +20.0 (acetone, *c* 2.0 g/dl).

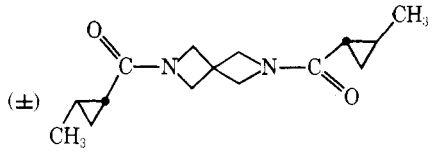
The (−)-isomer-rich diacid recovered from the quinine salt was dissolved in acetone, in which the racemic acid was insoluble: mp 181–182.5° (lit.[7] mp 175–180°); $[\alpha]^{20}D$ −18.9° (acetone, *c* 1.0 g/dl); $[\alpha]^{25}D$ −19.5° (acetone, *c* 2.0 g/dl).

(±)-*trans*-2-Methylcyclopropanecarboxylic Acid. This was synthesized according to the method of Applequist and Peterson:[9] bp 104–105° (22 mm) [lit.[9] 91–91.5° (14 mm)]. The melting point of the amide derived from the above acid and aqueous ammonia was 110–111° (lit.[9] 111.3–112.0°).

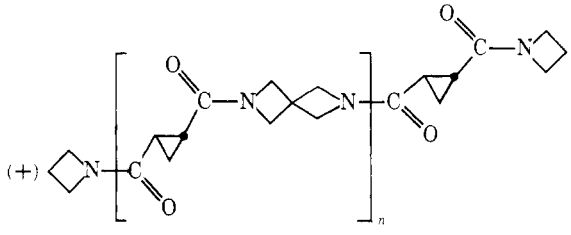
Acid Chlorides. The acid chlorides of (+)-(*S*)- and (±)-*trans*-1,2-cyclopropanedicarboxylic acid, (+)-, (−)-, and (±)-*trans*-1,2-cyclohexanedicarboxylic acid, and *trans*-2-methylcyclopropanecarboxylic acid were prepared by treating the acids with an excess of purified thionyl chloride:[4] (+)-C3 bp 29.5–30° (0.12 mm), mp 32–33° [lit.[4] bp 40° (0.08 mm)]; $[\alpha]^{24}D$ +252° (CCl_4, *c* 1.0 g/dl); (±)-C3 bp 38–39° (0.8 mm); (+)-C6 bp 65–66° (0.15 mm) (lit.[7] bp 61–62° (0.04 mm)), $[\alpha]^{24}D$ −19.5° (CCl_4 *c* 2.6 g/dl), $[\alpha]^{25}D$ −18.2° [CCl_4, *c* 2.0 g/dl)]; (−)-C6 bp 61–62° (0.10 mm), $[\alpha]^{24}D$



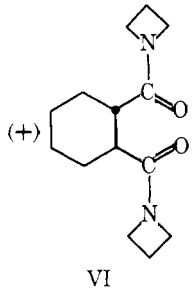
I II



III



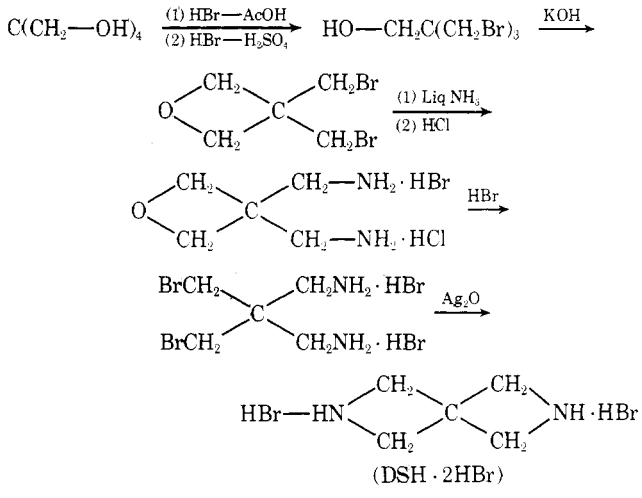
IV, $n = 1$
V, $n = 3.5$



VI

+19.8° (CCl_4, *c* 2.7 g/dl); (±)-C6 bp 60–61° (0.10 mm); (±)-*trans*-2-methylcyclopropanecarbonyl chloride bp 63–64° (88 mm).

2,6-Diazaspiro[3.3]heptane (DSH). The spirodiamine, DSH, was prepared by the following processes.



(DSH · 2HBr)

A mixture of pentaerythritol (640 g, 4.70 mol), 48% hydrobromic acid (2370 ml), and glacial acetic acid (470 ml) was boiled for 18 hr.[10] To this mixture an additional 48% hydrobromic acid (2370 ml) was added followed by the addition of sulfuric acid (1185 ml). The solution thus obtained was boiled for 8 hr. When the reaction mixture was cooled, the solution separated into two layers. The lower layer was dissolved in chloroform (1000 ml), washed with water, and dried over anhydrous potassium carbonate. After the separation of chloroform by distillation, the residue was fractionally distilled under reduced pressure to give 1272 g (83%) of colorless liquid which crystallized during the distillation: bp 130–155° (0.7–2.0 mm). The solid was recrystallized three times from carbon tetrachloride: mp 65–66° (lit.[10] 68–69.5°); nmr ($CDCl_3$) δ 3.52 (s, 6 H, CH_2Br), 3.79 (s, 2 H, $-CH_2O-$), 1.65 (s, 1 H, OH).

3,3-Bis(bromomethyl)oxatane was prepared by applying the procedure for 3,3-bis(chloromethyl)oxatane reported by Farthing.[11] The ring closure reaction was accomplished with potassium hydroxide in ethanol. Thus, a mixture of potassium hydroxide (132 g) and 3-bromo-2,2-bis(bromomethyl)propanol-1 (750 g) in ethanol (900 ml) was refluxed for 15 min. After separation of potassium bromide by filtration, the filtrate was fractionally distilled under vacuum. Pure oxabutane was obtained by redistillation from CaH_2: yield 80%; bp 68–69° (0.65 mm); $n^{26}D$ 1.5290; nmr ($CDCl_3$) δ 3.80 (s, 4 H, CH_2) and 4.38 (s, 4 H, CH_2).

The synthetic procedure of 3,3-bis(aminomethyl)oxatane from 3,3-bis(chloromethyl)oxatane[12] was used with some modifications for the next step. 3,3-Bis(bromomethyl)oxatane (30 g, 0.12 mol) was placed in a 500 ml stainless steel bomb equipped with a pressure gauge; liquid ammonia (150 ml) was added to the frozen bromooxatane. The bomb was heated for 8 hr at 80°. After cooling to room temperature, the excess ammonia was evaporated. The residue was then dissolved in 50% aqueous methanol and a sufficient amount of HCl gas was passed through the solution. The solid thus obtained was recrystallized from 95% methanol: yield 60–65%; mp 230–235°; nmr (D_2O) δ 3.40 (s, 4 H, CH_2) and 3.75 (s, 4 H, CH_2).

The final two steps were accomplished according to the methods of Govaert and Beyaert.[13] 3,3-Bis(aminomethyl)oxatane hydrobromide hydrochloride (5 g, 0.018 mol) and 49% hydrobromic acid (13 ml) were placed in a 20–25 ml glass ampoule with a thick wall (~2 mm). Hydrogen bromide gas was passed through the solution which had been cooled with Dry Ice. The ampoule was then sealed and heated for 7.5 hr at 230°. The mixture was poured into cold ethanol; the precipitate was isolated by filtration. The crude product was recrystallized from diluted hydrobromic acid: yield 4.6 g (61%); mp 284–286° dec [lit.[13] 286° dec]; nmr (D_2O) δ 3.34 (s, 4 H, CH_2) and 3.70 (s, 4 H, CH_2).

Silver oxide (2.75 g, 0.012 mol) was added to 2,2-bis(bromomethyl)propane 1,3-dihydrobromide (5.0 g, 0.012 mol) dissolved in 25 ml of water. After 1 hr the precipitate was separated by filtration. Water in the filtrate was evaporated until a solid appeared. Ethanol (50 ml) was added to the above mixture and the solid was filtrated. The crude product (DSH · 2HBr) was recrystallized from about 90% ethanol: yield 2.6 g (85%); mp 225–226° dec [lit.[13] 225° dec]; nmr (D_2O) δ 4.40 (s, 8 H, CH_2).

Anal. Calcd for $C_5H_{12}N_2Br_2$: C, 23.07; H, 4.62; N, 10.77. Found: C, 23.07; H, 4.64; N, 10.79.

C3 · DSH Polyamides. The polyamides were synthesized by interfacial polycondensation reactions of diacid chlorides with DSH.[3,4] (+)-(*S*)-*trans*-1,2-Cyclopropanedicarbonyl chloride (1.23 g, 7.34 mmol) in a sealed glass ampoule and 77 ml of dichloromethane (Merck, reagent grade) were placed in a Waring semimicro blender, which was then externally cooled to 0° with Dry Ice. DSH · 2HBr (2.10 g, 8.09 mmol) was dissolved in 16.1 ml of 2 *N* NaOH and 2.2 ml of water which had been precooled to 0° and added to the blender. The glass ampoule was broken in the blender with vigorous stirring. The reaction was continued for 10 min keeping the temperature at 0–10°. The solvents were evaporated under reduced pressure and the residue was added to 40 ml of water–methanol (1:1). The insoluble part was separated with a centrifuge. The polymer solution was dropped into 500 ml of ethanol to precipitate the high molecular weight polymer [(+)-C3 · DSH]. The isolated polymer was reprecipitated twice from water–methanol (1:1) in ethanol; the yield of the polymer was 0.39 g (29%) after drying over phosphorous pentoxide for 48 hr at 110° under high vacuum. The polymer dissolved in water–methanol (1:1) formed no precipitate when silver nitrate was added. The polymer was soluble in water–methanol (1:1), H_2SO_4, and 2,2,2-trifluoroethanol (TFE), partially soluble in water and chloroform, and insoluble in methanol and tetramethylene sulfone. The elemental analysis of the polymer indicated that the polymer contained about 1% ash which may be due to imperfect combustion[4] and *ca.* 0.5 molecule of water per one repeating monomer unit. The data corrected for the ash and the water agreed with the calculated value. The intrinsic viscosity of the polymer was 3.20 dl/g in TFE at 25°. Another run of the polymerization under the same reaction conditions gave a polymer with $[\eta]$ = 2.75 dl/g in 26% yield.

Anal. Calcd for $(C_5H_4O_2)(C_5H_8N_2)$: C, 62.4; H, 6.3; N, 14.6. Found (corrected): C, 62.3; H, 6.2; N, 14.5.

On the other hand, the filtrate (ethanol) of the polymer precipitation contained low molecular weight polymer, which was isolated by gel permeation chromatography (Sephadex LH-20, H_2O–MeOH (50/50)] and dialysis in water. The polymer was soluble in

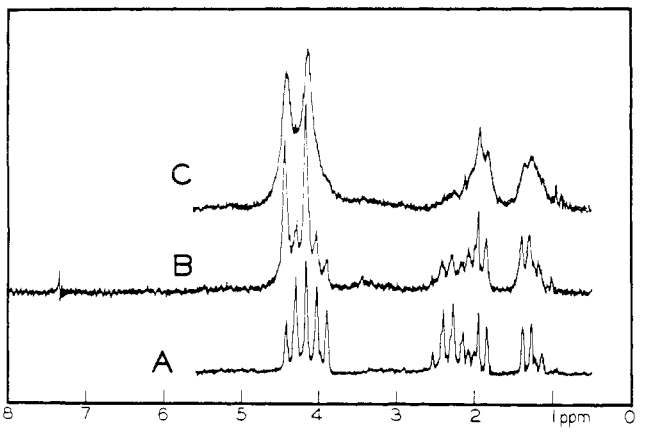


Figure 1. Nmr spectra of model compounds II (A), IV (B), and V (C) in $CDCl_3$ at 60 MHz.

water. The yield of the polymer was 0.27 g (20%): [η] 0.23 dl/g (TFE, 25°).

Anal. Found (corrected): C, 62.3; H, 6.2; N, 14.5.

The polyamides, (±)-C3 · DSH, and (±+)-C3 · DSH were also prepared in the same manner as described above. A mixture of 76% (+)-C3 and 24% (−)-C3 was used for the preparation of (±+)-C3 · DSH. The yields and intrinsic viscosities of ethanol-insoluble polymers were: (±)-C3 · DSH yield 63%, [η] 1.34 dl/g (TFE, 25°); (±+)-C3 · DSH yield 32%, [η] 3.4 dl/g (TFE, 25°). Microanalysis data (corrected) agreed with calculated values. All C3 · DSH polyamides had melting points higher than 300°.

C6 · DSH Polyamides. The polyamides were also prepared by interfacial polycondensation reaction. (−)-*trans*-1,2-Cyclohexanedicarbonyl chloride (1.13 g, 5.36 mmol) in a sealed glass ampoule and dichloromethane (54 ml) were charged in the blender and cooled at 0°. Just before the reaction, DSH · 2HBr (1.53 g, 5.90 mmol) was dissolved in 2 *N* NaOH (11.8 ml) and 2.7 ml of water and added into the blender. The reaction was performed for 10 min at 0–10°. Evaporation of the solvents left a mixture of the polymer and inorganic salts, which was taken up in chloroform (40 ml) to separate the salts by filtration. The filtrate was added dropwise into ethyl acetate (400 ml); the polymer [(−)-C6 · DSH] was reprecipitated from $CHCl_3$ in ethyl acetate. The polymer was soluble in TFE, water, methanol, and $CHCl_3$ and insoluble in acetone, ether, and ethyl acetate. The yield of the polymer was 0.44 g (35%) after drying for 48 hr at 110°; [η] 0.68 dl/g (TFE, 25°). From the filtrate of the polymer precipitations (ethyl acetate) an additional polymer (0.32 g, 26%) was recovered; [η] 0.46 dl/g (TFE, 25°). The polymers contained less than 1% ash. The elemental analysis data corrected for ash were in accordance with calculated values.

Anal. Calcd for $(C_8H_{10}O_2)(C_5H_8N_2)$: C, 66.6; H, 7.7; N, 12.0. Found: C, 66.3; H, 8.2; N, 11.9.

Polyamides, (+)-C6 · DSH, (±)[C6 · DSH, and (±+)-C6 · DSH were also prepared in the same manner. A mixture of 75% (+)-C6 and 25% (−)-C6 was used for the preparation of (±+)-C6 · DSH. The yields and intrinsic viscosities in TFE at 25° of the ethyl acetate-insoluble polymers were: (+)-C6 · DSH yield 44%, [η] 0.22 dl/g; (±)-C6 · DSH yield 33%, [η] 0.54 dl/g; (±+)-C6 · DSH yield 66%, [η] = 0.30 dl/g. The elemental analysis data corrected for ash agreed with calculated values. All polymers had melting points higher than 300°.

Model Compound I. (±)-*trans*-2-Methylcyclopropanecarbonyl chloride (0.45 g, 4.0 mmol) was added dropwise to a solution of azetidine (Eastman Kodak, 0.25 g, 4.4 mmol) and triethylamine (0.4 g) in 20 ml of ether at room temperature. Triethylamine hydrochloride was separated by filtration. The solvent of the filtrate was evaporated. The residue was passed through a Florisil column (1 × 10 cm) with chloroform as the solvent. From a fraction of 10–50 ml of chloroform elution, 0.25 g (45%) of the product was isolated: ir (neat) 1640 cm^{-1} (amide); nmr ($CDCl_3$) δ 1.1 (d, 3 H, CH_3), 0.5–1.2 (m, 4 H, cyclopropane), 2.3 (qi, 2 H, CH_2), 4.0 and 4.3 (two t, 2 H, 2 H, NCH_2).

Anal. Calcd for $C_8H_{13}NO$: C, 69.03; H, 9.41; N, 10.06. Found: C, 69.09; H, 9.79; N, 9.63.

Model Compound II. This was synthesized in the same manner as described in the polymerizations. (+)-(*S*)-*trans*-1,2-Cyclopropanedicarbonyl chloride (1.02 g, 6.13 mmol) and dichloromethane (61 ml) were charged in the blender and cooled to 0°. To this solution, azetidine (0.77 g, 13.4 mmol), 2 *N* NaOH (6.1 ml), and water (8 ml) were added. The reaction was carried out for 10 min at 0–10° with stirring. The solvents were evaporated and the residue was dried under high vacuum overnight. The reaction mixtures thus obtained were taken up in chloroform to exclude insoluble salts. The crude product was recrystallized twice from carbon tetrachloride–*n*-hexane mixture (4:3): yield, 0.89 g (70%); mp 112–113°; ir (Nujol) 1635 cm^{-1} (amide); nmr spectrum is shown in Figure 1; $[\alpha]^{25}D$ +123° ($CHCl_3$, *c* 1.0 g/dl), +98° (H_2O, *c* 1.0 g/dl).

Anal. Calcd for $C_{11}H_{16}N_2O_2$: C, 63.44; H, 7.74; N, 13.45. Found: C, 63.31; H, 7.65; N, 13.48.

Model Compound III. This was prepared using the same method as described above. The crude product was recrystallized from a CCl_4–*n*-hexane mixture (2:1): yield 55%; mp 165–167.5°; ir (Nujol) 1620 cm^{-1} (amide); nmr ($CDCl_3$) δ 1.1 (d, 6 H, CH_3), 0.6–1.2 (m, 8 H, cyclopropane), 4.1 and 4.4 (two s, 4 H, 4 H, N-CH_2).

Anal. Calcd for $C_{15}H_{22}N_2O_2$: C, 68.67; H, 8.45; N, 10.68. Found: C, 68.54; H, 8.41; N, 10.50.

Model Compounds IV and V. These compounds were prepared by two-step condensation reactions. First, (+)-(*S*)-*trans*-1,2-cyclopropanedicarbonyl chloride (0.81 g, 4.8 mmol) in dichloromethane (48 ml) was allowed to react with azetidine (0.29 g, 5.1 mmol) in 24 ml of 2 *N* NaOH in a blender for 2.5 min at 10–20°. Immediately after the reaction, DSH · 2HBr (0.66 g, 2.5 mmol) in 5.0 ml of 2 *N* NaOH was added with stirring to the above reaction mixture. The reaction was continued for 10 min at 10–20°. The solvents were evaporated and the residue was dried under vacuum overnight. The reaction mixture thus obtained was dissolved in chloroform to separate inorganic salts by filtration. The filtrate (5 ml) was dropped into acetone (40 ml) to precipitate oligomer V which was filtrated and dried. The solvents of the filtrate were evaporated. The residue was dissolved in chloroform again, followed by the addition into diethyl ether to precipitate IV. Model compounds IV and V were reprecipitated from chloroform in ether and acetone, respectively. The corresponding yields of IV and V were 0.04 and 0.25 g. Both compounds did not melt below 300°. The filtrate (ether) of IV contained about 0.3 g of II: ir (Nujol) IV 1620 cm^{-1} (amide); V 1620 cm^{-1} (amide). Nmr spectra in $CDCl_3$ are shown in Figure 1. The molecular weights determined by a vapor phase osmometer in TFE were 420 (calculated value 400.5) for IV and 880 for V. The latter molecular weight showed that the oligomer had an average of 3.5 DSH units in a molecule which agreed with the value determined by the nmr spectrum.

Anal. Calcd for IV, $C_{21}H_{28}N_4O_4$: C, 62.98; H, 7.05; N, 13.99. Found: C, 62.83; H, 7.13; N, 14.05.

Anal. Calcd for V, $C_{46}H_{58}N_9O_9$: C, 62.7; H, 6.6; N, 14.3. Found (corrected): C, 62.7; H, 6.5; N, 14.3.

Oligomer V contained about two molecules of water per one oligomer molecule.

Model Compound VI. This compound was prepared from (+)-*trans*-1,2-cyclohexanedicarbonyl chloride and azetidine in the same manner as described for I. The crude product was recrystallized twice from *n*-hexane: yield 56%; mp 94–95°; $[\alpha]^{25}D$ −31.7° ($CHCl_3$, *c* 1.0 g/dl), +21.9° (H_2O, C 1.0 g/dl); ir (Nujol) 1640 cm^{-1} (amide); nmr ($CDCl_3$) δ 1.3–2.5 (m, 10 H, cyclohexane), 2.2 (qi, 4 H, CH_2), 4.0–4.4 (m, 8 H, NCH_2).

Anal. Calcd for $C_{14}H_{22}N_2O_2$: C, 67.17; H, 8.86; N, 11.19. Found: C, 67.26; H, 8.81; N, 11.15.

Measurements. The nmr spectra were measured with a Varian T60 spectrometer at 60 MHz using tetramethylsilane as an internal standard. The ir spectra were taken with a Perkin-Elmer Model 257 spectrometer. The uv, ORD, and CD spectra were measured with a Jasco-Durram ORD/CD/UV-5 spectropolarimeter using a 0.1-mm cell at 23–25°. TFE (Matheson Coleman and Bell), methanesulfonic acid (MSA) (Eastman Kodak), and sulfuric acid (J. T. Baker Chemical) were used without further purification. The optical rotation was obtained with an ETL-NPL Automatic Polarimeter Type 143A. The molecular weights were determined with a Hitachi Perkin-Elmer Model 115 vapor pressure osmometer using TFE as a solvent at 40°. A calibration curve was made with benzil as a standard. Melting points were corrected. The solution viscosities of the polymers were measured with an Ubbelohde viscometer at 25.00 ± 0.02°.

Results and Discussion

It has been reported that free DSH is very unstable at room temperature.[13] To get a high molecular weight poly-

Table I
Optical Data for II, IV, V, (+)-C3·DSH, VI, and (+)-C6·DSH in TFE and MSA

	CD				ORD			
	TFE		MSA		TFE		MSA	
Compd	λ, mμ	$[\theta]^a$	λ, mμ	$[\theta]^a$	λ, mμ	$[m]^b$	λ, mμ	$[m]^b$
II	220	−32,000	216	−61,800	230	−9,900	229	−22,400
	210	0	205	0	221	0	219	0
	~200	+32,000	~194	+64,500	207	+50,600	202	+93,700
IV	219	−41,800	219	−64,000	229	−18,700	229	−23,800
	209	0	206	0	219	0	220	0
	~199	+37,400	195	+58,500	207	+49,800	203	+91,000
V	219	−57,700	219	−75,500	227	−24,000	229	−29,000
	208	0	207	0	219	0	220	0
	~199	+37,000	~195	+61,500	207	+69,600	204	+98,000
(+)-C3·DSH	219	−62,500	219	−76,700	227	−23,600	229	−33,800
	209	0	206	0	217	0	219	0
	~200	+35,500	~195	+59,500	207	+76,000	205	+99,000
VI	214	+4,800	203	−15,200	204	−14,500	212	−8,900
	209	0			195	0	201	0
	~195	−22,400					~195	+7,500
(+)-C6·DSH	207	−34,400	206	−31,900	214	−24,200	212	−17,800
					204	0	204	0
					~195	+16,700	~195	+22,800

[a] (deg cm²)/dmol of amide residue. [b] m = 3300Δε (deg cm²)/dmol of amide residue.

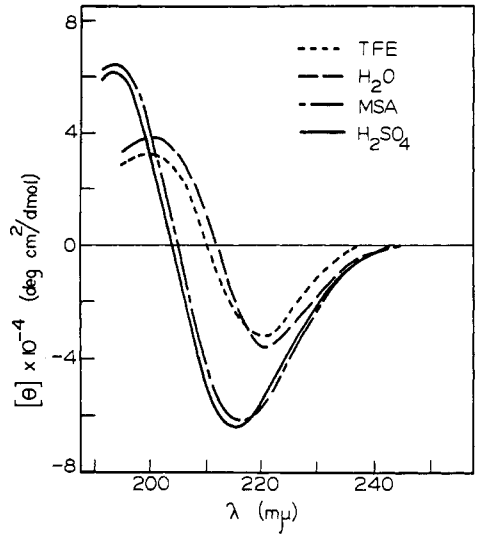


Figure 2. CD spectra of model compound II in various solvents.

mer, therefore, caution must be exercised in the step to liberate free amine from DSH · 2HBr. In the present method, we obtained polymers of sufficiently high molecular weight to study their conformation. Since DSH has a very rigid structure and good symmetry, one would expect that the polymers derived from DSH will have a high melting point. As shown in the Experimental Section, all polymers had melting points higher than 300°.

The uv/ORD/CD spectra were measured in various solvents such as TFE, water, 12% HCl, MSA, and sulfuric acid. Since there was no noticeable change in the spectra in concentrations of 2–6 × 10^{-3} mol of amide residue per liter for (+)-C3 compounds and 3–8 × 10^{-3} mol of amide residue per liter for (+)-C6 compounds, the spectra were taken at concentrations *ca.* 5 × 10^{-3} mol of amide residue per liter for (+)-C3 compounds and 7–8 × 10^{-3} mol of amide residue per liter for (+)-C6 compounds. Identical spectra were obtained repeatedly at different times (0.5–120 hr)

Table II
Intrinsic Viscosities of Polymers in TFE and Sulfuric Acid at 25°

	[η], dl/g	
Polymer	TFE	H_2SO_4[a]
(+)-C3·DSH	2.75	2.60
(±)-C3·DSH	1.34	1.33
(+)-C6·DSH	0.22	0.20
(±)-C6·DSH	0.54	0.51

[a] Viscosities did not change even after 24 hr.

after dissolving in the solvents, except in 12% HCl where the amide bonds were slowly hydrolyzed. The low and high molecular weight polymers showed the same spectra.

The CD spectra of II are shown in Figure 2. The spectra of other (+)-C3 compounds usually exhibited a strong peak at 195–200 mμ and a strong trough at 206–211 mμ. The intensity was stronger in a strong acid, MSA, than in a nonacidic solvent, TFE, as shown in Table I. The spectral data in water and sulfuric acid were similar to those in TFE and MSA, respectively. The peak and trough may be assigned to split π–π* transition due to an exciton coupling of two amide chromophores based on the position and intensity.[4] The n–π* transition was not observed probably because of overlap with stronger π–π* transition. The strength of the negative CD band at around 200 mμ increased with increasing molecular weight. The CD spectra of V which has an average of 3.5 DSH units were almost identical with high molecular weight (+)-C3 · DSH. Similar results have been reported on oligo-L-proline.[14]

The ORD spectra of II in various solvents and the ORD data for other (+)-C3 compounds are shown in Figure 3 and Table I, respectively. Cotton effects were observed corresponding to the CD band. The ORD intensity was also stronger in acidic solvents and increased with an increase in the molecular weight as found in the CD spectra. Although there are slight changes in the CD and ORD spectra

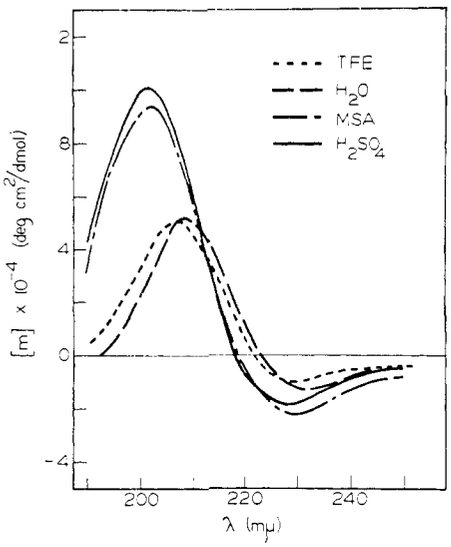


Figure 3. ORD spectra of model compound II in various solvents.

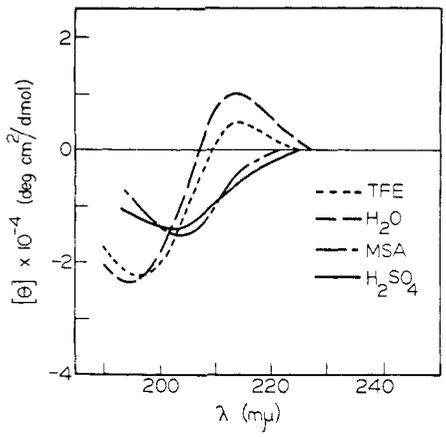


Figure 4. CD spectra of model compound VI in various solvents.

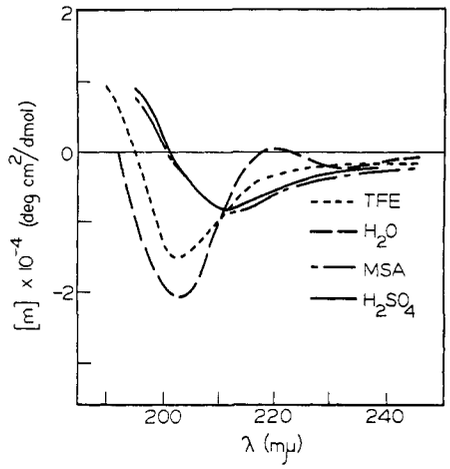


Figure 5. ORD spectra of model compound VI in various solvents.

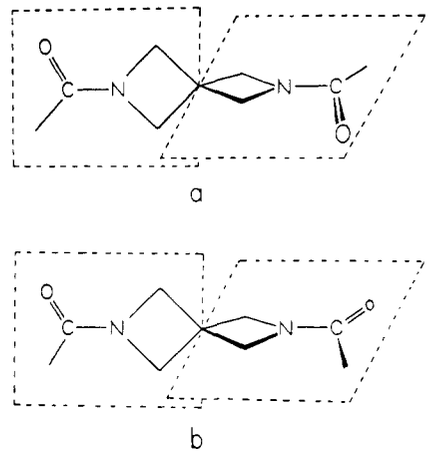


Figure 6. Rotation of the amide group due to DSH: (a) clockwise rotation; (b) counterclockwise rotation.

in the various solvents, the spectral patterns are quite similar. Consequently, it seems safe to conclude that these compounds have the same conformation with respect to the cyclopropane ring, which is not varied in the strong acids.

The solvent effects on the CD spectra of (+)-C3 piperidine diamide and (+)-C3 piperidine polyamide were reported previously.[4] The model compound II and (+)-C3 · DSH exhibited much stronger CD intensities than (+)-C3 · piperidine diamide and (+)-C3 · piperidine polyamide, respectively. In the latter CD spectra, the trough at around 220 mμ in TFE was red shifted by *ca.* 7 mμ with a decrease in intensity in MSA. The quite different solvent effect may indicate that the conformations of II and (+)-C3 · DSH are different from those of (+)-C3 · piperidine diamide and (+)-C3 · piperadine polyamide.

In Figure 4 are shown the CD spectra of VI in various solvents. In TFE and water, we could see a trough at around 195 mμ and a peak at around 214 mμ which may be assigned to a split π–π^* transition, while in MSA and sulfuric acid, we could see only a trough at around 204 mμ. This rather drastic spectral change on VI may imply that a conformational change occurs on going from the nonacidic solvents to the strong acids. On the other hand, (+)-C6 · DSH showed no spectral change in the same solvent systems (Table I). The ORD spectra of VI also demonstrated a rather drastic change (Figure 5), whereas (+)-C6 · DSH showed no change (Table I). (−)-C6 · DSH exhibited the exact opposite CD and ORD spectra to (+)-C6 · DSH.

The solvent effects on the CD spectra of (+)-C6 · piperidine diamide and (+)-C6 · piperadine polyamide were rather similar to those observed on VI and (+)-C6 · DSH, respectively.[15,16] The conformation of VI and (+)-C6 · piperidine diamide in TFE and water may be different from those of (+)-C6 polyamides and the model compounds in strong acids. One of the probable conformations is an extended form where two amide carbonyls lay close to each other and the piperidine or the azetidine rings are placed in the outside position,[16] although we cannot say in which solvent system this conformation is preferred.

The CD and ORD spectra of II, VI, (+)-C3 · DSH, and (+)-C6 · DSH in 12% HCl were almost the same as those in water. The (±+)-C3 · DSH and (±+) · C6 · DSH polyamides (see Experimental Section) exhibited CD and ORD spectra very similar to the corresponding optically pure polymers except in intensity; (±+)-C3 · DSH and (±+)-C6 · DSH had about 70–80% intensity compared with the corresponding optically pure polymers.

The uv absorption maxima of (+)-C3 compounds were observed in the range of 207–213 mμ and red shifted with increasing molecular weight. There was no significant solvent effect on the spectra. The uv maxima of VI and (+)-C6 · DSH were observed at 195–201 mμ and 198–204 mμ, respectively, and blue shifted in the strong acids.

The intrinsic viscosities of (+) and (±)-C3 · DSH and (+)- and (±)-C6 · DSH were measured in TFE and in sulfuric acid (Table II). The viscosities were the same in both

solvents within experimental error. This may imply that the optically active polymers have no special conformation, although the strong peaks in the CD and ORD spectra are due to a rigid structure.[17] The optical data depend very much on the conformations of two carbonyl groups on the cyclopropane and cyclohexane rings. Probably the conformations in the polymers are not varied in all the solvents. However, the DSH unit in the polymers can rotate the amide groups clockwise or counterclockwise by 90° as shown in Figure 6. Since there are no differences in the steric interactions and the dipole–dipole interactions between the two structures, the rotation may be random in the polymers. This may be the reason why the optically active polymers and the racemic polymers demonstrated the same viscosity behavior.

In the cases of (+)-C3 · piperidane and (+)-C3 · *trans*-2,5-dimethylpiperadine polyamide, the solution viscosities in TFE and MSA were somewhat different; the viscosity in MSA was much greater than that in TFE.[18] The difference in the viscosity behavior also indicates that (+)-C3 · DSH may have a different conformation from (+)-C3 · piperadine and (+)-C3 · *trans*-2,5-dimethylpiperadine polyamides as stated in the solvent effect on the CD spectra.

The nmr studies of the polymers and the model compounds, especially I and III, will be reported in a future publication.

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References and Notes

(1) L. Mandelkern in "Poly-α-Amino Acids," G. D. Fasman, Ed., Marcel Dekker, New York, N.Y., 1967.
(2) P. R. Schimmel and P. J. Flory, *Proc. Nat. Acad. Sci. U.S.*, **58**, 52 (1967).
(3) C. G. Overberger, G. Montaudo, Y. Nishimura, J. Sebenda, and R. A. Veneski in "Kinetics and Mechanism of Polyreaction," F. Tudos, Ed., Akademiar Kiado, Budapest, 1971, p 127.
(4) C. G. Overberger and Y. Shimokawa, *Macromolecules*, **4**, 718 (1971).
(5) G. Montaudo, P. Finocchiaro, P. Maravigna, and C. G. Overberger, *Macromolecules*, **5**, 197, 203 (1972).
(6) Y. Inoue, T. Sugita, and H. M. Walbarsky, *Tetrahedron*, **20**, 1695 (1964).
(7) Y. Nishimura, Ph.D. Thesis, Polytechnic Institute of Brooklyn, Brooklyn, N.Y., 1966.
(8) D. E. Applequist and N. D. Werner, *J. Org. Chem.*, **28**, 48 (1963).
(9) D. E. Applequist and A. H. Peterson, *J. Amer. Chem. Soc.*, **82**, 2372 (1960).
(10) A. I. D'yachenko and M. Yu. Lukima, *Izv. Acad. Nauk. SSSR*, 2237 (1966).
(11) A. C. Farthing, *J. Chem. Soc.*, 3648 (1955).
(12) T. W. Campbell, *J. Org. Chem.*, **22**, 1029 (1957).
(13) F. Govaert and M. Beyaert, *Bull. Soc. Chim. Belg.*, **55**, 106 (1946).
(14) H. Okabayashi, T. Isemura, and S. Sakakibara, *Biopolymers*, **6**, 323 (1968).
(15) G. Montaudo and C. G. Overberger, *J. Polym. Sci., Polym. Chem. Ed.*, **11**, 2739 (1973).
(16) G. Montaudo, P. Finocchiaro, P. Maravigna, and C. G. Overberger, *Macromolecules*, **5**, 197 (1972).
(17) M. Kasha, *Radiat. Res.*, **20**, 55 (1963).
(18) C. G. Overberger and Y. Shimokawa, to be published.

Polymerization of Hexachlorocyclotriphosphazene. The Role of Phosphorus Pentachloride, Water, and Hydrogen Chloride[1]

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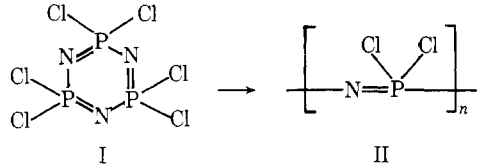
ABSTRACT: The polymerization of hexachlorocyclotriphosphazene (I) (also known as phosphonitrilic chloride trimer) to high molecular weight poly(dichlorophosphazene) (II) has been studied in the presence of phosphorus pentachloride, water, and hydrogen chloride. Phosphorus pentachloride is a powerful polymerization inhibitor, water is a polymerization catalyst or cocatalyst, and hydrogen chloride is a mild inhibitor. The results are discussed in terms of possible reaction mechanisms.

The thermal polymerization of hexachlorocyclotriphosphazene (phosphonitrilic chloride trimer) (I) to the rubbery, high molecular weight poly(dichlorophosphazene) (II) was first reported by Stokes in 1897.[3] More recently a number of investigators have studied this reaction with a view to understanding the reaction mechanism,[4-14] yet the details of this process are still only poorly understood. Interest in this polymerization reaction has grown rapidly in recent years, mainly because poly(dichlorophosphazene) is now a critical intermediate in the substitutive synthesis of high molecular weight poly(organophosphazenes).[9,15-20] These latter polymers constitute an important new class of applicable elastomers and thermoplastics.



I II

The thermal polymerization of hexachlorocyclotriphosphazene (I) is a complex reaction. The pure, molten trimer polymerizes at an observable rate only at temperatures above 230°, with the rate accelerating as the temperature is raised to 300°. However, polymerization is eventually accompanied by the formation of an insoluble modification.[9,15] This latter species is unsuitable as a substrate for substitution reactions, and the choice of a time–temperature relationship for polymerization requires a delicate assessment of the relative rates of polymerization and insolubilization.

The overall reaction is further complicated by the fact that traces of impurities appear to function as powerful accelerators or inhibitors for the polymerization. Catalysts are known which permit polymerizations to be effected at temperatures as low as 200°.[6,7,21] Finally, it is known that,