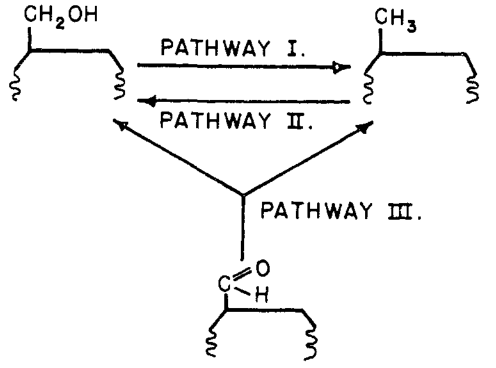

Fig. 2.

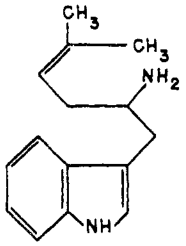

Fig. 3.

chanoclavine-C^{14} (biosynthesized from tryptophan-β-C^{14} by *Claviceps purpurea*) does not according to our findings,[11a] prove to be either the precursor or the metabolite of agroclavine. Rather agroclavine seems to be a common precursor of the other clavine-type ergot alkaloids,[12] which we have found to be converted into festuclavine, pyroclavine, setoclavine[11b] and isosetoclavine by *Claviceps purpurea*, a sequence which was proposed by Yamatodani and Abe.[13,11a]

Lastly our present finding that there is no change in the oxidation level at C–2 of mevalonate during its conversion into agroclavine (Table I) indicates that of the three possible pathways (Fig. 2) pathway II accounts for the appearance of the different substituents at C–8 (C–17 of ergot alkaloids) of ergot alkaloids. This finding is in good agreement with another observation in this laboratory, that chemically prepared lysergol-T and lysergene-T do not incorporate into agroclavine, thus ruling out the reaction sequence from elymoclavine into agroclavine through lysergol and lysergene as has been proposed[13] and confirming the report that agroclavine is converted irreversibly into elymoclavine.[12]

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(11) (a) Similar interrelationships were established by S. Agurell and E. Ramstad, personal communication. (b) C. I. Abon Chaar, D. Groger, L. R. Brady and V. E. Tyler, Jr., *Lloydia*, **24**, 159 (1961).

(12) S. Agurell and E. Ramstad, *Tetrahedron Letters*, 501 (1961).

(13) S. Yamatodani and M. Abe, *Bull. Agr. Chem. Soc. Japan*, **20**, 95 (1956).

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SOLVENT EFFECT ON THE DISPROPORTIONATION OF MONOSODIUM TETRAPHENYLETHYLENE

Sir:

The sodium adducts of tetraphenylethylene (TPE) exhibit anomalous behavior in ethereal solvents, in that the value of K appears to be abnormally large.[1–6] No e.s.r. signals have been

$$2\mathrm{ArH}^-, \mathrm{Na}^+ \overset{K}{\rightleftarrows} \mathrm{ArH} + \mathrm{ArH}^{-2}, 2\mathrm{Na}^+ \qquad (1)$$

detected in sodium–TPE solutions in dioxane or diethyl ether, even in the presence of a large excess of TPE.[7] The effects of anionic solvation,[2,6c] ionic aggregation,[6a] and possible changes in geometry[2,6b,6c,6d] all have been suggested as being responsible for this behavior.

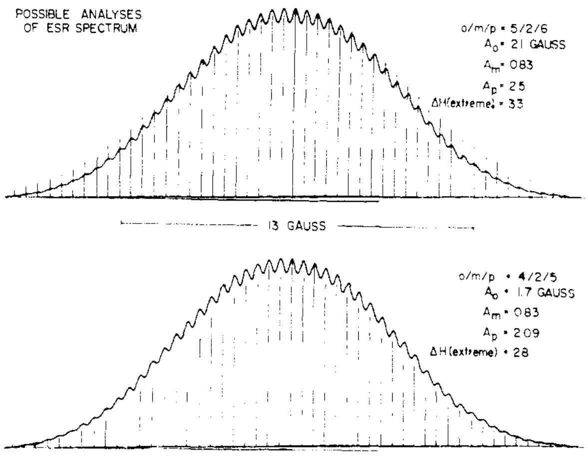

Fig. 1.—(a) Upper: Thirty-two lines of the calculated spectrum, all of intensities less than 3.2% of that of the central line, are not shown. (b) Lower: Twenty lines of the calculated spectrum, all of intensities less than 0.6% of that of the central line, are not shown.

We have observed that a change in solvent from diethyl ether to 1,2-dimethoxyethane changes the magnitude of K_{TPE} by a factor of at least 10^5 at room temperature (*ca.* 22° in our laboratories).

Dissolution of sodium in a TPE solution in 1,2-dimethoxyethane leads directly to a blue, paramagnetic solution with absorption maxima at 6350 ± 100 and 4900 ± 50 Å., the relative intensities of which vary with the amount of dissolved sodium.[8]

The e.s.r. spectrum[8a] of the blue solution exhibits the same hyperfine pattern whether the alkali metal employed is Li, Na, K, or Cs. Figure 1 shows an integrated version of the spectrum together with the spectra predicted from two possible coupling constant analyses, $A_o/A_m/A_p$ = 5/2/6 and 4/2/5, the best fits we have been able to find. These ratios are in reasonable agreement

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(1) For leading references to work on alkali metal adducts of aromatic hydrocarbons see A. Streitwieser, Jr., "Molecular Orbital Theory," John Wiley and Sons, Inc., New York, N. Y., 1961, p. 159 ff.

(2) N. S. Hush and J. Blackledge, *J. Chem. Phys.*, **23**, 514 (1955).

(3) W. Schlenk, J. Appenrot, A. Michael and A. Thal, *Ber.*, **47**, 473 (1914); W. Schlenk and E. Bergmann, *Ann.*, **463**, 1 (1928).

(4) N. B. Keevil and H. E. Bent, *J. Am. Chem. Soc.*, **60**, 193 (1938).

(5) H. Gilman and R. V. Young, *J. Org. Chem.*, **1**, 315 (1936).

(6) (a) D. W. Ovenall and D. H. Whiffen, *Chemical Society Special Publication No. 12*, 1958, p. 139; (b) discussion of M. J. S. Dewar, *ibid.*, p. 164; (c) discussion of N. S. Hush, *ibid.*, p. 164; (d) discussion of P. Gray, *ibid.*, p. 166.

(7) (a) Solvent dioxane, reference 6a; (b) solvent diethyl ether, this work.

(8) (a) Preparation of a blue solution of sodium tetraphenylethylene in tetrahydrofuran by taking care to insure a large excess of TPE has been described recently. The authors attribute the blue color, as do we, to TPE⁻. See A. G. Evans, J. C. Evans, E. D. Owen, B. J. Tabner and J. E. Bennett, *Proc. Chem. Soc.*, 226 (1962). (b) See also H. P. Leftin and W. K. Hall, *J. Phys. Chem.*, **64**, 382 (1960).

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 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]

Acknowledgments.—The authors gratefully acknowledge discussions with and assistance of their colleagues at U.C.R., especially Professor S. Chan, Mr. James Sharp, and Mr. Larry Thompson. The work was supported by Army Research Office (DURHAM) Grant DA-ARO(D)-31-124-GII8, and the National Science Foundation, which supported R.S.C. through the Undergraduate Research Participation Program.

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[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).

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).