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Nitrogen 1s Binding Energy Shifts Detected from a Homologous Series of Cyanine Dyes

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The recent interest in the study of dyes has been greatly stimulated by their potential applications in the field of electronic and optical switching and as chemical-vapor sensing coatings for transducers.[1] Such transducers through the rapid development of minaturization techniques have opened up an area of pollution technology that should ultimately result in a proliferation of a low cost, rugged and versatile array of point-contact detectors for toxic vapor and liquid detection.

Recently we at NRL have undertaken a study of a class of cyanine dyes,[2] which have long been employed as photosensitizers for photographic emulsions in the infrared.[1] They also possess probable semiconducting properties since their optical band gaps fall in the 2.4–1.7 eV regions. These low-energy electronic gaps arise from the delocalization of the mobile π-electrons which are capable of being either thermally or optically excited from the top of the valence band states into the unoccupied conduction band states.

It is well-known that these dyes and dyes in general exhibit a greater degree of electronic conduction with an increase in conjugation, i.e., adding of more carbons to the dye structural backbone.[3] Moreover, this increase in conjugation has been observed to produce a "bathochromic shift" of the main electronic absorption band. Figure 1 shows a plot of the shifts in the maximum wavelength as a function of the increase in the carbon chain addition for a homologous series of symmetric cyanine dyes. This series was selected since conjugation is restricted to the carbon chain of the dye backbone, leaving the end groups structurally unchanged, except for the case of cryptocyanine iodide, where the end rings are rotated by 90°.

It was expected that this restriction would result in a more direct and simpler interpretation of the binding energy shifts with linear carbon–carbon addition. Note, in Figure 1, that increasing the number of carbon atoms between the benzene rings from one to five produces electronic band shifts for both the maximum wavelength and its associated shoulder from 517 and 487 nm (i.e., pseudo cyanine iodide) to 715 and 653 nm (i.e., 1,1′-diethyl-2,2′-dicarbocyanine iodide). Note also that, although cryptocyanine iodide has only three carbons, its absorption band maxima fall at nearly the same wavelengths as the five-carbon-chain analogue. This phenomena is probably associated with the 90° orientation of the outer double rings, which apparently results in an effective increase in conjugation equivalent to the simple addition of two more carbons to the dye skeleton. Figure 1 also shows that the measured optical densities or strengths of the electronic transitions also increases with conjugation. Again cryptocyanine iodide possesses an optical density for both electronic bands of comparable magnitude to the five-carbon analogue.

If these conjugation effects reflect the delocalization of the mobile π-electrons, it is assumed that the addition of carbon atoms to the dye skeleton should in turn produce a delocalization of charge at the nitrogen atom site and hence result in an effective reduction in binding energy of the 1s core electrons.[4] Indeed, this effect is displayed in Figure 2 where the principal electronic wavelengths for this homologous series are plotted vs. the nitrogen 1s binding energy. For the ESCA measurements, each dye was put on a silver planchette in either a solid film (i.e., evaporation of a 10^{-5} M solution in methanol) or in the form of a mull. The two data points shown in Figure 2 for each dye represent these two sample conditions studied. Considering the variability in sample preparation, the reproducibility of this data appears reasonably good. Note that the binding energy decreases linearly with the increase in the maximum dye wavelength and hence dye conjugation. The data were obtained with a McPherson ESCA-36 spectrometer. For each run a gold standard, i.e., Au 4f5/2, Au 4f7/2 spectrum, was taken and showed that the peak maxima were reproducible to within ±0.01 eV via computer fit of the line shape displaying data points 0.12 eV apart. The data shown in Figure 2 for the nitrogen (N1s) binding energies were corrected for sample charging by setting the carbon (C1s) line at 284.6 eV; the C1s binding energies for aromatic and aliphatic carbons seem to be very similar.[5] The iodide counterion was also investigated by

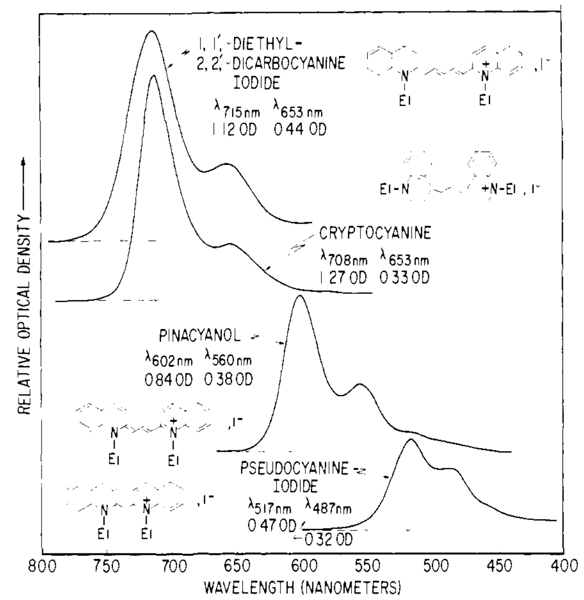

Figure 1. Electronic absorption band shifts as a function of conjugation for a homologous series of symmetrical cyanine dyes. The relative optical density for the principal electronic and secondary bands are given together with the molecular structure for each dye.

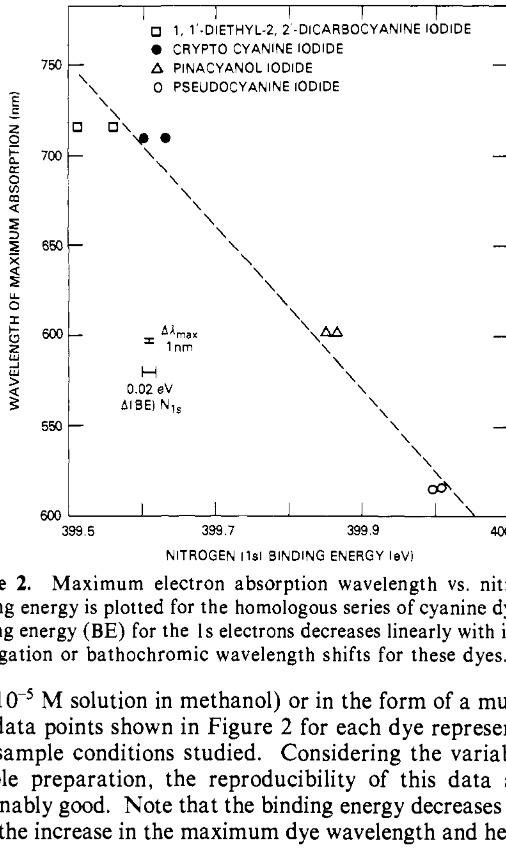

Figure 2. Maximum electron absorption wavelength vs. nitrogen 1s binding energy is plotted for the homologous series of cyanine dyes. The binding energy (BE) for the 1s electrons decreases linearly with increased conjugation or bathochromic wavelength shifts for these dyes.

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(1) Meier, H. *Top.* in *Curr. Chem.* **1976**, *61*, 85–128.

(2) Fisher, N. I.; Hamer, F. M. *Proc. R. Soc. London, Ser. A* **1936**, *154*, 703.

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(4) Jack, J. J.; Hercules, D. M. *Anal. Chem.* **1971**, *43* (6), 729.

(5) "Handbook of X-ray Photoelectron Spectroscopy", Wagner, C. D., Riggs, W. M., Davis, L. E., Moulder, J. F., Muilenburg, G. E., Eds.; Perkin-Elmer Corp.: Eden Prairie, MN, 1979.

ESCA and showed no measurable binding-energy shifts from one dye to the next in this series.

In summary, our data show that for a symmetric cyanine dye series, the principal electronic absorption band shifts with conjugation are directly reflected in the delocalization of the nitrogen 1s core electrons in which the binding energy decreases linearly with increased conjugation. We believe that the ESCA analysis could be an important complementary tool for the assessment of solid dye films with respect to their semiconduction and photoconduction potential for various optical and electronic device coatings.

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Registry No. 1,1′-Diethyl-2,2′-dicarbocyanine iodide, 14187-31-6; cryptocyanine, 4727-50-8; pinacyanol, 605-91-4; pseudocyanine iodide, 977-96-8.

Structure and Reactivity of the Zirconaenolate Anion $(Cp_2Zr(\eta^2\text{-}OCCH_2\text{-}C,O)CH_3)Na\cdot 2THF$. Synthesis of Homo- and Heterobinuclear Ketene Complexes[1]

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Transition-metal acyl complexes are key intermediates in numerous stoichiometric and catalytic transformations.[2] Despite the ubiquitous use of enolate anions in organic synthesis, deprotonation of acyl ligands to form the corresponding metallaenolate anions has been only recently reported.[3] Preparation of these reactive species appears to necessitate use of a bulky, non-nucleophilic base and a metal with electron-donating ancillary ligands.[4] As previously reported, a good leaving group such as halide as a ligand on the central metal leads to neutral metal ketene complexes.[3a,5,6] Herein we report structural details of the metallaenolate (ketene) anion $(Cp_2Zr(\eta^2\text{-}OCCH_2\text{-}C,O)CH_3)Na\cdot 2THF$ (**2a**·2THF) and describe its reactivity toward organic and metal halides.[7] The latter reactions lead to isolation of a variety of neutral binuclear ketene-bridge structures.[8,9]

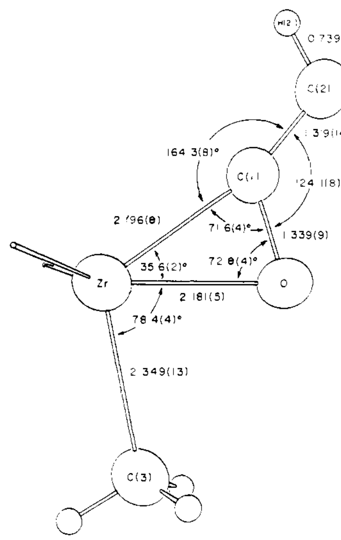
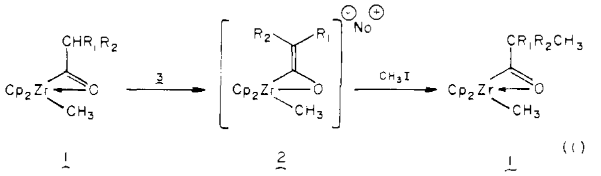


Figure 1. Molecular geometry of the equatorial ligands in **2a**·2THF.

Zirconaenolate anion **2a**·Et_2O precipitates instantly on addition of an ethereal solution of $NaN(Si(CH_3)_3)_2$ (**3**) to a stirred solution of $Cp_2Zr(COCH_3)CH_3$ (**1a**)[10] in ether at −30 °C (eq 1). The resulting white powder is pyrophoric in air and moderately light sensitive. The complex is insoluble in pentane, ether, and benzene but dissolves readily in THF, yielding **2a**·2THF upon removal of solvent in vacuo. The latter complex is benzene soluble. Crystals of **2a**·2THF suitable for X-ray structural analysis[11] have been obtained by slow cooling of a pentane–THF solution of **2a**. The geometry of the planar $Zr(COCH_2)CH_3$ moiety is presented in Figure 1. The C(1)–O and C(1)–C(2) bond lengths are typical of single and double bonds, respectively. The $OCCH_2$ moiety is virtually identical with that in the neutral ketene complex $(\eta^5\text{-}C_5Me_5)_2Zr(\eta^2\text{-}OCCH_2\text{-}C,O)(py)$[5] (py = pyridine) except for the slightly shorter Zr–O bond in the latter (2.126 (1) Å), which may reflect the greater donor strength of CH_3 vs. the pyridine ligand. The Zr–C(3) bond length is similar to the Zr–C(methyl) distance in **1a** (2.336 (7) Å)[10] but considerably longer than in the more electron deficient $Cp_2Zr(CH_3)_2$ (2.276 (7) Å).[12] To our knowledge this is the only structurally characterized metallaenolate anion.



1a, $R_1 = R_2 = H$ — **2a**, $R_1 = R_2 = H$
b, $R_1 = H; R_2 = CH_3$ — b, $R_1 = H; R_2 = CH_3$
c, $R_1 = R_2 = CH_3$ — c, $R_1 = R_2 = CH_3$

Although the NMR spectroscopic and structural data do not indicate high negative charge density at C(2), reaction of **2a**·2THF with CH_3I gives $Cp_2Zr(COCH_2CH_3)CH_3$[3a] quantitatively without production of ethane (^1H NMR). Alkylation of **2a**·2THF with CD_3I yields only $Cp_2Zr(COCH_2CD_3)CH_3$ (^1H NMR). Sequential alkylation and deprotonation as above leads cleanly and quantitatively to anions **2b** and **2c** (eq 1). Particular noteworthy is production of only one isomer of the zirconaenolate **2b**·Et_2O

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(1) In memory of Professor Ernst G. Straus.

(2) (a) Kuhlmann, E. J.; Alexander, J. J. *Coord. Chem. Rev.* **1980**, *33*, 195. (b) Calderazzo, F. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 299. (c) Henrici-Olive, G.; Olive, S. *Transition Metal Chem.* (*Weinheim, Ger.*) **1976**, *1*, 77. (d) Carr, D. B.; Schwartz, J. *J. Am. Chem. Soc.* **1979**, *101*, 3521.

(3) (a) Straus, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 5499. (b) Theopold, K. H.; Becker, P. N.; Bergman, R. G. *Ibid.* **1982**, *104*, 5250. (c) Liebeskind, L. S.; Welker, M. E. *Organometallics* **1983**, *2*, 194. (d) Straus, D. A. Ph.D. Thesis, California Institute of Technology, Pasadena, CA, 1983.

(4) Compare, for example: Johnson, R. W.; Pearson, R. G. *Inorg. Chem.* **1971**, *10*, 2091. Heck, R. F.; Breslow, D. F. *J. Am. Chem. Soc.* **1963**, *85*, 2779. Malisch, W.; Blau, H.; Haaf, F. J. *Chem. Ber.* **1981**, *114*, 2956.

(5) Moore, E. J.; Straus, D. A.; Armantrout, J.; Santarsiero, B. D.; Grubbs, R. H.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2068.

(6) For a novel synthesis of a mononuclear neutral η^2-ketene-C,O complex, see: Casey, C. P.; O'Conner, J. M. *J. Am. Chem. Soc.* **1983**, *105*, 2919.

(7) This complex has been briefly reported with ^1H and ^{13}C NMR spectroscopic data (THF-d_8), ref 3a,d.

(8) Two examples of μ-$OCCH_2$ ketene structures are reported: (a) Lin, Y. C.; Calabrese, J. C.; Wreford, S. S. *J. Am. Chem. Soc.* **1983**, *105*, 1679 (Ru, Ru). (b) Morrison, E. D.; Steinmetz, G. R.; Geoffroy, G. L.; Fultz, W. C.; Rheingold, A. L. *Ibid.* **1983**, *105*, 4104. See also: Ott, K. Ph.D. Thesis, California Institute of Technology, Pasadena, CA, 1983. Certain dimeric substituted ketene complexes also fall into this category: (c) Fachinetti, G.; Biran, C.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1978**, *17*, 2995. (d) Bristow, G. S.; Hitchcock, P. B.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1982**, 462. See also ref 3a,d.

(9) A structurally characterized trinuclear $(Zr_2Al)(\mu,\eta^2\text{-}OCCHCH_2C(CH_3)_3\text{-}C,O)_2$ complex has been prepared by reaction of $Al(CH_3)_2Cl$ with $(Cp_2Zr(OCCHCH_2C(CH_3)_3))_2$ (ref 3a,d): Waymouth, R. M.; Grubbs, R. H., unpublished results.

(10) Fachinetti, G.; Fochi, G.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1977**, 1946.

(11) Complex **2a**·2THF crystallized in the space group $P\bar{1}$ with: a = 10.745(5) Å, b = 14.449 (5) Å, c = 12.060 (4) Å, α = 119.40 (3)°, β = 91.26 (4)°, γ = 114.83 (4)°, V = 1123 (1) Å^3, Z = 2.

(12) Average value from: Hunter, W. E.; Hrncir, D. C.; Bynum, R. V.; Peuttila, R. A.; Atwood, J. L. *Organometallics* **1983**, *2*, 750.

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