of $Fe(CO)_4$ with respect to CO loss,[19] we propose that instead of iron tetracarbonyl the cycle is carried by di- and monoolefin-substituted iron tricarbonyl complexes.[20] Termination is by recombination of $Fe(CO)_3$(pentene) with CO.

From all experiments performed thus far, it appears the pulsed-laser initiation method yields time-averaged results identical with conventional thermal and continuous photochemical systems. The time resolution of this method (limited only by the length of the laser pulse), however, will permit transient spectroscopic studies of previously unobservable intermediates and dynamics of organometallic catalytic systems. In work currently in progress we are attempting to spectroscopically and dynamically characterize the $Fe(CO)_5$-based systems by direct, time-resolved observation of intermediates in both liquid and entirely gas-phase photocatalytic systems.

Acknowledgment. We gratefully acknowledge Koppers Company Inc. for generous support of this research.

Registry No. $Fe(CO)_5$, 13463-40-6; 1-pentene, 109-67-1; *trans*-2-pentene, 646-04-8; *cis*-2-pentene, 627-20-3.

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(18) Masters, C. "Homogeneous Transition-Metal Catalysis"; Chapman and Hall: London, 1981.

(19) Engelking, P. C.; Lineberger, W. C. *J. Am. Chem. Soc.* **1979**, *101*, 5569.

(20) This mechanism is supported by the comparison to the behavior of group 6 systems where diolefin complexes are stable and where isomerization appears to require the absorption of more than one photon per conversion. For relevant experiments see: Wrighton, M. S.; Hammond, G. H.; Gray, H. B. *J. Organomet. Chem.* **1974**, *70*, 283. Tumas, W.; Gitlin, B.; Rosan, A. M.; Yardley, J. T. *J. Am. Chem. Soc.* **1982**, *104*, 55. The problem is analyzed theoretically in Elian and Hoffmann (Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058.

Circular Dichroism of 1,1′-Spirobi[benzindans]: Demonstration of Nongenerality of the C_2 Rule

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Received December 21, 1981

Previously, Hug and Wagnière presented the rule of C_2 symmetry (C_2 rule) whereby they pointed out that if the chirality of a chromophore in a C_2 molecule is right handed, transitions of A symmetry will lead to negative Cotton effects and transitions of B symmetry to positive ones. They gave evidences in support of this rule for many different types of C_2 molecules.[2,3]

However, the C_2 rule cannot be considered a general one in view of the fact that the *chirality of chromophore*[4] is independent of the *helicity of transition*.[5] This situation is shown schematically by use of an exciton model (Figure 1). For both cases a and b, the chirality of the chromophore is left handed and the coupling mode of local transition moments ($\vec{\mu}_1$ and $\vec{\mu}_2$) is of A symmetry. The rotational strength R^A is evaluated as follows:[6]

$$R^A = 2\pi\sigma\mu^2 m_1 n_1 p_1$$

where σ is the excitation wave number of the local chromophore, $\mu = |\vec{\mu}_1| = |\vec{\mu}_2|$, (l_1, m_1, n_1) denotes the direction cosines of the point dipole $\vec{\mu}_1$, and $(p_1, 0, 0)$ are the coordinates of P_1, the point of intersection of $\vec{\mu}_1$ (or its extrapolation) and the x axis. Thus the rotational strength R^A assumes positive or negative value according to the sign of $m_1 n_1 p_1$, which corresponds with the helicity of transition (right handed for a and left handed for b). Evidently the C_2 rule takes only case a into consideration.[8] Therefore, it is not valid in principle to deduce the sign of the Cotton effect solely from the chirality of the chromophore and the symmetry of transition.

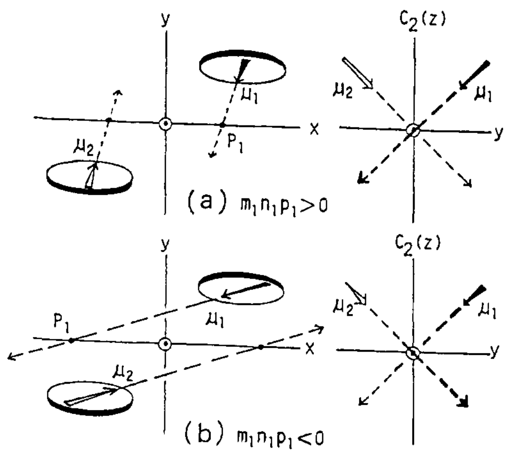

Figure 1. A symmetry coupling of local transitions in a left-handed chirality of a chromophore. The chromophore is located in the $+z$ region and viewed along the $C_2(z)$ axis (left) and x axis (right).

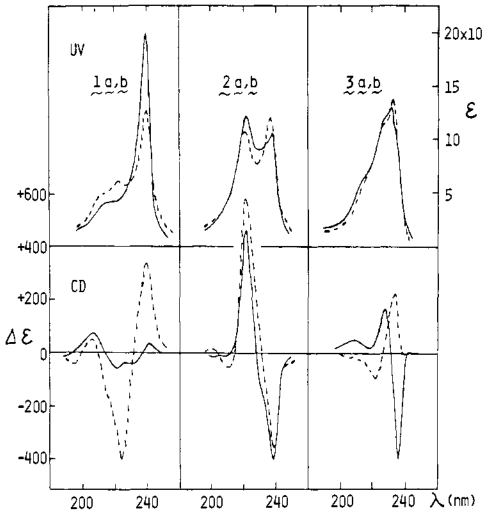

Figure 2. UV and CD spectra of 3,3′-di-*tert*-butyl-1,1′-spirobi[benzindans] **1–3**, in isooctane [(1*S*,3*R*,3′*R*)-**a** (—) and (1*S*,3*S*,3′*S*)-**b** (---)].

Moveover, even if the C_2 rule is accepted, its application to the prediction of absolute configurations will require an identification of the symmetry of transition for individual CD bands. For this purpose an apparent regularity that a transition of B symmetry is found at lower energy, followed by a transition of A symmetry, for many C_2 chromophores has often been employed.[3,9] However,

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(1) Present address: Suntory Institute for Biomedical Research, Wakayamadai, Shimamoto-cho, Mishima-gun, Osaka, 618 Japan.

(2) Wagnière, G.; Hug, W. *Tetrahedron Lett.* **1970**, 4765–8.

(3) Hug, W.; Wagnière, G. *Tetrahedron* **1972**, *28*, 1241–8.

(4) Hug and Wagnière[3] defined the chirality of a chromophore as follows: "A chromophore is visualized in the energetically most easily accessible planar conformation of effective C_{2v} symmetry. The C_2 axis lies in this plane and it divides the plane into a right part and a left part. The molecule (chromophore) is then twisted into its assumed real conformation. If the right-hand part of the molecule (chromophore) is twisted counterclockwise, the left part clockwise, then the chirality is right-handed." This is an expression of the handedness of the mutual arrangement between the local chromophores (molecular subunits) in the whole chromophore (molecule). We followed this definition throughout our arguments.

(5) Helicity of the transition refers to the helical relationship between local transition moments (transition moments in the local chromophores) which constitute the transitions (A and B symmetry) in the whole chromophore (molecule).

(6) This equation is derived from the general formula[7]

$$R = (\pi\sigma/2)(\vec{\mu}_1 \cdot \vec{R}_{12}\vec{\mu}_2)$$

(7) Schellman, J. A. *Acc. Chem. Res.* **1968**, *1*, 144–51.

(8) Wagnière and Hug[2] indicated the mathematical underpinning of the C_2 rule by using a model that is virtually identical with Figure 1a.

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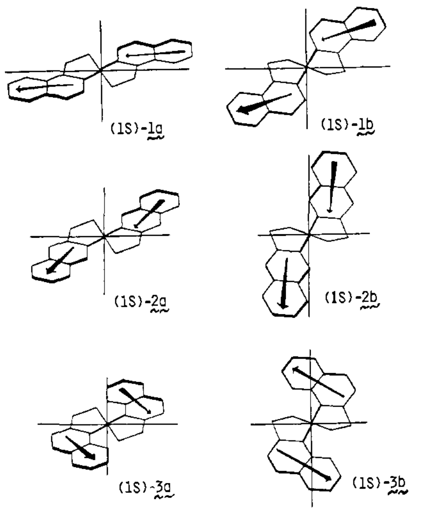
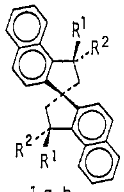


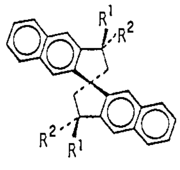
Figure 3. Lower-frequency coupling modes of the ^1B_b transition moments in 1,1′-spirobi[benzindans].

this regularity does not always hold well. Evaluation of the interaction energy V_{12} between local transition moments using the point–dipole–point–dipole approximation shows that the lower energy coupling mode can be of either symmetry, depending upon the mutual disposition of the local transition moments.[7,10]

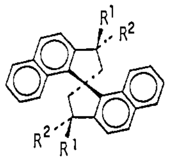
One type of evidence corroborative of the foregoing arguments is our recent study of the three positional isomers, 3,3′-di-*tert*-butyl-1,1′-spirobi[benz[*e*]indan] (**1**),[11] -spirobi[benz[*f*]indan] (**2**),[12] and -spirobi[benz[*g*]indan] (**3**),[13] each of which includes two



1a,b



2a,b



3a,b

(1S,3R,3′R)-a; $R^1 = Bu^t$, $R^2 = H$
(1S,3S,3′S)-b; $R^1 = H$, $R^2 = Bu^t$

diastereomers with C_2 symmetry. Figure 2 shows the UV and CD spectra in the ^1B_b region[14] observed for these spiro compounds having the 1*S* configuration. According to the definition by Hug and Wagnière,[4] chirality of the chromophore is left handed for all of them. The spectral features were found to be sensitive to changes in the mutual arrangement of the local moments with a large dipole strength and a distinct polarization direction along the long axis of each naphthalene ring.[15] Since the lower energy coupling modes of local transitions located at the centers of the naphthalene rings are undoubtedly of *B* symmetry for **1a,b** and **2a,b** (V_{12}^A, ca. 1900 cm^{-1}; Figure 3, top and center),[16] the positive signs of couplets for (1*S*)-**1a,b** are obviously in conflict with the C_2 rule, while the negative ones for (1*S*)-**2a,b** are consistent with that. On the other hand, the exciton analysis can explain not only all of these CD signs but also the spectral features semiquantitatively. Thus the very weak CD of **1a** is attributable to its conformation, in which the two local moments are directed almost parallel to each other; besides, a close resemblance between the features of **2a** and **2b** agrees with the insensitiveness of the calculated rotational strength and splitting energy to the difference between their conformations.

The signs of couplets, negative for (1*S*)-**3a** and positive for (1*S*)-**3b**, are not contradictory to the C_2 rule, since the lower energy coupling mode of local transitions is of *B* symmetry for **3a** (V_{12}^A, ca. 500 cm^{-1}) and of *A* symmetry for **3b** (V_{12}^A, ca. −1300 cm^{-1}) (Figure 3, bottom). This CD behavior, however, affords a good illustration of the fact that a relatively small change in conformation causes, in some cases, the inversion of energy levels of *A* and *B* coupling and accordingly the reversal of CD signs regardless of identical chirality of the chromophore.

In conclusion, the presented results show that the C_2 rule is no longer a general one; thus, even for C_2 molecules, the determination of CD signs requires the examination of the helicity and energy relationship of transitions, as is the case for other types of chiral molecules.[7]

Registry No. **1a**, 73294-82-3; **1b**, 73346-61-9; **2a**, 79264-94-1; **2b**, 79299-37-9; **3a**, 82166-56-1; **3b**, 77210-75-4.

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[9] A similar choice between two coupling modes was also made in the application of the aromatic chirality rule to some non-C_2 compounds (Harada, N.; Nakanishi, K. *Acc. Chem. Res.* **1972**, *5*, 257–63).

[10] Mason, S. F.; Vane, G. W. *J. Chem. Soc. B* **1966**, 370–4.

[11] Imajo, S.; Nakamura, A.; Shingu, K.; Kato, A.; Nakagawa, M. *J. Chem. Soc., Chem. Commun.* **1979**, 868–70.

[12] Imajo, S.; Kato, A.; Shingu, K.; Kuritani, H.; *Tetrahedron Lett.* **1981**, 2179–82.

[13] Imajo, S.; Shingu, K.; Kuritani, H. *Tetrahedron Lett.* **1980**, 4279–82.

[14] The Cotton effects observed at ca. 210 nm are possibly due to the ^1C_b transition.[15] In the UV spectrum of **1a**, the higher-frequency band with low intensity is hidden by the following ^1C_b band.

[15] (a) Platt, J. R. *J. Chem. Phys.* **1949**, *17*, 484–95. (b) Klevens, H. B.; Platt, J. R. *Ibid.* **1949**, *17*, 470–81.

[16] ^{1}H NMR spectroscopy showed that the dihedral angle between two aromatic planes is smaller for (1*S*,3*R*,3′*R*)-**a** (ca. 60–75°) than for (1*S*,3*S*,3′*S*)-**b** (ca. 90–110°), owing to the opposite sense of puckering of the five-membered rings in which the *tert*-butyl groups tend to assume quasi-equatorial orientations for each diastereomer.[11-13]

Carbanion Photochemistry. 6. Formation of a Reactive Carbene via Photoinduced Halide Elimination[1]

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Received December 28, 1981

Although cyclopentadienylidene[2] and various phenylated derivatives,[3a-f] as well as the 2,3-benzo[3g,h] and 2,3,4,5-dibenzo derivatives[3i,j] have been synthesized and studied, the corresponding 3,4-benzo derivative has not. For this carbene, the electronic demand from two potentially aromatic rings should favor mixing in of states containing electrons in the formal p orbital. We now report evidence for the synthesis of 1,3-diphenylisoindenylidene (**1**) using a novel photoelimination reaction from a carbanion. Unlike other members of this series, this carbene undergoes hydrogen atom abstraction in preference to addition.

Simple Hückel molecular orbital theory predicts an increased electron density at the C-2 position of photoexcited allyl anions. Thus a 2-bromo-substituted allyl anion should undergo photoelimination provided the ground-state elimination is avoided. The 2-bromo-1,3-diphenylindenyl anion (**2a**), although only formally an allyl anion, is known to be thermally stable[4] and satisfies the Hückel model for increased C-2 electron density in the excited state.

Solutions of the requisite anion (ca. 0.1 M) were produced by 10% excess potassium *tert*-butoxide treatment of 2-bromo- or 2-chloro-1,3-diphenylindene[4] in dimethyl sulfoxide. A 10-fold

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[1] For previous papers, see: (a) Tolbert, L. M.; Merrick, R. D. *J. Org. Chem.* **1982**, *47*, 2808. (b) Tolbert, L. M.; Siddiqui, S. *Tetrahedron* **1982**, *38*, 1079.

[2] (a) Dürr, H. *Top. Curr. Chem.* **1973**, *40*, 103. (b) Baron, W. J.; DeCamp, M. R.; Hendrick, M. E.; Jones, M., Jr.; Levin, R. H.; Sohn, M. B. "Carbenes"; (Jones, M., Jr., Moss, R. A.; Eds.; Wiley: New York, 1973; Vol. 1, p 51.

[3] (a) Schönleber, D. *Chem. Ber.* **1969**, *102*, 1789. (b) Dürr, H., Schrader, L. *Ibid.* **1969**, *102*, 2026. (c) Dürr, H.; Kober, H. *Justus Liebigs Ann. Chem.* **1970**, *740*, 74. (d) Dürr, H.; Sergio, R.; Scheppers, G. *Ibid.* **1970**, *740*, 63. (e) Moss, R. A.; Przybyla, J. R. *J. Org. Chem.* **1968**, *33*, 3816. (f) Moss, R. A. *Ibid.* **1966**, *31*, 3296. (g) Weil, T.; Cais, M. *Ibid.* **1963**, *28*, 2472. (h) Wasserman, E.; Barash, L.; Trozzolo, A. M.; Murray, R. W.; Yeager, W. A. *J. Am. Chem. Soc.* **1964**, *86*, 2304. (i) Jones, M., Jr.; Rettig, K. R. *Ibid.* **1965**, *87*, 4013. (j) Jones, M., Jr.; Rettig, K. R. *Ibid.* **1965**, *87*, 4015.

[4] Koelsch, C. F. *J. Org. Chem.* **1960**, *25*, 130.