dichroism curve with greater accuracy. This is all subject to the other assumptions already mentioned, and these do place a limit on the extent to which the present method could thereby be improved.

ACKNOWLEDGMENTS

The major portion of this work was done in collaboration with the late Professor William E. Moffitt at Harvard University, where the author was holder of a National Research Council-American Chemical Society Petroleum Research Fund Postdoctoral Fellowship.

The numerical work was carried out on the IBM 704 computer at the Bell Telephone Laboratories in Murray Hill, New Jersey. It is a pleasure to acknowledge the generous hospitality of the Bell Laboratories made available through the kind courtesy of Dr. S. O. Morgan and Dr. W. P. Slichter. The author also would like to express his appreciation to Dr. M. E. Terry and Miss Shirley Reed for their competent help and advice in connection with the computational procedures.

REVIEWS OF MODERN PHYSICS VOLUME 32, NUMBER 2 APRIL, 1960

Theory of the Optical Activity of Bimesityl Derivatives*

EDEL WASSERMAN

Bell Telephone Laboratories, Inc., Murray Hill, New Jersey

IN the previous paper, Dr. Moscowitz mentions the importance of the rotational strength in determining the contribution of an electronic state to the optical activity of a molecule. From Rosenfeld's equation we may represent the observed rotation, employing light of frequency ν, as

$$[M] \propto \sum_k \nu^2 R_k/(\nu_k^2-\nu^2),$$

where $[M]$ is proportional to the optical activity per molecule. The rotational strength R_k is given by $\boldsymbol{\mu}_e \cdot \boldsymbol{\mu}_m$ except for a phase factor. Here, μ_e and μ_m are the electric and magnetic moments associated with the ground to k state transition of frequency ν_k.

For optically inactive systems, μ_e and μ_m may be perpendicular, so that R_k vanishes. With an active molecule, a natural approach for theory has been to consider the interaction of individually inactive portions, the electric moment of one group having a component parallel to the magnetic moment of another. This is the approach used in the coupled oscillators model of Born,[1,2] Kuhn,[2,3] and Kirkwood.[4] A recent example is found in Moffitt's treatment of polypeptides.[5]

Although the decomposition into groups is frequently arbitrary, one system in which it is particularly attractive is the active biphenyls. The ortho substituents prevent coplanarity and extensive conjugation between the rings. Except for the dipolar interactions the pi electrons of the two rings may be considered separately.

An attractive series for the study of the optical activity of biphenyls is the substituted bimesityls (Fig. 1). The four ortho methyl groups should prevent extensive motion about the interring bond. Theoretical computations can therefore be restricted to a single conformation. The symmetry of the three methyl groups in each ring permits the 3,3′-disubstituted bimesityl to be considered as two interacting monosubstituted benzene rings. The axis of rotation greatly simplified the computations. Finally, Adam and Moyer's preparation and resolution of the diaminobimesityl[6] and the synthetic versatility of the aromatic amino group allowed the preparation of other symmetrical, optically active, bimesityl derivatives.

Assuming that the optical activity in the visible and near ultraviolet is adequately described by the lowest

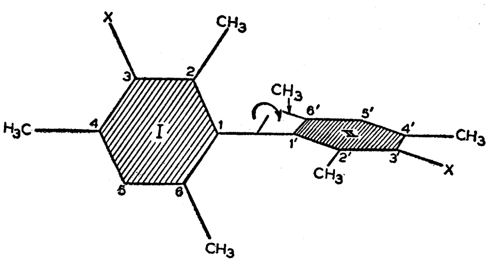

FIG. 1. 3,3′-disubstituted bimesityl. Arrow designates axis of rotational symmetry.

---

* Presented at the William E. Moffitt Memorial Session.

[1] M. Born, *Optik* (Verlag Julius Springer, Berlin, 1933).

[2] T. M. Lowry, *Optical Rotatory Power* (Longman's Green and Company, Inc., New York, 1935).

[3] W. Kuhn in *Stereochemie*, edited by K. Freudenberg (Franz Deuticke, Leipzig and Vienna, 1933).

[4] J. Kirkwood, J. Chem. Phys. **5**, 479 (1937).

[5] W. E. Moffitt, J. Chem. Phys. **25**, 467 (1956).

[6] W. W. Moyer and R. Adams, J. Am. Chem. Soc. **51**, 630 (1929).

excited states of the molecule, the pi-electron approximation is used in formulating the wave functions for the bimesityl derivatives. The molecular wave functions are of the form

$$\Omega_{S_{\substack{A\\B}}} = (2)^{-\frac{1}{2}}(\Theta_{N\mathrm{I}}\Theta_{S\mathrm{II}} \pm \Theta_{S\mathrm{I}}\Theta_{N\mathrm{II}}),$$

where $\Theta_{N\mathrm{I}}$ and $\Theta_{S\mathrm{I}}$ represent the ground and s excited states of ring I. The A refers to those functions which are symmetric with respect to the axis of rotation, the B to those that are antisymmetric. Overlap and exchange between rings are neglected, as are any effects of nuclear vibrations.

The individual benzene rings are described by the four LCAO-ASMO functions of Goeppert-Mayer and Sklar.[7] The three methyl groups are considered by assuming that the energies of these states are those observed for the corresponding states of mesitylene. The 3,3′ substituents are taken into account by introducing two excited state functions representing transfer of charge from the substituent to the ring. These six Θ_S states may interact by means of one-electron (intraring) perturbations. These are the resonance integral between the substituent and the adjacent carbon atom and the change in the coulomb integral at the 3,3′ carbon atoms.

In addition to the intraring perturbation, the "exciton" (dipole-dipole) interaction between rings was examined. This perturbation can split the degeneracy of A and B states. But since the intraring and interring perturbations are of A symmetry, neither can mix A and B states. Thus, each compound requires the eigenvalues and eigenvectors of two sixth-order energy matrices.

The one-electron perturbations were evaluated from observed spectra. The shift of the lowest energy band of the ortho and meta identically disubstituted derivatives from that of the corresponding monosubstituted benzene yielded the resonance integral. Similar comparison of the para with the corresponding ortho and meta derivatives yielded the change in the Coulomb integral. The dipole-dipole interaction was obtained by direct computation from the wave functions .

It was found that the deviation of the rings from perpendicularity was extremely important in determining the magnitude of the optical rotation computed. Only two Ω_S functions, one of each symmetry, can give rise to optical activity. These correspond to one of the degenerate states responsible for the intense E_{1u} band of benzene (the Θ_Y state in Moffitt's notation[8]). The other bimesityl states become active only by mixing with them. These Ω_Y functions have allowed electric and magnetic moments so that their rotational strengths are large, but they cancel one another exactly. Their degeneracy is not directly resolved by dipole-dipole interactions when the rings are perpendicular. The splitting which does occur, due to mixing with other states, yields only a small predicted rotation; much less than that observed in most cases.

Table I. Rotations of nonperpendicular bimesityls at 5790 A.

Substituent	Calc	Obs
F		−1.6
OH	30.0	13
NH_3^+		53
$N(CH_3)_2$	44.4	53
NH_2	36.6	78
Cl	96.0	98
O^-		185
Br	93.6	213
I	334.2	432

That the rings do deviate from perpendicularity is indicated by an examination of the Van der Waals' interactions between the groups attached to the benzene rings. By using known potential functions it is found that the adjacent ortho methyl groups are displaced by the 3,3′ substituents. The 2,2′ methyls are closer than the 6,6′ methyls. This leads to a slight rotation about the interring bond (2° for the largest substituent). The Ω_Y functions are now split directly by the exciton interaction and much larger rotations are possible.

With all the elements of the energy matrices determined, the eigenvalues and eigenvectors were computed by means of an IBM 650. They were substituted into Rosenfeld's equation to produce the optical activities. The values at 5790 A are given in Table I. Similar agreement between theory and experiment, within a factor of 2.5, is found at other wavelengths. Suitable potential functions are not available for F, NH_3^+, and O^-, but we may utilize evidence of their "size" from other sources to demonstrate a good correlation between the magnitudes of steric interactions and optical rotation.

In conclusion, we may note that the absolute configuration of Fig. 1 is predicted to be levorotatory in the visible for all compounds studied except difluorobimesityl.

ACKNOWLEDGMENT

This problem was suggested by the late Professor William E. Moffit. Much is owed to his inspiring direction of its prosecution both by his conversations with the author and through his papers in which many of the procedures employed are discussed.

---

[7] M. Goeppert-Mayer and A. L. Sklar, J. Chem. Phys. **6**, 645 (1938).

[8] W. E. Moffitt, J, Chem. Phys. **22**, 324 (1954).