mobility, but still undergo relatively fast rotational motion about some molecular axis. (In fact, this is the conclusion arrived at by Brüssau and Sillescu[39] from their study of spin-lattice relaxation times of $CDCl_3$ in dilute PVP–chloroform solutions.)

Summary and Conclusions

We consider as a main point of our study to have shown that interactions of peptide groups of lactams with hydrogen donating solvents, particularly with water, are much more complicated than generally assumed. Specifically, our results indicate that the local site of such interactions is not only the carbonyl group but may also involve adjacent "closely coupled" reactive centers, such as the C–N group. One should thus be wary of accepting, without unambiguous proof, certain concepts in the literature which propose specific *atoms* of complicated reactive interaction sites to be the sole center of the dynamic interaction between the site and molecules in the liquid phase.[40] Interaction at the tertiary nitrogen atom of a peptide group had been invoked by Granzhan, *et al.*,[22] for the system water–methylpyrrolidinone. However, this was done in an *ad hoc* fashion; they place one molecule of water each at the C=O group and at the N atom in order to account for their hypothetical 1:2 lactam–water complex.

More generally, our data indicate that water–PVP interactions are relatively strong in comparison with those observed with other hydrogen donating molecules. There are no solution compositions where one could consider the mobility of the water molecules unaffected: in water-rich solutions, the lactams studied here induce structure-promoting effects on water with the subsequent redistribution of hydrogen bonds; in the intermediate concentration range down to water-poor solutions, the water molecules find themselves increasingly at or near the peptide bonds.

Our work also shows that the concept of "degree of binding" is of questionable meaning without reference to the time scales involved and the particular phenomena observed. For instance, the viscosity measurements are particularly sensitive to the interactions involving the largest species in the solutions but rather insensitive to the multiple equilibria present. (Hence, conclusions in the literature on definite compositions[22,41] and solution dynamics[42] of substrate–ligand complexes, derived from viscosity data, must be considered with caution.) The self-diffusion measurements give a more detailed account since they observe different molecular species, but they do not identify the species. The infrared spectral frequency and relative intensity measurements are on the fastest time scale (about 10^{-13} sec); they observe the effect of the interactions on the susceptible local oscillators. Hence, such data identify the interaction sites as well as reflect the complexity of the existing equilibria, but they cannot predict the time scales of the slower individual equilibrium steps nor the stoichiometry of the molecular entities involved in them.

Acknowledgments. I would like to express my gratitude for stimulating discussions and helpful criticism to Dr. R. Ullman and Professor S. Krimm. Dr. Zinbo of our laboratory kindly performed the gel permeation analyses.

(39) R. G. Brüssau and H. Sillescu, *Ber. Bunsenges. Phys. Chem.*, **76**, 31 (1972).

(40) See, for instance, P. Combelas, C. Garrigou-Lagrange, and J. Lascombe, *Ann. Chim. (Paris)*, **5**, 315 (1970.

(41) D. D. Macdonald, D. Dunay, G. Hanlon, and J. B. Hyne, *Can. J. Chem. Eng.*, **49**, 420 (1971).

(42) See, for instance, J. Czubryt, E. Tomchuk, and E. Bock, *Ber. Bunsenges. Phys. Chem.*, **75**, 243 (1971).

Optical and Magnetic Properties of Anions of Hexahelicene

S. I. Weissman* and Raymond Chang

Contribution from the Department of Chemistry, Washington University, St. Louis, Missouri 63130, and the Department of Chemistry, Williams College, Williamstown, Massachusetts 01267. *Received July 5, 1972*

Abstract: The optical rotatory dispersion spectra of the mono-, di-, and trianion of (+)-hexahelicene were determined. The mono- and trianion are paramagnetic. The dianion appears to be diamagnetic.

Hexahelicene has served, since its synthesis and resolution by Newman,[1] as a model substance for observation and calculation of various features of optical activity.[2] Our interest was directed toward it because of its usefulness in the study of dependence of electron-transfer rate on relative optical configuration of reactants.[3] The observation that the rate constants for electron transfer between anion and neutral molecules of hexahelicene are markedly dependent on the relative optical configurations of the reacting pair suggested that knowledge of the optical activity of the anions might be useful in interpreting the data. Accordingly, we have measured the optical rotatory dispersion (ORD) of the anions of hexahelicene. We have as yet not found any illuminating relations between the optical and rate data, but, in view of the intrinsic interest of the optical data and their bearing on the theories of optical activity, we report the results of our optical studies. Included in this report are the electron spin resonance (esr) studies of the anions of hexahelicene.

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

(2) C. W. Deutsche, D. A. Lightner, R. W. Woody, and A. Moscowitz, *Annu. Rev. Phys. Chem.*, **20**, 420 (1969).

(3) R. Chang and S. I. Weissman, *J. Amer. Chem. Soc.*, **89**, 5968 (1967).

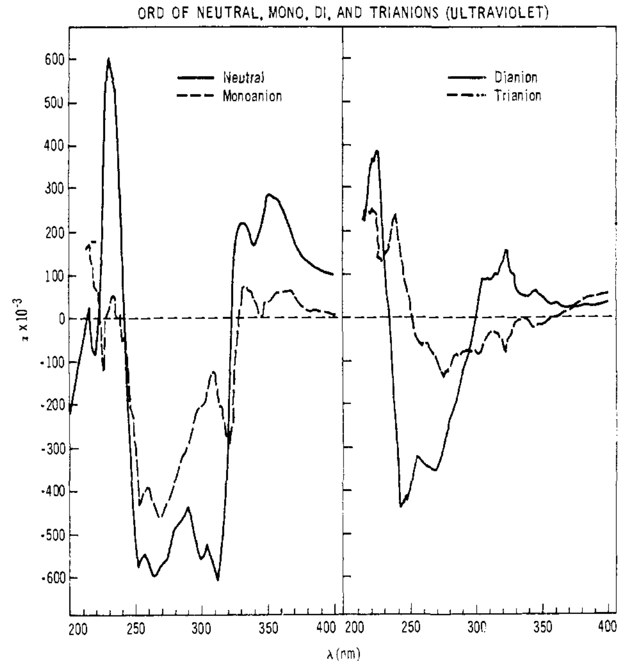


Figure 1. Ultraviolet ORD spectra of neutral hexahelicene and its anions.

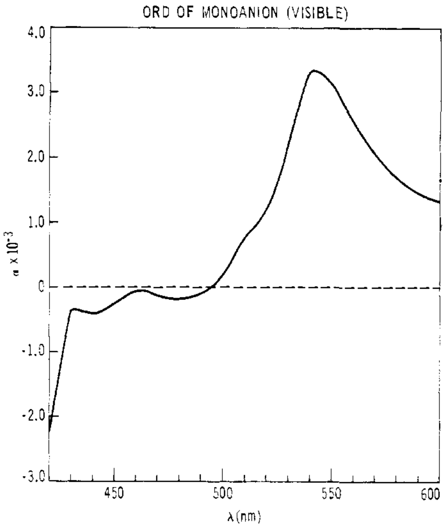


Figure 2. ORD spectrum of the monoanion of hexahelicene in the visible.

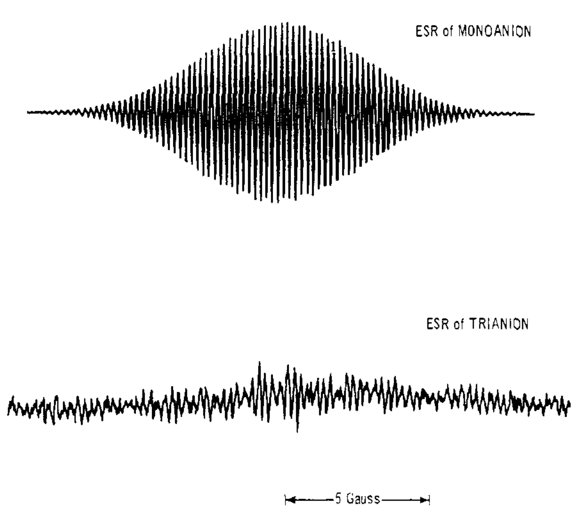


Figure 3. Resolved esr spectra (dX''/dH *vs.* H) of the monoanion and trianion of hexahelicene.

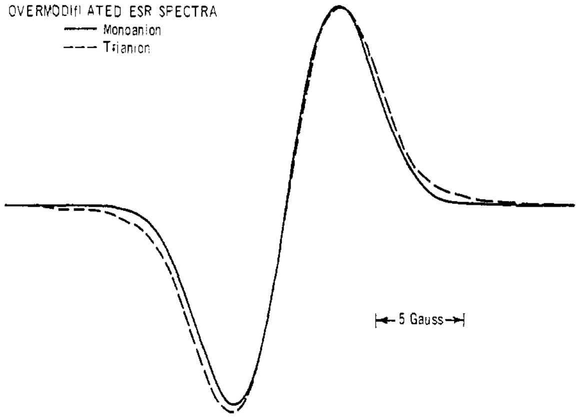


Figure 4. Esr spectra at high-modulation amplitude under identical conditions at maximum concentrations of monoanion and trianion.

Experimental Section

The usual high-vacuum methods for preparation of the anions were employed.[4] For measurements of the ORD a completely sealed system which could be accommodated in the cell compartment was used. The alkali metal mirror was isolated from the rest of the system by a breakseal. Because of the necessity for accurate reproducibility of the placement of the cell in the measurements of optical rotation, the cell was clamped permanently into the cell holder for each experiment, and the entire arrangement was removed for further reactions. All the ORD spectra were recorded on a Cary Model 60, electronic absorption spectra on Cary 14, and esr spectra on a Varian E-3 spectrometer.

Results and Discussion

Hexahelicene is well behaved in its reduction by alkali metals in solvents such as 1,2-dimethoxyethane (DME) and tetrahydrofuran (THF). Progressive reduction of a dilute solution (*ca.* 10^{-4} *M*) of hexahelicene results in a succession of changes of color from olive green to pink to green with the corresponding changes in its optical rotation and paramagnetism. These changes can be reversed upon the addition of neutral hexahelicene. Prolonged reduction resulted in a dark green solution which still possessed optical activity but apparently contained decomposed products. Figure 1 shows the ultraviolet ORD spectra of the neutral, mono-, di-, and trianion of hexahelicene in DME at room temperature.

These spectra were obtained from the observed spectra of the mixtures which were produced by progressive reduction by the following iterative procedure. During the initial stages of reduction it was assumed that only the neutral molecule and its monoanion were present. The ORD curve for the neutral molecule, multiplied by an arbitrarily assumed mole fraction, was substracted from the ORD curve of the solution after first reduction. This difference, after a readjustment in the mole fraction, was then used together with the curve of the neutral molecule to synthesize the ORD curve for the solution after the second reduction. If no fit could be obtained, a new mole fraction was then tried for the first solution and the process was repeated until the best fit was found. For the latter stages of

---

[4] D. E. Paul, D. Lipkin, and S. I. Weissman, *J. Amer. Chem. Soc.*, 78, 116 (1956).

reduction it was necessary to assume the presence of three species. By systematically varying the mole fractions it is possible to first obtain the ORD curve of the monoanion and then the di- and trianion. The electronic absorption spectra of the anions of hexahelicene show very broad bands in the visible range that are insensitive to the change in relative concentrations. Consequently, they were of little use in following the progress in reduction or correlating with the rotations in the ORD curves.

In the visible region the spectrum of only the monoanion is given (Figure 2). The spectra of the dianion and trianion in the visible were so lacking in structure that we were unable to disentangle them from each other.

Both mono- and trianion are paramagnetic; their esr spectra are shown in Figure 3. The analysis of the esr spectrum of the monoanion has recently been reported.[5] The trianion spectrum has not yet been analyzed; however, it is obvious that the spin density distributions in the two ions are drastically different.

The intensity of the esr spectrum of the monoanion first increases as reduction proceeds and then decreases; in the final stages of reduction the intensity of the trianion spectrum reaches a maximum. The integrated intensity of a completely reduced solution is equal to the intensity of the monoanion spectrum at the stage of reduction at which it is maximum (Figure 4). Attempts to find triplet spectra in rigid media or broad spectra in fluid solution of the dianion failed, presumably because it is diamagnetic.

Acknowledgments. We wish to thank Professor M. S. Newman for generous samples of the racemic and optically active hexahelicene used in these experiments. The work has been supported by the National Science Foundation, the National Institutes of Health, and the Petroleum Research Fund of the American Chemical Society.

---

(5) R. D. Allendoerfer and R. Chang, *J. Magn. Resonance*, 5, 273 (1971).

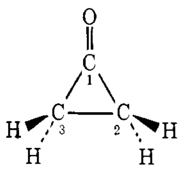
Ring Opening of Cyclopropanone

A. Liberles,* A. Greenberg, and A. Lesk

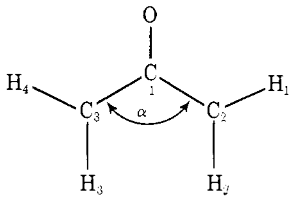
Contribution from the Department of Chemistry,
Fairleigh Dickinson University, Teaneck, New Jersey 07666.
Received February 8, 1972

Abstract: We report the results of INDO and *ab initio* SCF calculations on cyclopropanone, oxyallyl, and allene oxide, and the con- and disrotatory openings of the closed ketone. The *ab initio* results indicate that singlet oxyallyl is 83 kcal/mol less stable than cyclopropanone, while allene oxide is 21 kcal/mol less stable. The internal $C_3C_1C_2$ angle in singlet oxyallyl is predicted to be near 105°. Although the conrotatory opening of cyclopropanone passes through a true transition state, the disrotatory opening is the lower energy pathway, and oxyallyl appears to be at, or near, the disrotatory energy maximum.

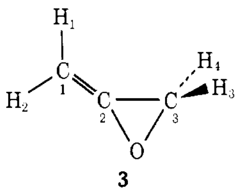
Cyclopropanone is one of the more interesting molecules in organic chemistry and much effort has gone into studying its behavior and that of its derivatives.[1-4] The parent molecule has recently been prepared[5,6] and its microwave spectrum studied.[7,8] While there is little doubt that the molecule exists, much of its chemistry is difficult to explain in terms of the conventional structure **1**, and it has been postulated that it may isomerize to oxyallyl (**2**) or allene oxide (**3**).[1,2,9] This appears to be a problem that molecular quantum chemistry can handle, and several semiempirical theoretical calculations have been reported.



1



2



3

Extended Hückel calculations by Hoffmann indicate that **2** is the most stable, being 23 kcal/mol more stable than **1**, and 21 kcal/mol more stable than **3**.[10] The disrotatory opening of **1** is preferred, and **2**, once formed, is reported to have an internal angle α equal to 121°.

More recently, Bodor, Dewar, Harget, and Haselbach[11] have performed MINDO/2 calculations. Their

---

(1) N. J. Turro, *Accounts Chem. Res.*, 2, 25 (1969).

(2) N. J. Turro, R. B. Gagosian, S. E. Edelson, T. R. Darling, J. R. Williams, and W. B. Hammond, *Trans. N. Y. Acad. Sci.*, 33, 396 (1971).

(3) D. G. Sclove, J. F. Pazos, R. L. Camp, and F. D. Greene, *J. Amer. Chem. Soc.*, 92, 7488 (1970).

(4) A. S. Kende, *Org. React.*, 11, 261 (1960).

(5) N. J. Turro and W. B. Hammond, *J. Amer. Chem. Soc.*, 88, 3672 (1966).

(6) S. E. Schaafsma, H. Steinberg, and T. J. De Boer, *Recl. Trav. Chim. Pays-Bas*, 85, 1170 (1966).

(7) J. M. Pochan, J. E. Baldwin, and W. H. Flygare, *J. Amer. Chem. Soc.*, 91, 1896 (1969).

(8) J. M. Pochan, J. E. Baldwin, and W. H. Flygare, *ibid.*, 90, 1072 (1968).

(9) J. G. Burr and M. J. S. Dewar, *J. Chem. Soc.*, 1201 (1954).

(10) R. Hoffmann, *J. Amer. Chem. Soc.*, 90, 1475 (1968).

(11) N. Bodor, M. J. S. Dewar, A. Harget, and E. Haselbach, *ibid.*, 92, 3854 (1970).