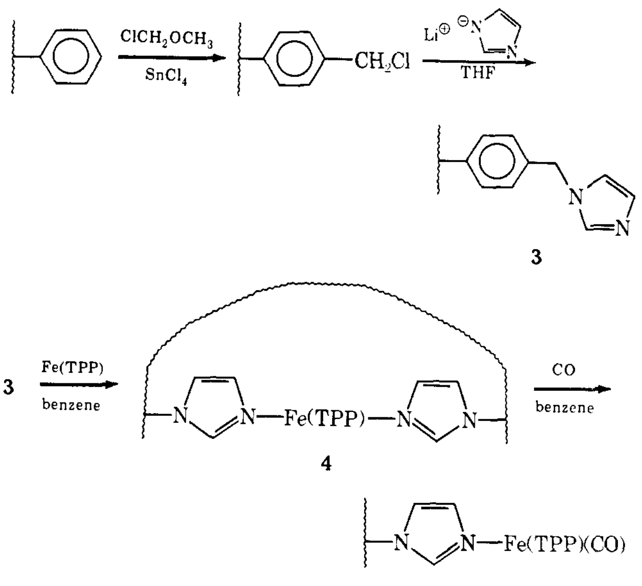
actions, we have forced iron into a situation which appears to minic the coordination in deoxymyoglobin. This was based on our hypothesis that 2-methylimidazole (2-Me-imid) should be unable to form a strong coordinate bond with an in-plane iron porphyrin because of severe nonbonded repulsive interactions between the hydrogen atoms on the methyl group and the electrons of the porphyrin ring so that coordination of two 2-Me-imid groups is improbable. Thus reaction between 2-methylimidazole and Fe(TPP) in benzene–ethanol afforded well formed single crystals of Fe(TPP)(2-Me-imid)·C_2H_5OH (**2**). [*Anal.* Calcd for $C_{50}H_{40}N_6OFe$: C, 75.4; H, 5.05; N, 10.55; Fe, 7.0. Found: C, 75.65; H, 5.15; N, 10.2; Fe, 7.5. Crystal data: $M_{calcd} = 797$; monoclinic C_c from systematic absences hkl, $h + k = 2n + 1$, and $h0l$, $l = 2n + 1$ on precession films; $a = 17.10$, $b = 16.51$, and $c = 14.71$ Å; $\beta = 98.7°$; $d_{measd} = 1.295$ by flotation in aqueous $ZnBr_2$, $Z = 4$; $d_{calcd} = 1.29$. The density agreement gives an unequivocal proof of the formulation.] Like deoxyhemoglobin (μ = 5.1 BM)[12] **2** is high spin (μ = 5.2 BM at 25°), and we suspect **2** has a similar square-pyramidal coordination with a large out of plane displacement of the iron atom toward the axial 2-Me-imid ligand.

The possibility that **2** is in fact six-coordinate with an ethanol molecule in the sixth position cannot be rigorously excluded in the absence of a full crystallographic study, but three observations are inconsistent with six-coordination. Firstly, the predicted "out of plane" position of the iron away from a sixth ligand makes this site very unfavorable for coordination by what is already a very poor ligand. Secondly, addition of ethanol to a benzene solution of Fe(TPP) in the presence of 2-Me-imid does not significantly perturb its visible spectrum.[12] Thirdly, it should be noted that recrystallization from benzene–methanol affords only four-coordinate Fe(TPP) even in the presence of a large excess of 2-Me-imid. Apparently the ethanol molecule stabilizes the lattice of **2** as a solvate. Otherwise the lattice of Fe(TPP) is more stable (less soluble).

X-Ray crystallographic studies are planned to test the hypotheses advanced in this paper. Such detailed structural data should be useful in assessing the Perutz[11] model for cooperative oxygen binding in hemoglobin.

Reversible oxygenation of myoglobin appears to result from a five-coordinate high-spin iron(II) porphyrin immobilized within a hydrophobic pocket.[13] Our attempts to prepare a model for oxygenated myoglobin by treating Fe(TPP) with resin-bonded imidazole, **3**, afforded **4** whose diamagnetism and electronic spectrum suggest six-coordinate Fe(II) (Scheme I). Treatment of **4** with CO yielded the diamagnetic carbonyl **5** (ν_{CO} 1970 cm^{-1}) but prolonged heating of **5** under vacuum afforded only slight paramagnetism. These results are consistent with our earlier report concerning the mobility of cross-linked polystyrene ligands.[15] Treatment of either **4** or **5** with O_2 in benzene caused leaching of the oxidized product $O[FeTPP]_2$.

Scheme I



Acknowledgments. We wish to thank W. T. Robinson and R. Gagne for assistance. This work was supported by National Institutes of Health Grant GM-17880.

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[12] λ_{max}: Fe(TPP) in benzene, 540; Fe(TPP)(imid)$_2$ in benzene, 535, 560, 610; Fe(TPP) with excess 2-Me-imid in benzene–ethanol, 530, 570, 610 nm.

[13] Apparently irreversible oxygenation of iron results from either an interaction involving two Fe(II) complexes and one O_2 molecule,[14] or protonation affording H_2O_2 which subsequently reacts with the Fe(II). Coordinatively unsaturated Fe(II) seems to be necessary for reaction with O_2.

[14] G. S. Hammond and C. S. Wu, *Advan. Chem. Ser.*, **No.** 77, 186 (1968).

[15] J. P. Collman, L. S. Hegedus, M. P. Cooke, J. R. Norton, G. Dolcetti, and D. N. Marquardt, *J. Amer. Chem. Soc.*, **94**, 1789 (1972).

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Optical Activity Associated with Isolated Olefinic Bonds. I. The Allylic Bond Polarization (ABP) Model and Its Extension to Homoconjugated Systems

Sir:

Although a definitive theoretical understanding of the electronic spectra of substituted ethylenes has yet to emerge,[1] the optical activity associated with nonconjugated olefinic linkages has come under increased scrutiny now that circular dichroism can be determined down to 185 nm routinely, and a number of empirical rules have been advanced.[2,6] The reversed octant rule of Scott and Wrixon[2] (SW rule) offers the most consistent explanation for the reported data for the λ_2

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[1] Three transitions from the π_x state (to the π_y^*, π_x^*, and σ^* states, in decreasing order of energy) have been considered (see ref 2b and 3 and references cited therein). The latter, a Rydberg-like transition, appears to account for the low-energy tail of the electronic spectra, but is not expected to be optically active.[4] Yogev, Sagiv, and Mazur[5] have recently demonstrated that the major olefin uv band is a composite of two transitions ($\lambda_1 \sim$ 185–190 and $\lambda_2 \sim$ 200–210 nm) of comparable intensity but differing polarization. In many of the cyclohexenes examined[2b,c] two CD extrema of opposite sign are observed in the 185–220-nm energy span, again reflecting the composite nature of the electronic spectrum.

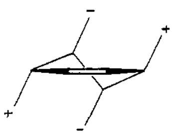
[2] (a) A. I. Scott and A. D. Wrixon, *Chem. Commun.*, 1182 (1969); (b) *Tetrahedron*, **26**, 3695 (1970); (c) *Tetrahedron*, **27**, 4787 (1971).

[3] C. C. Levin and R. Hoffmann, *J. Amer. Chem. Soc.*, **94**, 3446 (1972).

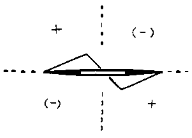
[4] M. Yaris, A. Moscowitz, and R. S. Berry, *J. Chem. Phys.*, **49**, 3150 (1968); S. F. Mason and G. W. Vane, *Chem. Commun.*, 540 (1965).

[5] A. Yogev, J. Sagiv, and Y. Mazur, *J. Chem. Soc.*, *Chem. Commun.*, 411 (1972).

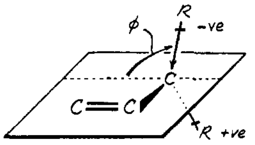
band of endocyclic olefins.[2,7,8] In contrast, Fétizon and Hanna reported that *exo*-methylene steroids generally show a correspondence in the sign of the CD Cotton effects for the C=O (n → π^*) and C=CH_2 ($\pi \rightarrow \pi^*$) transitions;[9] more recently Kirk, *et al.*, have shown that this sign correspondence extends to the C=O (n → σ^*) transition of cyclohexanones as well.[10] Axial allylic and homoallylic bond chiralities have been advanced as predictive rules in the latter cases.[6] These two rules are shown below for P-helicity cyclohexene.



axial bond chirality sign convention[11]

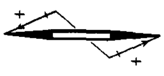


the Scott–Wrixon "reversed octant" rule

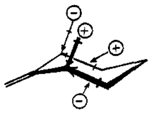


ABP model sign convention

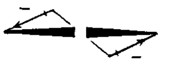
The axial bond chirality signs are in direct variance with those of the SW rule; in fact, only by ascribing a dominant role to allylic C–H bonds[6d] can it be applied to endocyclic olefins with any success. In our view (the ABP model), the λ_2 bond is dominated by the rotatory contribution of more polarizable allylic bonds (C–CH, C–O, C–X). The sign depends on the *sense of polarization of the bond and its chiral relationship to the π orbital.* The magnitude is maximal with optimum overlap (ϕ = 90°, negative; 270°, positive); thus the contributions of axial substituents dominate. The positive λ_2 CD of P-helicity cyclohexenes reflects, in our view, the reinforcing contributions of the two allylic bonds within the ring (A, below).



A



B

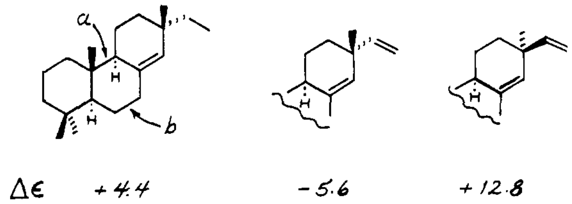


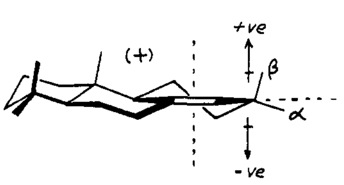
C

The symmetry of *exo*-methylenecyclohexanes (B, above) requires dissymmetric axial substitution to generate rotatory strength by the ABP model, suggesting that the nonapplicability of the SW rule to *exo*-methylene steroids is the result of the reduced rotatory strength of the λ_2 transition in the absence of axial allylic substituents or other perturbations of local symmetry about the plane containing the σ bond and perpendicular to the π nodal plane.[12] In support of this we present CD data for a series of rigid *exo*-methylenecyclohexanes bearing polarizable axial allylic substituents: methyl zizanoate ($\Delta\epsilon_{192} = -6.4$), (+)-$\beta$-cedrene ($\Delta\epsilon_{200} = -4.7$), (+)-zizaene ($\Delta\epsilon_{193} = -3.8$), (−)-$\beta$-longipinene ($\Delta\epsilon_{201} = +10$),[13] and (+)-prezizaene ($\Delta\epsilon_{193} = +5.6$)[14]—in each case consistent with the sign rule of the ABP model. A series of *exo*-methylenecyclopentanes[15] shows distinct λ_2 CD bands of the sign predicted by the ABP model even in the absence of asymmetric allylic substitution, consistent with the C_2 symmetry of this system (C, above).

The inclusion of sense of polarization as a determinant of CD sign, although without obvious theoretical basis, does offer a pleasing explanation for "abnormal" contribution due to the hydroxyl group of allylic alcohols.[2c] The increased electron demand of sp^2-hybridized carbon suggests that homoconjugated dienes should be analyzed in the same manner.

The three olefins below[16] demonstrate a strong contribution by the vinyl substituent which is opposite in sign to that of an alkyl substituent similarly located.





A series of spiradienes[17] offers additional support for this analysis. The 2,8-dienes display CD spectra typical of cyclohexenes with the same sign for the λ_2 band as displayed by the 2-enes. The homoconjugated 2,7-dienes show a single symmetrical CD band[18] of the sign predicted. α-Vetispirene (I)[19] illustrates that a homoconjugated component can dominate the CD of a butadiene when the conjugated system has no distinct inherent skew.[20] The selinenes (II and III) illustrate the importance of a sense of polarization; the analysis of each double bond (unlike the spiradiene cases) indicates opposing contributions, but the vinylic substitution pattern suggests the polarization shown which correctly predicts the negative CD band observed for each.

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(6) (a) A. Yogev, D. Amar, and Y. Mazur, *Chem. Commun.*, 339 (1967); (b) A. W. Burgstahler and R. C. Barkhurst, *J. Amer. Chem. Soc.*, **92**, 7601 (1970); (c) J. K. Gawronski and M. A. Kielczewski, *Tetrahedron Lett.*, 2493 (1971); (d) W. Hug and G. Wagnière, *Tetrahedron*, **28**, 1241 (1972).

(7) A. W. Burgstahler, J. N. Marx, and D. F. Zinkel, *J. Org. Chem.*, **34**, 1550, 3716 (1969).

(8) R. Rossi and P. Diversi, *Tetrahedron*, **26**, 5033 (1970).

(9) M. Fétizon and I. Hanna, *Chem. Commun.*, 462 (1970).

(10) D. N. Kirk, W. Klyne, W. P. Mose, and E. Otto, *J. Chem. Soc., Chem. Commun.*, 35 (1972).

(11) It has been noted that the sign convention for allylic axial bonds is consistent with theoretical expectations assuming that the double bond plus the axial bond constitute a single chromophore[6a] of pseudo-C_2 symmetry with the electronic transition polarized perpendicular to the pseudoaxis.[6d]

(12) We designate olefins of such local symmetry as class II olefins. The factor determining their CD spectra will be the subject of subsequent communications.

(13) This is a new sesquiterpene isolated from *Scapania undulata*. Its structure rests on spectral evidence and its conversion to (−)-longibornyl bromide, establishing its absolute configuration as that of (−)-β-pinene ($\Delta\epsilon_{198} = +15.2$).

(14) N. H. Andersen and M. S. Falcone, *Chem. Ind.* (*London*), 62 (1971).

(15) CD spectra of phyllocladene[2a] and (−)-kaurenes[2c] have been reported. In addition we have examined (+)-longifolene ($\Delta\epsilon_{198} = +19.4$) and the Wittig methylenation products of (+)-camphor ($\Delta\epsilon_{203} = -4.4$), (+)-fenchone ($\Delta\epsilon_{200} = +8.5$), and (−)-longicamphor (positive $\pi \rightarrow \pi^*$ Cotton effect).

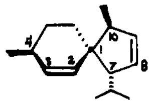
(16) The CD data on these olefins were disclosed in a personal communication (May 1970) by Professor M. Fétizon.

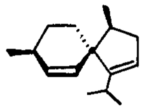
(17) The synthesis of these and other acoradienes appears as part of the Ph.D. thesis of D. D. S. (University of Washington, 1971).

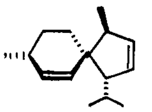
(18) Davydov splitting would be one explanation for these enhanced rotatory strengths; however, such coupling leads to two CD bands of opposite sign. The negative low-energy CD band observed for (5*R*)-spiro[4.4]nona-1,6-diene, in accord with the ABP model, has recently been predicted by CNDO-CI calculations.[6d]

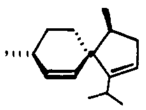
(19) N. H. Andersen, M. S. Falcone, and D. D. Syrdal, *Tetrahedron Lett.*, 1759 (1970).

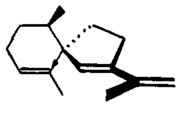
(20) A similar effect due to allylic hydroxyls has been noted by A. F. Beecham [*Tetrahedron*, 27, 5207 (1971), and references cited therein].



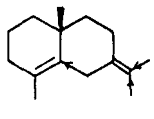




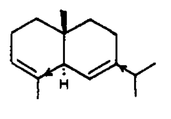




I



II



III

These limited (by space) examples should serve to illustrate the ABP model and its relationship to the other, apparently conflicting, viewpoints on this topic. An examination of the effects of specific vinylic and allylic substitution in rigid systems is in progress in order to delineate the relationship between ABP and torsional[3] contributions.

Acknowledgments. N. H. A. wishes to acknowledge stimulating conversations with Professors Scott, Fétizon, and Burgstahler on this subject. We are grateful to Professors Fétizon and Scott for sending preprints and unpublished results. The work was partially supported by National Institutes of Health Grant GM-18143.

(21) Alfred P. Sloan Foundation Fellow.

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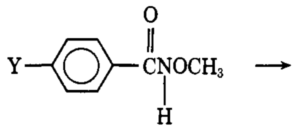
Reaction of *O*-Methylbenzohydroximoyl Chlorides with Sodium Methoxide. Inversion of Configuration at Trigonal Carbon during Nucleophilic Substitution

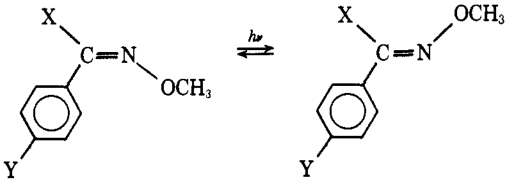
Sir:

The reaction of phosphorus pentachloride with alkyl benzohydroxamates provides a general preparative method for *O*-alkylbenzohydroximoyl chlorides.[1,2] This previous work[1] indicated that only one geometric isomer of a hydroximoyl chloride is formed in the reaction. In order to study the stereochemistry of the nucleophilic substitution reactions of these compounds, we have prepared and identified the *E* and *Z* isomers of *O*-methylbenzohydroximoyl chloride (**2a** and **3a**) and *O*-methyl-*p*-nitrobenzohydroximoyl chloride (**2b** and **3b**). The reaction of phosphorus pentachloride with methyl benzohydroxamate (**1a**) gave **2a** (71%) as a colorless oil, bp 53–54° (0.1 mm).[3] Ultraviolet irradiation (200-W medium-pressure lamp) of a 0.15 *M* solution of **2a** in hexane for 6 hr produced a photostationary state of the isomers **2a** and **3a** in a 62:38 ratio. The mixture was separated by preparative glc and isomer **3a** was obtained as a colorless oil, bp 43–44° (0.1 mm). The geometric isomers of *O*-methyl-*p*-nitrobenzohydroximoyl chloride (**2b**, mp 121–122° and **3b**, mp 110–112°) were prepared in a similar manner. Stereochemical assignments for the hydroximoyl chlorides were made on the basis of the dipole moment data given in Table I.



$Y{-}C_6H_4{-}C(=O)N(H)OCH_3 \longrightarrow$

1a, Y = H
b, Y = NO_2



2a, X = Cl; Y = H
b, X = Cl; Y = NO_2
c, X = Br; Y = H

3a, X = Cl; Y = H
b, X = Cl; Y = NO_2

Table I. Dipole Moment Data for *E* and *Z* Isomers of *O*-Methylbenzohydroximoyl Chloride and *O*-Methyl-*p*-nitrobenzohydroximoyl Chloride

Hydroximoyl chloride	Con- formation	Theor dipole moment, D[a]	Exptl dipole moment, D[b]
2a	*s-trans*	1.13	1.38 (1.41)[c]
2a	*s-cis*	2.46	
3a	*s-trans*	2.00	1.99
3a	*s-cis*	1.65	
2b	*s-trans*	3.55	3.60
2b	*s-cis*	1.76	
3b	*s-trans*	2.98	2.96 (3.00)[c]
3b	*s-cis*	2.78	

[a] Calculated using the following bond (or group) moments and bond angles: CH_3—O, 1.06 D; N—O, 0.30 D; C═N, 1.40 D; C—Cl, 1.75 D; NO_2, 4.20 D; 110° for N—O—CH_3; 120° for C═N—O; 120° for N═C—Cl. [b] The experimental dipole moments were determined in benzene at 25° using the method of E. A. Guggenheim, *Trans. Faraday Soc.*, **45**, 714 (1949); J. W. Smith, "Electric Dipole Moments," Butterworths, London, 1955, pp 58–64. [c] Duplicate determination.

We have investigated the stereochemistry of the reaction of sodium methoxide with the hydroximoyl chlorides **2** and **3** in 90% dimethyl sulfoxide (DMSO)–10% methanol. Reaction of a 0.07 *M* solution of **2a** at 45° with sodium methoxide (0.09 *M*) resulted in almost exclusive formation of a compound with inverted configuration, methyl (*Z*)-*O*-methylbenzohydroximate (**4a**, 68% yield). Only about 2% of the product could be attributed to the *E* isomer (**5a**) by glc. Under identical reaction conditions the (*Z*)-hydroximoyl chloride (**3a**) gave predominantly the product with inverted configuration, **5a** (ratio of **4a** to **5a** = 23:77 by glc, 62% yield). In order to establish the configuration of **4a** and **5a**, they were independently synthesized by methylation of the *Z* and *E* isomers of methyl benzo-

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(1) J. E. Johnson, J. R. Springfield, J. S. Hwang, L. J. Hayes, W. C. Cunningham, and D. C. McClaugherty, *J. Org. Chem.*, **36**, 284 (1971).

(2) For recent reviews concerning imidoyl chlorides, see (a) H. Ulrich, "The Chemistry of Imidoyl Halides," Plenum Press, New York, N. Y., 1968; (b) R. Bonnett in "The Chemistry of the Carbon-Nitrogen Double Bond," S. Patai, Ed., Interscience, New York, N. Y., 1970, pp 628–642.

(3) All new compounds reported herein gave spectral and elemental analyses in accord with the assigned structures.