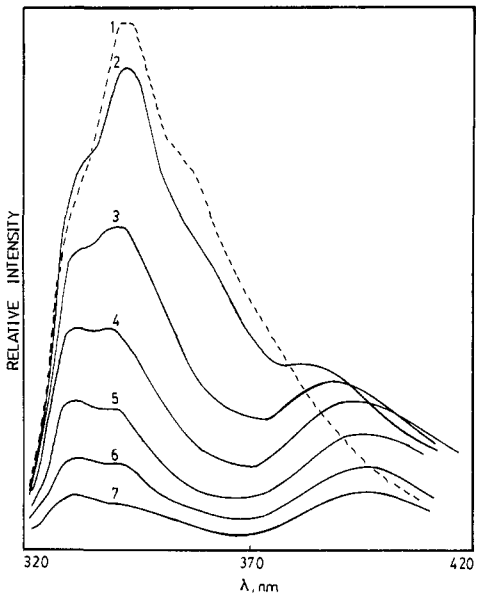


Figure 2. Fluorescence spectra of 1-naphthol (2.0×10^{-4} M) in the presence of 0, 4, 8, 12, 16, 20 and 25 mM of NND for curves 1-7, respectively, in dioxane at 20 °C.

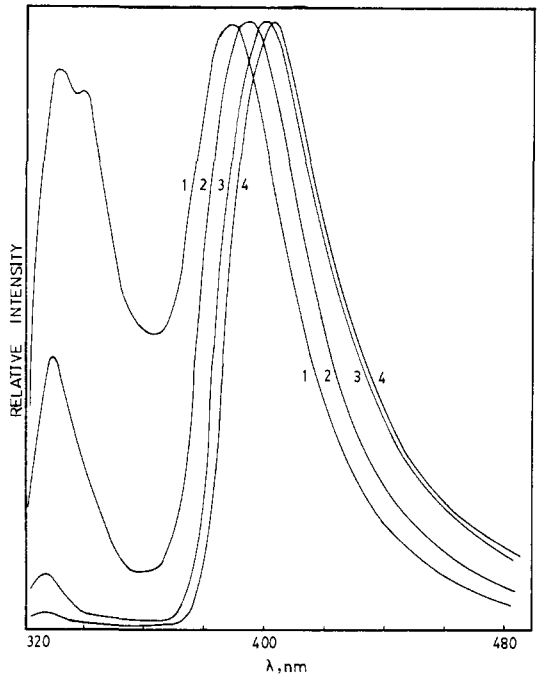


Figure 3. Fluorescence spectra of 1-naphthol (2.0×10^{-4} M) in the presence of [NND] at 0.01, 0.03, 0.07, and 0.10 M for curves 1-4, respectively, in acetonitrile at 20 °C: curves 2-4 were normalized at 390-410 nm with respect to curve 1.

to the 1-naphtholate fluorescence in the ion pair **3**. Its intensity is low probably owing to the rapid decomposition to the aminium and nitric oxide radicals as in **3** → **4**. The precise mechanism of this step is unclear but may be regarded as energy migration within the ion pair **3** to cause the homolysis of proton associated NND.[24] Within exciplexes, the lowest singlet-excited-state phenolates certainly possess enough energy to cause the homolysis of the N-N bond of NND (≈40 kcal/mol).[25]

(24) The energy level of the lowest singlet-state NND is calculated from the longest absorption maximum of NND (375 nm) at −150 °C in ethanol-methanol to be 76 kcal/mol. However, within exciplexes, the classical collisional energy transfer is not necessarily the only way for the energy migration.

(25) (a) Gowenlock, B. G.; Pritchard-Jones, P.; Major, J. R. *Trans. Faraday Soc.* **1961**, *57*, 23. (b) Fisher, I. P.; Henderson, E. *Trans. Faraday Soc.* **1967**, *63*, 1342.

While there are a number of mechanisms that can be written for the nitrosation step from 4, electron transfer followed by radical coupling as in **4** → 5 → monooxime is the simplest route. In conclusion, singlet-state phenols can provide enhanced acidity and excitation energy to promote a substantial chemical transformation if such reactions occur within the lifetimes of phenol-phenolate couples.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for generous financial support and to Professor S. Nagakura, Okazaki Institute of Molecular Science, for stimulating discussions.

Registry No. 1-NpO⁻, 17545-30-1; NND, 62-75-9; 1-NpOH, 90-15-3; 2-allyl-1-naphthalenol ion (1-), 95739-59-6; 2-naphthalenol ion (1-), 15147-55-4; 1-anthracenol ion (1-), 22718-00-9; 9-anthracenol ion (1-), 56709-95-6; 2-allyl-1-naphthalenol, 28164-58-1; 2-naphthalenol, 135-19-3; 1-anthracenol, 610-50-4; 9-anthracenol, 529-86-2; 1,4-naphthalenedione monooxime, 4965-30-4; 2-allyl-1,4-naphthalenedione 4-oxime, 95739-60-9; 1,2-naphthalenedione 1-oxime, 2636-79-5; 1,4-anthracenedione monooxime, 31619-42-8; 9,10-anthracenedione monooxime, 14090-75-6.

Supplementary Material Available: Tables of analytical data for oximes, a graph of the quenching of 1-naphthol fluorescence, and a plot of the fluorescence spectra of 2-naphthol (4 pages). Ordering information is given on any current masthead page.

syn-[2.2]Metacyclophane: Synthesis and Facile Isomerization to *anti*-[2.2]Metacyclophane. The use of (Arene)chromium Carbonyl Complexes To Control the Stereochemistry of Cyclophanes[1]

Reginald H. Mitchell,* Thottumkara K. Vinod, and Gordon W. Bushnell

Department of Chemistry, University of Victoria Victoria, British Columbia, Canada V8W 2Y2

Received December 27, 1984

anti-[2.2]Metacyclophane (**1**) was probably prepared as early as 1899,[2] though definitely in 1950,[3] and since that time has been the subject of much study.[4] *syn*-[2.2]Metacyclophane (**2**), however, has remained unknown. We now report its preparation and facile isomerization to **1**.

In 1970,[5] we thought that we had prepared a bis(methylthio) derivative of **2**, but on reinvestigation we have found that this compound was a mixture of two *anti*-cyclophanes **4**, whose 100-MHz ^{1}H NMR fortuitously was consistent with the syn structure previously assigned. Repeated careful chromatography separated the mixture, and 250 MHz ^{1}H NMR spectra then led to their assignment as the 1(e),3(e) and 1(e),4(e) anti isomers **4A** and **4B**, respectively. Thus the only authentic *syn*-[2.2]metacyclophane derivatives known[5b,6] are those with internal methyl substituents, where the substituent raises the barrier for the syn → anti isomerization. interestingly even there the parent compound has not yet been prepared.

It has been observed that the presence of electron-withdrawing substituents on one benzene ring favors *syn*-2,11-dithia[3.3]-metacyclophane formation over that of the anti conformer.

(1) Presented in part at the 66th Chemical Institute of Canada Conference, Calgary, Alberta, Canada OR7-2, June 6, 1983, and the 38th American Chemical Society Northwest Regional Meeting, Honolulu, HI, paper 138, Dec. 29, 1983.

(2) Pellegrin, M. M. *Recl. Trav. Chim. Pays-Bas* **1899**, *18*, 458.

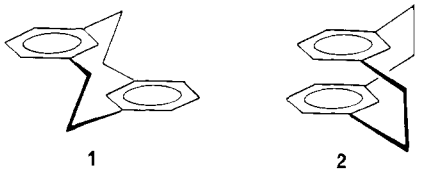
(3) Baker, W.; McOmie, J. F. W.; Norman, J. M. *Chem. Ind. (London)* **1950**, *77*; *J. Chem. Soc.* **1951**, 1114-1118.

(4) Reviews: (a) Griffin, R. W. *Chem. Rev.* **1963**, *63*, 45-54. (b) Smith, H. B. "Bridged Aromatic Compounds"; Academic Press: New York, 1964. (c) Vögtle, F.; Neumann, P. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 73-83. (d) Keehn, P., Rosenfeld, S., Eds. "Cyclophanes"; Academic Press: New York, 1983.

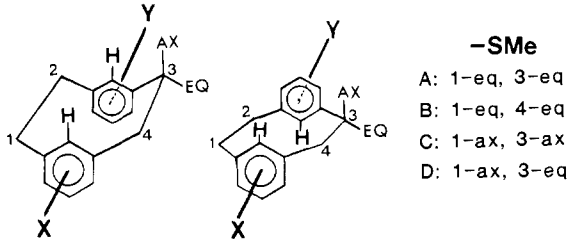
(5) (a) Mitchell, R. H.; Boekelheide, V. *J. Am. Chem. Soc.* **1970**, *92*, 3510-3512; (b) *Ibid.* **1974**, *96*, 1547-1557.

(6) Kamp, D.; Boekelheide, V. *J. Org. Chem.* **1978**, *43*, 3470-3475.

0002-7863/85/1507-3340$01.50/0



1 2

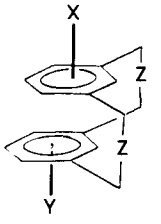


-SMe
A: 1-eq, 3-eq
B: 1-eq, 4-eq
C: 1-ax, 3-ax
D: 1-ax, 3-eq

X	Y	X	Y
3: Absent	Absent	4: Absent	Absent
6: $Cr(CO)_3$	Absent	7: $Cr(CO)_3$	Absent
9: $Cr(CO)_3$	$Cr(CO)_3$	10: $Cr(CO)_3$	$Cr(CO)_3$

However, subsequent removal of such substituents after expulsion of sulfur and ring contraction to give the parent cyclophanes has not yet proved possible.[6,7] We therefore thought that use of an (arene)chromium tricarbonyl derivative would solve this problem, in that the strong electron-withdrawing nature of the $Cr(CO)_3$ fragment would stabilize *syn*-cyclophanes by charge transfer across the cofacial decks[6] and yet would be easily removed[8] later.

No (arene)chromium tricarbonyl derivatives of simple thiacyclophanes are known;[9] however, reflux of *syn*-2,11-dithia[3.3]metacyclophane with $Cr(CO)_6$ in *n*-Bu_2O readily gave 70% of *syn*-**5**. The internal hydrogens of **5** appeared at δ 7.23 and 4.83 clearly confirming the syn configuration.



5: X=$Cr(CO)_3$, Y=Absent, Z=S
8: X=Y=$Cr(CO)_3$, Z=S
11: X=$Cr(CO)_3$, Y=Z=Absent
12: X=Y=$Cr(CO)_3$, Z=Absent

Methylation of **5** with $(CH_3O)_2CHBF_4$ followed by Stevens rearrangement[5] gave (70%) the *syn*-[2.2]metacyclophane **6D**, as yellow crystals, mp 120-121 °C. The syn configuration of **6D** was confirmed by (i) the internal hydrogen signals at δ 6.93 and 5.51, (ii) an X-ray crystallographic structure determination,[11] and (iii) isomerization (80 °C, 1 h) to the *anti*-cyclophane in which both SMe groups are now axial, **7C**, mp 128 °C, internal hydrogens at δ 5.91 and 3.42. This was further confirmed by removal of the chromium from **7C** with Ce^{IV} in CH_3CN to give **4C**.[5b] Treatment of **4C** with $Cr(CO)_6$ in *n*-Bu_2O regenerated **7C**, confirming its structure. Treatment of **6D** with Ce^{IV} in CH_3CN at -35 °C, followed by isolation and chromatography of the product also at -35 °C, gave the first *syn*-[2.2]metacyclophane, **3D**, in which the internal hydrogens were at δ 7.04 and 6.75 and the other aromatic hydrogens were shielded by the cofacial rings at δ 7.00-6.30. If a solution of **3D** were allowed to warm above 0 °C, isomerization to the *anti*-cyclophane **4A** occurred.

When **6D** isomerizes to **7C**, the 3(e)-SMe → 3(a)-SMe, i.e., the noncomplexed ring flips, whereas when **3D** isomerizes to **4A**, the 1(a)-SMe → 1(e)-SMe, indicating that the opposite ring has flipped. Attempted removal of the SMe groups from either **3D** or **6D** by Li/NH_3 reduction at -40 °C unfortunately only gave complexed and uncomplexed *anti*-cyclophane **1**, because ring flip of the uncomplexed ring probably occurred during the reduction, along with some decomplexation. We thus, using excess $Cr(CO)_6$, prepared in 62% yield the bis complex **8**, mp 199-201 °C, which would not be expected to ring flip readily. Stevens rearrangement gave **9D** in 40% yield, which on reduction with Li/NH_3 at -40 °C yielded a mixture of **11** and **12**, the first derivatives of unsubstituted **2** known. **11** isomerizes on heating by flipping the uncomplexed ring to give the known complexed *anti*-cyclophane.[12] The ^1H NMR spectrum of **12** shows the internal hydrogens at δ 5.09 and the external hydrogens at δ 5.10 and 4.75, with bridge protons at δ 2.98-2.79, which leaves no doubt as to its structural assignment. Removal of the complexing $Cr(CO)_3$ moiety with *m*-chloroperbenzoic acid or Ce^{IV} at -45 °C in CH_3CN yielded *syn*-[2.2]metacyclophane (**2**), which rapidly isomerized to **1** above 0 °C. The ^1H NMR spectrum of **2** at -40 °C showed the internal hydrogens at δ 6.58, the external hydrogens at δ 6.36 and 6.60, and the bridge hydrogens at δ 3.14 and 2.85. In due course we hope to obtain a solid sample of **2** and study the kinetics of its isomerization of **1**. Thus at last some 25 years after the synthesis of **1** was confirmed, a synthesis of **2** has proved possible using a $Cr(CO)_3$ moiety to control cyclophane stereochemistry.

(7) Mitchell, R. H.; Williams, R. V., unpublished results.
(8) Nicholls, B.; whiting, M. C. *J. Chem. Soc.* **1959**, 551-556. Card, R. J.; Trahanovsky, W. S. *J. Org. Chem.* **1980**, *45*, 2560-2566.
(9) Balbach, B. K.; Koray, A. R.; Okur, H.; Wülknitz, P.; Ziegler, M. L. *J. Organomet. Chem.* **1981**, *212*, 77-94.
(10) Note, however, we find that whereas *syn*-9,18-dimethyl-2,11-dithia[3.3]metacyclophane reacts readily with $Cr(CO)_6$ to give (70%) the $Cr(CO)_3$ adduct (mp 202 °C dec, the anti isomer is resistant and requires the more reactive $Cr(CO)_3(CH_3CN)_3$ and then only gives 20% of product mp 220 °C dec.
(11) The crystal structure was triclinic, space group $P\bar{1}$ (No. 2), with a = 10.087 (6) Å, b = 11.276 (7) Å, c = 9.739 (5) Å, α = 112.42 (4)°, β = 98.21 (4)°, γ = 82.91 (4)°, D_{meas} = 1.422 g/cm^{-3}, D_{calcd} = 1.434 g/cm^{-3}, Z = 2 molecules per cell. Measurements were made on a Picker 4-circle diffractometer, automated with a PDP11 computer. The structure was solved by direct methods and refined by least squares to R = 0.0391 and R_w = 0.0517 for 1599 observations [$I > 2\ \sigma(I)$] and 302 parameters. the angle between the aromatic ring mean planes is 28.8°. the structural details will be published elsewhere.
(12) Langer, E.; Lehner, H. *Tetrahedron* **1973**, *29*, 375-383.

Characterization of 10-Hydroxybacteriochlorophyll *a* by ENDOR and TRIPLE Resonance Spectroscopy

W. Lubitz,*† F. Lendzian,‡ and H. Scheer§

Institut für Organische Chemie and Institut für Molekülphysik, Freie Universität Berlin 1000 Berlin 33, West Germany
Botanisches Institut der Universität München 8000 München 19, West Germany

Received October 22, 1984

Although the bacteriochlorophyll *a* (BChl *a*, see Figure 1) radical cation plays a central role as a primary photoproduct in bacterial photosynthesis,[1-4] a detailed map of its spin density distribution was difficult to obtain for the following reasons: (i) the parent compound BChl *a* was unstable and was frequently

† Institut für Organische Chemie.
‡ Institut für Molekülphysik.
§ Botanisches Institut.
(1) Hoff, A. J. in "Light Reaction Path of Photosynthesis"; Fong, F. K., Ed.; Springer: Berlin, 1982; pp 80-151, 322-326. Hoff, A J. *Biophys. Struct. Mech.* **1982**, *8*, 107-150.
(2) Parson, W. W. *Ann. Rev. Biophys. Bioeng.* **1982**, *11*, 57-80.
(3) Norris, J. R.; Katz, J. J. In "The Photosynthetic Bacteria"; Clayton, R. K., Sistrom, W. S., Eds.; Plenum: New York, 1978; pp 397-418.
(4) Feher, G.; Hoff, A. J.; Isaacson, R. A.; Ackerson, L. C. *Ann. N. Y. Acad. Sci.* **1975**, *244*, 239-259.

0002-7863/85/1507-3341$01.50/0