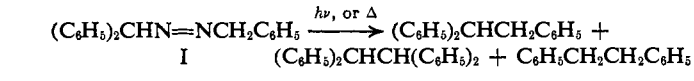
of the radical pair. The reactions chosen were the formation of 1,1,2-triphenylethane from diphenylcarbene and toluene, as described in ref 2, and the thermal or photochemical decomposition of the azo compound I. It is generally accepted that acyclic



$$\underset{\mathrm{I}}{(C_6H_5)_2CHN{=}NCH_2C_6H_5} \xrightarrow{h\nu,\ \text{or}\ \Delta} (C_6H_5)_2CHCH_2C_6H_5 + (C_6H_5)_2CHCH(C_6H_5)_2 + C_6H_5CH_2CH_2C_6H_5$$

azo compounds decompose through the singlet state,[7] and there can be little doubt as to the triplet character of the reacting diphenylmethylene. The comparison of the chemistry of the two systems reveals a spin correlation effect because the ratio of unsymmetrical to symmetrical products is higher in the reaction of I (1.5:1) than in the methylene reaction (1:1).

Figure 1 shows the spectra obtained from the two reactions showing the opposite polarizations, in striking confirmation of the considerations outlined above. Analysis of the spectra shows that the triplet reaction produces overpopulation in the nuclear substates with m_{j_z} closest to zero ($\pm 1/2$) and the singlet reaction gives product with overpopulation of substates with m_{j_z} furthest away from 0 ($\pm 3/2$).

It should be pointed out that since the formation of polarized product requires separation of the components of the radical pair, cyclic azo compounds should not give polarized products if decomposed from a singlet state. To deduce the multiplicity of the precursor it is also necessary to know the absolute sign of the nuclear spin coupling constants in the reaction product.

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[2.2]Paracyclophane System Optical Activity. I. Theory[1]

Sir:

Certain chemical systems show optical activity that can be accounted for by the simplest quantum models.[2,3] The experimental study of such synthetically modified systems is important to a better understanding of the origins of the extraordinary molecular spectroscopy associated with optical activity. This communication describes a semiempirical exciton theory that gives straightforward interpretation to observed circular dichroisms of ring-substituted paracyclophanes.[4] There emerges as well a sensitive scheme for defining the sign of Platt's "spectroscopic moments" for benzene $^1L_b \leftarrow {}^1A$ transitions[5] and possibly refining the numerical values assigned to them.

The secular determinant of first-order degenerate perturbation theory[6] for a pair of substituted benzene molecules (A and B) will assume diagonal form with the excited state wave functions

$$\Psi_i^+ = 2^{-1/2}[A_0B_i + A_iB_0] \quad (1)$$

and

$$\Psi_i^- = 2^{-1/2}[A_0B_i - A_iB_0]$$

where, for instance, A_0 and A_i are isolated molecule wave functions for molecule A in the ground state ^1A and excited state ^1L_b, respectively. The perturbation matrix elements are based on the *inter*benzene nuclei and electron electrostatic potential terms, H'. *Inter*benzene overlap and thus also *inter*benzene electron exchange are neglected. Additional higher order terms will mix in higher states under the perturbation. Unequal weighting of A_0B_i and A_iB_0 in Ψ_i^+ and Ψ_i^- obtains insofar as the interaction of excited A and ground state B differs slightly from that of excited B and ground state A. This will be the case to some degree since A and B represent phenyl rings which bear different substituents.

The wave functions of eq 1 give first-order perturbation energies for the states

$$E_\pm^{(1)} = (A_iB_0|H'|A_iB_0) \pm (A_iB_0|H'|A_0B_i) \quad (2)$$

relative to the separated (noninteracting) members of the pair. The nondegenerate ground state has a wave function $\Psi_0 = A_0B_0$ at the corresponding level of approximation with a first-order perturbation energy $(A_0B_0|H'|A_0B_0)$[6] relative to separated members of the pair both in the ground state.

The electric dipole operator $\vec{m} = \vec{m}(A) + \vec{m}(B)$ gives the familiar "in phase" and "out of phase" transition moments of substituted benzenes such that the dipole strengths from the ground state to the states with degeneracy now lifted according to eq 2 are

$$D_{0,\pm} = |\vec{m}_{0,\pm}|^2 = 1/2|\vec{m}(A)_{0i} \pm m(B)_{0i}|^2 \quad (3)$$

The magnetic dipole operator may be defined with respect to an arbitrary origin[7]

$$\mu = \frac{e}{2mc}\{[\vec{R}(A) \times \vec{p}(A)] + \vec{l}(A) + [\vec{R}(B) \times \vec{p}(B)] + \vec{l}(B)\} \quad (4)$$

where $R(A)$ and $\vec{R}(B)$ are vectors to the centers of gravity of the benzenes, $\vec{p}(A)$ and $\vec{p}(B)$ are linear momenta, and $\vec{l}(A)$ and $\vec{l}(B)$ are angular momentum operators referred to the respective benzene centers of gravity. Most conveniently, one may choose the arbitrary origin to be midway between the benzene centers of gravity, such that $\vec{R}(A) = \vec{R}(B)$.

Neglecting small terms,[8] it follows that the rotatory

(1) This work supported by Public Health Service Grant GM 11644.

(2) (a) W. J. Kauzmann, J. E. Walter, and H. Eyring, *Chem. Rev.*, **26**, 339 (1940); A. Moscowitz, *Advan. Chem. Phys.* **4**, 67 (1962); (b) O. E. Weigang, Jr., and E. H. Höhn, *J. Amer. Chem. Soc.*, **88**, 3673 (1966).

(3) J. Tinoco, Jr., and R. W. Woody, *J. Chem. Phys.* 40, 160 (1964).

(4) D. J. Cram and N. C. Allinger, *J. Amer. Chem. Soc.* 77, 6289 (1955); D. J. Cram and L. A. Singer, *ibid.*, **85**, 1078 (1963).

(5) J. R. Platt, *J. Chem. Phys.*, **19**, 263 (1951); J. Petruska, *ibid.*, **34**, 1111, 1120 (1961).

(6) H. Eyring, J. Walter, and G. E. Kimball, "Quantum Chemistry," John Wiley & Sons., Inc., New York, N. Y., 1948.

(7) The origin independence of rotatory strength in this model is assured. It persists even through the first order of perturbation of wave functions if only dynamic coupling terms are considered. See the appendix: E. G. Hohn and O. E. Weigang, Jr., *J. Chem. Phys.*, **48**, 1127 (1968).

(8) The neglected terms like $\vec{m}(A)_{0i}\cdot\vec{\mu}_{i0}(A)$ are zero for optically inactive benzene "monomers." But even at a level where one monomer is considered active from alkyl group substituents, these terms are demonstrably small for the $^1L_b \leftarrow {}^1A$ ($^1B_{2u} \leftarrow {}^1A_{1g}$) related transitions of benzene. The relevant experiment and theoretical reasons have been discussed by Moscowitz, *et al.*[9] The terms $\vec{m}_{0i}(A)\cdot\vec{\mu}_{i0}(B)$ can be expected to be small for the same reasons in the case of parallel-plane benzene systems.

(9) A. Moscowitz, A. Rosenberg, and A. E. Hansen, *J. Amer. Chem. Soc.*, **87**, 1813 (1965).

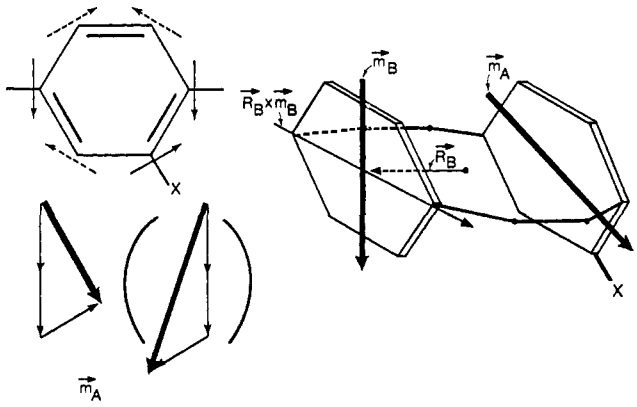

Figure 1. Vector constructions relating paracyclophane absolute configuration to $^1L_b \leftarrow {}^1A$ rotatory strength. Substituent spectroscopic moments are shown on the left as full arrows. They contribute in a fashion that depends on location of the substituent (full arrows) and the magnitude and sign given to the spectroscopic moment. The net transition vector dipole $\vec{m}_A$ is given for arbitrary magnitudes and a positive (negative) substituent spectroscopic moment. The vector cross-product on the right has a resultant directed in a right-handed sense.

strengths associated with the dipole strengths of eq 3 are[10]

$$R_{0,\pm} = -i\vec{m}_{0,\pm}\cdot\mu_{\pm,0}$$
$$= \pm\pi\bar{\nu}_{0i}\vec{m}(A)_{0i}\cdot\vec{R}(B)\times\vec{m}(B)_{0i} \qquad (5)$$

where $\bar{\nu}_{0i}$ is the frequency in cm^{-1} of the zero-order $i \leftarrow 0$ transition and use has been made of the relationship $\vec{p}_{0i} = (-2\pi imc/e)\bar{\nu}_{0i}\vec{m}_{0i}$. Some elaboration by adding special Franck–Condon overlap factors to eq 3 and 5 is necessary to account for lowest order vibronic coupling effects.[11]

The polarizations and magnitudes represented by the electric moments $\vec{m}_{0i}(A)$ and $\vec{m}_{0i}(B)$ for $^1L_b \leftarrow {}^1A$ in eq 3 and 5 can be inferred from Platt's semiempirical theory of spectroscopic moments for substituted benzenes.[5] Figure 1 shows the relevant vector constructions.

The theory affords a quantum mechanical assignment of the *absolute configuration* that is in agreement with the experimental assignment.[12] The theory suggests, and experimental examples[13] have confirmed, that *for the given absolute configuration, the sign of the longest wavelength singlet–singlet CD of the transition pair follows (and will be opposite to) that of the signed parameter, the spectroscopic moment of its substituent.* As Figure 1 shows, the out-of-phase, then in-phase (going to higher frequency) combination of benzene electric moments for the two states results in a reversal of the projection of vector $\vec{R}(B)\times\vec{m}(B)_{0i}$ on $\vec{m}(A)_{0i}$ while preserving the projection magnitude. The initial sign of this projection depends on the spectroscopic moment for the additional substituent on A through its contribution to $\vec{m}(A)_{0i}$.

Platt's work suggests that this scheme will fail for the $^1L_a \leftarrow {}^1A$ related transitions where significantly large experimental intensity changes are not observed. Indeed, on theoretical grounds Moffitt[14] points out that $^1L_a \leftarrow {}^1A$ bands are expected to be insensitive to inductive effects relative to the $^1L_b \leftarrow {}^1A$ bands. On the other hand, the former bands are expected to be the *more* sensitive to vibronic coupling effects.

(10) See also: H. Eyring, J. C. Liu, and D. Caldwell, *Chem. Rev.*, **68**, 525 (1968); J. A. Schellman, *Accounts Chem. Res.*, **1**, 144 (1968).
(11) O. E. Weigang, Jr., *J. Chem. Phys.*, **43**, 71 (1965).
(12) H. Falk and K. Schloegel, *Angew. Chem. Int. Ed. Engl.*, **7**, 383 (1968).
(13) M. J. Nugent and O. E. Weigang, *J. Amer. Chem. Soc.*, **91**, 4556 (1969).
(14) W. Moffitt, *J. Chem. Phys.*, **22**, 320 (1954).

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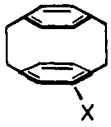
[2.2]Paracyclophane System Optical Activity. II. Circular Dichroism of Ring-Substituted Paracyclophanes[1]

Sir:

The ring-substituted paracyclophanes afford the rare opportunity[2] to compare observed optical activity to the parameters of a simple theory.[3] The optically active 4-substituted [2.2]paracyclophanes **1** used in this study,



1a X = CO_2H
1b X = CH_3
1c X = CH_2Br
1d X = CH_2OH

with the exception of 4-methyl[2.2]paracyclophane (**1b**), have been described previously.[4] However, neither their circular dichroism (CD) nor optical rotatory dispersion has been reported.

The absolute configuration of (+)-(*S*)-4-carboxy-[2.2]paracyclophane has been assigned to **1a** by kinetic arguments.[5] The prediction of its absolute configuration by a semiempirical exciton theory[3] is found to be successful. This communication examines the correspondence of the experimental data for **1** to this and other details of the theory.

With the exception of the methyl derivative, the CD measurements were carried out on derivatives of (+)-(*S*)-4-carboxy[2.2]paracyclophane (**1a**) that therefore have the *S* configuration. (−)-(*R*)-4-Methyl-[2.2]paracyclophane, enantiomeric to **1b**, was derived from (−)-(*R*)-acid.[6] The (−)-(*R*)-methyl derivative, derived from 92% optically pure (−)-(*R*)-acid, had $[\alpha]^{25}D$ −75.0° (*c* 4.0, chloroform), mp 150–151°, and gave satisfactory analysis.

(1) This work supported by Public Health Service Grant GM 11644.
(2) See also the systems considered by: S. F. Mason and G. W. Vane, *J. Chem. Soc., B*, 370 (1966); S. F. Mason, G. W. Vane, K. Schofield, R. J. Wells, and J. S. Whitehurst, *ibid.*, 553 (1967).
(3) M. J. Nugent and O. E. Weigang, Jr., *J. Amer. Chem. Soc.*, 91, 4555 (1969).
(4) D. J. Cram and N. C. Allinger, *ibid.*, **77**, 6289 (1955); D. J. Cram, and L. A. Singer, *ibid.*, **85**, 1078 (1963).
(5) H. Falk, and K. Schloegel, *Angew. Chem. Int. Ed. Engl.*, **7**, 383 (1968).
(6) (−)-(*R*)-4-Methyl[2.2]paracyclophane was prepared by treatment of (+)-(*R*)-4-bromomethyl[2.2]paracyclophane with sodium and *t*-butyl alcohol in tetrahydrofuran. *Cf.* P. G. Gassman and P. G. Pape, *J. Org. Chem.*, **29**, 160 (1964).