

Scheme I. Arrangement of the interturn hydrogen bonds in β helices with different sense of twist for generic Boc- and MeO-protected, DL-alternating heptapeptides (a) and octapeptides (b) having the same sequence as the oligopeptides considered in this work. β helices with 14- and 16-membered hydrogen-bonded rings (~ 4.4 residues per turn) are considered.

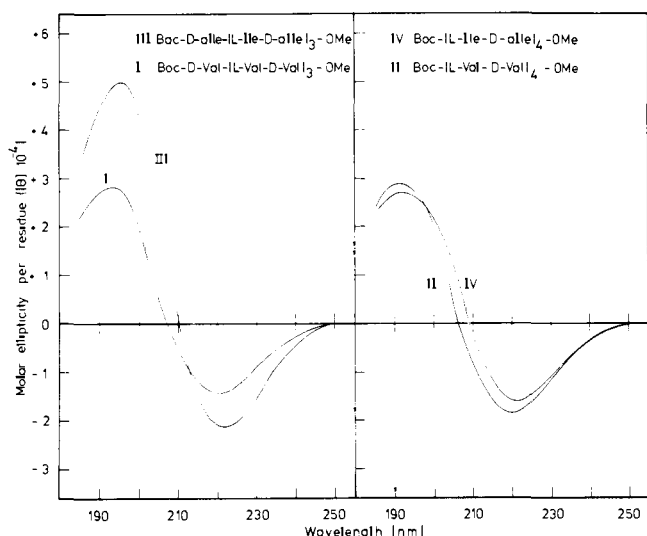
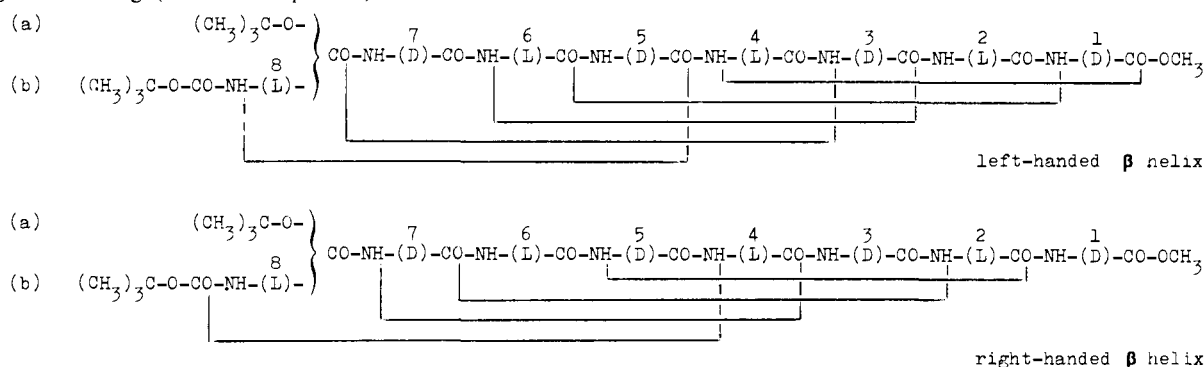


Figure 1. CD spectra of oligopeptides I-IV in cyclohexane solution: concentration, 0.2 mg/mL; T , 25 °C. The ellipticity values represent the molar ellipticities of the protected oligopeptides divided by the number of the residues.

at a non-H-bonded urethane NH. Thus the NMR data strongly suggest that the predominant sense of twist is left-handed. Support for this assignment comes from Bayley's⁶ preliminary theoretical calculations of CD properties of β helices, where left-handed β helices with ~ 4.4 residues per turn have a negative ellipticity band near 200 nm and a positive one near 180 nm. The calculated positions relative to the signs of these bands coincide with those characterizing the CD spectra of Figure 1. Thus, we conclude that the predominant sense of twist of the β -helical conformations of the oligopeptides I-IV is left handed.

In the case of the alternating oligomers of DL-valine the preference for one sense of twist can only be determined by the sequence of the residues. Since the same left-handed helical sense is adopted predominantly by I and II, the preference for this particular helical sense must be related to the D residues' being in odd positions and the L-residues' being in even positions, these positions being numbered starting from the methoxy end group. It is possible that sequences of this type, with a D residue at the C-terminus, preferentially stabilize the left-handed sense, because there is one more interturn hydrogen bond for this sense than for the right-handed sense (Scheme I). III and IV have the same sequence pattern as I and II, and also favor the same handedness. Therefore, it appears likely that the sequence, and not the chirality of the side groups, is the determining factor for the preferential winding in the left-handed sense of the chains of III and IV. As long as the

nature of the side chains play only a minor role, if any, in the stabilization of a particular β -helical sense, any similarly protected DL-alternating oligopeptide having a D residue at the C-terminus should exhibit this preference for a left-handed sense for β helices in solution. Conversely, if the sequence of such oligopeptides terminates with an L residue, the right-handed sense should be favored. It is interesting to observe that a preference for the left-handed sense of twist has been proposed⁷ for the β -helical conformation of samples of poly(L-Glu(OBzl)-D-Glu(OBzl)), and can be inferred from the CD spectrum for the β -helical conformation attributed⁸ to poly(L-Ala-D-Val). Indeed, on the basis of the arguments of Heitz and Spach,⁷ the same type of relationship between sequence and the preferred sense of twist as that established for protected oligopeptides should also hold for nonprotected polypeptides.

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References and Notes

- (1) G. P. Lorenzi, and T. Paganetti, *J. Am. Chem. Soc.*, **99**, 1282-1283 (1977).
- (2) T. Paganetti, V. Rizzo, A. Baici, P. Neuenschwander, and G. P. Lorenzi, paper presented at the 5th American Peptide Symposium, La Jolla, Calif., June 20-24, 1977.
- (3) P. De Santis, S. Morosetti, and R. Rizzo, *Macromolecules*, **7**, 52-58 (1974).
- (4) Owing to the low solubility of I in cyclohexane, the NMR spectrum of this heptapeptide could not be measured.
- (5) M. Branik, and H. Kessler, *Chem. Ber.*, **108**, 2176-2188 (1975).
- (6) P. M. Bayley, *Prog. Biophys. Mol. Biol.*, **27**, 3-76 (1973).
- (7) F. Heitz and G. Spach, *Macromolecules*, **8**, 740-745 (1975).
- (8) F. Ascoli, G. De Angelis, F. Del Bianco, and P. De Santis, *Biopolymers*, **14**, 1109-1114 (1975).

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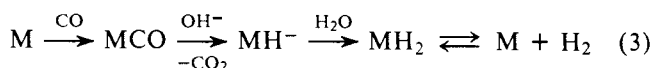
Reductions with Carbon Monoxide and Water in Place of Hydrogen. 1. Hydroformylation Reaction and Water Gas Shift Reaction

Sir:

When compared with the conventional method of performing the hydroformylation reaction, the Reppe modification of this process¹ reveals several features of interest and potential importance. In the normal process an olefin is converted to the next higher aldehyde or alcohol through reaction with carbon monoxide and hydrogen with use of a cobalt or rhodium carbonyl catalyst (eq 1). In the Reppe modification

as applied to the reaction of propylene + CO + H₂O to give *n*- and isobutyraldehyde are given in Table I, together with comparable data using Fe(CO)₅. (It should be noted that the exact nature of the catalyst species present under the reaction conditions has not yet been established.)

If the polynuclear carbonyls catalyze the reaction in a manner similar to that described for Fe(CO)₅, then, in the absence of olefin, they could also be catalysts for the generation of hydrogen via the water gas shift reaction; i.e., CO + H₂O → CO₂ + H₂. Hydrogen formation would be expected to occur via the steps given in eq 3. This catalytic generation of hydrogen is indeed observed; in the final column of Table I is given the efficiency of the generation of hydrogen under the same conditions as used in the hydroformylation reaction except for the exclusion of olefin.¹⁸



From Table I it is seen that catalysts which are efficient for the hydroformylation reaction are also efficient for the water gas shift reaction, but, not surprisingly, the converse is not always true.

Further studies directed at the development of catalysts for these and other reductions using CO + H₂O in place of H₂ will be reported later.

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References and Notes

- W. Reppe and H. Vetter, *Justus Liebig's Ann. Chem.*, **582**, 133 (1953).
- C. W. Bird, "Transition Metal Intermediates in Organic Chemistry", Academic Press, New York, N.Y., 1967, p 138.
- N. von Kutepow and H. Kindler, *Angew. Chem.*, **72**, 802 (1960).
- W. Hieber and H. Vetter, *Z. Anorg. Allg. Chem.*, **212**, 145 (1933).
- (a) M. B. Smith and R. Bau, *J. Am. Chem. Soc.*, **95**, 2388 (1973); (b) L. F. Dahl and J. F. Blount, *Inorg. Chem.*, **4**, 1373 (1965).
- The pH measurements were made at room temperature on samples withdrawn from the autoclave.
- As the reaction proceeds, the pH drops owing to the liberation of CO₂.
- H. W. Sternberg, R. Markby, and I. Wender, *J. Am. Chem. Soc.*, **79**, 6116 (1957).
- N. M. Bogorodovskaya, N. S. Imyanitov, and D. M. Rudkovskii, *Kinet. Katal.*, **11**, 584 (197).
- We have found that HFe₃(CO)₁₁⁻, under a CO pressure at 100 °C, is converted to species **1**, consistent with the observations of F. Wada and T. Matsuda, *J. Organomet. Chem.*, **61**, 365 (1973).
- R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, **83**, 4023 (1961).
- L. Malatesta and G. Caglio, *Chem. Commun.*, 420 (1967).
- P. Chini, *Inorg. Chim. Acta, Rev.*, **2**, 31 (1968).
- F. Piacenti, M. Bianchi, P. Frediani, and E. Benedetto, *Inorg. Chem.*, **10**, 2759 (1971).
- C. W. Bradford and R. S. Nyholm, *Chem. Commun.*, 384 (1967).
- B. F. Johnson, J. Lewis, and P. A. Kitty, *J. Chem. Soc. A*, 2859 (1968).
- G. Longoni and P. Chini, *J. Am. Chem. Soc.*, **98**, 7225 (1976).
- Ru₃(CO)₁₂ in conjunction with KOH has recently been shown to be a homogeneous catalyst for the water gas shift reaction: R. M. Laine, R. G. Pinker, and P. C. Ford, *J. Am. Chem. Soc.*, **99**, 252 (1977). A soluble rhodium complex has also been reported to effect the reaction in an acidic medium: C. Cheng, D. E. Hendrikson, and R. Eisenberg, *ibid.*, **99**, 279 (1977).

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Regarding a Generalized Scale of Solvent Polarities¹

Sir:

We have recently developed a scale of solvent "polarities", π , based on the solvent-induced solvatochromic shifts of seven

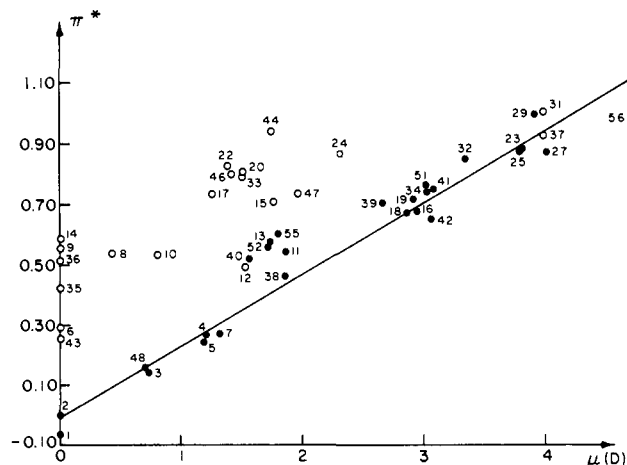


Figure 1. π^* vs. dipole moment of the solvents. Closed circles are for select solvents, $\pi \equiv \pi^*$. Open circles are for other solvents; cf. footnote 24.

Table I. Select Solvents for Use in Solvent Polarity Studies with Eq 1

Solvent ^a	$\pi (\equiv \pi^*)^b$	Solvent ^a	$\pi (\equiv \pi^*)^b$
Hexane, heptane (1)	-0.081	Butanone (16)	0.674
Cyclohexane (2)	0.000	Acetone (18)	0.683
Triethylamine (3)	0.140	Ethyl chloroacetate (39)	0.704
Tri- <i>n</i> -butylamine (48)	0.162	Triethyl phosphate (19)	0.715
Di- <i>n</i> -butyl ether (5)	0.239	Acetic anhydride (34)	(0.747) ⁵
Diisopropyl ether (4)	(0.271) ⁵	Cyclohexanone (41)	0.750
Diethyl ether (7)	0.273	Cyclopentanone (51)	0.756
Butyl acetate (38)	0.460	Nitromethane (32)	0.848
Tetrahydropyran (40)	0.513	Acetonitrile (50) ^c	(0.86) ⁵
Ethyl acetate (11)	0.545	γ -Butyrolactone (27)	0.873
Methyl acetate (52)	0.556	Dimethylformamide (25)	0.875
Methyl formate (55)	(0.596) ³	Dimethylacetamide (23)	0.882
Tetrahydrofuran (13)	0.576	Sulfolane (56)	(0.988) ⁴
Tri- <i>n</i> -butyl phosphate (42)	0.653	Dimethyl sulfoxide (29)	1.000

^a The solvents are numbered as in ref 2 and Figure 1. ^b The π^* values are classified as in ref 2 primary values obtained from at least six different data sets, and secondary values in parenthesis, for which 3 to 5 π^* have been averaged (indicated by superscript). ^c The π value indicated for CH₃CN from χ_R , P , E_K , $\log k$, and G values is 0.86 ± 0.02 , and this value fits well on the correlation with μ , Figure 1. We have noted that H-bonding contributions are likely to be involved with A_N and E_T values for CH₃CN (giving apparent π^* 0.99). The smaller π^* value of 0.713 is unaccounted for at the present time.

different indicators.² It was shown that this scale gives a very satisfactory quantitative description of the solvent effects on more than forty $\pi \rightarrow \pi^*$ and $p \rightarrow \pi^*$ electronic transitions.

We have critically examined the π^* values in the light of other empirical solvent scales based upon a variety of spectroscopic and/or chemical reactivity data.³ Eight of the most widely used "polarity" scales have been chosen: Dimroth's E_T ,⁴ Brooker's χ_R ,⁵ Lassau and Junger's $\log k(\text{Pr}_3\text{N} + \text{MeI})_{20^\circ\text{C}}$,⁶ Walther's E_K ,⁷ Knauer and Napier's A_N ,⁸ Allerhand and Schleyer's G ,⁹ Taft's P ,¹⁰ and Brownstein's S .¹¹ No general correlation of useful precision exists between these scales (Figure 3 of ref 2 illustrates a typical case).

We wish to report, however, that, for a group of selected solvents (Table I), all scales give very closely equivalent re-