Circular Dichroism Spectra of a Single Chirally Perturbed Naphthalene Chromophore

Sir:

The naphthalene chromophore has received growing attention in the last few years, and its electronic spectra have been investigated with polarized and unpolarized light. A series of interesting papers appeared in the literature on the circular dichroism (CD) arising from the dipole–dipole interaction of at least two naphthalene moieties disposed in a chiral arrangement.[1] By contrast, no relevant contribution has been reported on the CD of a simple naphthalene chromophore chirally perturbed by an alkyl environment only.

(*R*)-2,2-Dimethyl-3α-naphthylbutane (I) and (*R*)-2,2-dimethyl-3β-naphthylbutane (II) were prepared[2] as suitable systems in the frame of the investigation of chiroptical properties of isolated aromatic chromophores.[3] The relationship between the sign of the optical rotatory power and the absolute configuration and the relationship between the value of the optical rotation and the optical purity have been determined.[2]

The limiting case of the preferred conformations in solution, reported in Figure 1, was established as follows: (1) Inspection of the NMR signals for the aromatic protons under irradiation of the *t*-Bu, Me, and CH groups, as well as that of the CH group signal under irradiation of the *peri*-hydrogen of the naphthalene ring, with experimental conditions suitable for observing the interproton nuclear Overhauser effect (NOE) NMR enhancement, showed that the predominant conformer of I is characterized by the orientation of the CH hydrogen toward the *peri*-hydrogen of the naphthalene ring. Under the same NOE conditions, the spectra of II showed the absence of a strongly prevailing conformation and suggested the existence of an equilibrium between the two conformers, having the C–H bond near the plane containing the naphthalene nucleus (Figure 1). (2) Comparative analysis of the IR spectra of I and II at different temperatures as the crystal, glass, and liquid, and in a hydrocarbon solvent, indicates the presence of a strongly prevailing conformation for I and two equiprobable conformations for II, in solution. In the crystalline state, a single conformation has been found both for I and II, the structure of the latter (IIa, Figure 1) being identified by X-ray analysis.[4]

As is well-known,[5] the naphthalene chromophore shows three main absorptions connected with the $\pi \rightarrow \pi^*$ transitions in the range of 330–185 nm. The two long-wavelength bands are weak and are assignable to the symmetry-forbidden ^1L_b and ^1L_a transitions whereas the short wavelength one is strong and assignable to the electrically allowed ^1B_b transition. In addition, some other bands have been observed, but their position and assignement are still questionable.

In Figures 2 and 3 are reported the UV and CD spectra of I and II in *n*-heptane solution at room temperature. In the spectral range 330–250 nm, the UV spectra show the well-structured ^1L_b and ^1L_a bands, having the typical pattern expected for α- and β-alkyl-substituted naphthalenes. The CD spectra show two bands in the same spectral range with well-resolved fine structure, which have the same negative sign in I and the opposite sign in II (Figures 2 and 3). At shorter wavelengths, the UV spectrum of I exhibits a band at about 225 nm flanked by three main shoulders at about 218, 210, and 202 nm (Figure 2). Apart from the intensity pattern, the spectrum of II is similar to that of I with the exception of a well-resolved band at about 188 nm ($\epsilon \sim 14\,000$), instead of the shoulder at about 202 nm (Figure 3).

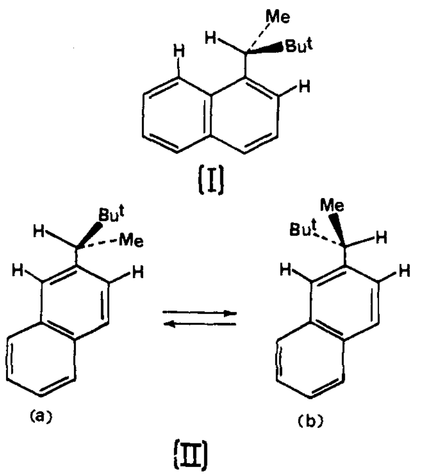


Figure 1. Limiting conformations for I and II in a hydrocarbon solution.

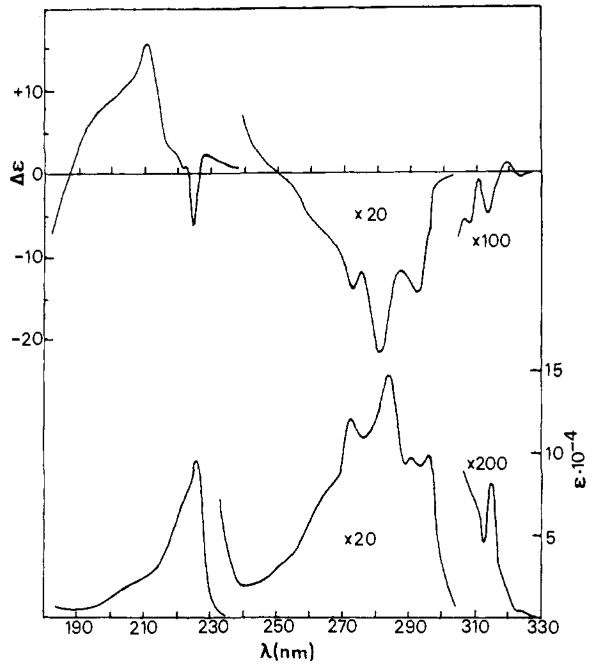


Figure 2. CD (upper) and UV (lower) spectra of I in *n*-heptane solution at room temperature. CD data are corrected for 100% optical purity of the sample.

The CD spectrum of I (Figure 2) shows a system of at least four bands in the same spectral range: a small positive band at about 230 nm, a sharp negative band at 225 nm, a relatively strong positive band at 211 nm, and a broad positive shoulder at about 200 nm. In contrast, the CD spectrum of II (Figure 3) shows clear evidence for the existence of two bands: one negative at 226 nm and the other positive at 194 nm, with a series of shoulders between them. The following reasonable interpretation of the UV and CD spectra between 250 and 185 nm can be given by comparing the results obtained. Low-temperature and vapor-phase measurements are needed in order to give the correct assignement of the 230-nm CD band in I.

Different assignements[6-8] were proposed for the absorption observed between the ^1L_a and ^1B_b bands in the UV spectrum of naphthalene in the vapor phase which may not correspond to the CD band in question. At shorter wavelengths the two next bands of opposite sign in I (225 and 211 nm; Figure 2) have probably the same sign in II (Figure 3) and correspond to the ^1B_b and ^1B_a

---

(1) (a) Mason, S. F.; Seal, R. H.; Roberts, D. R. *Tetrahedron* **1974**, *30*, 1671. (b) Ciardelli, F.; Salvadori, P.; Carlini, C.; Menicagli, R.; Lardicci, L. *Tetrahedron Lett.* **1975**, 1779. (c) Harada, N.; Takuma, Y.; Uda, H. *J. Am. Chem. Soc.* **1978**, *100*, 4029. (d) Imaio, S.; Nakamura, A.; Shingu, K.; Kato, A.; Nakagawa, M. *J. Chem. Commun.* **1979**, 868.

(2) Piccolo, O.; Menicagli, R.; Lardicci, L. *Tetrahedron* **1979**, *35*, 1751.

(3) Salvadori, P.; Lardicci, L.; Menicagli, R.; Bertucci, C. *J. Am. Chem. Soc.* **1972**, *94*, 8598.

(4) Marchetti, F., Private communication.

(5) Klevens, H. B.; Platt, J. R. *J. Chem. Phys.* **1949**, *17*, 470.

(6) Angus, J. G.; Morris, G. C. *Aust. J. Chem.* **1971**, *24*, 173.

(7) Robin, M. B., "Higher Excited States of Polyatomic Molecules", Academic Press: New York, 1974; Vol. II p 259.

(8) Kitagawa, T. *J. Mol. Spectrosc.* **1968**, *26*, 1.

0002-7863/80/1502-6859$01.00/0

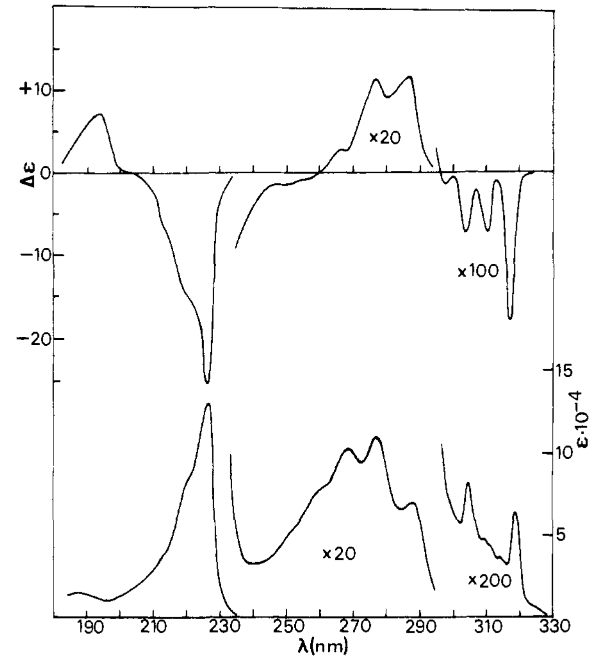


Figure 3. CD (upper) and UV (lower) spectra of II in *n*-heptane solution at room temperature. CD data are corrected for 100% optical purity of the sample.

degenerate transitions in benzene. Actually, the latter has been located by Klevens and Platt[5] at about 169–167 nm, but other authors place this band a few nm beyond the ^1B_b transition[6,9,10] toward shorter wavelengths. It is worth noting that the UV maximum of the main absorption in I (Figure 2) corresponds to the negative band at 225 nm in the CD spectrum, and this supports the ^1B_b assignment for this band.

Finally, the CD band at about 195 nm in II (Figure 3) corresponds to the UV maximum at 188 nm, and it could be due to the ^1C_b transition as suggested by Klevens and Platt[5] for naphthalene. In the CD spectrum of I, such a band could correspond to the shoulder at about 200 nm, overwhelmed by the relatively intense positive band at 211 nm due to the ^1B_a transition.

Acknowledgment. We are indebted to Professors E. Benedetti and C. A. Veracini for their assistance in the interpretation of the IR and NMR spectra, respectively.

---

(9) Hoshi, T.; Yoshino, J.; Funami, H.; Kadoi, H.; Inoue, H. *Ber. Bunsenges. Phys. Chem.* **1972**, *76*, 898.

(10) Peacock, T. E.; Wilkinson, P. T. *Proc. Phys. Soc., London* **1964**, *83*, 525, and references therein.

Piero Salvadori,* Oreste Piccolo, Carlo Bertucci
Rita Menicagli, Luciano Lardicci

Centro di Studio del C.N.R. per le Macromolecole
Stereoordinate ed Otticamente Attive
Istituto di Chimica Organica
Facoltà di Scienze M.F.N., Università di Pisa, Italy

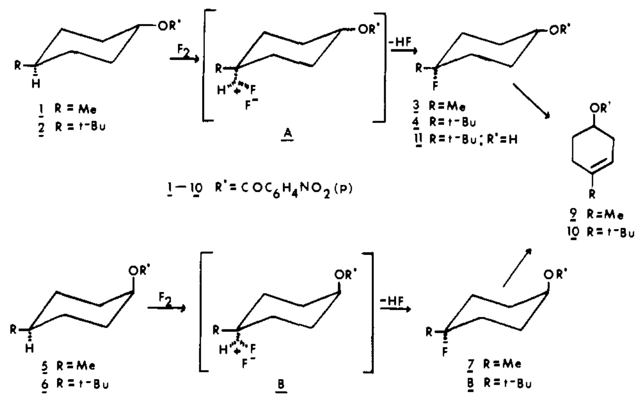
Received July 28, 1980

Remote and Selective Electrophilic Fluorinations at the Carbon-Hyrogen Single Bond

Sir:

Most of the organic syntheses performed today have one feature in common: they all require an anchor around which the reagents can group themselves. In fact, most organic chemical reactions are performed on, or around, functions such as carbonyl or hydroxyl groups, double bonds, heteroatoms, and so on. There are extremely few reactions on hydrogen atoms attached to an unactivated saturated carbon. It is even rarer for such reactions to be nonradical in character and to proceed with reasonable yield and high selectivity.[1]

Scheme I



In order to attack successfully an unactivated C–H bond, a very powerful electrophile has to be employed. However, this electrophile should be used in low concentration and low temperatures in order to take advantage of the differences in the electron density of the various covalent single hydrogen–carbon bonds, thus leading to regiospecific reactions. We have chosen for this purpose the most powerful electrophile, electrophilic fluorine. There are two main sources for such an unusual reactant: the first is already quite well-known and includes reagents with the fluoroxy function such as the commercial CF_3OF and SF_5OF[2] or such reagents which can be prepared in situ like CF_3CF_2OF and CF_3COOF.[3] The second and the more powerful source for an electrophilic fluorine seems to be elemental fluorine itself.[4,5]

We describe here a highly regiospecific and an absolutely stereospecific reaction on unactivated sites with this most reactive element of all. Scheme I, in which the starting materials are various 4-alkylcyclohexanol esters, can provide a good example of the synthetic potential of this fluorination reaction.

When 600 mg of *trans*-4-methylcyclohexanol *p*-nitrobenzoate (**1**) was treated with fluorine diluted with nitrogen (4%, v/v) at −70 °C, a single fluorinated product was obtained in 60% yield.[6] It was identified[7] as *trans*-4-methyl-4-fluorocyclohexanol *p*-nitrobenzoate (**3**), mp 115 °C. In a similar way, 700 mg of

---

(1) Representation of such reactions can be found in the works of N. C. Deno. Radical chlorination of certain straight chain alcohols in strongly acidic media shows a degree of perference for attack on sites remote from the hydroxyl group. The ionic hydroxylation of some hydrocarbons by trifluoroperoxyacetic acid is also able to functionalize positions remote from electronegative groups. These reactions, however, either radical or ionic, are also limited in scope, because complications arise with tertiary hydrogens. See: Frommer, U.; Ullrich, V. *Z. Naturforsch.* **1971**, *26B*, 322. Deno, N. C. "Methods in Free Radical Chemistry"; E. S. Huyser, Ed.; Marcel Dekker: N.Y., 1972; Vol. 3, p 135. Deno, N. C.; Eisenhardt, K. A.; Pohl, D. G.; Spinnelli, H. J.; White, R. C. *J. Org. Chem.* **1974**, *39*, 520. Deno, N. C.; Messer, L. A. *J. Chem. Soc., Chem. Commun.* **1976**, 1051. Deno, N. C.; Jedziniak, E. J.; Messer, L. A.; Meyer, M. D.; Stroud, S. G.; Tomezko, E. S. *Tetrahedron* **1977**, *33*, 2503. Deno, N. C.; Meyer, M. D. *J. Org. Chem.* **1979**, *44*, 3383.

(2) Hesse, R. H. *Isr. J. Chem.* **1978**, *17*, 60.

(3) (a) Rozen, S.; Lerman, O. *J. Am. Chem. Soc.* **1979**, *101*, 2782. (b) *J. Org. Chem.* **1980**, *45*, 672.

(4) There is one pioneering work in the whole chemical literature which deals with the functionalization of certain steroids with CF_3OF and F_2; see ref 5.

(5) Barton, D. H. R.; Hesse, R. H.; Markwell, R. E.; Pechet, M. M.; Rozen, S. *J. Am. Chem. Soc.* **1976**, *98*, 3036.

(6) The reactions were carried out in glass vessels with 2–4 mmol of substrate dissolved in 400 mL of $CHCl_3$–$CFCl_3$ (1:1). The mixtures of F_2 and N_2 were prepared in a vacuum line similar to the one described in the Matheson publication, report number G-115B. The fluorine gas as well as the gauges are also from Matheson. The delivery rate of the F_2/N_2 mixture was usually about 15 cm^3/min, but changes in this rate are not of much importance since the solubility of fluorine is poor in the solvents we usually work with (see ref 3b). It is important, however, to ensure a good suspension of the gas bubbles in the solution. This can be achieved with an efficient vibromixer (Chemapec Inc., Hoboken, NJ). The progress of the reactions was monitored by GC (SE-30, 3%). Unless otherwise stated, the reactions were stopped after about 90–95% of the starting material was consumed, and in our case it required 3–6 h. The yields reported in this work are absolute.

(7) All new compounds had the correct composition established by microanalysis. Their spectral data (IR,^{19}F and ^{1}H NMR, and mass spectra) are in excellent agreement with the assigned structures and stereochemistry.