ation of ArNOH· forms ArNO and 4-bromophenylhydroxylamine, which is reduced by four electrons from $ArNO_2$. The chloride analogue of Bamberger rearrangement[45] of the latter would give the observed 4-bromo-2-chloroaniline that is in the same state of oxidation as the hydroxylamine. The conversion by HCl of nitrosobenzene to 2,4-dichloroaniline[19] apparently does not occur under these weakly acidic conditions.

The recognition herein that second-order dependence on a reactant concentration for a photochemical reaction requires a quadratic expression and the treatment we have given it appear to be novel contributions. Indeed, whereas first-, second-, and third-order dependencies for ground-state reactions will appear as simple exponents of the concentration terms in the rate expression, for photochemical kinetics these dependencies appear in the Φ^{-1} expression in the form of binomial expansions, $(a + bx)^n$, where $x = [\text{reactant}]^{-1}$. This arises because each of the kinetically significant bimolecular partitionings along a photoreaction pathway will appear in the inverted quantum yield expression in the following form, $a + (b/[\text{reactant}])$.

Summary

We have elsewhere[17] presented evidence that photosubstitution of bromide ion by chloride ion in 3-bromonitrobenzene occurs by direct, heterolytic nucleophilic attack on the $^3\pi,\pi^*$ state. This reaction is first order in chloride ion, shows uncatalyzed reaction, and is catalyzed by acid, the catalysis being attributed to protonation of the π,π^* state. We conclude here that photosubstitution by chloride ion on 4-bromonitrobenzene involves electron transfer from chloride ion to the $^3n,\pi^*$ state as the primary process, the attachment of chloride at the para position occurring as an intermolecular reaction of an exciplex. This reaction is second order in chloride ion and is exclusively an acid-catalyzed process, the acid catalysis being attributed to protonative capture of the initial exciplex. The initial steps of this reaction can initiate efficient photoreduction by 2-propanol, whereas the heterolytic reaction occurs cleanly with no concomitant photoreduction in the presence of 2-propanol. Together these findings strongly support the postulate[1,15,16] that meta-to-nitro regioselectivity in nucleophilic aromatic photosubstitution on nitrobenzene derivatives reflects heterolytic bond changes, whereas para-to-nitro regioselectivity reflects electron transfer and radical coupling as the route to the σ complex.

These results, taken together, are grounds for qualifying the recently claimed[46] ubiquity of single electron transfer (SET) processes in organic reactions. The cited theoretical study[46] "sets out to demonstrate that all so-called two-electron (or polar) pathways actually involve the shift of a single electron and are far more closely related to the established SET pathways than has been recognized till now." If SET from the attacking nucleophile occurred in the meta-to-nitro photosubstitutions,[1-3,14,15,17] the regiochemistry would be controlled by the nitro aromatic radical, and bond formation would occur at the *ortho* or *para* carbons. This would make meta-to-nitro regioselectivity impossible, a conclusion at variance with the facts. We conclude that there is a real difference between the SET pathway and the heterolytic pathway in these photoreactions.

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Triene Photophysics and Photochemistry: Previtamin D₃

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Abstract: The origin of the wavelength dependent photochemical behavior of previtamin D₃ was investigated. The fluorescence spectrum and quantum yield of previtamin D₃ were determined at 302 and 307 nm, and both the intensity distribution and the fluorescence quantum yields were found to be independent of excitation energy. A large Stokes shift was observed which is consistent with an excited state torsional relaxation about the central double bond of the triene. The excited state displacement was reproduced by QCFF/PI calculations of the ground and excited states of a model compound. The excited state involved in the absorption and emission spectra is discussed.

Wavelength effects in solution photochemistry can arise from excited-state or ground-state properties.[1] This experimental variable has been studied in the photochemistry of polyenes, and it generally has been found that wavelength-dependent photochemistry arises from a variety of ground-state effects such as secondary reactions of the primary photoproduct,[2] independent excitation of conformational[3-9] and structural isomers,[10] and ex-

Table I. Quantum Yields of P_3 Conversion at Two Wavlengths

λ, nm	Pro₃	L₃	T₃
253.7	0.014	0.040	0.41
302.5	0.02	0.09	0.29

citation of ground-state complexes.[11,12] However, it has been suggested that wavelength dependencies may also result from the

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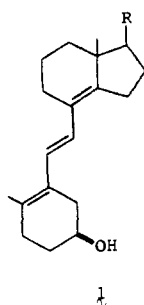(4) Dauben, W. G.; Rabinowitz, J.; Vietmeyer, N. D.; Wendschuh, P. H. *J. Am. Chem. Soc.* **1972**, *94*, 4285.

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Scheme I

$$R = \text{—}\curlyvee$$

T_3

Scheme II

Table II. Quantum Yields of P_3 Conversions at Five Wavelengths

λ, nm	Pro_3	L_3	T_3
295.0	0.04	0.06	0.43
297.5	0.04	0.06	0.42
300.0	0.04	0.08	0.36
302.5	0.04	0.09	0.27
305.0	0.08	0.18	0.29

involvement of more than one excited state or from the involvement of activation barriers in a single excited state. The latter processes permit new vibrational modes for relaxation into new minima on the excited state hypersurface.[7,13-15]

The effect of wavelength on the photochemical conversion of provitamin D_3 (7-dehydrocholesterol, Pro_3) to previtamin D_3 (P_3), thermally converted to vitamin D_3, has been studied because of the importance of yield maximization in the commercial production of the vitamin. A detailed study using light of different wavelengths (225–400 nm) for the formation of "potential vitamin D" found that 295-nm light was most effective.[16] More recently, a wavelength effect upon the four components in the previtamin D_3 (P_3) photostationary state (Scheme I) has been reported for two wavelengths (253.7 and 302.5 nm),[17] and the results are shown in Table I.

The relative percentage change in quantum yields for the case of the two electrocyclic ring closures to Pro_3 and L_3 is clearly larger than for the cis–trans isomerization to tachysterol_3 (T_3). It was concluded that it was not possible with these data to quantitatively assess the separate contributions of the ground-state and the excited-state properties to the wavelength effects observed.[17]

In 1982, the effect of excitation energy upon the P_3 photochemical stationary state was examined in our laboratories with greater wavelength resolution.[18] Using laser excitation wavelengths between 295 and 305 nm, the steady-state concentrations were determined, and the calculated quantum yields were reported,

as shown in Table II. From these results, it was concluded that the diminution in the quantum yield for the conversion of previtamin D_3 to its trans isomer tachysterol_3 with increasing wavelength was consistent with changes in absorbance in the wavelength region studied of the two conformations of P_3 (s-cis,s-trans and s-trans,s-trans) known to be involved in the cis–trans isomerization to form T_3.[19] The twofold increase in the quantum yields for the ring closure formation of provitamin D_3 and lumisterol_3 within an excitation range of 2.5 nm could not be attributed to a change in the absorbance of the s-cis,s-cis conformers which are assumed to be the conformations which undergo ring closure. A doubling of the absorbance value of the conformers within this short wavelength range would be required and such seems improbable since the molar extinction coefficient of P_3, itself, is decreased by 29% in the same wavelength range. It was suggested that the twofold increase was due to excited state effects of unknown origin.

A great amount of progress has been made in recent years toward the understanding of electronic excited states of polyenes. The research of Kohler and his co-workers has demonstrated in the case of octatetraene that the 2^1A_g state, which consists of a mixture of multiply excited electronic configurations, lies lower in energy than the 1^1B_u state which is primarily a π,π^* electronic excitation.[20-26] The effect of molecular geometry upon the spectroscopic properties has been observed by Andrews and Hudson in their studies of two rigid steroidal trienes, one in the s-trans,s-trans configuration and the other in the s-cis,s-trans configuration.[27] Application of the Strickler–Berg relation[28] to the absorption and fluorescence spectra was consistent for the s-cis,s-trans compound but not for the s-trans,s-trans compound. This inconsistency with the Strickler–Berg relation and the absence of a common absorbance and fluorescent origin for this latter compound led the investigators to the conclusion that the absorbing and emitting states were of different electronic character, namely the 1^1B_u and the 2^1A_g, respectively. The consistency of the Strickler–Berg relation and the overlap in the absorption and fluorescence spectra for the s-cis,s-trans isomer indicated that the 1^1B_u state of this triene was involved in both the absorption and emission. It was concluded that the state order of trienes depends on the chromophore geometry, mediated by alkyl substituent effects.

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More recently, Birge and his co-workers have reported the absorption, fluorescence, and two-photon excitation spectra of nonrigid isotachysterol (1), an all trans isomer of P_3.[29] From

R

OH

1

the fit of the observed spectra to the Franck–Condon profile calculated from semiclassical Gaussian wavepacket propagation theory, the authors concluded that the absorption and the fluorescence originate from different electronic excited states. The excited state origin of the fluorescence spectrum and the upper state in the two photon excitation spectrum were designated as 2^1A_g states for this nonrigid triene, a conclusion similar to that given for the rigid, s-trans,s-trans steroidal triene studied by Andrews and Hudson.[27]

Utilizing the fact that a triene chromophore has two close lying excited states, an electronic state model has now been devised to explain the excitation wavelength effect in the photochemical conversion of previtamin D_3 to provitamin D_3 and lumisterol$_3$. This model, which is consistent with the electronic excited state assignment discussed earlier,[27,29] is shown in Scheme II. The close proximity in energy of the two lowest electronic excited states in the proposed model is consistent with results calculated for 1,3,5-hexatriene by Nascimento and Goddard.[30] Since the triene moiety is nonplanar and unsymmetrically substituted, no symmetry labels will be used in connection with the ground and excited electronic states, and only S_0, S_1, and S_2 will be used.

With this model, since the quantum yields for ring closure are increasing with decreasing excitation energy, the origin of the wavelength effect could be a reduction in the relative rate of a nonphotochemical excited state process with decreasing excitation energy, assuming that the other individual rate constants do not vary with excitation energy. At excitation wavelengths shorter than 302.5 nm, excitation occurs to the S_2 electronic excited state. This state can either undergo radiative or nonradiative relaxation to the ground state ($k_{2,0}$) or relaxation to the S_1 electronic excited state ($k_{2,1}$). From the S_1 state, the molecule can undergo either relaxation to the ground electronic state ($k_{1,0}$) or undergo photochemical relaxation to form Pro$_3$ and L_3 ($k_{2,1}$ or k_{P_1}). At longer excitation wavelengths, the S_1 state can also be directly populated and therefore, the relaxation processes of the S_2 state are involved to a lesser extent in the overall photochemical conversion to Pro$_3$ and L_3.

In order to test this proposed excited state model, a study of the fluorescence spectrum of P_3 was undertaken. If, under the proper conditions, both the S_2 and S_1 states can undergo radiative relaxation to S_0, then the overall appearance of the fluorescence spectrum should change with decreasing excitation energy as the S_2 state is no longer highly populated. If this change is not observed, so that the observed fluorescence arises solely from the lower electronic excited state, then the fluorescence quantum yield should parallel the photochemical quantum yields of ring closure with a corresponding increase with decreasing excitation energy.

To gain more information about the excited state of P_3, the low-temperature absorption spectroscopy of the ground state and theoretical calculations related to the ground and excited states were also studied.
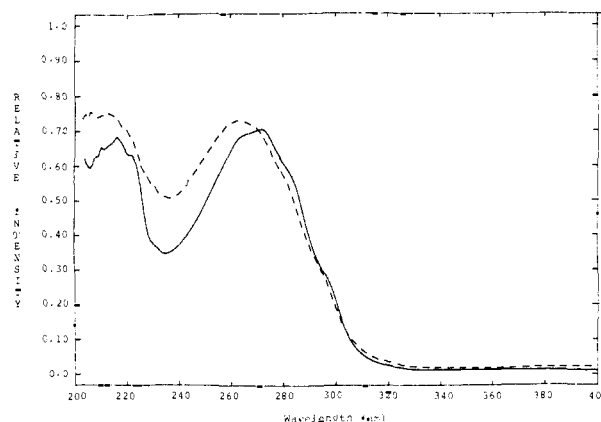
Figure 1. Previtamin D_3 absorption measured at 300 K (dashed) and 77 K (solid) (corrected for solvent contraction).

Results and Discussion

A. Low-Temperature Absorption Spectroscopy. In 1981, Gielen[31] reported that the absorption maximum of previtamin D_3 in solution shifted 9 nm to longer wavelength upon cooling the sample from ambient temperature to 77 K. This bathochromic shift was interpreted as evidence for an increase in the planarity of the triene moiety at lower temperature, resulting in an increase in the conjugation of the π-electronic system and a corresponding lowered electronic transition energy. In 1983, Maessen,[31] using the UTAH program,[32] calculated that the dihedral angle for the C_5–C_6 single bond in the minimal energy conformations of the s-cis,s-cis conformers was in the range of 50–60°. Thus, the conclusion that the bathochromic shift at low temperature was related to an increased planarity of the triene chromophore is in conflict with the calculated minimal geometry.[33] In view of this discrepancy, the low-temperature absorption spectrum of P_3 was investigated in greater detail. The absorption spectra measured at ambient temperature and at 77 K are shown in Figure 1.

It is apparent that although the absorption maximum shifts from 263 nm at 300 K to 273 nm at 77 K, there is no corresponding shift in the absorption spectrum between 273 and 320 nm. It is known that a changing population of conformers with temperature can lead to inhomogeneous broadening of the absorption spectrum.[34] Generally, this is found with compounds where the spectral change is large with conformational change. Such is not expected in previtamin D_3 since all low-energy conformations have a geometry of the triene chromophore which is similar.[33] If the red shift in the absorption maximum was due to an increased solvent polarization at lower temperatures which would stabilize the excited state, then the long wavelength edge of the spectrum should also shift to the red since the entire absorption band would be shifted.

There are two absorption bands in Figure 1. At 77 K, the first band has an absorption maximum at 273 nm, and the second band has a maximum which is approximately 210 nm. The decrease in temperature clearly decreases the intensity between the two maxima. The contribution of the long wavelength tail of the shorter wavelength absorption to the short wavelength edge of the longer wavelength absorption is correspondingly decreased with decreasing temperature. The bathochromic shift of the absorption maximum from 263 to 273 nm can be explained by a simple decrease in the overlap of the two electronic transitions

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(33) Dauben, W. G.; Funhoff, D. J. H., submitted for publication. Detailed calculations in this laboratory of the ground state of P_3 using the MMP2 program showed eight conformations within a 3-kcal range. The global minimum is the s-trans:s-cis conformation with an equatorial hydroxyl group, a result not in agreement with the previous postulations.[31d]

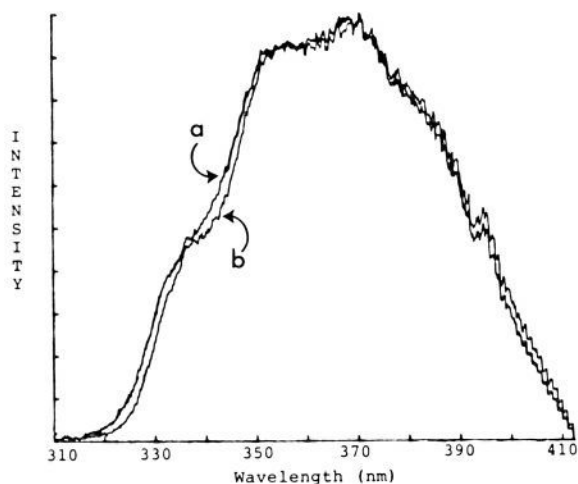(34) Myers, A. B.; Trulson, M. D.; Mathies, R. A. *J. Chem. Phys.* **1985**, *83*, 5000.

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Figure 2. Previtamin D_3 fluorescence spectra at 15 K: (a) 302-nm excitation and (b) 307-nm excitation.
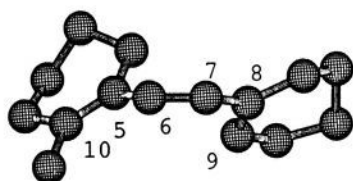

**Figure 3.** Spacial projection of calculated ground state.

with decreasing temperature dependent line widths. For example, as shown in Table IV, there are many vibration modes under 210 cm^{-1}, and the population of these bands could vary with temperature.

B. Low-Temperature Fluorescence Spectroscopy. As the low-temperature absorption spectrum provided no evidence for a change in conformational population between 77 and 300 K temperatures, the proposed comparison of the low-temperature fluorescence spectra and fluorescence quantum yields with the ambient temperature photochemical quantum yields was deemed reasonable. The spectra obtained with 302 and 307 nm excitation at 15 K are shown in Figure 2. Examination of the spectra reveals essentially to change in the spectral intensity distribution when the wavelength of excitation is changed from 302 to 307 nm, the spectral region where the large change in quantum yield is observed.

The fluorescence quantum yields were determined at these wavelengths and were found to be identical within experimental error, $\phi_f = 0.18 \pm 0.02$.

C. QCFF/PI Calculations of Previtamin D₃ Model. It has been determined by MMP2 molecular mechanics calculations that the global minimum ground state conformation of previtamin D_3 is a highly twisted s-trans:s-cis form with an equatorial hydroxyl group.[33] The ground- and excited-state geometries and normal modes of this conformation were investigated with the QCFF/PI method of Warshel and Karplus.[35]

In order to simplify the calculations, a model compound was selected for study, a compound which contained the triene moiety but with ring D, the sidechain, the C-18 methyl group, and the C-3 hydroxyl group removed was chosen. This model compound was *cis*-1-(2-methyl-1-cyclohexenyl)-2-(1-cyclohexenyl)ethylene. This compound, called *cis*-bicyclohexenylethylene for convenience, is shown below.
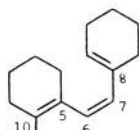
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Table III. Calculated Ground- and Excited-State Geometries of *cis*-Bicyclohexenylethylene

state	carbon atoms	dihedral angle (deg)	bond length (Å)
S_0	C_{10}–C_5–C_6–C_7	39.3 (+140.7)^a	1.49
	C_5–C_6–C_7–C_8	11.2 (−11.2)	1.35
	C_6–C_7–C_8–C_9	34.4 (−34.4)	1.48
S_1	C_{10}–C_5–C_6–C_7	12.7 (+167.3)	1.42
	C_5–C_6–C_7–C_8	46.7 (−46.7)	1.44
	C_6–C_7–C_8–C_9	12.2 (−12.2)	1.41

^{a} The indices + and − pertain to the sign of the torsional angle around the listed bond according to the convention of Klyne and Prelog (Klyne, W.; Prelog, V. *Experientia* **1960**, *12*, 521).
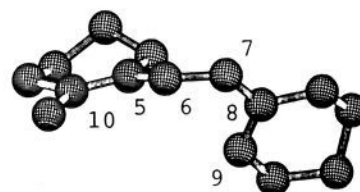
Figure 4. Spacial projection of calculated excited state.
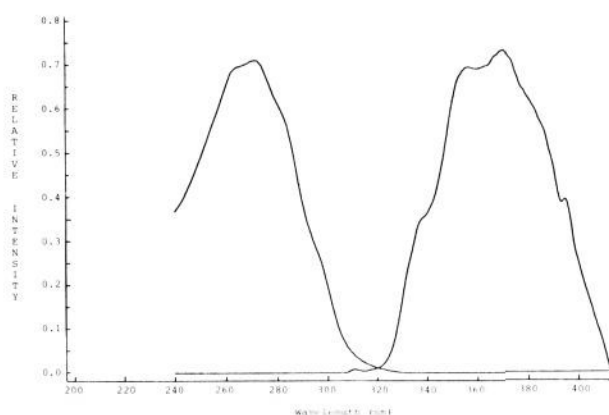
Figure 5. Absorption and fluorescence of previtamin D_3.

The initial geometry inputed into the QCFF/PI calculations was that found for this system in the conformational global minimum calculated for previtamin D_3 by the MMP2 method.[33] The ground-state geometry obtained from QCFF/PI calculations of the model was used to calculate the geometry of the excited-state minimum. The ground- and excited-state geometries obtained in these calculations are listed in Table III, and ball-and-stick three-dimensional projections of these two states are shown in Figures 3 and 4. The calculated excited-state geometry has the usual shortened carbon–carbon single bonds and lengthened carbon–carbon double bonds, relative to the ground state. The general shape of this s-trans:s-cis molecule is defined by the dihedral angle relationship of the three double bonds. In the excited state the result is increased coplanarity of the two terminal double bonds due to diminution of the dihedral torsional angles for the C_5–C_6 and C_7–C_8 carbon systems, a feature consistent with increased double bond character of the corresponding single bonds. Of particular interest is that the calculations indicate that the excited state molecule is substantially twisted about the central C_6–C_7 double bond and this is clearly shown in Figure 4.

The superposition of the low-temperature absorption and fluorescent spectra of previtamin D_3 is shown in Figure 5. The curves are scaled to equal intensity. The lack of overlap between these two spectral bands, which is typical of many linear trienes, has been taken as evidence for the 2^1A_g-like state being the lowest energy singlet state and/or for a large molecular distortion in the excited states.[20a,27]

Such a large molecular distortion in the excited state of previtamin D_3 was indicated by the QCFF/PI calculations by using the model compound, for example, the twisting of the central

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Table IV. Normal Modes and Displacements Calculated by Using the QCFF/PI Program

mode (cm⁻¹)	Δ	mode (cm⁻¹)	Δ
1690.26	0.59	776.22	0.11
1671.46	1.02	711.43	−0.32
1623.62	1.12	624.97	−0.25
1506.94	−0.30	608.48	−0.61
1482.31	−0.11	578.96	0.62
1428.35	0.12	533.36	−0.21
1402.56	0.32	517.41	0.46
1294.76	0.34	473.84	−0.19
1277.55	−0.18	458.32	−0.17
1271.57	0.30	442.48	0.75
1236.45	0.27	394.62	0.67
1142.26	0.11	294.16	−0.13
1116.06	0.30	280.99	−0.36
1027.98	0.15	247.40	0.28
1024.29	−0.35	209.37	1.97
1011.85	0.20	142.51	−0.89
1007.52	−0.48	134.14	−0.38
1002.21	0.26	113.08	0.73
946.83	0.31	95.96	0.20
896.46	−0.12	66.78	0.12
864.10	0.18	44.44	−0.75
854.49	0.11	37.96	−1.16

Figure 6. Ultraviolet absorption spectra: observed for P_3 (——), calculated for model with δ values of 3.0 (– – –) and 4.0 (— —).

C_6–C_7 double bond. The lack of overlap of the two spectral bands (Stokes shift) has also been reported for stilbenes, and the measured Stokes shift increase in the series *trans*-stilbene, *cis*-stilbene, and *trans*- and *cis*-α,α′-dimethylstilbenes. This increase parallels the calculated increase in the equilibrium value of the torsional angle about the central α,α′-bond on excitation.[36]

In order to quantify the extent to which the geometrical relaxation predicted by the QCFF/PI calculations of the model compound corresponded to the similar parameters of previtamin D_3, the Franck–Condon absorption profile of the model compound was compared with the experimental spectrum of P_3. This profile was calculated by using the normal mode frequencies and displacements obtained from a modified QCFF/PI program.[37] The calculated normal mode frequencies and displacements in the absorption profile calculation are listed in Table IV in the Experimental Section, and to obtain an absorption profile for the model compound which best fits the experimental absorption spectrum of previtamin D_3, it is necessary to evaluate the effect of twisting or stretching of bonds which possess a large δ value. This modified QCFF/PI calculation of the ^1B_u state does not mix the σ and π electrons and, thus, underestimates the effect of twisting of a double bond, and mixing of these electrons will increase the nonplanarity of the double bond.[37] The twisting mode of the central double bond at 209 cm⁻¹ has the largest δ value. An increase of the δ value for this important mode should increase the magnitude of the torsion angle. In the calculation of the absorption profile of the model compound it was found by changing the δ value from 1.9 as originally calculated to 3.0 and 4.0 gave the best fit with the experimental spectrum (see Figure 6). The profile obtained by using a δ value of 3.0 appears to have more structure related to the observed spectrum, but clearly both calculated profiles give an acceptable fit.

Because P_3 has essentially unstructured absorption and emission spectra, the spectral origin (i.e., 0–0 transition) cannot be accurately placed. By using the two calculated absorption profiles, the 0–0 transition was estimated to be 306 or 314 nm for the δ values of 3 and 4, respectively. The Stokes shift of both the absorbance and the fluorescence spectral maxima relative to the estimated 0–0 transition is approximately 4100 and 5600 cm⁻¹, respectively, for the 306-nm 0–0 transition and 4700 and 4700 cm⁻¹, respectively, for the 314 nm 0–0 transition. If, indeed, both the absorption and emission occurs from the 0–0 transition, this near or exact mirror image symmetry would suggest that the same
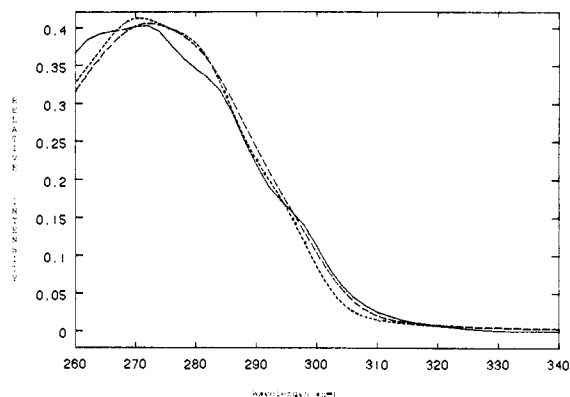
state is involved in each process.

The aforementioned experimental and calculational results can be summarized briefly: (a) the 10-nm bathochromic shift in the absorption maxima of P_3 between ambient temperature and 77 K can be due to a simple decrease in overlap of the two electronic transitions with decreasing temperature dependent line width or different populations of hot bands with varying temperature and not to an increase in the planarity of the triene chromophore as previously suggested;[31d] (b) the fluorescence spectrum of P_3, obtained for the first time by study at 15 K in a 1:1 methyl cyclohexane–decalin matrix, was found to be practically identical when the wavelength of the excitation was changed from 302 to 307 nm; (c) the fluorescence quantum yield at these two wavelengths, the spectral range where the large change in photochemical quantum yield for ring closure is observed, was found to be identical within experimental error; (d) the modeling of the excited state geometry, using a modified QCFF/PI computation with a simplified model, yielded results consistent with other related calculations,[36] but most important was the finding that the relaxed excited state molecule is highly twisted about the central C_6–C_7 double bond with concurrent shortening of the carbon–carbon single bonds and lengthening of the carbon–carbon double bond; (e) the calculated Franck–Condon profile of the model compound and the observed low-temperature absorption spectrum of P_3 were in excellent agreement after evaluation of the twist angle of the central double bond, indicating that the proposed geometrical distortion in the P_3 model excited state was consistent with the experimental P_3 data; (f) the superposition of the low-temperature absorption and fluorescence spectra show there is a lack of overlap between the spectra, consistent with a considerable degree of geometrical relaxation in the excited state of P_3 as indicated by the QCFF/PI calculations with use of a model compound; (g) the magnitude of the Stokes shift of both the absorbance and fluorescence spectra maxima relative to the estimated 0–0 transition at 306–314 nm suggests that the electronic state formed on excitation and from which the fluorescence originated are the same.

The foregoing indication of participation of only one excited state in the low-temperature absorption and fluorescence spectra casts doubt on the postulated two-state model to explain the large change of photochemical quantum yield in the ring closure of P_3 over a 2.5-nm change in excitation energy. However, all the spectroscopic data can only be considered as negative evidence against this two-state model at this time since other information, such as fluorescence lifetime, has not been able to be obtained. Furthermore, the relationship between the photochemistry and the photophysics of a molecule is not always clear, and, thus, the sudden change in the ring closure quantum yield of P_3 still awaits explanation. However, the involvement of a particular vibrational manifold process[38] in the ring closure reaction warrants consideration and extended wavelength studies in the 300–330-nm wavelength region will be of interest.

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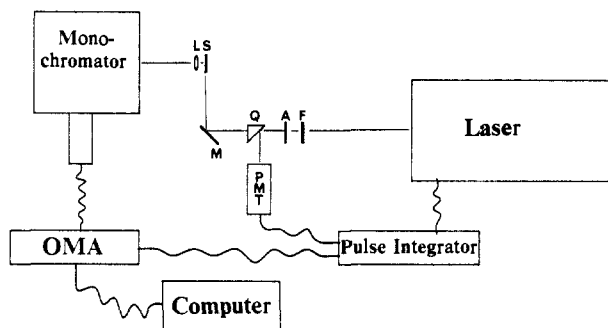
Previtamin D₃

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Figure 7. Apparatus configuration for fluorescence measurements. Symbols are as follows: L, lens; S, sample; M, mirror; Q, fused silica prism; A, pinhole aperture; F, filter.

Experimental Section

Unless otherwise noted, all solvents employed were of spectroscopic grade. The reagent grade indene and scintillation grade naphthalene used as standard were recrystallized twice from methanol. Eastman spectroscopic grade methylcyclohexane was used as obtained. The spectroscopic grade decalin used was a 44:56 mixture of the cis and trans isomers, respectively, as determined by coinjection of authentic samples of the pure isomers on a Hewlett Packard Model 5790 capillary GC. Ultraviolet absorption spectra were measured on a Hewlett Packard Model 8450 spectrometer. Previtamin D₃ was prepared and analyzed according to the method of Dauben and Phillips.[39] High pressure liquid chromatography was used for both purification and quantitative analysis. A Whatman M9 10/50 packed column was used in the purification, and a Waters 5μ silica column in a radial compression module and a Hewlett-Packard Model 3390A recording integrator were used in the quantitative analysis. Reagent grade hexane and HPLC grade ethyl acetate were used without purification other than filtration through Millipore filters and degassification under aspirator reduced pressure. The eluting solvent for both purification and analysis was 8% ethyl acetate in hexanes. Solvent flow rates of 5.0 and 3.0 mL/min were used in the preparative and analytical separations, respectively.

In order to avoid vitamin D₃ contamination, the HPLC purified material was collected in an ice-cooled flask under positive nitrogen pressure. The eluting solvent was removed by using a rotary evaporator, and the flask containing the residue was evacuated to less than 5 μ on a separate vacuum system. The flask was flushed with nitrogen and sealed with a septum. Approximately 15 mL of a 1:1 mixture of methylcyclohexane and decalin was added to afford a solution with an absorbance at the desired excitation wavelength between 0.4 and 1.0 au. This solution was purged with nitrogen and stored under positive nitrogen pressure in dry ice until sealed in the quartz cells within 24 h of purification. The samples were freeze–pump–thaw degassed at least 3 times each to a pressure less than 5 μ. Six or seven tubes containing the solution were sealed for each experiment. Sealed samples were stored in liquid nitrogen until use, generally within 12 h of sealing. By this procedure, the previtamin D₃ obtained was always greater than 98% pure, as verified by analytical HPLC, with no volatile impurities, and of a concentration less than 10⁻³ M.

The detection system used for the fluorescence measurements is shown in Figure 7. A Chromatix CMX-4 coaxial flash-lamp-pumped dye laser was used as the excitation source. For the experiments at 300 nm, the dye used was Rhodamine 6G in 1:1 methanol and water. For the experiments with 307-nm excitation, Rhodamine 6G with Ammonyx LO and water were utilized.

The reference photomultiplier used was a Thorn-EMI 1P28 equivalent in a locally made antimagnetic housing with a front section to hold standard filters.

The detector employed was a Princeton Applied Research Model 1205D with the proprietary UV scintillator coating. The optical multichannel analyzer was a PAR OMA-1 Model 1205A controller. The controller was adjusted such that the A and B channels acquired their signals from the same region of the detector, avoiding problems arising from asymmetry in the detection region. The polychromator used to disperse the incoming fluorescence was a McPherson Model 218 0.3 m monochromator, with the exit slit removed. The 300 groove/nm grating employed provided a dispersion of 100 nm across the faceplate of the 500 channel detector. The wavelength calibration was performed by using mercury lines from an Oriel spectral lamp as reference.

The samples were contained in quartz ampules constructed from 0.25 in. o.d. quartz tubing. The samples were mounted in a copper holder,

attached vertically to the cold stage of a CTI Cryogenics Model 21 two-stage, closed-cycle helium refrigerator and cooled to 15 K. A quartz condenser assembly from an Oriel Model 8120 500 watt mercury arc lamp was mounted directly on the outside of the refrigerator sample chamber, which focused the sample fluorescence on the entrance slit of the polychromator. The reference photomultiplier signal was integrated by an Evans Electronics (Berkeley, CA) gated integrator module, Model 4130A. Analysis of all irradiated samples by HPLC showed less than 10% of photoconversion to isomeric products of the starting triene P₃.

The normalization for the system spectral response was determined as follows. Indene was chosen as a reference standard because its fluorescence intensity was significant throughout the entire spectral window of interest. The indene was dissolved in isooctane to provide a solution with a maximum absorbance approximately 1 au. The fluorescence spectrum of this solution was measured on a Perkin-Elmer Model MPF-2A fluorescence spectrometer, with a P-E 150 Xenon source. Excitation at 305 nm, with 2-nm bandwith entrance, and 8-nm bandwidth exit slits were employed. The spectrum, measured between 310 and 410 nm, was manually digitized at 11 evenly spaced points which, in turn, were entered into a moving parabolic spline program on the HP-85 microcomputer to generate a 500 channel ideal response curve for the indene sample. The same indene solution was then sealed in a cell identical with those used for the previtamin D₃ fluorescence measurements, and the fluorescence spectrum was acquired with the OMA spectrometer, with the CMX-4 at 305.0 nm as the excitation source. The ideal response curve, after appropriate scaling, was divided by the actual response curve to generate a set of correction factors. Spectrum normalization for nonlinear response of the SIT and intermediate optics with respect to wavelength consisted of multiplying the spectrum by the set of correction factors. The validity of this approach was determined by the high correlation between subsequently normalized spectra of naphthalene and carbazole and published spectra of these compounds.[40]

The fluorescence quantum yields at 15 K were obtained by integration of the fluorescence spectrum, corrected for sample absorbance, and for excitation intensity as measured by the integrated reference signal. Naphthalene was used as the calibration standard to generate the proportionality factor between the integrated fluorescence spectrum and the integrated reference signal, by using the reported value of the naphthalene fluorescence quantum yield[41] and the measured absorbance of the naphthalene solution.

An Air Products Model AC-1-11 cryostat mounted onto the sample stage of a Hewlett-Packard Model 8450 spectrometer was used to obtain the absorption spectrum of previtamin D₃ in 1:1 methylcyclohexane–decalin at 77 K. A quartz cell 1 in. in diameter with a pathlength of 0.125 in. was used to hold the solution. The quartz cell was sealed under vacuum after 3 freeze–pump–thaw cycles at less than 5 μ.

Structural minimizations were performed by using the QCFF/PI calculations of Warshel and Karplus[35] on a VAX 8800 owned and operated by the Computer Facilities and Operations Department of the University of California, Berkeley. The normal mode calculation was performed by using a modification of the QCFF/PI calculation[37] on the VAX 8800. The sum-over-states absorption spectrum calculation was performed by using the FCSUMS program[42,43] on a Vaxstation II.

The initial geometry for the model compound was derived by removing the D-ring, the C-18 methyl group, and the hydroxyl group from the global minimum energy conformation of previtamin D₃[32] as calculated by MMP2 and reminimizing this structure by using MMP2. This was then used as input geometry to calculate the QCFF/PI ground-state minimum energy conformation. This structure was reminimized until the change in the geometry of the conformation was negligible. The final conformation, shown in Figure 3, was used as input geometry to calculate the QCFF/PI excited state minimum energy conformation, Figure 4. Both the ground- and excited-state minima were then used to calculate the normal modes. All modes with a displacement greater than 0.1 were used in the sum-over-states absorption spectrum calculation and are listed in Table IV. To simulate a larger excited state twist in the central double bond, the δ of the mode at 209.37 was increased from 1.97 to 3.00. The calculated absorption spectra were fit to the low-temperature experimental absorption spectrum, thus permitting placement of the 0–0 transition.

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Host–Guest Complexation. 47. Carcerands and Carcaplexes, the First Closed Molecular Container Compounds[1,2]

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Abstract: The design, synthesis, and properties are reported for the first carcerand (**1**), a closed-surface container compound in whose interior are trapped simple organic molecules, a gas, and inorganic ions as permanent guests (G). A mixture of carcerand **1** and carcaplex **1·G** was formed by shell closure of two bowl-shaped cavitands, each containing a C_4 axis with four CH_2–X groups on their rims. The shell closure involved the reaction $(\sim CH_2-Cl)_4 + (\sim CH_2SCs)_4 \rightarrow (\sim CH_2SCH_2\sim)_4 + 4CsCl$ and was conducted in a mixture of $(CH_3)_2NCHO$, $(CH_2)_4O$, and Cs_2CO_3 under Ar. The insoluble carcerand–carcaplex mixture produced was purified by extensive extraction of byproducts with a variety of solvents (29% yield) and characterized. Elemental analysis demonstrated the following: the presence of N, indicating entrapped $(CH_3)_2NCHO$; the presence of Cs^+ and Cl^- in stoichiometric amounts, indicating the absence of CH_2–Cl bonds and the entrapment of at least one of these ions; carbon, hydrogen, nitrogen, and sulfur ratios compatible with **1·G** in which **1** is $C_{80}H_{72}O_{16}S_4$ and G is $(CH_3)_2NCHO$, $(CH_2)_4O$, CsCl, and Ar. An FT-IR spectrum indicated the presence of $(CH_3)_2NCHO$. The solid-state ^{13}C NMR spectrum was compatible with the structure of **1**. FAB-MS gave high-resolution m/z values (± 10 ppm) corresponding to the carcerand and its various

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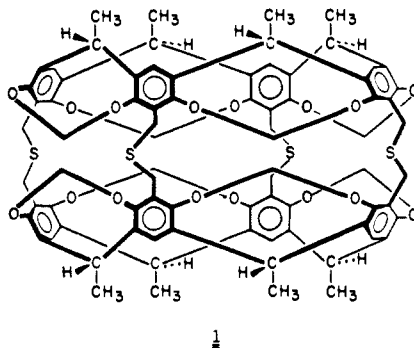
carcaplexes (relative intensities): $(M + H)^+$ (86); $(M + (CH_3)_2NCHO + H)^+$ (98); $(M + (CH_2)_4O + H_2O)^+$ (39); $(M + Cs)^+$ (100); $(M + Cs + H_2O)^+$ (61); $(M + (CH_3)_2NCHO + Ar)^+$ (28); $(M + (CH_3)_2NCHO + Cs)^+$ (32); $(M + Cs + Cs + H_2O + H)^+$ (14). Lower resolution peaks were observed as follows: $(M + Cs + ^{35}Cl)^+$ (21); $(M + Cs + Cs + ^{35}Cl)^+$ (4). No peaks were observed corresponding to masses for host–guest combinations that could not be made with CPK molecular models. Experiments with D_2O followed with FAB-MS indicated that H_2O can enter the interior of **1**. When the shell closure was conducted under an atmosphere of $ClCF_2CF_2Cl$ gas, **1·G** was shown to contain trace amounts of this gas.

Although cubane,[3] pentaprismane,[4] and dodecahedrane[5] are closed-surface compounds, their interiors are much too small to contain simple organic compounds or inorganic ions. In 1983, we formulated what to our knowledge was the first closed-surface hydrocarbon sphere with an enforced interior of sufficient size to embrace simple organic compounds, inorganic ions, or gases. We also discussed the interesting questions that arose regarding the physical and chemical properties of imprisoned guests.[6]

In CPK models, the envisioned hydrocarbon (**2a** or **2b**, $C_{96}H_{72}$) appears essentially strain free and is about the size of a large cantalope, with an interior the size of a large orange. The surface is composed of 12 benzene rings woven together with 24 methylene groups substituted in the 1, 2, 4, and 5 positions of the benzenes in patterns that compose six macrorings of structure **3** and eight medium rings of structure **4**. In **2a** the eye views the interior through an expanded **3** unit, and in **4** through an expanded **4** unit. In CPK models these holes are much too small to allow entrance or egress of chemical entities larger than electrons or protons.

"Soccer ball", a conceptually new form of carbon (C_{60}), and its higher oligomers are also closed-surface, hollow spheres with potentially enough internal volume to contain small molecules or ions. The 1986 report of lanthanum encapsulated in C_{60}[7] has been

(1) We warmly thank the National Science Foundation for NSF Grant CHE 21-09532, which supported the research at UCLA, and NASA Grant NAG 9-41, which supported the argon and thermal analysis at UCSD done by K. Marti and R. M. Sampson.

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