ther test the validity of **6** as a model for reaction center chlorophyll.[15]

Note Added in Proof. We note that Katz and co-workers (*Proc. Natl. Acad. Sci., U.S.A.*, **73,** 1791 (1976)), having had full access to our data and interpretation, consider a structure equivalent to ours as a viable alternative to their previous model of P-700.

Acknowledgments. We would like to thank Dr. Martin H. Studier of the Argonne National Laboratory for running a mass spectrum of **3** and Dr. Edward Bunnenberg of Stanford University for providing the CD spectra of **4**.

References and Notes

(1) Supported by NSF Grants MPS73-08517-A02 and CHE76-01795.
(2) G. L. Closs, J. J. Katz, F. C. Pennington, M. R. Thomas, and H. H. Strain, *J. Am. Chem. Soc.*, **85,** 3809 (1963); J. J. Katz, G. L. Closs, F. C. Pennington, M. R. Thomas, and H. H. Strain, *ibid.*, **85,** 3801 (1963).
(3) J. J. Katz and J. R. Norris, *Curr. Top. Bioenerg.*, **5,** 46 (1973).
(4) F. K. Fong and V. S. Koester, *J. Am. Chem. Soc.*, **97,** 6888 (1975); F. K. Fong, *ibid.*, **97,** 6890 (1975).
(5) C. Houssier and K. Sauer, *J. Am. Chem. Soc.*, **92,** 779 (1970).
(6) H. C. Chow, R. Serlin, and C. E. Strouse, *J. Am. Chem. Soc.*, **97,** 7230 (1975).
(7) H. Isenring, E. Zass, K. Smith, H. Falk, J. Luisier, and A. Eschenmoser, *Hel. Chim. Acta*, **58,** 2357 (1975).
(8) S. J. Baum, B. F. Burnham, and R. A. Plane, *Proc. Natl. Acad. Sci. U.S.A.*, **52,** 1439 (1964).
(9) The term "locked" is not meant to imply a static or rigid structure (all NMR evidence pertains at most to averages), rather it is used to convey the remarkably good fit which can exist between two molecules of water and the diester in **6**.
(10) The ^{1}H NMR spectrum of the "locked" form is assigned by the well-established method of titrating with a solvent (pyridine) capable of strongly coordinating Mg and following each signal as it returns to its assigned "open" position.
(11) Three different ways of folding can be visualized depending on the sidedness of the rings in the locked form. The propionic acid side chains might both project toward the center of the structure (in-in), both outside (out-out), or one inside and one outside (in-out). The "in-out" form can be excluded because chemical shift changes vastly different from what is observed are predicted. Though the ten atom chain is long enough to accommodate the "out-out" structure, a model shows that the 8a methyl protons will fall within the deshielding region of the other ring; no shift is observed. One is then left with the "in-in" form (**6**) as the only one consistent with the ^{1}H NMR data. This is important because it predicts that the chlorophyllides containing the carbomethoxy group at position 10 and located trans to the propionic side chain,[2,6] will be able to fold the same way without encountering any steric crowding.
(12) The CD spectrum (associated with the low energy transitions) in benzene containing water shows strong maxima at 698 and 603 nm both of negative sign.
(13) In addition to chemical shift differences, line broadening is observed in the alcohol indicating that an exchange process is occurring. It has not been possible to freeze out two populations at temperatures to −80 °C, indicating, as expected, a low activation barrier to exchange.
(14) We have constructed an accurate three-dimensional model of **6** using bond lengths and angles from the crystal structure.[6] The *y* axes of the two chromophores are nearly antiparallel, the interplanar separation is about 3.4–3.6 Å and the inter-Mg distance is 9 Å. A possible structure in which the *y* axes subtend an angle of 120° is believed to be less favorable.
(15) Small scale preparations of the dimer containing the 10-carbomethoxy group have been accomplished. Preliminary experiments indicate optical properties equivalent to **4**.
(16) ANL-ERDA Laboratory Graduate participant.

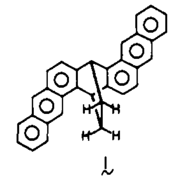
S. G. Boxer,[16] G. L. Closs*
Department of Chemistry, The University of Chicago
Chicago, Illinois 60637
Received April 23, 1976

The Absolute Stereochemistries of 6,15-Dihydro-6,15-ethanonaphtho[2,3-*c*]pentaphene and Related Homologues as Determined by Both Exciton Chirality and X-Ray Bijvoet Methods

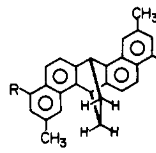
Sir:

It is well known that in addition to the x-ray Bijvoet method, the circular dichroic Cotton effects due to a chiral exciton coupling between two or more chromophores enable one to determine the absolute stereochemistry in a nonempirical manner.[1-6] In this optical method it is important to choose the proper electronic transition of proper chromophores which satisfy the following requirements of chiral exciton coupling:[7] (i) large extinction coefficient values in uv spectra; (ii) isolation of the band in question from other strong absorptions; (iii) established direction of the electric transition moment in the geometry of the chromophore; (iv) unambiguous determination of the exciton chirality in space, inclusive of the configuration and conformation; and (v) negligible molecular orbital overlapping between the chromophores.

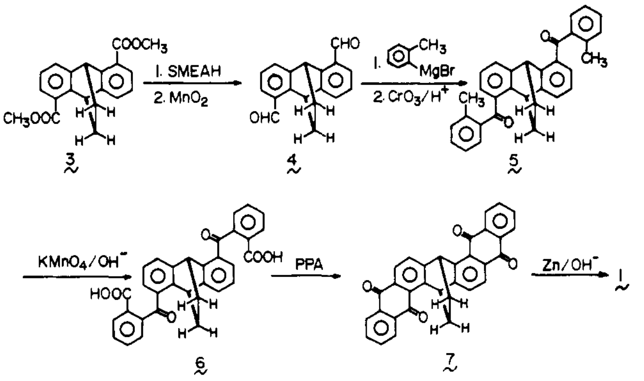
This communication reports the very strong chiral exciton coupling of the ^1B_b transition of polyacene chromophores in (6*R*,15*R*)-(+)-6,15-dihydro-6,15-ethanonaphtho[2,3-*c*]pentaphene (**1**) and the related homologues, **2a** and **2b**, which rigidly meet the above requirements of the exciton chirality method. Namely, the allowed ^1B_b transition of the component chromophore of **1**, i.e., anthracene, exhibits a very strong ϵ value of the order of 10^5; ϵ_{max} = 134 300 for **1**. The location of the present band around 260 nm is sufficiently separated from weak ^1L_a and ^1L_b transitions around 400-320 nm and also from the ^1C_b transition around 200 nm so that the minor contribution from the weak absorption bands can be neglected (see Figure 1). Next, the polarization of the ^1B_b transition in polyacenes is well established to be along the long axis of the chromophore. Furthermore, because of the rigidity of the present hydrocarbon **1**, one can unambiguously determine the positive exciton chirality in space (see Figure 1). Finally there is no direct conjugation between the two component chromophores, and the contribution of homoconjugation is also negligible, if any, because of the large exciton dipole-dipole coupling term.[8] Thus compound **1** ideally meets the above-mentioned criteria.



1



2a R;H
2b R;CH₃



The hydrocarbon **1** was synthesized[9] from (9*R*,10*R*)-(+)-1,5-dimethoxycarbonyl-9,10-dihydro-9,10-ethanoanthracene (**3**), the absolute configuration of which has been established by the x-ray Bijvoet method[10] and by chemical correlations.[11] Reduction of **3** with $NaAlH_2(OC_2H_4OCH_3)_2$ (SMEAH) in benzene and successive oxidation with activated MnO_2 in acetone gave dialdehyde **4**, mp 128-129.5 °C, which was then treated with *o*-toluyl magnesium bromide in ether, followed by oxidation with Jones reagent to afford diketone **5**, mp 151-152.5 °C. Selective oxidation of the methyl groups of **5** was achieved by refluxing with $KMnO_4$ in aqueous NaOH-pyridine to give dicarboxylic acid **6**. Cyclization of **6** in polyphosphoric acid afforded quinone **7**, mp 268-268.5 °C, as the sole product; the yield of **7** from **5** was 64%. Reduction

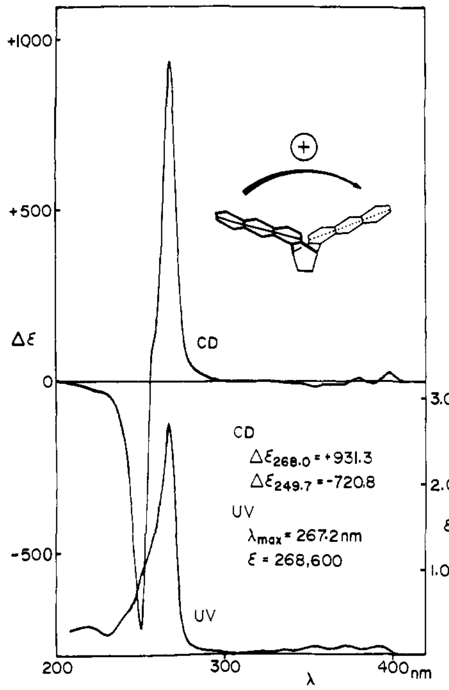


Figure 1. Uv and CD spectra of (6*R*,15*R*)-(+)-6,15-dihydro-6,15-ethanonaphtho[2,3-*c*]pentaphene (**1**) (see text for the solvent systems).

of **7** with zinc powder in alkaline medium gave a strong fluorescent hydrocarbon **1** in solid masses:[12] $[\alpha]_D$ +1157° (*c* 0.034, dioxane); mass spectrum *m/e* 406 (M^+), 378 ($M - C_2H_4$); NMR ($CDCl_3$) δ 1.79 (br s, 4 H), 5.41 (br s, 2 H), 6.8-8.1 (m, 12 H), 8.22 (s, 2 H), 8.75 (s, 2 H); ir (KBr) ν_{max} 3040, 1615, 1150, 874, 740, 467 cm^{-1}; uv (0.08% dioxane in EtOH) λ_{max} 391.0 (ε 9100), 371.2 (ε 11 200), 352.7 (ε 9000), 267.2 nm (ε 268 600); CD (0.18% dioxane in EtOH) $\Delta\epsilon_{397.2} = +26.4$, $\Delta\epsilon_{388.1} = -2.3$, $\Delta\epsilon_{378.0} = +6.3$, $\Delta\epsilon_{362.9} = -9.7$, $\Delta\epsilon_{352.8} = -14.5$, $\Delta\epsilon_{268.0} = +931.3$, $\Delta\epsilon_{249.7} = -720.8$.

The CD spectrum of **1** clearly exhibits very strong positive first and negative second Cotton effects due to coupling of the ^1B_b transitions ($\Delta\epsilon_{268.0} = +931.3$ and $\Delta\epsilon_{249.7} = -720.8$; $A (= \Delta\epsilon_1 - \Delta\epsilon_2) = +1652.1$), the positive sign of the *A* value being in accord with the positive exciton chirality,[2,7] i.e., the clockwise screwness, between the two long axes of the anthracene moieties in **1** (see Figure 1).

The related homologues **2a**, mp 209.5-211.0 °C, and **2b**, mp 124-126 °C, synthesized[9] from **3** also show clearly split Cotton effects arising from the ^1B_b transition of naphthalene chromophores ($\Delta\epsilon_{240.6} = +371.5$, $\Delta\epsilon_{227.0} = -149.4$ for **2a** and $\Delta\epsilon_{242.0} = +340.3$, $\Delta\epsilon_{212.5} = -139.3$ for **2b**).[13] The present data thus demonstrate ideal cases of chiral exciton coupling in CD spectra, and provide the most unambiguous evidence which demonstrates the consistency between nonempirical circular dichroic and x-ray Bijvoet methods. The quantitative calculation of the chiral exciton coupling in these compounds is now in progress.

Acknowledgments. One of the authors (N.H.) thanks Professor Koji Nakanishi, Columbia University, for invaluable discussions during his stay in New York.

References and Notes

(1) I. Tinoco, Jr., *Radiat. Res.*, **20,** 133 (1963).
(2) The theoretical determinations of absolute stereochemistries of 1,1′-bianthryl derivatives: R. Grinter and S. F. Mason, *Trans. Faraday Soc.*, **60,** 274 (1964); S. F. Mason, R. H. Seal, and D. R. Roberts, *Tetrahedron*, **30,** 1671 (1974); see also x-ray and chemical correlation data, H. Akimoto and Y. Iitaka, *Acta Crystallogr., Sect. B*, **25,** 1491 (1969); H. Akimoto and S. Yamada, *Tetrahedron*, **27**, 5999 (1971).
(3) J. A. Schellman, *Acc. Chem. Res.*, **1,** 144 (1968).
(4) B. Bosnich, *Acc. Chem. Res.*, **2,** 266 (1969).
(5) N. Harada and K. Nakanishi, *Acc. Chem. Res.*, **5,** 257 (1972).
(6) A. D. Buckingham and P. J. Stiles, *Acc. Chem. Res.*, **7,** 258 (1974).
(7) The quantitative calculations of chiral exciton coupling in CD spectra: N. Harada, S. L. Chen, and K. Nakanishi, *J. Am. Chem. Soc.*, **97,** 5345 (1975), and references cited therein.
(8) It is worth noting that in contrast to the case of naphthalene and anthracene compounds, the homoconjugation effect is important in the CD spectra of benzene compounds, e.g., 9,10-dihydro-9,10-ethanoanthracene and bis-1,1′-spiroindane derivatives; see (a) S. Hagishita and K. Kuriyama, *Tetrahedron*, **28,** 1435 (1972); (b) S. Hagishita, K. Kuriyama, K. Shingu, and M. Nakagawa, *Bull. Chem. Soc. Jpn.*, **44,** 2177 (1971), and references cited therein.
(9) Experimental details for compounds **1**, **2a**, and **2b** will appear elsewhere.
(10) N. Sakabe, K. Sakabe, K. Ozeki-Minakata, and J. Tanaka, *Acta Crystallogr., Sect. B*, **28,** 3441 (1972); J. Tanaka, C. Katayama, F. Ogura, H. Tatemitsu, and M. Nakagawa, *J. Chem. Soc., Chem. Commun.*, 21 (1973).
(11) Y. Shimizu, H. Tatemitsu, F. Ogura, and M. Nakagawa, *J. Chem. Soc., Chem. Commun.*, 22 (1973); H. Tatemitsu, F. Ogura, and M. Nakagawa, *Bull. Chem. Soc. Jpn.*, **46,** 915 (1973).
(12) Since the hydrocarbon **1** solidified as masses instead of crystals, it was purified by preparative thin layer chromatography on silica gel.
(13) A similar CD spectrum was reported for 7,14-dihydro-7,14-ethanodibenz[*a,h*]anthracene-15,16-dicarboxylic acid, the absolute configuration of which was determined by kinetic resolution methods; see ref 8a.

Nobuyuki Harada,* Yuki Takuma, Hisashi Uda
Chemical Research Institute of Nonaqueous Solutions
Tohoku University
2-1-1 Katahira, Sendai, 980, Japan
Received March 12, 1976

Laser Excitation of Spin Forbidden Bands. Triplet Photochemistry of Cobalt(III) Ammines

Sir:

States related to the ground state by a spin forbidden band play a very large role in the attempt to account for reaction pathways in transition metal photochemistry. Since phosphorescence is not generally observed, it is often difficult to develop experimental tests of hypotheses concerning "spin forbidden states". Direct population of such states by light absorption is highly desirable but requires a light source meeting two limiting characteristics: (1) the source must be intense; (2) the source must be highly monochromatic so that irradiation can be at a well-defined wavelength which allows for precise determination of the absorbance in the spin forbidden band with a limited and calculable contribution from absorbance in the tails of more intense spin allowed bands. A laser can meet these criteria and should find important uses.

In this report, we describe the direct population of ^3T (O_h approximate microsymmetry) states of the d^6 Co(III) complexes $Co(NH_3)_6^{3+}$ and $Co(NH_3)_5Cl^{2+}$ using the 647.1-nm line of a Spectra Physics krypton ion laser. In these experiments, we have used a Perkin-Elmer polarimeter cell as an irradiation vessel and absorbance matched ammonium reineckate for actinometry. Dark controls were run in the thermostat bath used to circulate water around the polarimeter cell. The methodology is very close to that of ref 1, and we find good agreement for the experiments which overlap ref 1 as a check on our approach. Radiation times ranged up to 8 h and involved approximately 3% conversion. In the reaction with $Fe(CN)_6^{4-}$, there is no correction for absorbance by $Fe(CN)_6^{4-}$ at 647 or 514 nm, but correction for product absorption was carried out by both graphical approximation and rigorous calculation.

The population of spin allowed ligand field singlets $^1T_{1g}$ and $^1T_{2g}$ (O_h approximate microsymmetry) of $Co(NH_3)_6^{3+}$ and $Co(NH_3)_5Cl^{2+}$ leads to a substitutional photochemistry which is to be contrasted to other d^6 systems mainly in respect of the low total quantum yield (near 10^{-3}).[1] The singlet and triplet excited states of Co(III) correspond to the ligand field electron configurations $t_{2g}^5e_g^1$ and are thought to be appropriate for efficient photosubstitution[2] in consequence of the population of a single σ antibonding orbital. The low quantum yield following irradiation of singlet bands has been attributed by some