$[P(Me)_3]_2[C_3(C_6H_5)_3]]^{+}$[7] and 2.06 and 2.10 Å in the [[*endo*- and [[*exo*-$C_4(C_6H_5)_4(OC_2H_5)]Pd(\mu_2\text{-}Cl)]_2$ complexes, respectively.[34a] The C—Cl bond lengths which average 1.715 (3) Å (six values, range 1.710–1.721) are typical of C—Cl distances found in many chloro-substituted olefins.[35]

The short C—C and C—Cl bond distances, the planarity of the C_3Cl_3 moiety, and its orthogonality to the Ni—Ni bond, are indicative of a completely delocalized $Ni_2(\mu_2\text{-}C_3Cl_3)$ fragment. One aspect of the bonding can be explained in terms of the modified Dewar-Chatt-Duncanson model[36] used to describe the bonding in dinuclear acetylene bridged complexes where the C—C vector of the acetylene triple bond (and consequently the π electron cloud) is orthogonal to the M-M vector. In the $[Ni_2(CO)_2(\mu_2\text{-}C_3Cl_3)(\mu_2\text{-}Cl)_2]$ complex the open three-carbon propenyl fragment C(1,2,3) with its π cloud is also positioned orthogonal to the Ni-Ni vector. However, this bonding rationale is not totally satisfactory since opening of the strained cyclopropenium ion results in a three-carbon fragment which possesses considerable electron density on the terminal carbon atoms, C(1) and C(3). A more in-depth molecular orbital analysis is required to rationalize fully all aspects of the delocalized $Ni_2(\mu_2\text{-}C_3Cl_3)$ bonding.

The preparation and isolation of this novel perchlorinated propenyl cluster complex extends our current ideas of the mode of coordination of cyclopropenyl and propenyl species from those involving only one metal atom as enumerated previously to binuclear and possibly polynuclear types of metal interactions. The oxidative addition adduct $[Ir(CO)Cl[P(CH_3)_3]_2[C_3(C_6H_5)_3]]^+$ cation[7] where a four-membered iridocycle is formed serves as an example of a mononuclear precursor to the binuclear complex reported here. It also suggests that the use of halosubstituted C_3X_4 and $C_3X_3^+$ species may prove a fruitful synthetic approach into perhalogenated organometallic complexes. We are currently pursuing synthetic work to probe the utility of these ideas.

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(14) $[Ni_2(CO)_2(\mu_2\text{-}C_3Cl_3)(\mu_2\text{-}Cl)]_2$: triclinic; $P1$; Delaunay reduced cell parameters are $a = 7.141$ (1), $b = 10.637$ (2), $c = 13.950$ (2) Å, $\alpha = 88.41$ (1), $\beta = 91.35$ (1), $\gamma = 104.58$ (1)°; $V = 1025.0$ Å^3; $\rho_{\text{obsd}} = 2.23$ vs. $\rho_{\text{calcd}} = 2.28$ g/cm^3 for $Z = 2$. The centrosymmetric $P1$ space group was suggested by the statistical distribution of the normalized structure factors calculated from a Wilson plot. The structure was solved by MULTAN and refined by full anisotropic least-squares analysis to $R_1(F) = 4.8\%$ and $R_2(F) = 6.1\%$ for the 2304 independent reflections with $I > 2\sigma(I)$.
(15) These two molecules are similar and minor variation in the bond distances and bond angles for the most part are attributable to slightly different crystal packing forces. Differences where significant are noted; otherwise average bond distances and angles for the two independent half-molecules are reported.
(16) The 0.016 Å difference between the two crystallographically independent Ni-Ni distances more than likely indicates that the ESDs of 0.001 Å noted are underestimates. Since the two molecular units are chemically equivalent, one may independently derive the magnitude of the likely errors by direct comparison of the chemically equivalent bonds. Such a procedure suggests that the true uncertainty in the Ni-Ni distance is ~0.005 Å.
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Sterically Hindered Isomers of Retinal from Direct Irradiation of the All-Trans Isomer. Isolation of 7-*cis*-Retinal[1]

Sir:

Wald, Hubbard, and Brown established that the all important 11-*cis*-retinal can be obtained by direct irradiation of the all-trans isomer in a dilute ethanol solution.[2] In a steady-state mixture, the amount of 11-cis was estimated to reach 25% of the combined isomer composition. They further showed in a simple and elegant experiment that from the photolysate all-trans, 13-cis, and 11-cis isomers can be isolated by fractional recrystallization.[2b] To the vision researchers this procedure remains the most direct route to small amounts of pure 11-*cis*-retinal.

The mechanistic details of the photoreaction have since been examined in great detail, but much confusion still exists. The product mixtures have been analyzed by UV spectroscopy,[3-5] thin layer chromatography (TLC),[4] and more recently by high pressure liquid chromatography (HPLC),[6] quantum yields determined under direct and sensitized irradiation condi-

Table I. Direct Irradiation of *all-trans*-Retinal. Product Distribution and Relative Quantum Yield

Solvent[a]	Primary products (relative quantum yield)[b]
	350-nm Irradiation[c]
n-Hexane	13-cis, 9-cis (1:0.28)
Ethanol	13-cis, 11-cis, 9-cis, 7-cis (1:0.81:0.24:0.04)
Acetonitrile	13-cis, 11-cis, 9-cis, 7-cis (1:1.9:0.70:0.27)
	440-nm Irradiation[d]
n-Hexane	13-cis, 9-cis (1:0.25)
Ethanol	13-cis, 11-cis, 9-cis, 7-cis (1:1.0:0.31:0.05)
Acetonitrile	13-cis, 11-cis, 9-cis, 7-cis (1:2.0:0.78:0.20)

[a] Reagent grade solvents without further purification. [b] Less than 10% of conversion. Average of three-five samples. Corrected for different absorbance of isomers at 254 and 360 nm. [c] Peak width 20 nm. [d] Peak width 30 nm.

tions[3-6] and triplet yields by microsecond[7] and nanosecond flash spectroscopy.[5,8] The triplet yield of *all-trans*-retinal in nonpolar solvents (such as *n*-hexane) is higher than in polar solvents such as methanol, but the reported values range from 0.5 to 0.7. The quantum yield of isomerization also appears solvent dependent, but again there is a large spread of reported values (e.g., in nonpolar solvents the quantum yield of trans to 13-cis varied between 0.04 and 0.2).[3,6] Even the question of the formation of the 11-cis isomer in alcoholic solvents appears to require further confirmation or scrutiny. Waddell et al.[6] reported that 13-*cis*-retinal is the only photoproduct from a methanol solution of *all-trans*-retinal. However, they noted that Wald et al.[2] carried out the experiment at a wavelength (>410 nm) different from theirs (350 nm); therefore the suggestion of a possible wavelength dependence of the isomerization reaction was made.[6] One may add that certain aspects of spectroscopic properties of retinal are indeed wavelength dependent.[9]

To this date there are no indications in the literature that the more hindered 7-cis isomers are present in the photomixtures. Their absence could be considered consistent with the one time commonly held notion that such sterically crowded compounds are unlikely to exist,[10] but, of course, four such retinal isomers have recently been prepared in our laboratory.[11]

In conjunction with the study of the photochemistry of the hindered 7-cis isomers,[12] we have reinvestigated the photoisomerization of *all-trans*-retinal in several solvents. In this paper we wish to report the portion of the results dealing with the formation of the hindered 11-cis and 7-cis isomers under direct irradiation. Some of the contradictory observations in the literature will be clarified and we will show that *the previously unnoticed 7-cis isomer is present in the photolysate in sufficient quantities for isolation.*

First we conducted the study in the two commonly used solvents: hexane and ethanol. Acetonitrile was also used as a solvent. It was not employed in previous direct irradiation studies, although its use was recently described in a triplet sensitized study.[6]

Irradiation was carried out on an optical bench equipped with a mercury arc lamp, a quartz lens, and a Schoeffel monochromator. Two different monochromator settings were used (350 and 440 nm). At a slit width of 2 μ, the average half-height width of the beam is 25 nm. Solutions were not deoxygenated.[13] Product mixtures were analyzed by HPLC with two UV detectors at 254 and 360 nm. The peaks were identified by comparison with reported retention times[14] and with those of authentic samples.

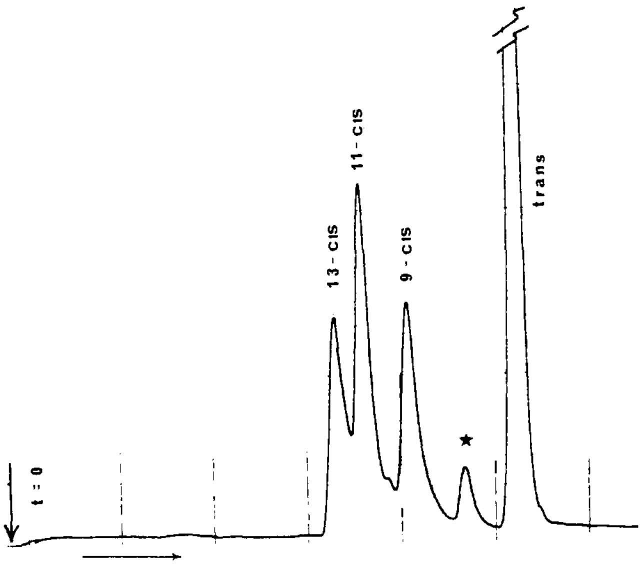

Figure 1. HPLC chromatogram of a mixture of retinal isomers obtained from direct irradiation of the all-trans isomer in CH_3CN. The peak with * was identified as being due to the 7-cis isomer (see text). Analytical conditions: Du Pont 830 lc equipped with Waters μ-Porasil column and Varian VARICHROM detector (360 nm).

The results summarized in Table I (after correction of different molar absorptivity of isomers at 360 nm) show that the initial product mixture in hexane is, as reported, mostly 13-cis, but in ethanol, in addition to 13-cis, 11-cis and 9-cis are also present in the initial product mixture at both wavelengths of irradiation. Furthermore, we noticed in the HPLC chromatogram (Figure 1) the appearance of a small peak. It never exceeded 1-2% of the total product mixture but interestingly it has a retention time identical with that of the hindered 7-*cis*-retinal.

When acetonitrile was used as the solvent, we were pleasantly surprised to find that (1) the minor peak in ethanol now approaches 6% of the total product mixture along with an increase of the amount of 11-cis and (2) the relative quantum yield of isomerization appears higher than in ethanol and with less degradation of retinal. The UV spectra of all product peaks were then recorded in the flow cell of the HPLC detector (Varian VARICHROM). First the spectra verified the assignment of the peaks corresponding to the 13-cis, 11-cis, and 9-cis isomers; further the spectrum corresponding to the minor peak is, one may safely say, that of a retinal geometric isomer and not of an overirradiated product. The structure of this minor component was unambiguously assigned when a solution of 35 mg of *trans*-retinal in 35 mL of CH_3CN was irradiated with light >400 nm (Corning 3-74 filter) and the product isolated by preparative HPLC separation.[15] A total of 0.78 mg of the minor product was collected.[16] Its ^1H NMR spectrum (XL-100, in $CDCl_3$) is identical with that of 7-*cis*-retinal:[17] δ 1.52 (s, 18-CH_3), 1.93 (s, 19-CH_3), 2.31 (s, 20-CH_3), 5.99 (d, 7-H), 6.11 ppm (d, 8-H) ($J_{7,8}$ = 11.3 Hz).

The maximum amount of the 7-cis among all of the retinal isomers during the course of irradiation in ethanol (as determined by HPLC analyses) is <2%. This amount would not be detectable by UV or TLC methods, and even by HPLC without authentic material its detection and identification would have been difficult. Therefore, it is not surprising that this hindered isomer was overlooked by previous workers. The reason why the 11-cis isomer was not reported to be a primary photoproduct[6] is not immediately obvious to us. Our method of analyses (HPLC) is essentially that of Waddell et al.[6] with the exception of the wavelength of detection. Waddell used exclusively the 350-nm beam while we used the 254- as well as the 360-nm beam, the 254-nm beam being four times more sensitive for detection of 11-cis. Also Waddell et al. carried out their irradiation in methanol, while Wald et al. used ethanol. To check for a possible solvent dependence we irradiated a sample of *all trans*-retinal in methanol. Again all four mono-cis products were detected during the early stage of irradiation. The ratios of 11-cis and 9-cis to 13-cis are 0.56 and 0.19, respectively (350-nm excitation), somewhat different from those in ethanol. Clearly our results show that 11-cis is formed in both alcoholic solvents and the results do not support the wavelength dependent explanation.[18]

Although we have yet to carry out experiments to elucidate the mechanistic details related to the formation of the 7-cis isomer, some comments on excited-state intermediates based on the limited information now available are perhaps appropriate. The formation of the hindered isomers appears to be favored in solvents of high dielectric constant (in which retinal also has low intersystem crossing efficiency).[8a,19] This is consistent with possible involvement of singlet, zwitterionic intermediates, as those suggested by Salem.[20] That the hindered isomers are formed along with 13-cis and 9-cis would further suggest that the twisted dipolar intermediates, once formed, do not interconvert. To confirm these tentative conclusions, and to have a better understanding of the solvent effect, more extensive studies with a large variety of solvents will have to be conducted.

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*Book Reviews**

Handbook for Chemical Technicians. By H. J. STRAUSS (Gould, Inc.). Edited by M. KAUFMAN (Electronic Writers and Editors, Inc.). McGraw-Hill Book Co., New York, N.Y. 1976. vii + 454 pp. $19.50.

The amount of information available to the chemist and chemistry technician is often overwhelming. In many cases, the usefulness of the data is limited by a lack of understanding as to how to use the data to arrive at a practical answer. The purpose of this handbook was to collect some of the most practical information and present it in a format intelligible to the average chmistry technician. The book includes ten chapters and a short subject index. The first two chapters present a detailed discussion of units and measurements, including extensive tables of data. Chapters 3 and 4 present a review of chemical fundamentals of organic chemistry. Chapter 7 discusses metals and alloys; Chapter 8 considers fluid mechanics, and Chapter 9 reviews a number of engineering operations. The last chapter is devoted to a discussion of safety practices for all types of operations. Each chapter is filled with useful information in the form of tables and graphs. Throughout the book, examples are provided as to typical problems which can be solved using the data included in the handbook. These examples are an especially valuable part of the book since they show precisely how to use the data presented in the numerous tables scattered throughout the book.

The author has prepared a highly practical handbook. Since it is a handbook, the material is highly condensed and must be read carefully. The handbook will prove of great value to the practical chemist as a one-volume source for most information of routine interest, although it will not replace the use of the larger reference volumes.

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Negative Ions. Third Edition. By H. S. W. MASSEY (University College London). Cambridge University Press, New York and London. 1976. xvii + 741 pp. $69.50.

This monograph contains a detailed and orderly account of the formation, stability, and properties of negative ions in gases; the methods, both experimental and theoretical, for investigating them; and the results of these investigations. Since the publication of the second edition in 1950, there has been great advancement, both theoretical and experimental, in the study of negative ions, and these are covered thoroughly in this edition. For example, the third edition has an extensive discussion of the formation of negative ions by radiative attachment and polar photodissociation, the use of lasers in negative ion formation, the study of autodetaching states of negative ions, collision processes involving negative-ion production and destruction, and the application of the most recent negative-ion data to problems of gases in planetary and stellar atmospheres as well as to trace analysis of halogenated pesticides.