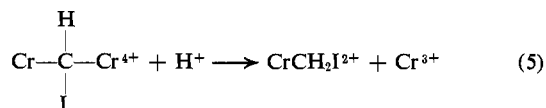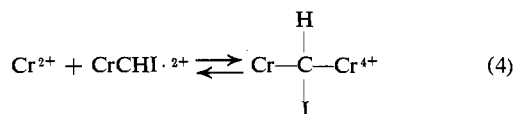of the label was found in the unreacted Cr^{2+} [7] and in the CrI^{2+} product. In order to explain these observations a rapid equilibrium between $[CrCHICr]^{4+}$ and $Cr^{2+} + CrCHI \cdot {}^{2+}$ is suggested.[8] The complete mechanism would then be

$$Cr^{2+} + CrCHI_2{}^{2+} \longrightarrow$$

$$CrI^{2+} + CrCHI \cdot {}^{2+} \quad \text{rate determining} \quad (3)$$

$$Cr^{2+} + CrCHI \cdot {}^{2+} \rightleftarrows \underset{\underset{I}{|}}{\overset{\overset{H}{|}}{Cr-C-Cr^{4+}}} \quad (4)$$

$$\underset{\underset{I}{|}}{\overset{\overset{H}{|}}{Cr-C-Cr^{4+}}} + H^+ \longrightarrow CrCH_2I^{2+} + Cr^{3+} \quad (5)$$

Step 4 involves a homolytic breakage of a carbon–Cr bond and this type of scission has been found in a number of organochromium compounds.[10,11]

Further evidence for a rapid equilibrium (4) is provided by the specific activities (counts/minute/mmole) of $CrCH_2I^{2+}$ compared to the total specific activities of all the products. (It was necessary to group together the specific activities of CrI^{2+} and Cr^{3+} due to the relatively rapid aquation of CrI^{2+} to Cr^{3+}.)[12] Starting with labeled $CrCHI_2{}^{2+}$ and unlabeled Cr^{2+}, the specific activity ratio of $CrCH_2I^{2+}$ to total specific activity of all the products would be 0.50 if step 4 was not reversible. For experiments done at $[H^+] = 1.0 \ M$, the ratio ranged from 0.38 to 0.45, depending upon the amounts of the reactants and the allowed reaction time. If step 4 is reversible part of the label will appear in Cr^{2+} and thus eventually in CrI^{2+}, and this will decrease the ratio of specific activity of $CrCH_2I^{2+}$ to total in products.

In the reaction between labeled Cr^{2+} and unlabeled $CrCHI_2{}^{2+}$, the expected specific activity ratio of $CrCH_2I^{2+}$ to total products would be 0.25 if no equilibrium steps were involved. The experimental values, ($[H^+] = 1.0 \ M$), ranged from 0.28 to 0.32 depending on reaction conditions. This deviation can be explained by noting that part of the label will be transfered to $CrCHI \cdot {}^{2+}$ in step 4, thus resulting in the possibility of forming fully labeled $[*CrCHI*Cr]^{4+}$. The further reaction of this species would result in an increase in the specific activity ratio of $CrCH_2I^{2+}$.

Attempts were made to separate the species present in the reaction mixture using ion-exchange columns thermostatted at low temperatures and using a nitrogen atmosphere. No species of charge $4+$ was detected so that if $[CrCHICr]^{4+}$ is formed it must rapidly dissociate to form the final products.

In labeling experiments which were identical except that the $[H^+]$ was 0.1 M instead of 1.0 M, the devia-

tion of the specific activity ratio of $CrCH_2I^{2+}$ to total products to that expected assuming step 4 was not reversible was greater for the lower acidity. This is qualitative evidence that the reaction of the intermediate to form the final products, step (5), is $[H^+]$ dependent. Further work to obtain more information about the intermediate is in progress.

The general form of the proposed mechanism (3–5) may be applicable to reduction of other polyhalo-organic compounds[13-15] by Cr(II). Castro[13] has proposed a mechanism for the reduction of geminal halides by Cr(II) which does not involve carbon-bridged dinuclear chromium intermediates. However, his mechanism cannot accommodate the results of the labeling experiments in the present study.

(13) C. E. Castro and W. C. Kray, Jr., *J. Amer. Chem. Soc.*, **88**, 4447 (1966).
(14) F. A. L. Anet and E. Leblanc, *J. Amer. Chem. Soc.*, **79**, 2649 (1957).
(15) H. Lux, D. Sarre, and I. Schaffelhofer, *Ber.*, **97**, 2301 (1964).

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[2.2]Paracyclophane System Optical Activity. III. Theory for Isotopic Substitution Chirality[1]

Sir:

The circular dichroism (CD) due to ring substitution by deuterium in [2.2]paracyclophane has been reported recently.[2] This observation affords an opportunity to compare the effects of mass-induced perturbations through vibration to the earlier observed effects[3,4] of substituents electronically different from hydrogen. The sign and approximate intensity of the long wavelength CD of such ring-substituted paracyclophanes can be predicted by a theory that accounts for the electronic perturbations of the benzene rings.[5] Also, since variation of the substituent in the same absolute configuration can change the sign of CD, the twist of benzene rings around the interplanar axis which has been observed in crystalline [2.2]paracyclophane[6] is not significantly operative by a substituent steric effect.

Therefore the CD observed for the deuterium substituent, which is only isotopically different from hydrogen, cannot be reasonably ascribed to either steric or electronic perturbations. We outline here a vibronic coupling theory for the source of rotatory strength.

The vibrational structure of the long wavelength

(7) Recovered as the oxygen oxidation product, octaaquodi-μ-hydroxodichromium(III) ion.
(8) Another way of obtaining labeled Cr(II) would be through an exchange with labeled Cr(III). However, this reaction has been discounted due to the relatively long half-life of the reaction ($t_{1/2} = 1.5$ days at 25°).[9]
(9) A. Anderson and N. Bonner, *J. Amer. Chem. Soc.*, **76**, 3197 (1954).
(10) R. Schmidt and T. W. Swaddle, *J. Chem. Soc. A*, 1927 (1970).
(11) J. K. Kochi and D. Buchanan, *J. Amer. Chem. Soc.*, **87**, 853 (1965).
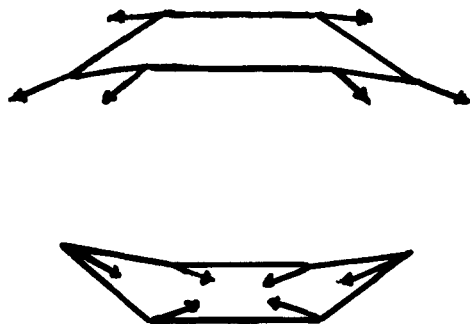(12) T. W. Swaddle and E. L. King, *Inorg. Chem.*, **4**, 234 (1965).

(1) Taken in part from the Master of Science Thesis of M. A. Hassloch, Tulane University, 1973.
(2) P. H. Hoffman, E. C. Ong, O. E. Weigang, Jr., and M. J. Nugent, *J. Amer. Chem. Soc.*, **96**, 2620 (1974).
(3) M. J. Nugent and O. E. Weigang, Jr., *J. Amer. Chem. Soc.*, **91**, 4556 (1969).
(4) H. Falk, P. Reich-Rohrwig, and K. Schloegl, *Tetrahedron*, **26**, 511 (1969).
(5) O. E. Weigang, Jr., and M. J. Nugent, *J. Amer. Chem. Soc.*, **91**, 4555 (1969).
(6) O. Schnepp, private communication.

Figure 1. Out-of-phase combination of ring breathing modes in bent benzene rings of [2.2]paracyclophane.

ordinary absorption of unsubstituted single crystal [2.2]paracyclophane has been observed at low temperature.[7,8] A recent reinterpretation of the vibrational analysis[9] applies the dimer vibronic coupling theory of Fulton and Gouterman[10] and defines a vibrational mode significantly coupled to the electronic structure. The major features of the uv absorption edge are accounted for by theory parameter values[10] of $\epsilon = 1.5$ and $\lambda = 2.0$ for the 235 cm^{-1} coupled vibrational mode[9] similar to that shown in Figure 1. The theory assumes variation with nuclear position of the *inter*-ring electronic potential to be the primary vibronic interaction. It has been observed previously[5] that such theory should account for details of band shape in the long wavelength CD of the ring-substituted paracyclophanes.

A more recent extension of the theory by Fulton[11] adds consideration of the variation of *intra*-ring electronic structure with such nuclear displacement as is depicted in Figure 1. Extending the right-hand side of eq 38 in ref 11 to include additional states and considering also the transition magnetic dipole form of eq 40 in ref 11, the model of ref 5 yields a vibronic coupling rotatory strength (*cf.* eq 5, ref 5)

$$R_{0.\pm} = \pm \pi \bar{\nu}_{0i} \frac{\partial m(A)_{0i}}{\partial Q_r^A} \cdot R(B) \times \frac{\partial m(B)_{0i}}{\partial Q_r^B} \xi_r \qquad (1)$$

where $\bar{\nu}_{0i}$ is the frequency in cm^{-1} of the zero-order $i \leftarrow 0$ transition. Q_r^A and Q_r^B are modified ring breathing modes shown in Figure 1 with a phase convention such that Q_r^A itself and the *negative* of Q_r^B are depicted, ξ_r is the zero-point mean square displacement of the normal mode. Equation 1 applies to a low temperature limit with no vibrational modes excited in the electronic ground state. Equation 1 can account for ^1L_b rotatory strength in [2.2]paracyclophane ring substituted by deuterium.

The extended form of eq 38 in ref 11 will define dipole derivatives that can be deduced as shown in Figure 2. Normal mode displacements have been assumed that would generate the observed $^1L_{b_2}$ circular dichroism of (−)-(S)-4-deuterio[2.2]paracyclophane.[2]

The *vibronic* rotation of transition dipole in ring A is

(7) A. Ron and O. Schnepp, *J. Chem. Phys.*, **37**, 2540 (1962); **44**, 19 (1966).
(8) S. Iwata, K. Fuke, M. Sasaki, S. Nagakwa, I. Otsubo, and S. Misumi, *J. Mol. Spectrosc.*, **46**, 1 (1973).
(9) M. A. Hassloch and O. E. Weigang, Jr., in preparation.
(10) R. L. Fulton and M. Gouterman, *J. Chem. Phys.*, **41**, 2280 (1964).
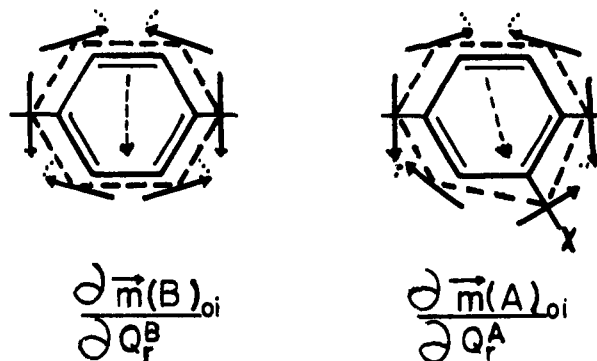(11) R. L. Fulton, *J. Chem. Phys.*, **56**, 1210 (1972).

Figure 2. Paracyclophane rings B and A under the distortion (exaggerated) of ring-breathing type modes. The reorientation (dotted arcs) of spectroscopic moment vectors relative to those for equilibrium position rings is shown. The resultant differential increments with vibration (dashed arrows), $\partial m(B_{0i})/\partial Q_r^B$ and $\partial m(A_{0i})/\partial Q_r^A$, are consistent with more general symmetry arguments.

completely analogous to the electronically induced rotation discussed in ref 5. Thus the vector relationships and the feature of opposite signed rotational strength with equal magnitude in the electronic theory[5] is preserved also in the vibronic theory detailed here.

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**[2.2]Paracyclophane System Optical Activity.**
IV. The Circular Dichroism of
(−)-(S)-4-Deuterio[2.2]paracyclophane[1]

Sir:

Few examples of CD arising from deuterium–hydrogen chirality have been reported.[2] We wish to report the first such uv transition CD observed for a system which has a broadly verified model for the origin of transition rotatory strength.

(−)-(S)-4-Deuterio[2.2]paracyclophane (**1**), $[\alpha]^{25}_{546}$
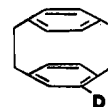
1

−4.0 ± 1.1° (*c* 0.87, chloroform) mp 280–285, was synthesized by deuterolysis of (S)-4-lithio[2.2]paracyclophane which in turn was derived from optically pure (+)-(S)-4-carboxy[2.2]paracyclophane.[3] Mass spectral analysis showed 90% deuterium incorporation into the [2.2]paracyclophane.[4]

(1) Taken in part from the Undergraduate Honors Thesis of P. H. Hoffman, Tulane University, 1971.
(2) For a recent review of optically active deuterium compounds, see L. Verbit, *Progr. Phys. Org. Chem.*, **7**, 51 (1970).
(3) A. Guest, P. H. Hoffman, and M. J. Nugent, *J. Amer. Chem. Soc.*, **94**, 4341 (1972).