CONFORMATIONAL ASPECTS OF POLYPEPTIDES. VII. REVERSAL OF THE HELICAL SENSE OF POLY-L-ASPARTATE ESTERS[1]

Sir:

We wish to report a reversal in the helical sense of poly-β-benzyl-L-aspartate in chloroform resulting from the introduction of a nitro group in the para position of the aromatic ring in the side chain.

In order to ascertain the sense of the helical conformation of poly-β-*p*-nitrobenzyl-L-aspartate, copolymers of β-*p*-nitrobenzyl-L-aspartate with β-benzyl-L-aspartate were prepared. The dependence of the b_0 coefficient of the Moffitt equation,[2] the λ_c values from the Drude equation and $[\alpha]_{546}$ on copolymer composition were determined in chloroform. Figures 1, 2, and 3 summarize the data obtained. It can be seen that a distinct transition occurs between 35 and 40% nitro residue content in each of these figures. Unfortunately, copolymers with nitro residue contents greater than 66% are insoluble in chloroform.

Blout[3] and Bradbury[4] have shown that copolymers of poly-γ-benzyl-L-glutamate and poly-β-benzyl-L-aspartate exhibit an irregular progression of optical rotatory properties. This is attributed to a difference in the sense of the helix of the homopolymers. Furthermore, Fasman[5] showed that copolymers of poly-L-tyrosine and poly-L-glutamic acid (although the respective homopolymers have b_0 values of $+494$ and -560) show a linear change of rotatory properties. He concludes that both homopolypeptides have the same sense of helical conformation. Moreover, Schellman,[6] assuming a mixture of poly-γ-benzyl-L-glutamate and poly-β-benzyl-L-aspartate helices, calculated that λ_c values of copolymers of these amino acids change from 141 mμ at 0% glutamate to 279 mμ at 80% glutamate. At higher glutamate concentrations, the Drude dispersion plots become nonlinear.

Figure 1 reveals a region of rapid change in b_0 with percentage nitro residue content; (all data refer to mole per cent.) the b_0 changes from $+354$ at 20% nitro residue content to -1016 at 54% nitro residue content. An even more striking transition is shown in Fig. 2. The specific rotation, $[\alpha]_{546}$, is not only non-linear, but it changes in direction after 40% nitroresidue content. We found that the λ_c values from the Drude equation range from 153 mμ at 0% nitro residue content to 284 mμ at 66% nitro residue content. This is in agreement with Schellman's predictions for copolymers of opposite helical sense.

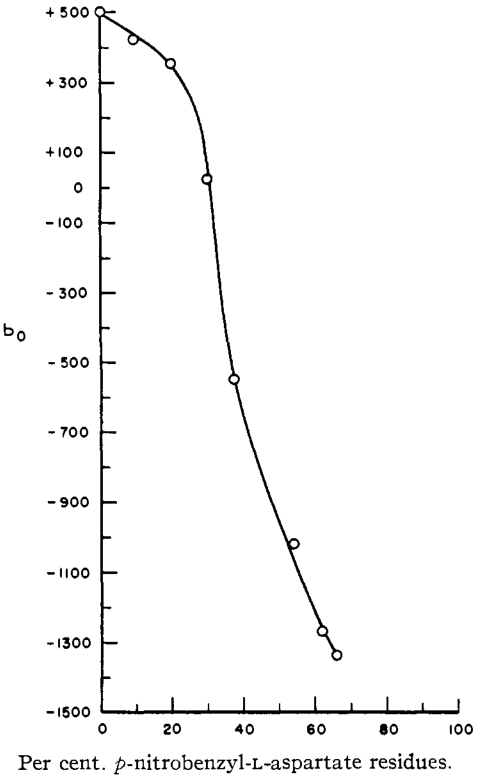

Fig. 1.—The b_0 values for the wave length range 435 to 589 mμ of copolymers of β-*p*-nitrobenzyl-L-aspartate: β-benzyl-L-aspartate as a function of mole % of *p*-nitrobenzyl-L-aspartate residues in chloroform at 25.0°.

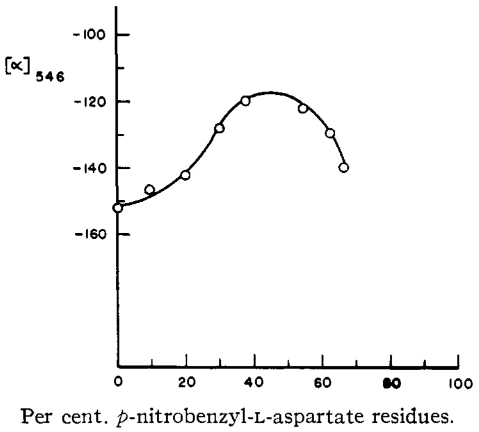

Fig. 2.—The specific rotation at the wave length 546 mμ of copolymers of β-*p*-nitrobenzyl-L-aspartate: β-benzyl-L-aspartate as a function of mole % of *p*-nitrobenzyl-L-aspartate residues in chloroform at 25.0°.

We have also prepared copolymers of β-*p*-nitrobenzyl-L-aspartate with γ-benzyl-L-glutamate. Preliminary observations indicate that the $[\alpha]_{546}$ as well as b_0 values vary regularly with copolymer composition in dimethylformamide. There are no regions of sharp transition. These results demonstrate that poly-β-*p*-nitrobenzyl-L-aspartate and poly-γ-benzyl-L-glutamate are most probably of the same helical sense. Since Blout[3] and Bradbury[4] have shown that poly-β-benzyl-L-aspartate and poly-γ-benzyl-L-glutamate are of opposite helical sense, it follows that poly-β-*p*-

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[1] Previous paper in this series: M. Goodman and I. Listowsky, *J. Am. Chem. Soc.*, **84**, 3770 (1962).

[2] W. Moffitt and J. T. Yang, *Proc. Natl. Acad. Sci.*, **42**, 596 (1956).

[3] E. R. Blout, *Tetrahedron*, **13**, 123–133 (1961); E. R. Blout and R. H. Karlson, *J. Am. Chem. Soc.*, **80**, 1259 (1958); and R. H. Karlson, K. S. Norland, G. D. Fasman and E. R. Blout, *ibid.*, **82**, 2268 (1960).

[4] E. M. Bradbury, L. Brown, A. R. Downie, A. Elliott, W. E. Hanby and T. R. R. MacDonald, *Nature*, **183**, 1736 (1959).

[5] G. D. Fasman, *ibid*, **193**, 681 (1962).

[6] J. A. Schellman and C. G. Schellman, *J. Poly. Sci.*, **49**, 129 (1961)

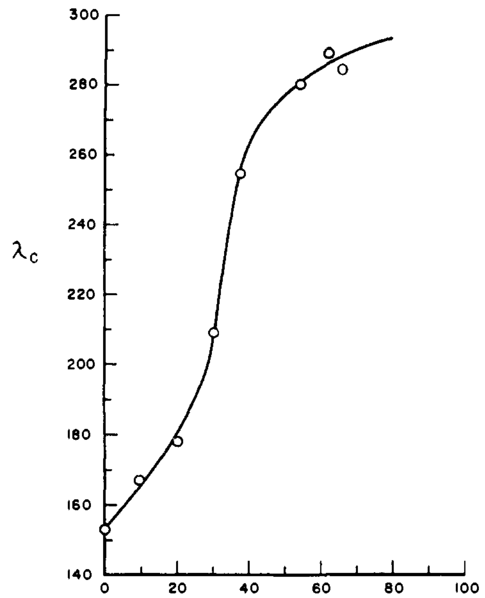


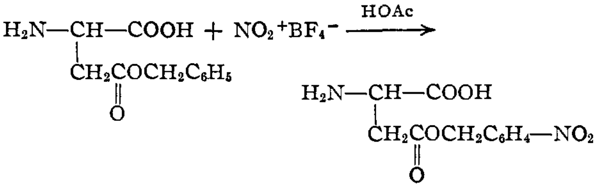
Fig. 3.—The values of λ_c from the Drude equation for copolymers of β-*p*-nitrobenzyl-L-aspartate: β-benzyl-L-aspartate as a function of mole % of *p*-nitrobenzyl-L-aspartate residues in chloroform at 25.0°.

nitrobenzyl-L-aspartate and poly-β-benzyl-L-aspartate are of opposite helical sense.

Thus, we conclude that the introduction of a *p*-nitro group into the β-benzyl-L-aspartate molecule does indeed reverse the sense of the helix.

The unusually large negative b_0 values (*e.g.*, −1338 at 66.0%, −1268 at 62.0% and −1016 at 54.0% nitro residue contents) may be attributed to the presence of groups in the side chain which produce Cotton effects in the near ultraviolet spectral region. Alternatively, the nitro side chain groups which can be assumed to form a rigid helix of their own may have an additive effect on the b_0 values.

β-*p*-Nitrobenzyl-L-aspartate was prepared[7] by nitration of β-benzyl-L-aspartate using nitronium fluoroborate[8] in glacial acetic acid, then neutralization with sodium bicarbonate.



$$H_2N-\underset{\underset{\underset{O}{\|}}{CH_2COCH_2C_6H_5}}{\overset{}{CH}}-COOH + NO_2{}^+BF_4{}^- \xrightarrow{HOAc} H_2N-\underset{\underset{\underset{O}{\|}}{CH_2COCH_2C_6H_4-NO_2}}{CH}-COOH$$

The N-carboxyanhydride[9] of β-*p*-nitrobenzyl-L-aspartate was prepared by phosgenation of the amino acid in dioxane. It was then polymerized using diethylamine initiator in dimethylformamide and isolated by precipitation with ethyl ether.

Exclusive *para*-nitration was proved by hydrolysis of β-*p*-nitrobenzyl-L-aspartate with 10% hydrochloric acid. *p*-Nitrobenzyl alcohol was isolated and characterized unambiguously.

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[7] Details of the synthesis will be published elsewhere.

[8] S. Kuhn and G. Olah, *J. Am. Chem. Soc.*, **83**, 4570 (1961).

[9] A. Berger and E. Katchalski, *ibid.*, **73**, 4084 (1951).

[10] Undergraduate research participant for 1961 under NSF Grant G15814.

[11] Supported by grant RG 8974 from the National Institutes of Health.

DEPARTMENT OF CHEMISTRY MURRAY GOODMAN
POLYTECHNIC INSTITUTE OF
BROOKLYN CHARLES M. DEBER[10]
BROOKLYN, N. Y. ARTHUR M. FELIX[11]

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PHOTOCHEMICAL ISOMERIZATION OF SQUARE COMPLEXES

Sir:

We wish to report photochemically effected isomerizations of platinum(II) complexes. Both sunlight and a General Electric 275 watt sunlamp cause rapid isomerization of solutions of *cis*- and *trans*-bis-(triethylphosphine)-dichloroplatinum(II), $[(Et_3P)_2PtCl_2]$.[1] Mixtures of isomers were analyzed spectrophotometrically utilizing differences in the electronic absorption spectra; with known mixtures each isomer could be analyzed to ±1%. No filter was used in the experiments with sunlight; a solution of potassium hydrogen phthalate (5 g./l.) was used as a filter[2] (sharp cut-off at 304 mμ) with the sunlamp. The electronic absorption spectra are shown in Fig 1; they indicate that it is the low intensity, d→d transition at long wave length that is active in the isomerization. When the isomers were irradiated with unfiltered light from the sunlamp, a dark precipitate formed indicating decomposition.

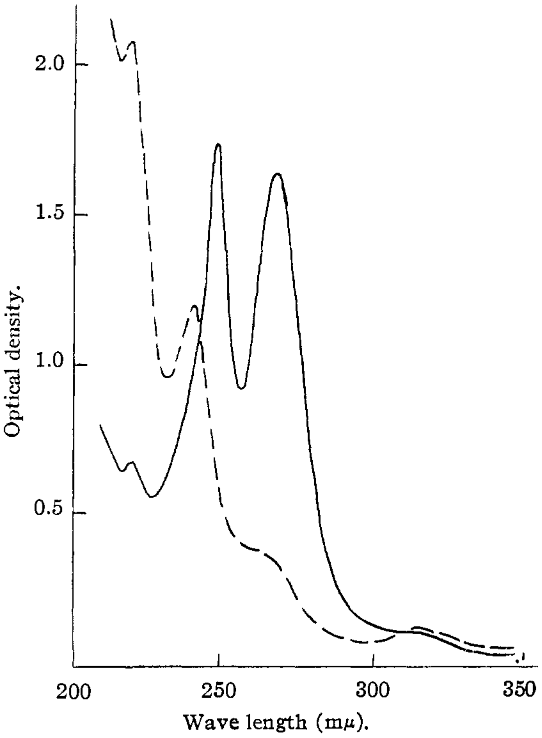

Fig. 1.—Spectra of $(Et_3P)_2PtCl_2$ isomers in methanol: *trans*, 1.592 × 10^{-4}*M*, ——; *cis*, 1.863 × 10^{-4}*M*, — —.

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[1] Prepared by the procedure of K. A. Jensen, *Z. anorg. allgem. Chem.*, **229**, 238 (1936).

[2] M. Kasha, *J. Opt. Soc. Am.*, **38**, 929 (1948).