Table I
Selected Minimum Energy Conformations of GpC

Starting Conformation Dihedral Angles (deg) χ'	ψ'	ϕ'	ω'	ω	ϕ	ψ	χ	Sugar Pucker	Final Conformation Dihedral Angles (deg) χ'	ψ'	ϕ'	ω'	ω	ϕ	ψ	χ	Energy, E (kcal/mol)	Final Order
								C$_3$'endo										
15	50	225	180	290	180	60	15		2	62	205	296	279	183	56	25	−39.0	1
15	50	225	290	290	180	60	15											
15	50	225	60	60	180	60	15		5	61	181	183	79	194	60	44	−38.1	2
15	50	225	290	60	180	60	15		−7	62	240	315	106	205	76	39	−37.3	3
15	50	225	60	290	180	270	15		−3	61	190	129	238	100	350	39	−31.1	5
15	50	225	180	60	180	60	15		−2	62	187	214	59	169	53	33	−23.3	12
15	50	225	180	290	180	270	15		2	62	189	192	295	171	303	38	−18.7	17
								C$_2$'endo										
55	50	225	290	60	180	180	55		−15	294	299	332	282	178	171	153	−16.7	1

Table II
Dihedral Angles Proposed for Helical RNAs

RNA	ϕ'	ω'	ω	ϕ	ψ	χ	Ref
10-fold	203	285	257	188	88		5
		291.1	259.1	189.1	80.1	10.1	6
11-fold	216	273	282	165	74		5
	203.7	292.8	288.7	186.2	58.5	13.4	6
12-fold	193.8	298.0	282.9	175.6	63.3	18.5	6

atoms, q_i is the charge on atom i, a_{ij} and b_{ij} are the parameters in the 6–12 potential, and ϵ is the dielectric constant. The single summation extends over all eight flexible dihedral angles (Figure 1), where θ_k is the kth dihedral angle, and $V_{0,k}$ is the rotational barrier height for that rotation. Values computed in ref 1 were used for the parameters a_{ij} and b_{ij}, as well as for q_i, V_0, and ϵ. Units of energy are in kilocalories per mole.

The energy was minimized by a modified version of the algorithm of Powell,[4] the dihedral angles being the variable parameters. As starting conformations various combinations of the eight dihedral angles, representative of the allowed conformations of known di- and polynucleotides,[5,6] were chosen. In particular, the initial conformations used were $\chi' = 15°$ (anti), $\psi' = 50°$, $\phi' = 225°$, $\omega' = 60$, 180, and 290°, $\omega = 60$ and 290°, $\phi = 180°$, $\psi = 60$, 180, and 270°, and $\chi = 15°$ (anti). The sugar conformations were fixed at C$_{3'}$ endo for one series of trials and at C$_{2'}$ endo for another. Table I gives the results obtained for the three lowest energies, and for a selection of other conformations.

From the set of 18 starting conformations for C$_{3'}$-endo sugars, 17 different local minima were obtained. The lowest energy conformation, resulting from two different sets of initial conditions, has dihedral angles in the range of observed helical RNAs[5-7] (see Table II). Next in energy is an extended conformation comparable to one deduced from nmr data by Barry *et al.*[8] Figure 2a,b shows the lowest and next lowest energy form, respectively. For C$_{2'}$-endo sugars, the lowest energy conformation found here was extended, and was of much higher energy than the best C$_{3'}$-endo value (see Table I).

The above computations were extended to include the effects of intermolecular hydrogen bonding, as well as additional parameters to minimize the energy with respect to position and orientation of the GpC molecule in the unit cell. Further details of these calculations, which relied heavily on use of a PDP-10/LDS-1 interactive computer graphics system, will be supplied in the future. The results indicate that the helical RNA conformation found by energy minimization, with additional refinement, satisfies our X-ray diffraction data and is in agreement with the general nature of an independent structure determination of GpC using standard crystallographic methods by Seeman *et al.*[9] The extended conformation which was near in energy to this helical form could not be packed into our crystal cell. Thus, the conformation of GpC both in the crystal and in solution, appears to be predictable by elementary energetic considerations.

Acknowledgment. We thank Dr. A. Lesk for many helpful discussions pertaining to the computational, conformational, and crystallographic aspects of this problem. The molecular modeling was performed at the Princeton University Computer Graphics Laboratory, supported by NIH Grant RR-00578; other support was received from NIH GM-16539 and NSF GB-28021.

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Received May 16, 1973

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Asymmetric Pentadiene Polymerization

By using a catalyst system consisting of titanium (−)-(menthoxide)$_4$ and Al(C$_2$H$_5$)$_3$, Natta and coworkers succeeded in obtaining optically active 1,3-pentadiene polymers having a prevailingly cis-1,4 isotactic structure.[1] The sign of rotation of the polymers was (−).

Thinking of the true catalyst complexes as containing a reactive titanium–carbon bond and at least one (−)-menthoxide substituent, as suggested by the above authors, we tried to polymerize *trans*-1,3-pentadiene in the presence of catalyst systems prepared by reacting (−)-menthol with

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Table I

Catalyst System[a]	Ti:(−)-$C_{10}H_{19}OH$:Al Molar Ratio	Crude Polymer Ir Anal.[b]			$[\alpha]_{546}^{20}$ (deg)[c]	Polymer (g)	Time (Days)
		% Cis	% Trans	% 3,4			
$Al(C_2H_5)_3$-(−)-$Ti(OC_{10}H_{19})_4$	1:4:7	73	17	10	−6.5	1.16	12
$Al(CH_2C_6H_5)_3$-(−)-$Ti(OC_{10}H_{19})_4$	1:4:7	nd	nd	nd	∼−5	0.03	24
$Ti(CH_2C_6H_5)_4$-(−)-$C_{10}H_{19}OH$	1:1	53	35	12	∼0	0.11	10
$Ti(CH_2C_6H_5)_4$-$Al(CH_2C_6H_5)_3$-(−)-$C_{10}H_{19}OH$	1:1:1	66	23	11	+3.0	0.11	5
Bimetallic compound-(−)$C_{10}H_{19}OH$	1:1.06:1.5	66	22	12	+4.5	0.33	3
Bimetallic compound-$Al(CH_2C_6H_5)_3$-(−)-$C_{10}H_{19}OH$	1:4.2:7.9	69	20	11	−3.7	0.73	7

[a] The polymerizations were run at 0° in toluene (25 ml) solution by using 0.6×10^{-3} mol of Ti and 6 g of *trans*-1,3-pentadiene. [b] Determined as described in literature.[7] [c] Determined in *n*-hexane solution.

benzyltitanium derivatives.[2] The table shows the results so obtained compared with the results of a typical polymerization carried out using Natta's catalyst.

The most important facts are as follows. (1) The combination of tetrabenzyltitanium with (−)-menthol gives rise only to traces of polymer having a negligible optical activity (if any). (2) Very low polymer yields are also obtained using catalyst systems consisting of (−)-titanium tetramenthoxide and tribenzylaluminum. (3) A catalyst was formed by reacting a bimetallic compound containing Ti-C-Al bonds, prepared according to Zucchini from tetrabenzyltitanium and tribenzylaluminum,[2] with one (−)-menthol molecule. This catalyst yielded an optically active polymer having a mainly cis-1,4 isotactic structure, similar to that obtained in the presence of Natta's catalyst, *but surprisingly the sign of rotation is (+) instead of (−)*. A lower yield is obtained if a mixture of tetrabenzyltitanium, tribenzylaluminum, and (−)-menthol is used as the catalyst system. (4) The sign of rotation of the polymer can be *reversed* by addition to the above catalyst of $Al(CH_2C_6H_5)_3$ previously allowed to react with the correct amount of (−)-menthol to achieve the same Ti-Al-menthol molar ratio as in the Natta's catalyst system.[3]

These findings probably mean that at least two types of catalyst complexes of different structure exist in the catalyst. Their relative amount depends on the stoichiometry of the whole catalyst system. Both types of catalyst complexes show the same stereospecific behavior, but opposite signs of asymmetric induction. In addition the bimetallic compound seems to be a catalyst precursor.

The reason that the (−)-titanium tetramenthoxide-triethylaluminum mixture is an active catalyst system, while the (−)-titanium tetramenthoxide-tribenzylaluminum is not, probably lies in the fact that in the former case the formation of a bimetallic compound through elimination of ethane is easier than in the latter case, which involves toluene elimination. In the latter case, the bimetallic compound must therefore be formed by reacting tetrabenzyltitanium with tribenzylaluminum, as described by Zucchini and Giannini.[2]

Experimental Section

trans-1,3-Pentadiene was prepared by thermal decomposition of the sulfone[4] and purified by distillation over sodium hydride. Benzyltitanium derivatives, tribenzylaluminum, and titanium menthoxide were prepared according to the literature.[2,5,6] The (−)-menthol was a Fluka product, $[\alpha]_{546}^{20}$ −45°. The solvent was dried by distillation over $LiAlH_4$.[1] The polymerization was run under nitrogen atmosphere.

Acknowledgment. The authors thank Mr. G. Morelli for running the ir spectra of the polymers.

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Received April 17, 1973

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Far-Infrared Spectra of Copoly(γ-benzyl D,L-glutamates) and Sequential Copolymers of γ-Benzyl D- and L-Glutamates

Conformation of copoly(D,L-α-amino acids) has been studied with regard to the effect on the backbone structure of D- and L-amino acid residues in a single polypeptide chain.[1] Wada[2] and Tsuboi *et al.*[3] synthesized copoly(γ-benzyl D,L-glutamates) with various D- and L-residue ratios (PBD,LG) by the *N*-carboxyanhydride method and studied their conformation by means of dielectric dispersion,[2] infrared spectroscopy, and X-ray diffraction.[3] They found that each chain of the meso copolymers of γ-benzyl D- and L-glutamates has a random-coil portion and an α-helix portion and that the latter consists of the L and D residues with the ratio of D:L = 5:1 or 1:5. Based on this finding, they also proposed a simplified polymerization mechanism to this copolymer. Recently Heitz and Spach[4] synthesized poly(γ-benzyl-D-glutamyl-γ-benzyl L-glutamate) and studied its conformation in solution and in solid state. They concluded that the sequential copolymer takes the α-helical conformation and suggested that the meso copolymer of γ-benzyl D- and L-glutamates may assume the α-helical conformation even if it has a random sequence of the D and L residues. This is inconsistent with the hypothesis of Wada[2] and Tsuboi *et al.*[3]

In order to investigate in more detail the conformation and the D- and L-residue sequence of PBD,LG we measured the infrared spectra in a region from 700 to 200 cm^{-1} of PBD,LG and compared them with those of the

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