with the ratios calculated for (planar) TPE^- by the method of McLachlan,[9] 5/1.7/5.8 (or 4/1.3/4.7), but the magnitudes of the constants are higher than calculated by factors of 1.4 and 1.2, respectively. The e.s.r. spectrum is at least consistent with the assignment of the structure of the blue substance as TPE^-.

We estimate K_{TPE} in 1,2-dimethoxyethane at 22° as less than 1.8,[10] and in diethyl ether as greater than 10^5.[11]

It has been predicted that if anionic solvation were dominant in accounting for the anomalous value of K_{TPE} in diethyl ether or dioxane, its value should be larger in solvents of higher dielectric constant.[2,6c] *The direction of the observed solvent effect is the opposite of that predicted on this basis.* This, coupled with the observation that there is a distinct metal ion effect[12a] on K_{TPE} in 1,2-dimethoxyethane, leads us to conclude that *the chemical effects we have observed are consequences of variations in the kind or degree of ionic aggregation with solvent.*[12b,13]

A simple coulombic explanation of the results can be offered.[13] The additional electron–electron repulsive interactions in TPE^{-2} (over those present in TPE^-) represent unfavorable coulombic interactions, the magnitude of which can be decreased by the close proximity of one or more sodium ions, suitably situated. In a solvent which promotes separation of ionic charges (either by ionic dissociation[14] or through an influence on the structure of ionic aggregates[15]), the formation of TPE^- should be energetically more favored, with the consequence that K_{TPE} should be smaller (other factors being constant[16]) than in a solvent not as effective in promoting ionic charge separation. It is this observation we have made. Our results provide

(9) A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).

(10) A solution of 1.7×10^{-5} mole of TPE in 12.6 ml. of 1,2-dimethoxyethane was saturated in sodium and 2.3×10^{-6} mole of TPE added. An e.s.r. intensity measurement indicated 1.4×10^{-3} m./l. of spins. In the calculation of a limiting value, all errors were assumed to operate so as to maximize K_{TPE}. A 30% error in the intensity measurement was assumed.

(11) It was assumed that 10^{-5} m./l. of spins would have been detected in our experiments (Varian equipment with 100 kc. field modulation unit). A 6×10^{-3} molar solution of TPE was allowed to react with sodium until approximately 10^{-4} m./l. of TPE^{-2} was present. No resonance could be detected.

(12) (a) A. V. Tobolsky and D. B. Hartley, *J. Am. Chem. Soc.*, **84**, 1391 (1962), report that a blue color precedes formation of the red when lithium, but not sodium, is allowed to react with TPE in tetrahydrofuran. See, however, reference 8. When potassium is employed in 1,2-dimethoxyethane, only faint blue solutions can be prepared before they turn red upon dissolution of further metal. Lithium and cesium show a consistent trend. (b) The direction of the metal ion effect suggests that variations in the degree of ionic association have a greater effect on K_{TPE} than possible variations in the structure of ionic aggregates.[14b]

(13) Electrochemical data closely related to the present result have been discussed in terms of ionic association and solvation effects, by G. J. Hoijtink, E. de Boer, P. H. van der Meij and W. P. Weijland, *Rec. trav. chim.*, **75**, 487 (1956).

(14) (a) A. C. Aten, J. Dieleman and G. J. Hoijtink, *Discussions Faraday Soc.*, **29**, 182 (1960); (b) N. M. Atherton and S. I. Weissman, *J. Am. Chem. Soc.*, **83**, 1330 (1961).

(15) J. F. Garst, C. Hewitt, D. Walmsley and W. Richards, *ibid.*, **83**, 5034 (1961). References are given to solvent effects possibly related to that of the present communication.

(16) If the degree of ionic dissociation is important, it is to be expected that entropy factors may play a large role.[14,17]

(17) A. Mathias and E. Warhurst, *Trans. Faraday Soc.*, **56**, 348 (1960).

a partial solution to the TPE anomaly, in that while we conclude that ionic aggregation effects dominate direct anion solvation effects, we can make no deductions concerning the role of a possible change in geometry.

K_{TPE} in tetrahydrofuran apparently is intermediate between that in diethyl ether and that in 1,2-dimethoxyethane.[8,12a] Thus, K_{TPE} for these three solvents qualitatively correlates with the ketyl spectral shifts.[15]

DEPARTMENT OF CHEMISTRY   JOHN F. GARST
UNIVERSITY OF CALIFORNIA
RIVERSIDE, CALIFORNIA   RONALD S. COLE

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INHERENTLY DISSYMMETRIC CHROMOPHORES. OPTICAL ACTIVITY ASSOCIATED WITH A HOMOCONJUGATED DIENE[1]

Sir:

Our continuing concern with inherently dissymmetric chromophores[2] has prompted us to investigate the optical rotatory dispersion of (+)-(1R) - 5 - methylenebicyclo[2.2.2]hept - 2 - ene (I). This molecule is of exceptional interest in that (insofar as perturbing environmental effects can be ignored) the dissymmetrically disposed double bonds constitute a prototype helix of repeating units in which the chromophoric entities are not directly bonded. Molecular systems of this sort are the subject of much current concern,[3] and it might be hoped that such a simplified version as I would lend itself to quantitative interpretation and hence give further insight into extended helical arrays.

Extended helical systems (*e.g.*, polypeptides) have been treated in the past from a coupled-oscillator point of view.[4] An optically active coupled-oscillator represents a particular case of an inherently dissymmetric chromophore, but merits special attention since many theoretical treatments of optical activity, both classical[5] and quantum mechanical,[6] are based on such a

(1) Financial support from Alfred P. Sloan Foundation Fellowships (A.M. and K.M.) and the National Science Foundation (Grant No. G-15746) is gratefully acknowledged.

(2) See, *e.g.*, K. Mislow, *Ann. N. Y. Acad. Sci.*, **93**, 457 (1962), and references cited therein.

(3) See, *e.g.*, E. R. Blout, Chapter 17 of C. Djerassi, "Optical Rotatory Dispersion," McGraw-Hill Book Co., Inc., New York, N. Y., 1960; J. A. Schellman and C. G. Schellman, *J. Polymer Sci.*, **49**, 129 (1961).

(4) (a) D. D. Fitts and J. G. Kirkwood, *Proc. Natl. Acad. Sci. U. S.*, **42**, 33 (1956); **43**, 1046 (1957); (b) W. Moffitt, *J. Chem. Phys.*, **25**, 467 (1956); (c) W. Moffitt, D. D. Fitts and J. G. Kirkwood, *Proc. Natl. Acad. Sci. U. S.*, **43**, 723 (1957); (d) I. Tinoco, Jr., "Advances in Chemical Physics," Vol. IV, I. Prigogine, ed., Interscience Publishers, Inc., New York, N. Y., in press, and references cited therein.

(5) Amongst others, M. Born, *Physik. Z.*, **16**, 251 (1915); *Ann. Physik*, **55**, 177 (1918); C. W. Oseen, *ibid.*, **48**, 1 (1915); W. Kuhn, *Z. physik. Chem. (Leipzig)*, **B4**, 14 (1929); S. F. Boys, *Proc. Roy. Soc. (London)*, **144**, 655 (1934).
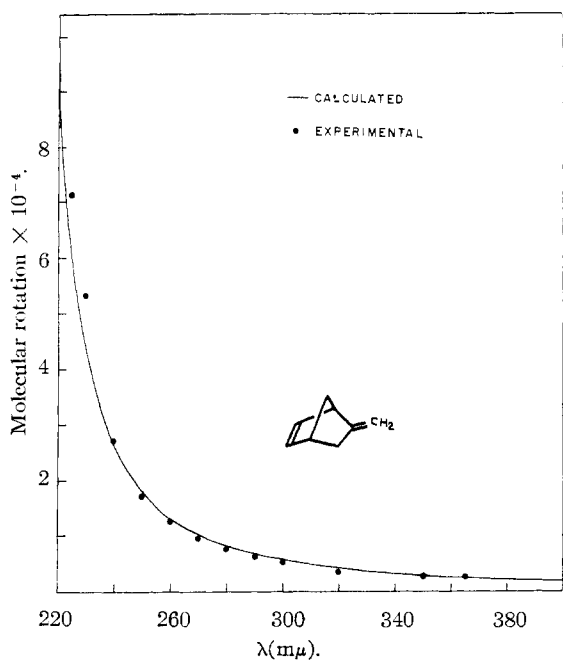
Fig. 1.—Calculated and experimental (corrected to optical purity) optical rotatory dispersion of (+)-(1R)-5-methylene-bicyclo[2.2.2]hept-2-ene.

model. That the π-electron system of I might function as a coupled-oscillator may be anticipated from the following evidence: (a) the reactions of racemic I[7] indicate homoconjugative interaction similar to that in symmetrical bicycloheptadiene, where theoretical calculations[8] can be interpreted in coupled-oscillator terms; (b) a comparison of $\lambda^{isooctane}_{shoulder}$ of I (207 mμ, ϵ 10,300), of $\lambda^{isooctane}_{max}$ of (+)-(1S)-2-methylenebicyclo[2.2.1]heptane (II) (195 mμ, ϵ 10,900), and of norbornene[9] (III) indicates a coupling between the double bonds of I that lifts the degeneracy of the erstwhile ethylenic $\pi \rightarrow \pi^*$ transitions.

Using a set of ethylenic π-orbitals limited to one electron promotions, and estimating the interaction matrix elements from the spectra of I, II, and III as 0.34 ev., one calculates on a dipole length basis (within the assumptions of the Kirkwood[6] approximation) two optically active $\pi \rightarrow \pi^*$ transitions of equal and opposite rotational strength lying at 186 and 207 mμ. For reasons stated elsewhere,[10] we prefer to use dipole velocities for the actual numerical computation of the optical activity, and this leads to reduced rotational strengths[11] of the order of 140 in magnitude. The results of the calculations are compared in Fig. 1

with the experimental data (corrected to optical purity), it being further assumed that the inherent dissymmetry of the π-electron system will account for the major portion of the observed optical activity in the spectral region of interest. The calculated positive sign correctly reflects the chirality of the (1R)-isomer, and the good agreement in magnitude seems to justify the assumptions made. The high rotation of I (compared to II[12]) is typical for extended dissymmetric π-systems.

The coupled-oscillator approach inherently precludes the possibility of transitions which involve the transfer of electronic charge from one ethylenic fragment to another. This model therefore represents, in principle, a lower order of approximation than that obtained by applying the Rosenfeld[13] equation directly to wave functions which permit the inclusion of charge transfer states, for example, those obtained from a Pariser-Parr[14] or related semiempirical approach. It is therefore of interest to note that calculations of this sort indicate that the inclusion of charge transfer changes the coupled-oscillator results by less than 3% in the present case, and hence lends considerable support to the neglect of interchromophoric charge transfer when considering the optical activity of extended helices in which the repeating chromophoric units are not directly bonded.

It can be justified theoretically that the rotatory dispersion should follow the *form* of the Moffitt equation[15] over a limited range of wave lengths. The experimental data for 589–240 mμ were analyzed on a least squares basis in terms of a Moffitt–Yang plot[15] to yield values for the rotational strengths which were within 15% of the calculated values cited above. These and other points will be discussed further in a later paper, along with details of the calculations.

Treatment of (1R)-bicyclo[2.2.1]hept-5-en-2-one ($[\alpha]^{26}_D$ + 553° (isoöctane), 48–50% optically pure)[16] with methylenetriphenylphosphorane by the standard procedure[17] (40% crude yield) gave (after fractional distillation) I, b.p. 112.5–114°, n^{25}_D 1.4806, $[\alpha]^{23}_D$ + 273° (c 5.5) and $[\alpha]^{27}_{220}$ + 40,500° (c 0.0022) in isoöctane,[18] 97.5% homogeneous by g.l.c.,[19] and identical in infrared and g.l.c. retention time with authentic racemic I. Found for C_8H_{10}: C, 90.24; H, 9.71.

DEPARTMENT OF PHYSICAL CHEMISTRY
UNIVERSITY OF COPENHAGEN   LESLIE S. FORSTER
COPENHAGEN, DENMARK   ALBERT MOSCOWITZ

DEPARTMENT OF CHEMISTRY
NEW YORK UNIVERSITY   JOEL G. BERGER
NEW YORK 53, N. Y.   KURT MISLOW

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