0.11 in acetone solution;[8,9] therefore, about 14% of the dioxetane molecules which decompose lead to excitation of the europium complex to its fluorescent excited state. However, both the rate and yield of the reaction were found to be sensitive to solvent impurities[7] so the yield values in Table I are minimum values and the figure for $k_1 = 1.3 \times 10^{-4}$ sec^{-1} at 50° is a maximum value. Quenching of C* by II without excitation of II is also a possibility.

In earlier experiments involving energy transfer from I to various molecules that subsequently underwent a "photochemical" change, the excited state generation was calculated to be about 0.5–4%.[4b] The energy required for the "photochemical" reactions (~55–70 kcal) was considerably higher than the ~47 kcal/mol excitation of the europium compounds. The excitation energy available from C* is not known but possibly the lower value previously obtained was a result of the greater energy requirement.

It was recently reported that a similar compound, *cis*-1,2-diethoxydioxetane, yields on thermal decomposition the excited product with 100% efficiency, *i.e.* $\alpha = 1$, based on observation of the sensitized fluorescence of dibromoanthracene and diphenylanthracene.[10] We found that *cis*-1,2-diethoxydioxetane[11] yielded less than 1% as much light as trimethyldioxetane when thermally decomposed in the presence of II. This may be due in part to a higher value of k_3 for excited ethyl formate[10] than for the product of decomposition of I. The possibility of contamination of the diethoxydioxetane sample also cannot be discounted.

Acknowledgment. We thank the Public Health Service for its financial support (Research Grant No. 5 RO 1 NS-07868 from the National Institute of Neurological Diseases and Stroke).

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Received August 14, 1971

Raman Spectrum of the 11-Cis Isomer of Retinaldehyde

Sir:

Complementing the series of Raman spectra[1] of the more common isomers of retinal, we report the results on the 11-cis isomer,[2] which is the chromophore of rhodopsin in the dark-adapted retina.[3] The spectra of 3.5 m*M* solutions in ethanol, carbon tetrachloride, and EPA[4] were uniquely characteristic of 11-cis retinal, and indicated its stability against krypton-ion-laser irradiation at 17,600 cm^{-1} (yellow) or 15,455 cm^{-1} (red). Uv absorption measurements confirmed this observation. The spectrum in CCl$_4$ is shown in Figure 1, where it is compared with the spectra of *trans*- and 13-*cis*-retinals. The strength of the Raman emissions is due to the resonance enhancement phenomenon, as discussed previously.[1,5] The detectable lines correspond to vibrations of the conjugated carbon skeleton or to modes strongly coupled to it. The most intense line (at 1577 cm^{-1} for the 11-cis isomer) is identified as the ethylenic mode. Its frequency, $\bar{\nu}$(C=C), is sensitive to the conjugation (degree of delocalization) of the π electrons, as shown by solvent studies which indicate a linear decrease of $\bar{\nu}$(C=C) with increasing wavelength of the lowest singlet $\pi^* \leftarrow \pi$ transition[6] (which, in turn, is accepted as an indicator of degree of conjugation).[7] Table I shows that for CCl$_4$ solutions such a simple relation does *not* hold from isomer to isomer: the values of $\lambda_{\max}$ and $\epsilon(\lambda_{\max})$ both indicate that the π conjugation, strongest in the trans isomer, is markedly perturbed in the 11-cis isomer,[4] yet $\bar{\nu}$(C=C) for the 11-cis isomer is very close to the respective value in *trans*-retinal. The same situation holds true in the two other solvents. This result is a consequence of the fact that vibrational frequencies are determined not only by the force constants (through which $\bar{\nu}$(C=C) depends on conjugation) but also by molecular geometry. Changes in the latter by cis isomerization at the 11–12 double bond have a stronger influence on $\bar{\nu}$(C=C) than the corresponding decreased conjugation. Table I also shows that the intensity of the "ethylenic mode," when measured against the CCl$_4$ standard, is not proportional to $\epsilon^2(\lambda_{\max})$. This indicates, in agreement with results for *trans*-retinal,[6] that the formula for the Raman excitation spectrum contains terms other than the ones contributed by the lowest $^1(\pi\pi^*)$ state. These other terms, which vary from isomer to isomer, probably are cross-products of $^1(\pi\pi^*)$ terms and some $^3(\pi\pi^*)$ terms, the latter being more sensitive to isomeric configuration than those contributed by the singlet state.

Table I. Comparison of the First $^1(\pi^*\pi)$ Transition $\lambda_{\max}$ (nm) with the Ethylenic Mode Frequency, $\bar{\nu}$(C=C) (cm^{-1}), the Molar Extinction ϵ at $\lambda_{\max}$, and the Calibrated Intensity of the Ethylenic Mode I(C=C)/I(CCl$_4$) Relative to ϵ^2

Isomer	$\lambda_{\max}$, nm	ν(C=C),[a] cm^{-1}	$\epsilon \times 10^{-3}$	$\epsilon^{-2}I$(C=C)/I(CCl$_4$)
Trans	382	1578	47.6	4×10^{-10}
13-Cis	377	1584	38.8	6.6×10^{-10}
11-Cis	376	1577	26.4	19×10^{-10}

[a] ν(C=C) is the frequency and I(C=C)/I(CCl$_4$) is the calibrated intensity of the ethylenic mode. ϵ is the molar extinction at $\lambda_{\max}$.

Table II lists the major Raman transitions and their plausible assignments. As discussed in earlier work,[1,8] the chain modes of the isoprenoid polyene can be grouped in bands, in analogy with phonons in a unidimensional crystal. The frequency spread within an indi-

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Table II. Frequencies (cm^{-1}) of the Major Resonance-Enhanced Raman-Active Modes of the Retinal Isomers, in CCl_4 Solution, with Assignments in Terms of the Band Model

11-Cis	Trans	13-Cis	Assignment
965	965	968	Chain C–H bending
999	1006	1010	C–C stretch of C(*n*)–CH_3; $n = 9, 13$
1018			
		1116	
1126			
1145	1160	1163	
1155			
1207	1198	1192	Admixed band of chain C–C stretch and C–H bend
		1224	
	1268		
1272	1278	1278	
	1327	1310	
1343		1352	
1388	1386	1401	
1431	1445	1450	C–H bend of protons on methyls bound to C(9) and C(13)
1448			
1523			Ethylenic band, mainly chain C=C stretch
	1546	1552	
		1575 (sh)	
1577	1578	1584	

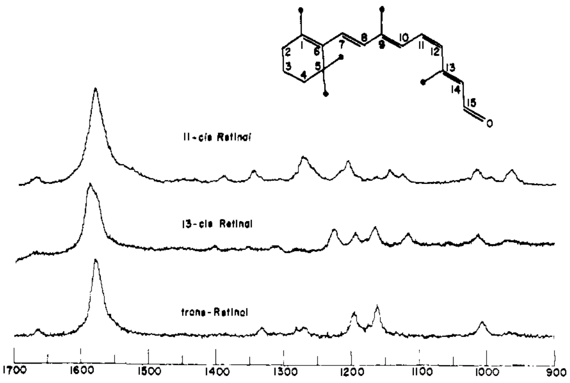

Figure 1. Raman spectra of three retinal isomers, 3.5 m*M* in CCl_4. The spectra of the 11- and 13-cis isomers were taken at an excitation frequency of 17,602 cm^{-1} (5680 Å). The trans isomer spectrum was obtained with 15,455-cm^{-1} (6471 Å) krypton-laser radiation. Scanning speed 20 cm^{-1}/min, integration time ~1 sec, spectral slit ~2 cm^{-1}. For this set of spectra there was no analyzer in the scattered beam; the incident radiation was polarized perpendicular to the scattering plane, and polarization measurements showed all lines essentially corresponding to diagonal Raman tensors. The structural formula given in the figure represents the conventional 11-cis, 12-*s*-trans isomer, which, according to recent X-ray data, is not that encountered in the solid, and which is probably only one of the possible equilibrium configurations in solution at room temperature (see W. Sperling, *Nature* (*London*), **232**, 187 (1971); B. Honig and M. Karplus, *ibid.*, **229**, 558 (1971)).

vidual band depends on interactions involving the parent vibration of the band. Clamped boundary conditions dictate a stationary pattern of vibrational modes, with an integral number of half-wavelengths ($\lambda/2$) matching the length of the conjugated segment of the chain. The bands derived from the C–C stretching and C–H in-plane bending parent modes are located in the 900–1300-cm^{-1} range, while the modes of the ethylenic band are in the 1400–1600-cm^{-1} range. The observed spectra of the various cis isomers reveal frequency shifts and large relative intensity changes in the 1000–1300-cm^{-1} range. In terms of the model, these features probably are determined by the position of the cis kink relative to the maxima of the modes which have zero amplitude at the end points of the chain. Cis isomerization may also remove the degeneracy of modes having equal frequencies and diverse wave vectors. Such degeneracies pertain to a zero-slope (flat) segment in the dispersion curve ($\bar{\nu} = \bar{\nu}(q)$; $q = 2\pi/\lambda$) of the band. A flat segment was calculated for the C–C stretching and C–H in-plane bending band near its frequency minimum which is at ~1160 cm^{-1} in *trans*-retinal.[9] The observed splitting of this line in the spectrum of 11-*cis*-retinal (Figure 1 and Table II) indicates that in *trans*-retinal it was at least triply degenerate.

An important result particular to the 11-cis isomer is the splitting of the lines which in *trans*-retinal are at 1010 and 1440 cm^{-1}. The 1010 mode has been assigned to the stretching of the C–C bond which connects chain carbons 9 and 13 with their respective methyl groups (Figure 1). The 1440-cm^{-1} mode, assigned to C–H bending within each methyl group, is resonance enhanced probably because of degeneracy with modes of the ethylenic band. In *trans*-retinal the methyl groups at positions 9 and 13 are unhindered, and their respective group vibrations are probably degenerate. The removal of this degeneracy in 11-*cis*-retinal by the hindrance of the methyl group attached to carbon 13 is a possible explanation of the splitting observed around 1010 and 1440 cm^{-1}. However, recent investigations[10,11] indicate that at room temperature 11-*cis*-retinal in solution exists as an equilibrium mixture of two conformations which differ in the C_{12}–C_{13} torsional angle (12-*s*-trans and 12-*s*-cis). Hence it is also possible that the splitting of the 1010- and 1440-cm^{-1} Raman lines results from the different frequencies contributed by the two conformations.

The question of whether the hindrance is relaxed at low temperatures in a glassy phase (as indicated by the rise in $\epsilon(\lambda_{max})$[4]) could not be tested in EPA glass because the Raman lines of the solvent masked the fingerprint modes of retinal. The ethylenic mode was observable and did not shift upon cooling to −125°.

In summary, we confirm the uniqueness of the Raman spectrum of each of the common mono-*cis*-retinal isomers, and thus indicate the usefulness of the spectra for monitoring isomerization reactions. The identification of the stereoisomers can be accomplished by relatively rapid scanning in the limited range of 1100–1300 cm^{-1}, even with far-red excitation (6740 Å). This would make possible the Raman study of rhodopsin and its less-stable bleaching intermediates.

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Received July 24, 1971

Molecular Structure of Palladium and Platinum Bis(ethylene-1,2-dithiolene). A Novel Metal–Metal Bonded Dimer

Sir:

The unusual properties and molecular structures of 1,2-dithiolene complexes have received considerable