This is the first measurement of the rates and barriers to electron transfer in these iron perovskite mixed-valence systems. These systems are structurally similar to the high $T_c$ superconductors, and the information about the mixed-valence metal–oxide–metal interactions may be useful in understanding the behavior of the YBaCuO systems. This research is being extended to lower dopant levels in order to decrease conductance, separate the Fe(IV) sites, and approach the electronic structure of systems more like the well understood parent compound.[6]

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**Registry No.** $La_{1-x}Sr_xFeO_3$ ($x$ = 0.1), 108601-52-1; $La_{1-x}Sr_xFeO_3$ ($x$ = 0.2), 109546-91-0; $La_{1-x}Sr_xFeO_3$ ($x$ = 0.3), 107121-72-2.

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# Preparation and Isolation of Polyenes Containing Up to 15 Double Bonds

Konrad Knoll, Steven A. Krouse, and Richard R. Schrock*

*Department of Chemistry 6-331*
*Massachusetts Institute of Technology*
*Cambridge, Massachusetts 02139*

*Received February 1, 1988*

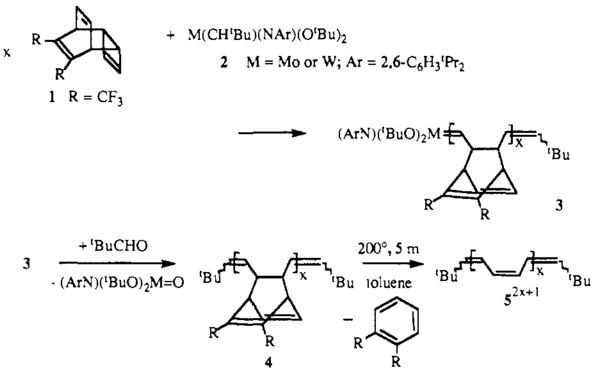
Conjugated polyene chains are important components of natural products[1] and are thought to be one of the most important features of polyacetylene.[2] Isoprenoid polyenes containing up to 19 double bonds in the backbone are known,[3] but no polyene having an unsubstituted backbone longer than a 10-ene appears to have been prepared.[4] It would be highly desirable to prepare well-characterized polyenes containing 10–20 double bonds in an unsubstituted backbone in order to address a variety of questions, inter alia those concerning excited states in polyenes[4c] and the nature of polyacetylene. Here we describe the preparation and isolation of individual polyenes containing as many as 15 double bonds by a controlled ring-opening polymerization.

**Table I.** $^{13}$C NMR Chemical Shifts for the Olefinic Carbon Atoms in **a** Isomers[13] of Several Di(*tert*-butyl)-Capped Polyenes (in $CDCl_3$) and One **b** Isomer[a]

| $\mathbf{5^{7}a}$ | $\mathbf{5^{9}a}$ | $\mathbf{5^{11}a}$ | $\mathbf{5^{7}b}$ |
|---|---|---|---|
| 147.86 | 148.01 (+0.15)[b] | 148.05 (+0.04) | 146.74 |
| 131.05 | 131.25 (+0.20) | 131.32 (+0.07) | 133.86 |
| | **130.39** | 130.57 (+0.18) | 133.27 |
| | | **130.29** | 132.93 |
| 129.84 | 129.75 (−0.09) | 129.70 (−0.05) | 132.37 |
| | | **129.58** | 131.15 |
| | **129.48** | 129.41 (−0.07) | 125.52 |
| 129.18 | 129.12 (−0.06) | 129.05 (−0.07) | |
| 128.27 | 128.21 (−0.06) | 128.19 (−0.02) | |
| 127.65 | 127.62 (−0.03) | 127.61 (−0.01) | |
| 120.57 | 120.56 (−0.01)[c] | 120.55 (−0.01) | |

[a] Estimated error ±0.005 ppm. The value in parentheses is the change in chemical shift relative to the shorter **a**-type polyene, and the boldface figures are the two chemical shifts for the four additional carbon atoms in the longer **a**-type polyene. Correlation of the 130.39 and 129.48 resonances in $\mathbf{5^{9}a}$ with the 130.57 and 129.41 resonances in $\mathbf{5^{11}a}$ (respectively) should be regarded as tentative. [b] $J_{CH}$ = 153 Hz. [c] $J_{CH}$ = 154 Hz.

Feast[5] has discovered that tricyclo[4.2.2.0$^{2,5}$]deca-3,7,9-trienes (e.g., the 7,8-bis(trifluoromethyl) derivative **1**; eq 1) and related molecules can be ring-opened by classical olefin metathesis catalysts[6] to give a polymer from which an arene is ejected upon heating to give polyacetylene. We have developed catalysts of the type M(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$(M = Mo or W; Ar = 2,6-$C_6H_3$-*i*-$Pr_2$) that will ring-open polymerize norbornenes in a controlled manner[7a,b] and now find that they can be used to ring-open polymerize (more accurately oligomerize) **1** in a controlled manner (eq 1).[8] Treating **3** with pivaldehyde gives the metal-free oligomer **4** via a Wittig-type reaction (eq 2).[9] Heating **4** to 200 °C for 5 m in toluene in a glass bomb yields a deep red solution, 90–95% of the contents of which is soluble in pentane. The most abundant polyenes[10] ($\mathbf{5}^{2x+1}$; $x$ = 3–7) having $2x + 1$ double bonds capped at each end by a *tert*-butyl group ($\mathbf{5}^{7}$–$\mathbf{5}^{15}$) can be isolated by chromatography on silica gel at −40 °C under dinitrogen in high yields[8] relative to theory.[10] The polyenes become increasingly unstable to air (a solution of $\mathbf{5}^{15}$ is rapidly decolorized) and thermally unstable in concentrated solution or in the solid state (after several days in the absence of air in the solid state



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(3) β-Carotene, one of the longest and most important of the naturally occurring polyenes, is an 11-ene isoprenoid.[1] The longest synthetic isoprenoid is "Dodecapreno-β-carotene", a 19-ene, obtained by derivatizing natural isoprenoids, see: Karrer, P.; Eugstler, C. H. *Helv. Chim. Acta* **1951**, *34*, 1805.

(4) A number of reviews are available.[4a–c] The longest well-characterized polyenes containing an unsubstituted backbone are 10-enes.[4d,c] Longer polyenes (e.g., the diphenyl-capped 15-ene[4a]) have been claimed,[4a,f] but no conclusive data were provided. Di(*tert*-butyl)-capped polyenynes containing up to 30 carbon atoms have been reported.[4g] (a) Kuhn, R. *Angew. Chem.* **1937**, *34*, 703. (b) Yanovskaya, L. A. *Russ. Chem. Rev.* **1967**, *36*, 400. (c) Hudson, B. S.; Kohler, B. E.; Schulten, K. In *Excited States*; Lim, E. C., Ed.; Academic Press: New York, 1982. (d) Bohlmann, F.; Mannhardt, H.-J. *Chem. Ber.* **1956**, *89*, 1307. (e) Sondheimer, F.; Ben-Efraim, D. A.; Wolovsky, R. *J. Am. Chem. Soc.* **1961**, *83*, 1675. (f) Nayler, P.; Whiting, M. C. *J. Chem. Soc.* **1955**, 3037. (g) Wudl, F.; Bitler, S. P. *J. Am. Chem. Soc.* **1986**, *108*, 4685.

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(8) Full details are available as Supplementary Material.

(9) The fact that the retro Diels–Alder reaction is occurring at 25° prevents accurate characterization of **4** by GPC methods. GPC studies at −17° of polyacetylene precursor polymers prepared with classical catalysts showed polydispersities to be between 2 and 3, see: Harper, K.; James, P. G. *Mol. Cryst. Liq. Cryst.* **1985**, *117*, 55.

(10) If we assume that initiation is the same rate or faster than propagation, the yields predicted by the Poisson equation (assuming a pyrolysis yield of 100%) are 3.4% ($\mathbf{5}^{5}$), 8.4% ($\mathbf{5}^{7}$), 14% ($\mathbf{5}^{9}$), 18% ($\mathbf{5}^{11}$), 18% ($\mathbf{5}^{13}$), 15% ($\mathbf{5}^{15}$), 11% ($\mathbf{5}^{17}$), 6.5% ($\mathbf{5}^{19}$), and 3.6% ($\mathbf{5}^{21}$).

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5–10% of **5**$^{15}$ cannot be redissolved in pentane).

Mass spectra and UV–vis spectra of each polyene are what might be expected on the basis of what is known for isoprenoids[1] and synthetic polyenes.[4] For example, the parent ion is the most intense with peaks for the doubly charged ions becoming significant for the longer polyenes, while the lowest energy transition[4c] ($^1B_u \leftarrow {}^1A_g$) in the UV–vis spectra is solvent dependent and red shifts with increasing chain length.[8]

$^{13}$C NMR spectra of samples of **5**$^7$, **5**$^9$, and **5**$^{11}$ show them to consist of ~75% of a single relatively symmetric isomer ($C_{2h}$ or $C_{2v}$) having 7, 9, or 11 olefinic resonances, respectively. The chemical shifts for **5**$^7$**a**, **5**$^9$**a**, and **5**$^{11}$**a** (**a** implies this major isomer) are listed in Table I. It should be noted that the chemical shift of the innermost carbon atoms in the chain in this isomer appear to be converging upon 130 ppm, a chemical shift close to that observed in *cis*-polyacetylene (128 ppm in the solid state).[11] Preliminary heteronuclear and homonuclear (H/H) correlation experiments suggest that the first olefinic carbon atom in the chain in the **a** isomer gives rise to the resonance at ~140 ppm, while the second gives rise to that at ~120 ppm.[13] Irradiation into the formally all-trans forbidden transition (the so-called cis band 140 nm above the origin of the $^1B_u \leftarrow {}^1A_g$ transition) in **5**$^7$ yields a material whose $^{13}$C NMR spectrum shows it to consist of >90% of another isomer (**5**$^7$**b**, Table I). On the basis of the observation that **5**$^7$**b** appears to be significantly less soluble and more crystalline than **5**$^7$**a** and on the basis of a characteristic strong, well-resolved, red-shifted UV–vis spectrum, we propose that **5**$^7$**b** is the all-trans isomer.

Several pieces of evidence suggest that the di(*tert*-butyl)-capped polyenes containing 17 or more double bonds are relatively unstable under the experimental conditions we have employed so far. First, significant amounts of **5**$^{17}$ and **5**$^{19}$ should be formed.[10] Second, attempts to prepare a distribution of longer polyenes by using 10 equiv of **1** gave only a reduced yield of qualitatively the same distribution of polyenes as that obtained employing 5 equiv of **1**. Third, from qualitative observations the longer the polyene the more extensively it decomposes to give pentane-insoluble material. We speculate that insoluble material results from cross-linking and that higher polyenes cross-link more readily. We hope to prepare longer polyenes by employing the parent tricyclo[4.2.2.0]deca-3,7,9-triene, since the retro Diels–Alder reaction in the polymer prepared by ring opening proceeds under relatively mild conditions.[5]

We believe that polyenes prepared by controlled ring-opening metathesis polymerization will help fill a significant gap in our knowledge of this important class of molecules. A valuable feature of the method is the ability to control the nature of at least one end group in the Wittig-like capping reaction. Extensions of such studies may allow us to prepare molecules with unusual nonlinear optical properties.[12]

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**Supplementary Material Available:** Full details of the preparation and isolation of the polyenes and partial spectroscopic data (1 page). Ordering information is given on any current masthead page.

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(12) *Nonlinear Optical Properties of Organic Molecules and Crystals*; Chemla, D. S.; Zyss, J., Eds. Academic Press, Inc.: New York, 1987; Vol. 1 and 2.

(13) **Note Added in Proof.** Homo- and heteronuclear correlation experiments suggest that the **a** isomer has a *trans(cis,trans)$_n$* configuration ($n$ = 7, 9, 11) as a result of stereoselective initiation, propagation, and capping reactions.

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## Phosphorescence Spectra of Bacteriochlorophylls

Larry Takiff and Steven G. Boxer*

*Department of Chemistry, Stanford University*
*Stanford, California 94305*

*Received December 29, 1987*

We wish to report phosphorescence spectra of the lowest triplet state of a number of bacteriochlorophylls (BChls) which provide the first accurate values for the triplet state energies of these chromophores. There have been many previous attempts to estimate the triplet state energies of bacteriochlorins motivated by the possible importance of triplet states in photosynthesis, the utility of these chromophores as sensitizers and quenchers of singlet oxygen, model studies of electron transfer, and intrinsic theoretical interest in the excited state energies of extended conjugated macrocycles.[1]

These observations were made possible by the recent development of liquid nitrogen cooled germanium photodiode detectors which are highly sensitive in the 800–1800 nm region. We recently reported phosphorescence spectra of photosynthetic reaction centers (RCs)[2] and have used identical methods in the present study. The absorbance, fluorescence, and phosphorescence spectra of BChl *a* are shown in Figure 1 and are typical of the spectra we obtain. Table I summarizes the results for several compounds. Luminescence decay kinetics were compared with the triplet lifetimes measured by transient absorption spectroscopy and were found to be the same within the experimental error.[3] The high sample concentrations and excitation light intensities required to observe this weak phosphorescence preclude the measurement of excitation spectra, as the luminescence intensity is not proportional to the sample absorbance under these conditions. The fluorescence quantum yield of BChl *a* is about 0.21;[4] we estimate that the phosphorescence quantum yield is roughly $10^{-7}$ by comparison of the integrated intensities of the emission bands, and this is typical of the bacteriochlorins.

It is seen that the singlet–triplet splittings of BChls are about the same as those measured for chlorophylls. The widths and shapes of the phosphorescence bands are about the same as their lowest energy absorbance and fluorescence bands. We find very little difference in the phosphorescence maxima of 5- and 6-coordinate BChl *a*, in contrast to those reported for Chl *a* (Table I, footnote i).[5]

These triplet energies may have important implications for triplet energy transfer from the BChl dimer to carotenoids in the

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(1) Connolly and co-workers (Connolly, J. S.; Gorman, D. S.; Seely, G. R. *Ann. N.Y. Acad. Sci.* **1973**, *206*, 649–669) estimated a $^3$BChl *a* energy of 5300–6100 cm$^{-1}$. Krasnovskii concluded that the energy of $^3$BChl *a* might be slightly higher than that of oxygen in its $^1\Delta_g$ state (7882 cm$^{-1}$) (Krasnovskii, A. A., Jr. *Photochem. Photobiol.* **1979**, *29*, 29–36). Song (Song, P. S. *Am. Chem. Soc. Symp. Adv. Chem. Plant Pigments*; Academic Press: New York, 1970; pp 33–74) calculated the energy of $^3$BChl *a* to be 7100 cm$^{-1}$. Weiss (Weiss, C. *J. Mol. Spectrosc.* **1972**, *44*, 37–80) predicted a value of 5600 cm$^{-1}$ for bacteriochlorin. Petke et al. (Petke, J. D.; Maggiora, G. M.; Shipman, L. L.; Christoffersen, R. E. *Photochem. Photobiol.* **1980**, *32*, 399–414) calculated a value of 9752 cm$^{-1}$ for ethylbacteriopheophorbide *a* and 7880 cm$^{-1}$ for ethylbacteriochlorophyll *a*. Sekino and Kobayashi (Sekino, H.; Kobayashi, H. *J. Chem. Phys.* **1987**, *86*, 5045–5052) estimated a triplet energy of 5200 cm$^{-1}$ for metallobacteriochlorin.

(2) Takiff, L.; Boxer, S. G. *Biochim. Biophys. Acta* **1988**, *932*, 325–334.

(3) For example, the $^3$BChl *a* lifetime at 77 K measured by transient absorption is 132 ± 1 μs and the phosphorescence lifetime is 124 ± 7 μs. Chlorin impurities absorbing around 680 nm are common contaminants of bacteriochlorins, but phosphoresce at much shorter wavelength with much longer lifetimes than the bacteriochlorins (Krasnovskii, A. A., Jr.; Romanyuk, V. A.; Litvin, F. F. *Dokl. Akad. Nauk SSSR* **1973**, *209*, 965).

(4) Tait, C. D.; Holten, D. *Photobiochem. Photobiophys.* **1983**, *6*, 201–209.

(5) It has been suggested that singlet fission may be important in the initial events of photosynthesis (Thurnauer, M. C.; Katz, J. J.; Norris, J. R. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 3270–3274. Merrifield, R. E.; Avakian, P.; Groff, R. P. *Chem. Phys. Lett.* **1969**, *3*, 155–157). This mechanism requires, however, that the $^3$BChl energy be less than or equal to half the excited singlet energy, which is ruled out by the data in Table I.