acyloxyalkyl radicals[16] is also compatible with the experimental data.

The proposed mechanism (Scheme II) shows that β-fission of **9a** to afford methyl benzoate competes directly with coupling with oxygen. Consequently, any structural change in R which increases the rate of β-fission should increase the yield of methyl benzoate. In fact, when the benzyl derivative **8b** was allowed to stand in air it was rapidly and quantitatively converted into a mixture of methyl benzoate and benzyl hydroperoxide. Apparently 9b, which is formally the structure of the intermediate in ipso attack of benzyl radicals on methyl benzoate, undergoes β-fission so rapidly that its coupling with oxygen cannot compete effectively.

The dependence of the rate of fission of **9** on the stability of the radical formed was also directly observed by ESR spectroscopy. UV irradiation of a mixture of **8c** and di-*tert*-butyl peroxide in the ESR cavity gave a good signal for **9c**, but similar treatment of **8b** gave only the signal for the benzyl radical.

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Electric Stimulus–Response Behavior of Liquid-Crystalline Viologen

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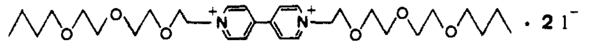
Molecular electronics seems to be a very promising new field of chemistry, since a variety of novel approaches have been successfully attempted.[1-3] We wish to report a novel stimulus–response system, in which liquid-crystalline (semiconducting) viologen iodide $V_{O6}{}^{2+}\cdot 2I^-$ (**1**), inserted between two In_2O_3–SnO_2



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electrodes, acquired ca 10^5-fold enhancement in electric conductivity, when an electric stimulus of 1–30 V was applied at 110 °C.

1 was prepared from bipyridyl and 3,6,9-trioxatridecyl iodide. Structure determination was performed by 400-MHz ^1H NMR ($CDCl_3$ δ from Me_4Si): 9.48 and 8.91 (AB quartet), 5.13 (triplet), 4.11 (α-CH_2), and others. Thermal analysis[5] and polarizing microscopic analysis showed a liquid-crystalline phase[6] at 63 °C(T_{C_1})–216 °C(T_{C_2}). **1** is a resistive material below T_{C_1} (L state, see Table I) ($\sigma = 10^{-11}$–(2×10^{-12}) Ω^{-1} cm^{-1} at 30 °C)[7] but becomes semiconducting ($\sigma = 4 \times 10^{-8}$ Ω^{-1} cm^{-1}) above T_{C_1} (M state).

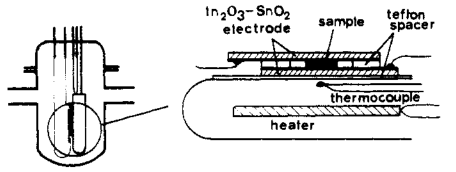


Figure 1. Apparatus and In_2O_3–SnO_2 sandwich cell. The thickness of the sample/spacer (0.1 mm) is grossly exaggerated.

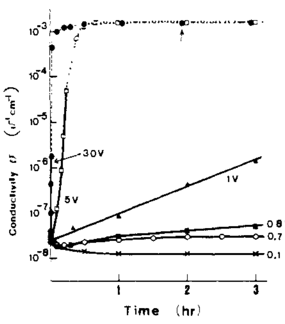


Figure 2. Dependence of conductivity (σ) vs. time plots on the applied voltage. Voltage was supplied through a variable resistor from a power source whose maximum output was set to 15 mA. Bald line represents the region where the indicated voltage initially applied was kept constant. In the broken line region, continuous voltage drop occurred to, e.g., 2.25 V, 15 mA at the arrow point.

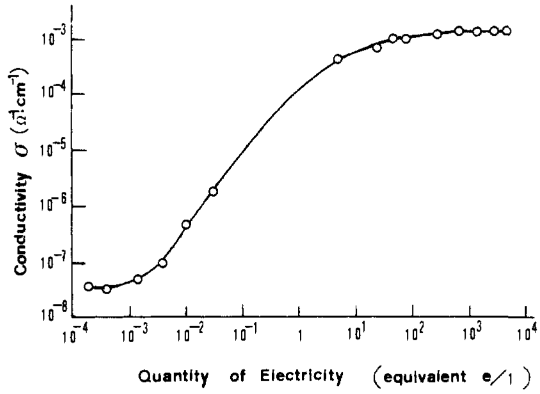
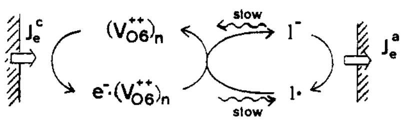


Figure 3. Conductivity change of **1** with the quantity of electricity passed through **1** at the liquid-crystalline state. At 110 °C initial voltage, 30 V, maximum current output was set to 15 mA.

Chart I



A remarkable further DC conductivity increase progressed autocatalytically, when a certain voltage, from 1 to 30 V, was applied to liquid-crystalline **1** of 0.1-mm thickness (Figure 1). The voltage–conductivity profile was very sensitive to the magnitude of the applied voltage (Figure 2). Except for the short induction period initially observed, the DC conductivity increment due to the electric stimulus was roughly proportional to the quantity of electricity passed through the liquid crystal (from $\sigma = 10^{-7}$ to 4.3×10^{-4} Ω^{-1} cm^{-1}) (see Figure 3), suggesting that a higher conductivity state, H, was produced by the electric current until saturation was attained at $\sigma = (1.2 \pm 0.2) \times 10^{-3}$ Ω^{-1} cm^{-1}. The σ value was ca. 2×10^{-3} Ω^{-1} cm^{-1}, when determined by the four-probe method. The H state, once formed, was kept for 3 days under Ar at room temperature without application of any "stimulating" voltage. The H state showed an electric response current of 23 μA, for example, on application of a "monitoring" voltage of 0.2 V. The state H was also stable toward further application of "monitoring" voltage (below 1 V) for 4 h at least, allowing 2900 electrons/1 viologen molecule to pass through.

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(7) Observed conductivity was varied depending on the solid layer preparation.

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Table I. DC Conductivity of **1**

T, °C	state and treatment	conductivity, Ω^{-1} cm^{-1}
30	solid untreated (L state)	(1×10^{-11})–(2×10^{-12})
110	liquid crystalline before "electric stimulus" (M state)	4×10^{-8} [a]
110	liquid crystalline after "electric stimulus" (H state)	$(1.2 \pm 0.2) \times 10^{-3}$ [b]

[a] Probably due to ionic current; see ref 4c. [b] Six independent experiments.

Below T_{C_1}, the conductivity enhancement was much smaller, or absent, and was not reproducible. Above T_{C_2}, a similar enhancement was observed but was followed by rapid electrolysis leading to carbonification. Therefore, the liquid-crystalline state is necessary for production and retainment of the H state.

A possible mechanism of the conductivity enhancement is accumulation of a $V_{06}{}^{\bullet+}$-type intermediate (probably together with I_2 and/or I), based on direct measurements of the electrode system at 535- and 550–560-nm absorption ascribable to $V^{\bullet+}Br^-$ and $V^{\bullet+}I^-$, respectively, in a highly polar medium. The amount of $V^{\bullet+}$ (30 V) was determined at 680 nm to be 0.13% (after 4 min), 0.71% (7 min), and 5.5% (30 min). A thin layer of the blue H-state solid cut out along the cathode surface was dissolved in carefully deoxygenated $CHCl_3$ and showed the typical $V^{\bullet+}$ absorption[8] at 605 nm (*A* = 0.31, amounting to 5% of **1** employed). However, the $V^{\bullet+}$ absorption very quickly disappeared ($\tau_{1/2}$, a few seconds) when *all* of the blue H-state solid was dissolved in carefully deoxygenated $CHCl_3$. These observations strongly suggest that a $V_{06}{}^{\bullet+}$ (and also a I_2/I) gradient was formed and that back electron transfer[9] regenerating $V^{2+}\cdot(I^-)_2$ took place readily in a solution but slowly in a liquid-crystalline or solid state (Chart I).

A conclusion then may be drawn that electrons are conducted via the less strongly bound electron on $V^{\bullet+}$, present probably in the form of aggregates (from the observed ESR broadening).

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Retinal Analogues with Locked 6–7 Conformations Show That Bacteriorhodopsin Requires the 6-*s*-*Trans* Conformation of the Chromophore

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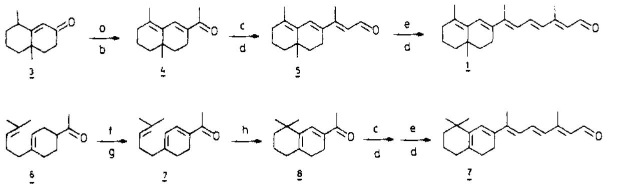
Bacteriorhodopsin (bR) functions as a light-driven proton pump in the purple membrane of *Halobacterium halobium*.[1,2] The chromophore is *all-trans*-retinal bound to the ε-amino group of lysine 216 via a protonated Schiff base (PSB) linkage.[3,4] It has recently been realized that the conformation about the C6–C7 single bond can play an important role in determining the spectroscopic properties of retinal-proteins.[5–7] In order to get more information how this conformation effects the properties of the chromophore both in vitro and in the protein, it is necessary to study bR analogues and model systems with a locked 6-*s*-*trans* and 6-*s*-*cis* chromophore. 8,16-Methanoretinal (**1**) is the retinal of choice in which the methylene group locks the polyene system in the 6-*s*-*trans* conformation with small or negligible changes in the electronic and steric factors. For comparison the interaction of a locked 6-*s*-*cis* analogue with bacterioopsin (bO) was also studied.

Scheme I.[a] Synthesis of 8,16-Methanoretinal (**1**) and 8,18-Methanoretinal (**2**)



[a] (a) Acetylene/*n*-BuLi/THF. (b) HCOOH. (c) $(EtO)_2POCH_2CN$/NaH/THF. (d) Dibal. (e) $(EtO)_2POCH_2C(CH_3){=}CHCN$/NaH/THF. (f) SO_2Cl_2/CCl_4. (g) DBN. (h) Concentrated H_2SO_4/toluene.

Table I. Absorption Maxima of Retinal Analogues, Their PSB's, and bR Analogues

analogue	retinal[a]	PSB[a]	bR	opsin shift,[b] cm^{-1}
all-trans-retinal	380 nm	440 nm	568 nm	5100
all-trans-**1**	400 nm	465 nm	564 nm	3800
all-trans-**2**	415 nm	485 nm	596 nm	3800

[a] Absorption maxima in methanol. [b] The opsin shift is the difference between the λ_{max} value of the protonated *n*-butylamine Schiff base of retinal analogue and that of the corresponding bR analogue.

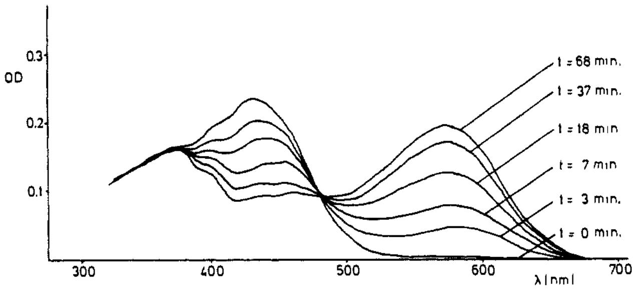


Figure 1. Formation of bR (**1**) analogue at 2 °C.

The synthesis of **1** and **2** is summarized in Scheme I. The starting bicyclic ketone **3** was prepared according to literature procedures.[8,9] Reaction of **3** with lithium acetylide at −60 °C and subsequent reaction with concentrated formic acid gives **4**,[10] which was extended by a Horner–Emmons type reaction[11] and Dibal reduction[12] to **5**. A Horner–Emmons reaction with the C_5-phosphonate and another Dibal reduction yielded retinal **1**. Retinal **2** was prepared starting from the Diels–Alder product of

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