of **1** (moles of **1** isomerized/moles of $^1O_2$ generated[9]) was 36%.

An attempt to measure the singlet O_2 quenching rate of **1** failed because complete isomerization to **2** occurred before sufficient product was formed from 2-methyl-2-pentene to be detected accurately by the usual techniques. The overall quenching rate measured in these runs agreed well with that previously determined for all-*trans*-β-carotene.

These results and those in the accompanying communication[1] support the mechanism suggested[4] for carotene quenching of singlet oxygen, in which energy transfer from $^1O_2$ to the carotene occurs, as shown below.

$$^3MB \xrightarrow[^3O_2]{k_{O_2}} {}^1O_2 \xrightarrow[k_A]{A} AO_2$$

$$^1O_2 + \text{carotene} \xrightarrow{k_Q} {}^3\text{carotene}$$

$$^3MB \xrightarrow{k_Q^T} {}^3\text{carotene}$$

$$^3\text{carotene} \longrightarrow \text{all-}trans\text{-}\beta\text{-carotene} \quad (2)$$

In this scheme, all terms have the previous meaning;[1] carotene is either *cis*- or *trans*-β-carotene, and ^{3}carotene is a carotene triplet. Radiationless decay processes for ^3MB and $^1O_2$ do not compete under these conditions and are omitted for clarity. ^{3}Carotene must collapse largely to all *trans*-β-carotene, whether formed from **1** or **2** initially.

The presence or absence of O_2 was found not to affect the rate of photochemical isomerization, which is consistent with the above scheme since $k_Q[car] \gg k_A[A]$.[1] On the other hand, if isomerization were caused only by ^3MB, O_2 would inhibit the reaction whereas if $^1O_2$ were the sole cause, isomerization would not occur under N_2.[10] In O_2 saturated solutions, isomerization occurs entirely by way of $^1O_2$, since $k_Q^T[car] \ll k_{O_2}[O_2]$.

The dependence of quenching rate on the length of the conjugated chain[1] is consistent with the above scheme if the compounds with 5 and 7 double bonds have triplet energies above 22 kcal (the energy of $^1\Delta_gO_2$) but below that of methylene blue. The triplet energy of the 9-double bond carotenoid would be near 22 kcal, and that of β-carotene (11 C=C) would be lower. No reliable energy data for any of these compounds are available.[11]

Alternative mechanisms are not ruled out. For example, reversible electron transfer from carotene to $^1O_2$ could accommodate both the isomerization results and the chain-length dependence. Such mechanisms are well established for quenching,[13] and the ionization potential of carotenoids should increase with decreasing conjugation, so that the rate should drop off, though perhaps not so sharply; furthermore, the carotene radical cation should isomerize relatively easily (although one might expect it to undergo other reactions as well). However, the energy-transfer mechanism seems more satisfactory.

The quenching of $^1O_2$ by carotenes not only explains at least part of the protective action of carotenes in natural systems, but also implicates singlet oxygen as a causative agent in photodynamic action, though probably not the sole one.

(9) Calculated by oxidizing 2-methyl-2-pentene under identical conditions, determining the amount of product produced,[1,4] correcting for the trapping efficiency by this olefin at the concentration used, and back-calculating to give the yield of $^1O_2$ based on NaOCl (50% in this solvent, 0°, 0.76 *M* 2-methyl-2-pentene, 0.11 *M* H_2O_2).

(10) Isomerization of two poly-*cis*-lycopenes is reportedly inhibited by O_2.[2b]

(11) The emission from β-carotene which was reported[12] is due to an impurity: P.-S. Song, private communication.

(12) R. J. Cherry, D. Chapman, and J. Langelaar, *Trans. Faraday Soc.*, **69**, 2309 (1968).

(13) C. S. Foote, *Science*, **162**, 963 (1968); N. J. Turro, *Photochem. Photobiol.*, **9**, 555 (1969).

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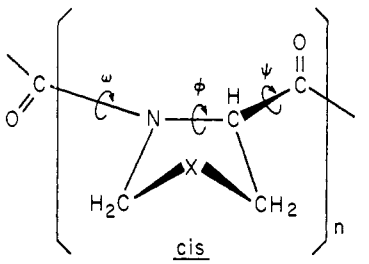
Conformational Aspects of Polypeptide Structure. XXXI. Helical Poly[(*S*)-thiazolidine-4-carboxylic acid] and Poly[(*S*)-oxazolidine-4-carboxylic acid]. Theoretical Results

Sir:

Conformational analysis of polypeptides has proven to be extremely useful in confirming and predicting ordered structures for isolated polymer chains.[1-3] We have calculated the structure for poly[(*S*)-thiazolidine-4-carboxylic acid], and believe that this polypeptide assumes a helical conformation. The structural relationship of this peptide to poly-L-proline is clear (Figure 1).



X = CH_2 Poly-L-proline
S Poly[(S)-thiazolidine-4-carboxylic acid]
O Poly[(S)-oxazolidine-4-carboxylic acid]

Figure 1.

Another related polypeptide, namely, poly[(*S*)-oxazolidine-4-carboxylic acid], is also under investigation in our laboratory. Although we have not succeeded in

(1) (a) R. A. Scott and H. A. Scheraga, *J. Chem. Phys.*, **45**, 2091 (1966); (b) *ibid.*, **46**, 4410 (1967).

(2) G. N. Ramachandran and C. M. Venkatachalam, *Biopolymers*, **6**, 1255 (1968).

(3) (a) J. E. Mark and M. Goodman, *J. Amer. Chem. Soc.*, **89**, 1267 (1967); (b) J. E. Mark and M. Goodman, *Biopolymers*, **5**, 809 (1967); (c) A. M. Liquori and P. DeSantis, *ibid.*, **5**, 815 (1967); (d) P. R. Schimmel and P. J. Flory, *Proc. Natl. Acad. Sci. U. S.*, **58**, 52 (1967).

Table I. The Helical Characteristics of Poly-L-proline, Poly[(*S*)-thiazolidine-4-carboxylic acid], and Poly[(*S*)-oxazolidine-4-carboxylic acid]

	Poly-L-proline		Poly[(*S*)-thiazolidine-4-carboxylic acid]		Poly[(*S*)-oxazolidine-4-carboxylic acid]	
Peptide unit	cis[a]	trans[b]	cis	trans	cis	trans
Internal rotation angles, deg ϕ	110	105	110	110	110	120
Internal rotation angles, deg ψ	340	335	350	340	350	340
Helical sense	Right	Left	Right	Left	Right	Left
Helical axial translation per peptide unit, Å	1.69	2.42	1.52	2.29	1.83	2.38
V (energy), kcal/mol of peptide unit	1.21	−0.82	3.86	−1.15	7.38	5.05
ΔV cis–trans, kcal/mol of peptide unit	2.03		5.01		2.33	

[a] W. Traub and U. Shmueli [*Nature (London)*, **198**, 1165 (1963)] carried out X-ray diffraction analysis on a fiber of poly-L-proline (I). They found two possible structures which are similar. They prefer the structure with 10 residues per unit cell and an axial translation per peptide unit of 1.90 Å. Our calculations agree somewhat better with the other structure which has 11 residues per unit cell and an axial translation per peptide unit of 1.73 Å. [b] P. M. Cowan and S. McGavin [*Nature (London)*, **176**, 501 (1955)] reported the axial translation per peptide unit for *trans*-poly-L-proline to be 3.12 Å. The discrepancy between this and our calculated value of 2.42 Å can arise from longer range intramolecular interaction (*i.e.*, greater than in the tripeptide we employed) and from packing factors for the fiber.

synthesizing poly[(*S*)-oxazolidine-4-carboxylic acid], we include calculations on this polymer with poly-L-proline and its sulfur analog.

Our conformational calculations for a tripeptide unit include nonbonded interactions, torsional potential functions, and electrostatic interactions. Coefficients for the pairwise Lennard-Jones potential functions were taken from Scott and Scheraga.[1] For interactions involving sulfur, we calculated the coefficients following the approach used to calculate the other interactions.[4] The electrostatic contributions were computed using a partial charge approximation suggested by Poland and Scheraga.[5] We employed standard bond lengths and bond angles[6] and developed a subroutine to our program to allow bond angles to deviate from their standard values.[7] In the case of the thiazolidine ring, we utilized preliminary X-ray diffraction information on (*S*)-thiazolidine-4-carboxylic acid which shows the ring to be puckered and the C–S–C bond angle to be approximately 90°.[8] To represent internal rotation angles, the convention suggested by Edsall, *et al.*,[9] was adopted. Details of our calculation will be presented in a subsequent paper. The preliminary results are tabulated in Table I. On the basis of the differences in energy of the cis and trans forms (Table I), we predict that poly[(*S*)-thiazolidine-4-carboxylic acid] should not mutarotate from the trans to the cis form. In the following communication we present experimental evidence on poly-[(*S*)-thiazolidine-4-carboxylic acid] that agrees with our calculations.

Poly[(*S*)-oxazolidine 4-carboxylic acid] shows two forms of helices with reasonable dimensions (Table I) and a cis–trans energy difference intermediate between the polyproline and its sulfur analog. The absolute values for the energy of the cis or trans tripeptide units are more positive because of the electrostatic contributions. We expect to observe mutarotation for poly[(*S*)-oxazolidine-4-carboxylic acid] under favorable conditions.

The succeeding paper presents initial experimental results which were carried out after we calculated the conformational characteristics for poly[(*S*)-thiazolidine-4-carboxylic acid]. We hope to extend these studies to the oxygen analog and other related polypeptides.

Acknowledgment. We wish to thank the National Science Foundation (Grant No. GB 7558) and the National Institutes of Health (Grant No. GM 08974) for their generous support of this research.

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Conformational Aspects of Polypeptide Structure. XXXII. Helical Poly[(*S*)-thiazolidine-4-carboxylic acid]. Experimental Results

Sir:

In the preceding paper we predicted that the all-trans polymer for poly[(*S*)-thiazolidine-4-carboxylic acid], a cyclic analog of poly-L-proline in which the γ-methylene has been replaced by sulfur, is more stable than the all-cis polypeptide by 5 kcal/mol of peptide unit. This compares with a difference between *trans*- and *cis*-poly-L-proline of about 2 kcal/mol of peptide unit.[1] Poly-L-proline[2–5] and its derivatives are the only poly-

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(6) "Tables of Interatomic Distances and Configuration in Molecules and Ions," The Chemical Society, London, 1958.
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(5) L. Mandelkern in "Poly-α-Amino Acids," Vol. 1, G. D. Fasman, Ed., Marcel Dekker, New York, N. Y., 1967, p 675.