Dicyano and Pyridine Derivatives of Retinal: Synthesis and Vibronic, Electronic, and Photophysical Properties

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Two new derivatives of all-trans retinal, one containing a pyridine and a cyanide substituent, *all-trans*-15cyano-15'-pyridylretinal (2), and the other containing two cyanide substituents, *all-trans*-15,15'-dicyanoretinal (3), have been synthesized from *all-trans*-retinal (1) by the Knoevenagel reaction. Compound 2 crystallizes in the space group $P\overline{1}$; compound 3 crystallizes in the space group $P2_1/n$. The polyene chains are bowed. The compounds exhibit C=N vibrations in the infrared and Raman regions and undergo irreversible oxidations. Compounds 2 and 3 display electronic absorptions with maxima located at 442 and 487 nm and emission peaks located at 583 and 500 nm, respectively. Density Functional Theory and Time Dependent Density Functional Theory calculations reveal that the electronic transition from the HOMO to the LUMO can be associated with the $A_g \rightarrow B_u$ electronic transition and a peak corresponding to the HOMO \rightarrow LUMO+1 transition can be associated with the "cis-peak".

Introduction

 β -Carotenes serve as antennas for absorbing light in spectral regions where chlorophylls do not absorb, and thus initiate photosynthesis.^{1–8} According to group theoretical treatments based on the C_{2h} point group, the electronic ground state is ${}^{1}A_{g}$ in character while the symmetry-allowed transition found in the visible region responsible for pigment coloration is due to the population of the ${}^{1}B_{u}$ state.^{1,9–22} Low-temperature (77 K) emission studies have shown that another ${}^{1}A_{g}$ excited state lies between the ground state and the ${}^{1}B_{u}$ excited state.^{1,3–15,23–26} Triplet states have also been previously investigated.^{27,28}

In this study, we have synthesized two cyanine derivatives of *all-trans*-retinal, β -carotene analogues (Scheme 1), as antennas for attachment to transition metal complexes using an acidcatalyzed approach. Crystal structures were determined for both compounds by using single crystal X-ray diffraction, and their electronic, vibronic and photophysical properties have been characterized. Density-functional theory (DFT) and Time Dependent Density Functional Theory (TDDFT)²⁹ calculations have also been employed to compare their spectral properties to those determined experimentally.

Experimental Section

Materials. The compound *all-trans*-retinal (Vitamin-A aldehyde) was obtained from Sigma. Malononitrile was obtained from Fluka while the compound 4-pyridylacetonitrile monohydrochloride was purchased from Acros Scientific. Butyronitrile used for emission and lifetime studies was obtained from Acros Scientific and was fractionally distilled prior to use. Dried benzene, diethyl ether, HPLC grade methanol, chloroform, methylene chloride, and optima grade acetonitrile for UV/visible spectral determination were purchased from Fisher Scientific. Propionic acid and ammonium carbonate were purchased from

SCHEME 1: Compounds 2 and 3 Derived from 1







All-trans-15-cyano-15'-pyridyl retinal (2)



All-trans-15,15'-dicyano-retinal (3)

Aldrich. IR grade potassium bromide used as a pellet for the infrared spectra and deuterated dimethyl sulfoxide (DMSO) for

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NMR analysis were obtained from Aldrich. Ferrocene standard and dried acetonitrile (sure-sealed bottle) used as an electrochemical solvent were purchased from Aldrich. Sulfur powder used as a standard to calibrate the FT-Raman spectrometer was provided by Thermo Nicolet. Electrochemical grade tetrabutylammonium perchlorate was purchased from Southwestern Analytical.

Preparation of all-trans-15-Cyano-15'-pyridylretinal (2). The following preparation was performed under an argon atmosphere. All-trans-retinal (100.0 mg, 3.49×10^{-4} mol) was placed in a 10 mL round-bottomed flask. The compound was then dissolved in benzene and allowed to stir for 5 min. After all the solid dissolved, 4-pyridylacetonitrile monohydrochloride $(58.3 \text{ mg}, 5.30 \times 10^{-4} \text{ mol})$ and ammonium carbonate (98.6 mg, 1.03 mmol) were added to the solution and the reaction was allowed to stir further for about 5 min. Then, 1.00 mL of propionic acid was added dropwise into the solution. After all the reagents were added, the reaction was heated overnight under argon with the temperature regulated at approximately 70 °C. The reaction was then allowed to cool in an ice water bath and the solvent was removed by lyophilization. The red-orange solid was redissolved in chloroform and subjected to column chromatography through an oven-dried neutral alumina (~ 10.0 g) stationary phase. The mobile phase used was 7:1 chloroform: methylene chloride. The first and final fractions were discarded while the middle fractions were saved and examined for purity by TLC. After combining the pure fractions, the solid was recovered after freeze-drying the solution to remove the solvent. The orange compound was dried in a vacuum oven and stored in a desiccator. Color: brick-red. Yield: 80%. Anal. Calcd for C₂₇H₃₂N₂: C, 84.31; H, 8.39; N, 7.29. Found: C, 84.05; H, 7.27; N, 7.27. IR (KBr pellet, cm⁻¹): (CN) 2208 w, (-C=C-) 1542 sh, 3745 m, 2924 m, 1097 m, 1023 m. Raman (solid, cm⁻¹): (CN) 2207 w, (-C=C-) 1534 sh, (C=C-H) 1211 sh. ¹³C NMR (CDCl₃): δ ppm 150.7 (pyr), 140.7, 140.2, 137.5, 135.6, 131.5, 130.3, 129.6, 127.1, 119.6 (CN), 39.9, 34.5, 33.4, 29.2 (β-ring), 22.0, 19.4, 13.9.

Preparation of *all-trans*-**15**,**15'**-**Dicyanoretinal (3).** Compound **3** was prepared analogous to compound **2** except malononitrile (58.3 mg, 5.30×10^{-4} mol) was substituted for 4-pyridylacetonitrile monohydrochloride (58.3 mg, 5.30×10^{-4} mol). The dark-red compound was dried in a vacuum oven and stored in a desiccator. Color: burgundy. Yield: 85%. Anal. Calcd for C₂₃H₂₈N₂: C, 83.07; H, 8.50; N, 8.43. Found: C, 82.98; H, 7.76; N, 8.45. IR (KBr pellet, cm⁻¹): (CN) 2219 m, (-C=C-) 1544 sh, 3746 w, 2926 w, 1244 w, 1188 w. Raman (solid, cm⁻¹): (CN) 2215, (-C=C-) 1528, (C=C-H) 1171 sh.

Measurements. Infrared spectra were obtained with Perkin-Elmer Model 1600 FT-IR and Nicolet Avatar model FT-IR spectrophotometers. All samples were prepared as potassium bromide pellets. Raman spectra were obtained with a Thermo Nicolet Nexus FT-Raman module spectrophotometer. The Nicolet instruments were accompanied by Omni software programs. Proton (1H) and 13C NMR spectra were obtained with Varian Mercury 300 MHz and Varian Inova 400 MHz Fourier Transform-NMR spectrometers (internal standard TMS). Ultraviolet spectra were obtained with a Hewlett-Packard Model 8452A diode array spectrophotometer interfaced with an OLIS software program. Elemental (C, H, N) analysis was performed by MHW Laboratories, Phoenix, AZ. An EG&G PAR model 263A potentiostat/galvanostat was used to obtain cyclic voltammograms. All measurements were carried out in a typical H-electrochemical cell, using a platinum disk working electrode (polished every run) and a platinum wire counter electrode. A Ag/AgNO₃ reference electrode in dried CH₃CN was freshly made and used for this study. The supporting electrolyte was 0.1 M tetrabutylammonium perchlorate. Ferrocene was added as a reference. The sample preparation for emission studies involved dissolving a small amount of sample in dried butyronitrile and then measuring the absorbance of the solution. The concentration of the solution was altered in order to achieve an absorbance of ~0.10 at the λ_{max} of the sample. The sample solution was placed in a quartz tube and was degassed a minimum of five times with the freeze-pump-thaw method prior to actual measurements. Emission quantum yields were calculated by using eq 1,

$$\log(\varphi_{\rm f}) = 0.919 \log\left[\frac{I_{\rm f}}{1 - 10^{-A}}\right] - 7.934$$
(1)

where φ_f is the emission quantum yield, I_f is the emission intensity, and *A* is the absorbance of the sample at the excitation frequency.³⁰ Low-temperature (77 K) emissions were measured with a Spex Fluorolog 212 spectrofluorometer equipped with a homemade sample holder connected to an Ar gas tank for continuous deaeration of the sample compartment.

Calculations. Calculations were affected with Gaussian 03 (Rev. B.03)²⁹ for UNIX. The molecules were optimized by using Becke's three-parameter hybrid functional B3LYP³¹ with the local term³² of Lee, Yang, and Parr and the nonlocal term³³ of Vosko, Wilk, and Nassiar. The basis set 6-311G** was chosen for all atoms and the geometry optimizations were all ran in the gas phase. TDDFT^{34–40} calculations were employed to produce a number of singlet excited states⁴¹ in the gas phase based on the optimized geometry. All oscillator values and singlet and triplet excited state values are presented in the Supporting Information.

X-ray Crystallography. all-trans-15-Cyano-15'-pyridylretinal (2) and all-trans-15,15'-Dicyanoretinal (3). Crystals were affixed to a nylon cryoloop with oil (Paratone-n, Exxon) and mounted in the cold stream of a Bruker Kappa-Apex II areadetector diffractometer. The temperature at the crystals was maintained at 150 K by using a Cryostream 700EX Cooler (Oxford Cryosystems). A scan with 0.3° and time of 10 s was employed along with graphite monochromated Molybdenum K α radiation ($\lambda = 0.71073$ Å) that was collimated to a 0.6 mm diameter. Data collection, reduction, structure solution, and refinement were performed with the Bruker Apex2 suite (v2.0-2).

The unit cell of **2** was determined from the setting angles of 50 reflections collected in 36 frames of data. Data were measured with a redundancy of 7 with a CCD detector at a distance of 50 mm from the crystal with a combination of φ and ω scans. All available reflections to $2\theta_{\text{max}} = 54^{\circ}$ were harvested (37745 reflections, 5276 unique) and corrected for Lorentz and polarization factors with Bruker SAINT (v6.45). Reflections were then corrected for absorption (numerical correction, $\mu = 0.064 \text{ mm}^{-1}$), interframe scaling, and other systematic errors with SADABS 2004/1 (combined transmission and other correction factors min/max = 0.9731/0.9911).

The unit cell of **3** was determined from the setting angles of 74 reflections collected in 36 frames of data. Data were measured with a redundancy of 7.8, using a CCD detector at a distance of 50 mm from the crystal with a combination of φ and ω scans. All available reflections to $2\theta_{\text{max}} = 54^{\circ}$ were harvested (37913 reflections, 4782 unique) and corrected for Lorentz and polarization factors with Bruker SAINT (v6.45). Reflections were then corrected for absorption (numerical

TABLE 1: Crystal Data and Structure Refinement for 2 and 3

empirical formula	$C_{27}H_{32}N_2$ (2)	$C_{23}H_{28}N_2$ (3)
formula weight	384.55	332.47
temperature	150 K	150 K
wavelength	0.71073 Å	0.71073 Å
crystal system	triclinic	monoclinic
space group	$P\overline{1}$	$P2_1/n$
unit cell dimensions	a = 6.8351(7) Å	a = 10.2960(7) Å
	b = 7.4409(7) Å	b = 11.5493(7) Å
	c = 24.397(2) Å	c = 17.6364(12) Å
	$\alpha = 89.250(6)^{\circ}$	$\alpha = 90^{\circ}$
	$\beta = 85.685(6)^{\circ}$	$\beta = 100.126(3)^{\circ}$
	$\gamma = 69.736(5)^{\circ}$	$\gamma = 90^{\circ}$
volume	1160.61(19)Å ³	2064.5(2) Å ³
Ζ	2	4
calcd density	1.100 g/cm^3	1.070 g/cm^3
absorption coeff	0.064 mm^{-1}	0.062 mm^{-1}
F(000)	416	720
crystal size	$0.43 \times 0.32 \times 0.14 \text{ mm}$	$0.39 \times 0.31 \times 0.22 \text{ mm}$
crystal habit	block	block
crystal color	dark red	dark red
θ range for data collection	1.67° to 25.00°	2.12° to 27.11°
limiting indices	$-8 \le h \le 7$	$-13 \le h \le 13$
	$-8 \le k \le 8$	$-14 \le k \le 14$
	$-28 \le l \le 28$	$-22 \le l \le 22$
no. of reflections collected/unique	33891/4069 [R(int) = 0.0862]	$36637/4549 \ [R(int) = 0.1076]$
completeness to $\theta = 25.00^{\circ}$	99.9%	99.6%
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data/restraints/parameters	4069/0/268	4549/0/231
refinement threshold	$I > 2\sigma(I)$	$I > 2\sigma(I)$
no. of data $>$ threshold	2417	2506
goodness-of-fit on F^2	1.022	1.048
final <i>R</i> indices $[I > 2\sigma(I)]$	R1 = 0.0627, wR2 = 0.1455	R1 = 0.0681, wR2 = 0.1570
R indices (all data)	R1 = 0.1182, wR2 = 0.1774	R1 = 0.1353, wR2 = 0.1968
largest diff peak and hole	0.471 and $-0.257 \text{ e}^- \text{\AA}^{-3}$	0.468 and $-0.172 \text{ e}^- \text{ Å}^{-3}$

correction, $\mu = 0.062 \text{ mm}^{-1}$), interframe scaling, and other systematic errors with SADABS 2004/1 (combined transmission and other correction factors min/max = 0.9796/0.9915).

The structures were solved (direct methods) and refined (fullmatrix least-squares against F^2) with the Bruker SHELXTL package (v6.14–1). All non-hydrogen atoms were refined by using anisotropic thermal parameters. All hydrogen atoms were included at idealized positions; hydrogen atoms were not refined. Pertinent crystal, data collection, and refinement parameters are given in Table 1.

Results and Discussion

Preparations. The preparation of **2** and **3** followed the Knoevenagel reaction, ^{42,43} which involved the condensation of the aldehyde, retinal, with substrates lacking α -hydrogen atoms adjacent to the coupling site. This criterion is required to enhance the acidity of the methylene (-CH₂-) protons.

Traditionally, this condensation reaction is catalyzed by using only a weak base such as piperidine or NaNH₂.⁴² In our case, we used simultaneous base- and acid-catalyzed condensation reactions to enhance the yield. The base catalyst used was NH₄CO₃ while the acid catalyst chosen was propionic acid (CH₃CH₂COOH). The reaction scheme is shown in Figure 1. The mechanism of formation of the pyridyl adduct is presented in Figure 2, which can be extended to the dicyano derivative. In this reaction, the base catalyst was added first to the reaction mixture to neutralize hydrochloride and to deprotonate one of the methylene ($-CH_2-$) protons. Then, the weak acid catalyst was added to protonate the carbonyl oxygen generating the carbonyl carbocation necessary to initiate the condensation reaction.

X-ray Results. The crystal structures of 2 and 3 were determined. Selected bond lengths, bond angles, and torsion angles were tabulated in Table 2 and ORTEP diagrams are shown in Figure 3. The retinal-pyridine adduct, in its crystal form, retained its all-trans configuration as can be seen clearly in Figure 3. The experimental bond distance for the C≡N group was 1.14 Å. For the polyene chain, localized C-C single bonds in both cases averaged 1.44 Å while double C=C bonds averaged 1.36 Å. The new C=C double bond that resulted between the methylene (-CH₂-) and carbonyl (CO) carbon after condensation gave an average bond distance of 1.36 Å but the bond angles at the condensation point were not the same. The C(22)-C(16)-C(17)angle was 117.9° for 2 while the C(17)-C(18)-C(22) angle of 3 was 121.1° . For 2 the C(14)-C(15)-C(16)-C(17) torsion angle was 177.8° while the C(21)-C(17)-C(16)-C(22) angle was 11.9°. For 3, the C(16)-C(17)-C(18)-C(22) torsion angle was 178.0°. The optimized structures of 2 and 3 were also calculated by using density functional theory (DFT) and the corresponding theoretical bond lengths and angles were correlated with the experimental data. Results showed good correlation with alternating single-double

bonds present in the polyene chain. Both the actual crystal and DFT optimized structures showed gradual bending in the polyene chain with the methyl groups pointed away from the curvature. From Figure 3, one also notes the lowering in symmetry of the polyene derivatives from $C_{\rm ex}$ suggested for $\beta_{\rm e}$ carotenes to

the polyene derivatives from C_{2h} suggested for β -carotenes to possibly C_s due to substituent effects and to twisting of the polyene chain. Calculations (DFT/TDDFT). The HOMO and LUMO orbit-

calculations (DF1/1DDF1). The HOMO and LUMO orbitals determined by DFT calculations are shown in Figure 4; lower energy HOMO and higher energy LUMO orbitals are shown in Figure 5.



Figure 1. Knoevenagel condensation of *all-trans*-retinal with (2) 4-pyridylacetonitrile monohydrate and (3) malononitrile.



Figure 2. Mechanism for the acid- and base-catalyzed Knoevenagel condensation of *all-trans*-retinal with 4-pyridylacetonitrile monohydrate.

Table 3 lists the population analysis data and the percentage electronic distribution of some selected states in 2 and 3. The HOMO is predominantly polyene in character with 87% occupancy in 2 and 67% in 3. The most remarkable difference is that the HOMO of 3 also showed some important contributions from the β -ring (19% occupancy) and the CN group (15% occupancy). Although the LUMO character lies on the chain of 2 and 3, the electron density of the LUMO in 2 is distributed throughout the molecule with a 10% occupancy coming out from the pyridyl group.

The pyridyl group in 2 plays an important role in hosting the excited electron. In some cases, the methyl groups of the polyene chain have minor contributions in one of the states such as that

observed in H - 1. In the latter case, a rather different π -bonding interaction was observed with a nodal plane arising every third atom of the polyene chain. In H - 3 the electron density is localized only on the pyridyl ring with no contributions coming from the polyene chain.

The electronic distributions of the orbitals in **3** are much more intriguing than the pyridyl derivative. The electron density in H-1 state is almost divided equally into three segments throughout the molecule. One segment is localized in the β -ring region; another segment is located in the middle of the polyene chain, while the last one is concentrated in the dicyano group. H-2, on the other hand, contains "banana-shaped" electron density lobes extended throughout the molecule. It is also

 TABLE 2: Selected Bond Lengths (Å) and Angles (deg) for 2 and 3

		(18)			
atoms 2	exptl	calcd	atoms 3	exptl	calcd
C(22)-N(2) (nitrile)	1.142	1.155	C(22)-N(1) (nitrile)	1.143	1.154
C(16)-C(22)	1.442	1.430	C(22)-N(2) (nitrile)	1.142	1.154
C(19)-N(1) (pyridyl)	1.329	1.334	C(5)-C(9)	1.469	1.471
C(20)-N(1) (pyridyl)	1.324	1.335	C(9)-C(10)	1.343	1.349
			C(10) - C(11)	1.451	1.449
C(6)-C(7)	1.479	1.549	C(11)-C(12)	1.364	1.365
C(7)-C(8)	1.328	1.342	C(12)-C(13)	1.423	1.428
C(8)-C(9)	1.458	1.457	C(13)-C(14)	1.353	1.360
C(9) - C(10)	1.351	1.361	C(14) - C(15)	1.428	1.437
C(10) - C(11)	1.440	1.432	C(15)-C(16)	1.386	1.372
C(11)-C(12)	1.346	1.357	C(16)-C(17)	1.395	1.416
C(12) - C(13)	1.443	1.442	C(17)-C(18)	1.370	1.371
C(13)-C(14)	1.357	1.368	C(18)-C(22)	1.425	1.426
C(14)-C(15)	1.424	1.427	C(18)-C(23)	1.430	1.427
C(15)-C(16)	1.355	1.366			
C(16)-C(17)	1.481	1.481			
C(22)-C(16)-C(17)	117.9	116.0	C(17)-C(18)-C(22)	121.1	120.7
C(22)-C(16)-C(15)	116.1	117.2	C(17) - C(18) - C(23)	122.9	122.0
			N(1) - C(22) - C(18)	176.3	179.2
			N(2)-C(23)-C(18)	178.4	178.7
C(14)-C(15)-C(16)-C(17) C(21)-C(17)-C(16)-C(22)	177.8 11.9	173.7	C(16)-C(17)-C(18)-C(22)	178.0	178.6

important to note that in all transitions, the dicyano groups are involved, particularly in the L+1 state.

Figure 6 shows the molecular orbital energy diagrams of **2** and **3**. The HOMO-LUMO gaps are consistent with the observed transition energy as discussed in the electronic absorption section (see Table 6).

Vibrational Properties. The infrared and Raman spectroscopy data are given in Table 4 while the Raman spectra of **2** and **3** are shown in Figure 7. Although the intensity of the Raman scattering in **2** is a lot weaker than that of **3**, the polyene mode of vibration in all cases remains IR and Raman active. The main points of interest in structural elucidation are the nitrile and polyene groups before and after condensation. As shown in Table 4, the carbonyl stretching frequencies of *all-trans*-retinal appeared at around 1655 cm⁻¹ (IR and Raman). The IR frequency of the C=N vibration for malononitrile was located at 2273 cm⁻¹ while its Raman frequencies were found at 2295



Figure 3. ORTEP diagram of 2 and 3.

TABLE 3: Electron Distribution (%) in 2 and 3

states	2	3
LUMO+1	60 (chain)	77 (chain)
	2 (β -ring)	12 (β -ring)
	1 (CN)	11 (CN)
	37 (pyridyl)	
LUMO	82 (chain)	72 (chain)
	1 (β -ring)	3 (β -ring)
	7 (CN)	25 (CN)
	10 (pyridyl)	
HOMO	87 (chain)	67 (chain)
	3 (β -ring)	19 (β-ring)
	5 (CN)	15 (CN)
	5 (pyridyl)	
HOMO-1	77 (chain)	35 (chain)
	5 (β -ring)	49 (β -ring)
	6 (CN)	15 (CN)
	11 (pyridyl)	
HOMO-2	1 (chain)	57 (chain)
	$0 \ (\beta \text{-ring})$	24 (β -ring)
	0 (CN)	19 (CN)
	99 (pyridyl)	

(sym) and 2265 cm⁻¹ (asym). After condensation, the carbonyl peak of retinal disappeared and peaks for the C≡N vibration appeared. The IR C≡N frequency for 2 was located at 2208 cm⁻¹ in close agreement with its Raman frequency at 2207 cm^{-1} . For 3, the related frequencies were 2219 cm^{-1} in the IR and 2215 cm⁻¹ in the Raman. It is notable that the CN stretching frequency in the pyridyl adduct is weaker than the malononitrile counterpart. This behavior may be due to the effect of pyridine ring that allows the CN to vibrate freely in the conjugation. Retention of the polyene groups after the condensation was best monitored by using Raman spectroscopy. These polyene group frequencies are also listed in Table 4. The frequency of alternating carbon-carbon double bond backbone in 1 was observed at 1574 cm^{-1} in the IR and at 1568 cm^{-1} in the Raman. For 2, the frequency of the polyene backbone was observed at 1542 cm⁻¹ in the IR and at 1534 cm⁻¹ in the Raman, while for **3** it was found at 1544 cm^{-1} in the IR and at 1528 cm^{-1} in the Raman.

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Figure 4. HOMO/LUMO pictures in 2 and 3 determined by DFT.





HOMO – 1 (**2**)









Figure 5. Orbital pictures of selected states involved in optical transition in 2 and 3.

 TABLE 4: Vibrational Stretching Frequencies (cm⁻¹) of CN and Polyene Groups

compd	functional group	exptl (IR)	exptl (Raman)
1	C=O stretch	1656	1654
	-C=C- skeletal	1574	1568
	=C-H in-plane bending		1268
	CH ₃ stretch	2934	
2	CN stretch	2208	2207
	-C=C- skeletal	1542	1534
	=C-H in-plane bending		1211
	CH ₃ stretch	2924	
3	CN stretch	2219	2215
	-C=C- skeletal	1544	1528
	=C-H in-plane bending		1171
	CH ₃ stretch	2925	

Alkene protons in conjugated systems are known to be Raman active modes. These proton frequencies of the methyl groups and the polyene backbone protons are also listed in Table 4.

Cyclic Voltammetry. Oxidations for 1, 2, and 3 were examined and the data are summarized in Table 5. Figure 8 shows the cyclic voltammograms of 2 and 3. Electrochemical results showed irreversible oxidation waves for all three, which is typical in most retinoids and carotenoids^{44–46} supporting their antioxidant properties; no reversible reduction was observed. For 2, the irreversible peak was observed at 0.78 V while for 3 it was observed at a higher potential of 0.98 V. Both were shifted to a lower electrode potential with respect to *all-trans*-retinal (1.10 V). The much larger shift for the 2 derivative may be related to additional π conjugation with the pyridine ring.



Figure 6. Molecular orbital energy diagrams of 2 and 3.

Some naturally occurring carotenoids (i.e., β -carotene) undergo cation radical formation. The irreversible oxidation observed in the CV of **2** resembles that of β -carotene.⁴⁵ It is possible for the compound to undergo a two-electron oxidation reaction at the electrode surface to generate a dication intermediate. This EC mechanism is well-established in most carotenoids. In the case of the dicyano adduct, another irreversible peak appears after the initial one. This behavior has been observed in naturally occurring compounds such as β -apo-8'carotenal wherein two- or three-electron-transfer processes are involved.⁴⁶

Electronic Spectra. The UV/visible spectral data of the compounds are given in Table 6 and shown in Figure 9. Relative to 1, compounds 2 and 3 showed bathochromic shifts. For 2, λ_{max} was shifted by 64 to 446 nm; for **3** it was shifted by about 82 to 464 nm. This bathochromic shift was due to the lengthening of the polyene chain (1-D box). After the condensation, a new double bond was generated between the carbonyl carbon of the retinal and the methylene groups of pyridine-CN and malononitrile. Simulated UV/visible absorption spectra of 1, 2, and 3 were determined by using TDDFT calculations and are overlaid with the actual electronic spectra (Figure 9). Results showed good correlation between experimental and calculated spectra. In the case of 2, the calculated spectrum underwent a hypsochromic shift from 446 to 441 nm in its lowest energy π * π^* transition while 3 underwent a bathochromic shift from 464 to 487 nm. Calculations revealed that the lowest energy transition occurred from the HOMO to LUMO in both 2 and 3 with an energy gap of 441 nm for the 2 and 489 nm for 3. Experimentally, two other major bands were observed in the spectra of both 2 and 3. For 2, a weak absorption band was also observed near 290 nm while a similar band was observed in the spectrum of 3 centered at 285 nm. These bands (Figure 9) correlated with the calculated 299 and 284 nm bands, respectively.

As expected, the polyene chain is the major contributor to the lowest-energy transitions. The HOMO of **2** (Figure 4) shows the electron density as located on the polyene chain while the LUMO shows some electron density has shifted to the pyridyl side increasing the conjugative ($\pi \rightarrow \pi^*$) behavior between the polyene and the pyridyl group. The HOMO of **3** is spread out over the polyene chain, the dicyano group, and the β -ring. Some p-orbital contribution in the case of methylene carbon is also observed. The LUMO, on the other hand, had a more distorted conjugated π -bonding system with its electron density shifted more toward the dicyano group.

As shown in Figure 9, the simulated UV/visible spectra obtained with TD-DFT calculations gave rise to four distinct theoretical bands in 2 while three bands were calculated for 3. Table 7 lists selected transitions, their corresponding oscillator strengths, and the major molecular orbitals that contribute in each transition.

The HOMO to LUMO transition of **2** has high oscillator strength in agreement with its high absorption coefficient and is the predominant peak calculated in the UV-visible spectrum with its maximum centered at 442 nm. The other calculated peaks merge pairwise into the peaks shown in Figure 9. For example, the calculated peaks at 305 and 299 nm when added together appear as one peak. The calculated peak at 299 nm gave oscillator strength of 0.23. Under this band lie the following transitions: HOMO \rightarrow L+1, HOMO \rightarrow L+3, and H-1 \rightarrow LUMO.

The calculated UV/visible data of **3** are also listed in Table 7. The HOMO–LUMO transition dominates with high oscillator



Figure 7. Raman spectra of 2 and 3.

TABLE 5: Oxidation Electrode Potentials of Retinoids^a

compd	<i>E</i> (V)
all-trans-retinal	1.10
2	0.78
3	0.98

^a 0.1 M TBAClO₄ in acetonitrile.

TABLE 6: UV/Visible data of $S_0 \ ^1\!A_g \to S_2 \ ^1\!B_u$ transition in 1, 2, and 3

compd	$E(\lambda_{\max})$ (exptl)	$\varepsilon \ (M^{-1} \ cm^{-1})$	$E(\lambda_{\max})$ (calcd)
1	382	44000	408
2	446	37673	442
3	464	86800	487

strength 1.5 times greater than the others. Two peaks also are observed located near the other calculated bands of high oscillator strength. The theoretical peak observed at around 284 nm has oscillator strength of about 0.14 and involves predominately the population of the L+1 state. This information can be related to symmetry adapted orbital labels deduced by using Group theory for naturally occurring retinoids and carotenoids. In general, the method uses A_g and B_u symmetry orbital labels deduced when symmetry operations in C_{2h} point group were applied to β -carotene rather than treating it with π (π^*) labels.



Figure 8. Cyclic voltammogram of 2 and 3.



Previous studies also showed that this approach can be extended to nonsymmetric polyene chains. $^{1,9-22,47-52}$

The electronic energy level diagram proposed for β -caroteness based on C_{2h} symmetry is shown in Figure 10. Direct absorption occurs from the S₀ (1 ¹A_g) \rightarrow S₂ (1 ¹B_u)² state. Vibrational relaxation and internal energy conversion occurs to the (2 ¹A_g) state from which emission takes place to the (1 ¹A_g) state. Previous calculations (semiempirical) have shown that the ¹A_g \rightarrow ¹B_u transitions in polyenes have high molar extinction coefficients.² The HOMO \rightarrow LUMO transitions of **2** and **3** located at 442 (f = 1.8) and 487 nm (f = 1.5), respectively, correspond to this criterion.

The optical transition at $\sim 280-290$ nm has been assigned as 1 A_g \rightarrow 3 A_g and labeled the "*cis*-peak" corresponding to perceived photoinduced *cis-trans* isomerization. From DFT calculations, this corresponds to the HOMO to LUMO+1 transition for **2** located at 299 nm and for **3** located at 284 nm.

Emission Studies. The emission properties of **2** and **3** were collected at 77 K; room temperature emission for both was weak. Population of this first excited $(2 \ ^{1}A_{g})$ state at 77 K by internal conversion resulted in an emission band at lower energy (λ_{em} for **2** = 583 nm and λ_{em} for **3** = 500 nm) as shown in Figure 11. One interesting feature valid for both compounds is that more intense emission occurred upon excitation at higher





Figure 9. Experimental and calculated UV/visible data for 2 and 3.

TABLE 7: Calculated UV/Visible Data for 2 and 3

		2			3
$\frac{\lambda}{(nm)}$	f	major contributors	λ (nm)	f	major contributors
442	1.8130	HOMO → LUMO	487	1.4752	HOMO → LUMO
337	0.2685	$H-1 \rightarrow LUMO$ HOMO $\rightarrow L+1$	374	0.6686	$H-1 \rightarrow LUMO$
327	0.0014	$H-2 \rightarrow LUMO$	330	0.0547	$H-2 \rightarrow LUMO$ HOMO $\rightarrow L+1$
305	0.0069	$H-3 \rightarrow LUMO$	284	0.1392	$HOMO \rightarrow L+1$ $H-2 \rightarrow LUMO$ $H-1 \rightarrow L+1$
299	0.2312	HOMO \rightarrow L+1 HOMO \rightarrow L+3 H-1 \rightarrow LUMO	265	0.0058	$H-3 \rightarrow LUMO$ $H-1 \rightarrow L+1$
279	0.0029	$\begin{array}{l} \text{HOMO} \rightarrow \text{L+2} \\ \text{HOMO} \rightarrow \text{L+3} \end{array}$	259	0.0184	$H-1 \rightarrow L+1$ HOMO $\rightarrow L+2$ H-3 $\rightarrow LUMO$
265	0.1569	$H-4 \rightarrow LUMO$ $H-6 \rightarrow LUMO$ $HOMO \rightarrow L+3$	255	0.0005	$H-4 \rightarrow LUMO$ HOMO $\rightarrow L+2$

wavelengths ($\lambda_{ex} = 290$ nm in **2** and $\lambda_{ex} = 280$ nm in **3**) rather than at the highly intense visible band. These data can be compared to the emission behavior of *all-trans*-retinal determined in our laboratories. Excitation at 380 nm resulted in emission at 570 nm. The emission intensity increased 50-fold at 77 K. The quantum yields of emission for *all-trans*-retinal determined in the lab with use of eq 1 at room temperature and 77 K are 0.001096 and 0.04465, respectively. The quantum yield compares favorably to that for **2** (0.005465) and **3** (0.005371) at 77K.

The excitation spectra peaked at 355 nm for 1, 445 nm in 2, and 410 nm for 3. However, according to the Franck–Condon principle, excitation occurs vertically to higher vibronic states of the ${}^{1}B_{u}$ state followed by internal conversion to the $2{}^{1}A_{g}$ excited state, which then leads to vibrational relaxation followed by fluorescence emission back to the ground (1 ${}^{1}Ag$) state. Emission lifetimes in all three cases were more rapid than 5 ns, which is the pulse width of our nanosecond laser.

Summary

Two new derivatives of *all-trans*-retinal synthesized via acidcatalyzed Knoevenagel condensation reaction, one containing a pyridine and a cyano substituents (15,15'-cyanopyridylretinal, 2) and the other containing two cyano substituents (15,15'-



Absorbance

Figure 10. Energy diagram for 2 and 3.

dicyanoretinal, 3), retained their *trans* geometry as determined by X-ray diffraction for each compound, but the chains were bowed. Molecular orbitals determined for the compounds by Density Functional Theory revealed that the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) were located primarily on the polyene chain and the energy gap between them was consistent with the observed optical spectrum with maxima located at 442 nm of 2 and 487 nm of 3. Optical transitions deduced from Time Dependent Density Functional Theory calculations correlated with experimental results and were interpreted based on the group theoretical approach as previously applied to β -carotene, with the lowest energy absorption in the visible region occurring from the ground state 1 ${}^{1}A_{g}$ (HOMO) \rightarrow 1 ${}^{1}B_{u}$ (LUMO) excited state. Low-temperature (77 K) emission observed at 583 nm of 2 and 500 nm of 3 were assigned to decay from the 2 ${}^{1}A_{g}$ state to its 1 ¹A_g ground state. TDDFT calculations further reveal that the electronic transitions in the 280-290 nm region are HOMO to LUMO+1 (1 ${}^{1}A_{g} \rightarrow 3 {}^{1}A_{g}$) transitions and most likely are associated with the "cis" peak, which is associated with photoinduced "*cis*-*trans*" isomerization in β -carotenes.



Figure 11. (a) Low-temperature (77 K) emission spectra of 2 and (b) low-temperature (77 K) excitation (red line) and emission (black line) spectrum in 3.

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Supporting Information Available: Tables of Cartesian coordinates and excited states for 1-3 and CIF files for 2 and 3. This material is available free of charge via the Internet at http://pubs.acs.org.

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