SOLVENT DEPENDENCE OF THE OPTICAL ACTIVITY OF HEXAHELICENE

Sir:

The purpose of this note is to report variations of the optical rotatory dispersion of hexahelicene[1] when observed in various hydrocarbon solvents. The literature contains several inferences that solvent effects should arise from shifts in the corresponding absorption spectra,[2] but no definitive experimental evaluation seems to have been made. Rather, studies of solvent effects on optical activity that are attributable to varying degree of ionization,[3] to conformational changes,[4] and to highly polar solvents contributing an asymmetry over and above that intrinsic in the optically active molecule[5] have been reported instead.

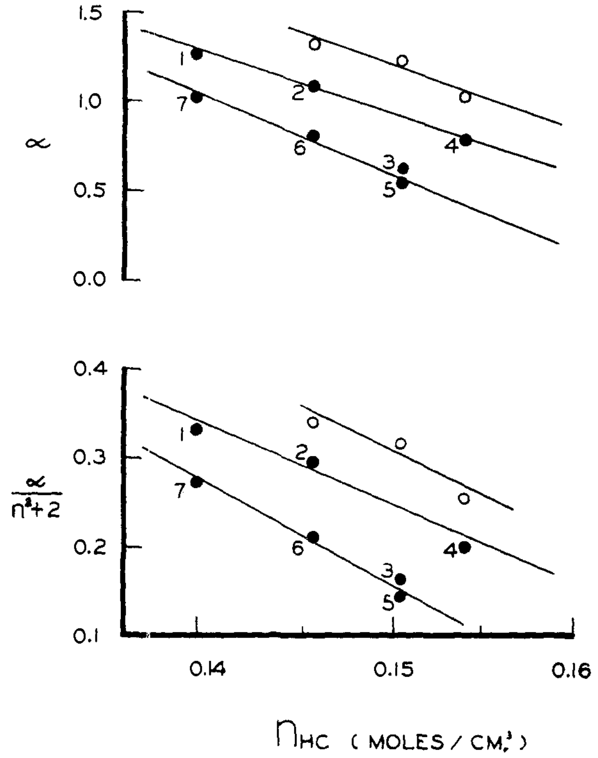


Fig. 1.—Relative specific rotations and relative rotivities of hexahelicene at a single wave length in (l. to r.) *n*-pentane, *n*-hexane, *n*-heptane, and *n*-octane *versus* a spectral shift parameter, the mole bond density.[11] The rotation scales for the two different samples (solid circles and open circles) are not relative one to another.

We have also studied the visible optical rotatory dispersion curves of (+)-carvone, (+)-camphor, and (+)-pulegone in various chlorinated hydrocarbons. The results could be interpreted qualitatively in terms of shifts to the red or blue of Cotton curves associated with the observed shifting near ultraviolet spectra. However, such systems are possibly complicated by the latter two effects mentioned above. Hexahelicene in hydrocarbon solvents should be free to the greatest degree from such effects.

Rotations were measured to the nearest 0.01° with a Bellingham and Stanley model A polarimeter using a direct vision prism eyepiece. A mercury–cadmium source gave five lines (6438, 5770–5791, 5461, 5086, 4358 Å.) suitable for observations. Two samples of partially resolved hexahelicene were used.[6] The results are shown in Fig. 1. Numbered solid data points represent successive measurements in normal hydrocarbon solvents (pentane, hexane, heptane, and octane). The first sample (about 1.3 mg., $[\alpha]_{546} = 4 \times 10^3$ deg./dm.) was retrieved for each subsequent measurement in the numbered order by evaporation of the solvent. The open circles show data obtained with a second sample (about 1.9 mg., $[\alpha]_{546} = 1 \times 10^3$ deg.) divided about equally among the solvents and observed at one time without intervening evaporations. (The measurement in pentane was frustrated by leakage from the polarimeter tube.) Relative concentrations were determined by systematic dilution of the polarimeter sample (1.2 ml.) followed by a scan of the absorbance from 2350 to 3800 Å. with a Beckman DK-1 recording spectrophotometer.

In each case it is evident that the specific rotation as well as the rotivity of the sample decreased with increasing density of the hydrocarbon solvents. Some racemization or oxidation caused by the repeated evaporations is evident in the plot of the first sample. One should note that the refractive index factor serves to enhance rather than remove the solvent dependence. The same effect occurred at all wave lengths used for the observations.

The hexahelicene molecule is relatively well understood with regard to its electronic states and the rotational strengths of their transitions through a simple molecular orbital treatment carried out by Moscowitz.[7] The calculations show that (1) the ^1L_b and ^1B_b transitions[8] arise from two excited states degenerate in the simple m.o. calculation and have equal moderately positive (for the left-hand helix) rotational strengths; (2) the effect of configuration interaction is to split the degenerate levels, the rotational strengths remaining positive but with the preponderance going to the higher energy (^1B_b) transition; (3) the ^1L_a transition corresponds to a non-degenerate upper energy level which also has a positive rotational strength somewhat greater than that for the degenerate levels.

More recently, Moscowitz has carried out a satisfactory calculation of the optical rotatory dispersion curve from 3100 to 4200 Å. using the experimental absorption curve of the transitions mentioned above.[9] The general relationship between absorption and optical rotatory dispersion is that of

---

(1) M. S. Newman and D. Lednicer, *J. Am. Chem. Soc.*, **78**, 4765 (1956).

(2) C. Djerassi, "Optical Rotatory Dispersion: Applications in Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1960, p. 61; A. Moscowitz, *ibid.*, p. 175.

(3) M. K. Hargreaves and P. J. Richardson, *J. Chem. Soc.*, 2260 (1957).

(4) C. Djerassi and L. E. Geller, *Tetrahedron*, **3**, 319 (1958); C. Djerassi, L. E. Geller and E. J. Eisenbraun, *J. Org. Chem.*, **27**, 1 (1960).

(5) C. O. Beckman and Karl Cohen, *J. Chem. Phys.*, **4**, 784 (1936).

(6) We are indebted to Prof. M. S. Newman of Ohio State University for samples of hexahelicene and the resolving agent.

(7) A. Moscowitz, Doctoral Thesis, Harvard University, 1957.

(8) W. Moffitt, *J. Chem. Phys.*, **22**, 320, 1820 (1954).

(9) A. Moscowitz, *Tetrahedron*, **13**, 48 (1961).

Moscowitz and Moffitt's case I where the ellipticity curve is simply proportional to the absorption curve.[10] The fitted rotatory strengths seem to be in accord with the points enumerated above.

We have observed that the spectrum of hexahelicene above 2200 Å. red-shifts with increasing hydrocarbon solvent density as do the spectra of other nonpolar polynuclear aromatics.[11] Thus, if the solvent dependence arises from shifting spectrum, the decrease of rotation cannot be accounted for by red-shifts of the positive Cotton curves. Most likely the decrease depends on a strong red-shifting negative Cotton curve centered at a wave length shorter than 3100 Å. Indeed, the m.o. calculation predicts such a rotational strength for a higher energy transition. In addition, the experimental rotatory dispersion measurements of Drs. Newman and Tsai out to 2750 Å.[12] are consistent with such a situation. That the change in optical activity arises from distortion of the helical pitch cannot be completely discounted but, to be sure, is not completely separable in theory from the origins of the spectral shift.

Certainly this study underscores the usefulness that parallel solvent effect studies on spectra and rotation might have in the interpretation of optical rotatory dispersion curves, especially were the latter measurements carried to the absorbing region. It also demonstrates what must be a contribution to environmental effects in more complex systems, one observable in the wings of the Cotton curve where nearly all characterizing measurements of protein and polypeptide systems are made,[13] and one not accounted for by the Lorentz field factor.

Acknowledgments.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. A grant from the National Science Foundation under its Undergraduate Research Participation Program is also gratefully acknowledged by the participants (N. C. K., N. J. K., and T. C. C.).

---

[10] W. Moffitt and A. Moscowitz, *J. Chem. Phys.*, **30**, 648 (1959).

[11] O. E. Weigang, Jr., *J. Chem. Phys.*, **33**, 892 (1960). Shifts in polar solvents may be treated similarly; O. E. Weigang, Jr., and D. D. Wild, submitted to *J. Chem. Phys.*

[12] M. S. Newman and Lin Tsai, private communication of unpublished measurements.

[13] For several reviews see: (a) I. Tinoco, R. W. Woody and K. Yamaoka, *Tetrahedron*, **13**, 134 (1961); (b) J. T. Yang, *ibid.*, **13**, 143 (1961); (c) B. Jirgensons, *ibid.*, **13**, 166 (1961); (d) J. Strem, Y. S. R. Krisna-Prasad and J. A. Schellman, *ibid.*, **13**, 176 (1961); (e) J. R. Fresco, *ibid.*, **13**, 185 (1961); (f) P. O. P. Ts'o and G. Helmkamp, *ibid.*, **13**, 198 (1961).

DEPARTMENT OF CHEMISTRY
TEXAS LUTHERAN COLLEGE
SEGUIN, TEXAS

N. C. KNETEN
N. J. KRAUSE
T. O. CARMICHAEL
O. E. WEIGANG, JR.

RECEIVED JANUARY 22, 1962

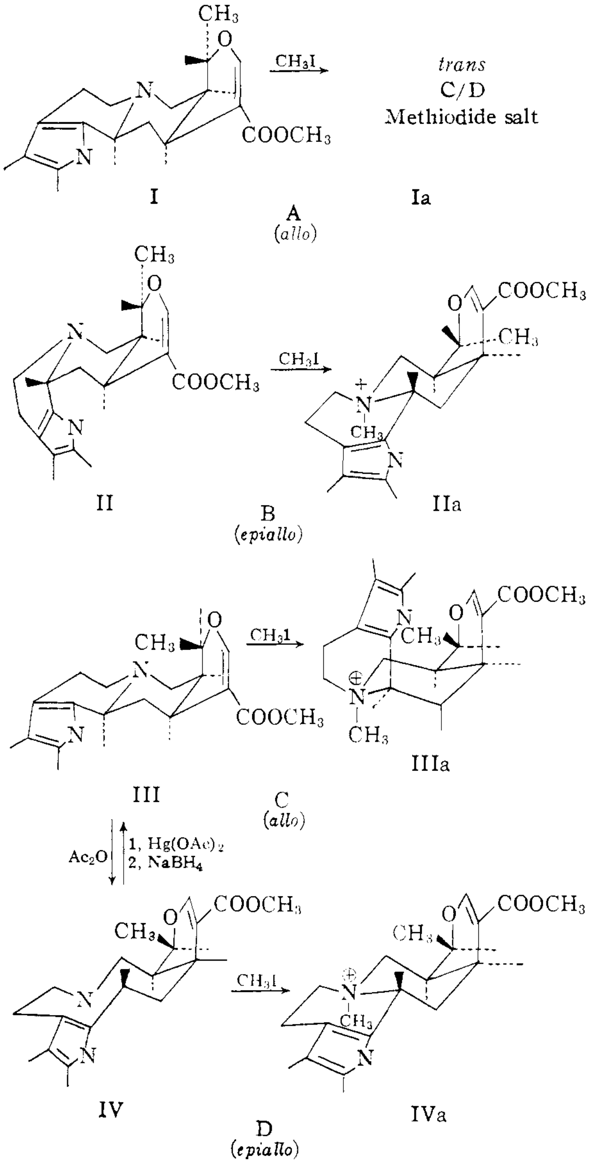
THE STEREOCHEMISTRY OF THE HETEROYOHIMBINE ALKALOIDS

Sir:

We here describe the complete stereochemistry of the alkaloids rauniticine, raunitidine, isoraunitidine, mayumbine, and raumitorine.[1,2]

The chemical shifts of the C-19 methyl groups in the n.m.r. spectra,[3] together with the known method of infrared analysis near 8.4 μ,[4] can be used to classify the heteroyohimbines into six stereochemical groups (represented by groups A to F in Table I).[5]

Despite the retention of the *trans*-quinolizidine system, the raunitidine to isoraunitidine isomerization involves only the asymmetric center at C-3,[6,7] since in our hands treatment of isoraunitidine with mercuric acetate and subsequent reduction of the Δ^3-perchlorate salt with sodium borohydride yielded only raunitidine.



---

[1] E. Wenkert, B. Wickberg and C. L. Leight, *J. Am. Chem. Soc.*, **83**, 5037 (1961).

[2] M. Shamma and J. B. Moss, *ibid.*, **83**, 5038 (1961).

[3] Measured with a 40 Mc. Varian NMR unit using deuteriochloroform as solvent and TMS as an internal standard.

[4] N. Neuss and H. E. Boaz, *J. Org. Chem.*, **22**, 1001 (1957).

[5] Although akuammigine was not in our possession, it can be placed in group B since it has been shown to be epimeric at C-3 with tetrahydroalstonine.

[6] R. Salkin, N. Hosansky and R. Jaret, *J. Pharm. Soc.*, **50**, 1038 (1961).

[7] F. Bohlmann, *Chem. Ber.*, **92**, 1798 (1959); and W. E. Rosen, *Tetrahedron Letters*, No. 14, 481 (1961).