The Optical Rotatory Dispersion of Triptycene Derivatives. The Direction of Electronic Polarization as a Determining Factor of the Sign of the RD Curve

By Fumio OGURA and Masazumi NAKAGAWA

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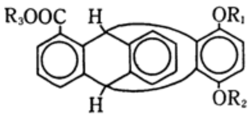
In a previous paper,[1] the present authors have reported the synthesis and optical resolution of 7-carboxy-2,5-diacetoxy-triptycene (I). The acetyl groups at 2,5-positions could be replaced by different groups.[2] Various kinds of optically-active triptycenes thus prepared (II–X)* have the same configuration as that of the parent triptycene (I), as the rigid cage structure of triptycene excludes the occurrence of any racemization or Walden inversion during the course of the transformation. In view of their rigid structure, the series of optically-active triptycenes bearing different substituents seems to offer the best tool for studying the effect of substituents on the rotatory properties.



I : $R_1=R_2=CH_3CO$, $R_3=H$, m. p. 269～270°C
II : $R_1=R_2=CH_3CO$, $R_3=CH_3$, m. p. 200～202°C
III : $R_1=R_2=H$, $R_3=CH_3$,
m. p. 294～297°C (decomp.)
IV : $R_1=H$, $R_2=R_3=CH_3$, m. p. 250～251°C
V : $R_1=R_3=CH_3$, $R_2=H$, m. p. 256～258°C
VI : $R_1=R_2=R_3=CH_3$, m. p. 261.5～262.5°C
VII : $R_1=CH_3CO$, $R_2=R_3=CH_3$, m. p. 270～271°C
VIII : $R_1=R_3=CH_3$, $R_2=CH_3CO$, m. p. 278～279°C
IX : $R_1=CF_3CO$, $R_2=R_3=CH_3$,
m. p. 262～263.5°C
X : $R_1=R_3=CH_3$, $R_2=CF_3CO$, m. p. 241～243°C

The compounds II, III, VI, VII, VIII, IX and X used in the measurements of the rotatory dispersion were derived from the *d*-isomer of I, while IV and V were derived from its *l*-isomer. The compounds I, II, III, IV, V, and VI exhibit plain curves of the same sign in so far as they have identical configurations. In sharp contrast to this fact, the sign of the plain curves of VII and IX are positive, whereas VIII and X show negative plain curves in spite of having the same configuration as VII and IX. Some representative RD curves are given in Fig. 1. The electronic spectra of VII, VIII, IX and X were found to be almost superimposable over a wide range of wavelengths. The only difference between VII and VIII and between IX and X are the relative positions of the electron-donating methoxyl groups and electron-attracting acyloxy groups in the *p*-disubstituted benzene ring in the triptycene molecules.

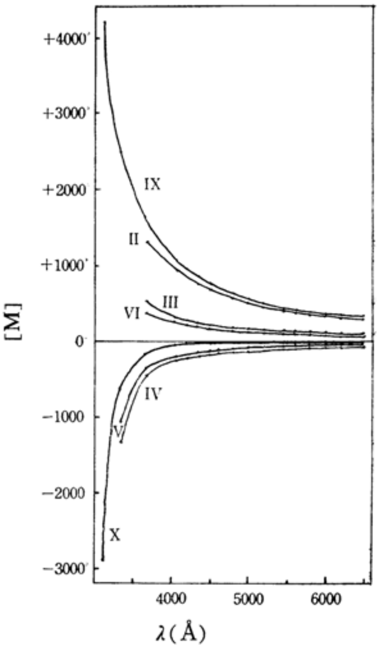


Fig. 1. The RD curves of the triptycenes.

These experimental results clearly indicate that the direction of electronic polarization is a determining factor in the sign of the RD curve. It seems evident that the inversion of the direction of electronic polarization exerts an inverse effect on the electric transition moment of the optically-active absorption band. However, the more extensive influence of the inversion of the direction of polarization is reflected in the fact that the RD curves of

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[1] A. Sonoda, F. Ogura and M. Nakagawa, This Bulletin, 35, 853 (1962).

[2] F. Ogura, Y. Toshiyasu. K. Kimura, R. Fujishiro and M. Nakagawa, ibid., 37, 757 (1964).

* All compounds described in this paper gave satisfactory IR spectra and elemental analyses.

II, III, IV, V, VI, VII and IX can be expressed by a one-term Drude equation, whereas in the cases of VIII and X the plots of 1/[M] versus λ^2 give no straight lines.

In order to obtain more precise information, the authors are now preparing to measure the optical rotatory dispersion at a shorter wavelength region and to measure the circular dichroism of the triptycene derivatives.

Department of Chemistry
Faculty of Science
Osaka University
Nakanoshima, Osaka