[Chem. Pharm. Bull.
30(2) 419—427 (1982)]

π-π^* Transition Energies of Steroid Polyenes and Steroid Polyenyl Cations

TOKIHIRO NIIYA,[a] YOSHINOBU GOTO,[a] KEIKI KOUNO,[b] YUKIO ONO,[b] and YO UEDA*,[b]

*Faculty of Pharmaceutical Sciences, Fukuoka University,[a] 11 Nanakuma, Nishi-ku,
Fukuoka 814, Japan and Faculty of Pharmaceutical Sciences, Kyushu
University,[b] 3-1-1 Maedashi, Higashi-ku, Fukuoka 812, Japan*

(Received July 18, 1981)

π-π^* Transition energies of steroid polyenes were calculated by the Pariser-Parr-Pople type LCAO-MO-CI method. Excellent coincidence was obtained between the calculated and the observed energies.

The method was applied to the calculation of π-π^* transition energies of steroid polyenyl cations having the structures assumed in the previous paper.1) Calculated energies of most of the cations were found to coincide very well with the wavelengths of maxima in the absorption spectra of steroid polyenes in strong acids. This result supports the validity of the assumptions made in the previous paper.

The method was not suitable for the calculation of π-π^* transition energies of steroid polyenyl cations having π electrons delocalized on more than nine carbon atoms.

Keywords——LCAO-MO-CI method; steroid polyene; steroid polyenyl cation; electronic spectrum; bisteroid; polyene; polyenyl cation

In our previous paper,1) the absorption spectral changes of strong acid solutions of steroid polyenes were found to be attributable to chemical changes of polyenyl cations formed by the dissolution of polyenes in strong acids. The chemical structures of steroid polyenyl cations are generally very difficult to determined, because these cations are not stable for long enough to permit the measurement of various kinds of spectra usually employed in the chemical structure determination of organic compounds, other than their electronic absorption spectra. Therefore, the chemical structures of the steroid polyenyl cations considered to be responsible for the coloration in strong acids had to be assumed in our previous paper.

The electronic absorption spectrum of a compound is known to give information only on the structure of the chromophore moiety of the molecule. However, such information is expected to be very useful in determining the chemical structure of the steroid polyenyl cation derived from a steroid polyene having a known chemical structure, because, it is considered that the addition of a proton to some of the carbon atoms of the conjugated unsaturated system of a steroid polyene is the initial step of cation formation, and is followed by change of the conjugated unsaturated system of the cation initially formed. Under these circumstances, it is of considerable interest to obtain information on the chemical structures of steroid polyenyl cations from the electronic absorption spectra.

In the cases of the absorption spectra of aliphatic and cyclic conjugated polyenes, including steroids, it is well-known that the wavelengths of the π-π^* transition bands coincide very well with the values calculated either by the empirical Woodward diene rule2) or by Fieser's modification.3) With regard to the quantum chemical investigation of the π-electronic spectra of polyenes, several papers have been published describing the results of investigations on aliphatic and cyclic conjugated polyenes, but unsaturated steroids have never been studied.

The theoretical calculations of the π-π^* transition energies of aliphatic and cyclic conjugated polyenes were first done for the "stripped chromophores," and the effect of substituents on the transition energy was not taken into account.4,5) Then, the method of calculation was expanded in order to account explicitly for the effect of substituents.6–12)

In contrast, the experimental correlation between wavelengths of absorption maxima of polyenyl cations and their chemical structures has not yet been investigated extensively.

The only correlation so far recognized is the linear dependence of the wavelengths of absorption maxima of polyenyl cations on the lengths of their conjugated systems in a series of cations having closely related chemical structures.[13,14] With regard to quantum chemical investigation, Oseen *et al.*[15] used the free electron theory to explain the observed linear correlation[13] of the wavelengths of absorption maxima of aliphatic polyenyl cations, $[(CH_3)_2C{=}CH{=}(CH{=}CH)_n{=}C(CH_3)_2]^+$, with the number of double bonds (n). Then Navangul *et al.*[16] and Honig *et al.*[10] both reported calculations of the π-π^* transition energies of the same series of cations by the Pariser–Parr–Pople type molecular orbital methods. The substituents of the above-mentioned cations are limited to methyl groups and they are located on only the terminal carbon atoms of the conjugated unsaturated systems. Therefore, the methods used by these two research groups are not expected to be applicable to steroid polyenyl cations having a variety of substituents on various kinds of carbon atoms of unsaturated systems.

Thus, no useful method for calculation of the π-π^* transition energy has yet been presented for steroid polyenes and polyenyl cations. Since the size of steroid molecules is too large for either non-empirical *ab initio* calculation or semi-empirical all-valence-electrons calculation, we sought a suitable method within the framework of the semi-empirical Pariser–Parr–Pople type LCAO–MO–CI method.[17,18]

The π-π^* transition energies calculated by the present method coincide well with the observed values in most cases of conjugated unsaturated steroids and alicyclic polyenyl cations. On the basis of the aforementioned results, the validity of the chemical structures of steroid polyenyl cations assumed in our previous paper is discussed.

Experimental

Molecular Geometry——Both **1**[19,20] and **2**[20,21] are known to have planar geometries. The geometries of **3**—**7** were assumed to be planar after the assumption made by Birge *et al.*[22] Compounds (**8**—**10**) are known to have planar diene moieties,[20] and compounds (**11**—**21**) were assumed to have planar unsaturated moieties, because Dreiding models show that the unsaturated moiety of every one of these compounds can be located on a plane. The cisoid diene system of compound (**22**) may have planar geometry, because four carbon atoms of the butadiene fragment of ergosterol are known to lie in a plane.[23] The transoid diene systems of compounds (**23**—**25**) were assumed to be planar, because Dreiding models show that the diene moiety of every one of these compounds can be located practically on a plane.[24] The geometries of the triene systems of compounds (**26**—**28**) have already been assumed to be planar.[5,11] The geometry of the triene system of **29** was assumed to be planar, because the Dreiding model of this compound shows that the triene moiety can be located practically on a plane. Bisteroids, **30**—**33**, were assumed to have planar unsaturated systems, because these bisteroids consist of two molecules having unsaturated systems already assumed to be planar, and the Dreiding model of (3,3′-bicholest)-3,3′-diene shows that the geometry of the 3,3′-diene moieties can be planar.

With regard to the geometries of polyenyl cations, no useful information is available in the literature, and all of the cations investigated in the present work were assumed to have planar unsaturated systems, because every one of these cations is formed by the addition of a proton to a polyene whose unsaturated system is either known or assumed to be planar.

Method of Calculation——The energies and oscillator strengths of the π-π^* transitions of compounds were calculated by the Pariser-Parr-Pople type LCAO-MO-CI method. The hetero-atom model was assumed for the alkyl group attached directly to the carbon atom of the unsaturated linkage.[25] The integral parameters necessary for the calculation are the atomic core integrals, H_{rr} and H_{rs}, and the electronic repulsion integrals, $(rr|rr)$ and $(rr|ss)$. Penetration integrals have been neglected throughout this work.

The diagonal core integrals, H_{rr}, were evaluated as usual.[17,18] The valence state ionization potentials of the carbon atom[25] and the hetero-atom[26] were taken from the literature, and the charge on the hetero-atomic core was made to be 2.

The off-diagonal core resonance integrals, H_{rs}, between all pairs of atoms r and s were evaluated according to the Wolfsberg-Helmholtz formula[27]

$$H_{rs} = -\frac{\kappa}{2} S_{rs}(I_r + I_s) \qquad (1)$$

where S_{rs} is the overlap integral between the Slater $p\pi$ atomic orbitals on atoms r and s, and I is the valence state ionization potential of an atom. The parameter κ was empirically assigned either a value of 0.86 in the calculation of polyenes or a value of 0.80 in the calculation of polyenyl cations.

The one-center repulsion integrals, $(rr|rr)$, were evaluated from the Pariser approximation.[28] The two-center repulsion integrals, $(rr|ss)$, were estimated according to the Nishimoto-Mataga formula.[29]

The effective nuclear charge, Z^*, of the hetero-atom was evaluated according to the equation given by Dewar *et al.*[30]

$$I_x/I_c = (Z_x^*/Z_c^*)^2 \qquad (2)$$

Subscripts x and c denote hetero-atoms and carbon atoms, respectively.

The numerical values of I_r, $(rr|rr)$ and Z^* used in this work are listed in Table I.

TABLE I. Selected Parameters

Atom(r)	I_r	$(rr\|rr)$	Z^*
C	11.16	11.13	3.25
Me	24.79	11.67	4.84

The configuration interactions were treated by including the lowest 36 (at maximum) singly excited configurations, because the strongly allowed transition observed at the longest wavelength is expected to be calculated from a simple singly excited configuration interaction treatment.[11]

Since the geometries of most of the compounds are not known, standard bond lengths and angles taken from the literature[31] were used in the calculation. This approximation can be expected to be pretty good.[11]

TABLE II. Compounds Used in This Work

Compound No.	Name
1	Butadiene
2	Hexatriene
3	Octatetraene
4	Decapentaene
5	Dodecahexaene
6	Tetradecaheptaene
7	Hexadecaoctaene
8	1,3-Pentadiene
9	2-Methyl-1,3-butadiene
10	2,3-Dimethyl-1,3-butadiene
11	2,4-Hexadiene
12	4-Methyl-1,3-pentadiene
13	2-Methyl-1,3-pentadiene
14	2,3-Dimethyl-1,3-pentadiene
15	3,4-Dimethyl-1,3-pentadiene
16	2,5-Dimethyl-2,4-hexadiene
17	2,6-Dimethyl-1,3,5-heptatriene
18	2,8-Dimethyl-1,3,5,7-nonatetraene
19	2,10-Dimethyl-1,3,5,7,9-undecapentaene
20	2,12-Dimethyl-1,3,5,7,9,11-tridecahexaene
21	2,14-Dimethyl-1,3,5,7,9,11,13-pentadecaheptaene
22	Ergosterol
23	Cholest-3,5-diene
24	Ergost-6,8(14),22-trien-3β-ol
25	Cholest-7,9(11)-dien-3β-ol
26	Ergost-2,4,6,22-tetraene
27	Ergost-4,6,8(14),22-tetraene
28	Cholest-5,7,9-trien-3β-ol
29	Ergost-3,5,7,22-tetraene
30	(3,3′-Bicholest)-3,3′,5-triene
31	3,3′-Bi(cholest-3,5-diene)
32	(3,3′-biergost)-28′-nor-3,3′,5,5′,7,22-hexaene
33	3,3′-Bi(ergost-3,5,7,22-tetraene)

The hetero-atom assumed for the alkyl group was placed at the position of the carbon atom of the alkyl group.

The coulombic interaction between the polyenyl cation and its counterion(s) was not included in the calculation because firstly the location of the counterion(s) is ambiguous and secondly it was reported that the transition energies of polyenyl cations, **34**—**38**, can be calculated fairly satisfactorily without considering the counterion effect.[10,32]

All calculations are carried out on a FACOM M-200 computer at the Computation Center of Kyushu University and on an ACOS 600 computer at the Computation Center of Fukuoka University.

All compounds used in this work are listed in Table II.

Isolation of the Substance formed by Dissolution of Ergost-3,5,7,22-tetraene (29) in H_2SO_4——A solution of **29** in HOAc (0.1 ml) was mixed with 20 ml of H_2SO_4. The mixture was neutralized with ice-cold aq. $NaHCO_3$ solution as quickly as possible after the preparation of the solution. The substance formed was extracted with 2,2,4-trimethylpentane, and the organic layer was washed with H_2O, and dried over anhyd. Na_2SO_4. The solvent was removed by evaporation *in vacuo*. The residue was used without any further purification for measurements of absorption spectra in strong acid.

Results and Discussion

π-π^* Transition Energies of Steroid Polyenes

Experimental π-π^* transition energies[33] of all-*trans* aliphatic polyenes, **1**[34] and **2**—**7**,[35] were used in the assignment of the empirical parameter κ, and a value of 0.86 was found to give satisfactory results (Table III).

Table III. π-π^* Transition Energies of All-*trans* Aliphatic Polyenes

Compound No.	Observed [cm^{-1}, (log ε)]	Calculated [cm^{-1}, (f)$^{a)}$]
1	46080(4.32)$^{b)}$	46650(0.91)
2	38910(4.63)$^{c)}$	38490(1.23)
3	34480(—)$^{d)}$	33830(1.52)
4	31550(5.06)$^{c)}$	30870(1.80)
5	29070(5.10)$^{c)}$	28860(2.07)
6	27170(—)$^{c)}$	27560(2.36)
7	25910(5.05)$^{c)}$	26550(2.63)

a) Oscillator strength.
b) In *n*-hexane.
c) In 2,2,4-trimethylpentane.
d) In cyclohexane.

The alkyl group adjacent to an unsaturated system exerts a bathochromic effect on the π-π^* transition energy and its magnitude is well-known to be approximately constant, whatever the kind of alkyl group.[3] In order to take into account the bathochromic effects of alkyl groups of polyenes in the LCAO–MO–CI calculation, the inductive model[6—8,10,11] and the hyperconjugative model[9,12] have been introduced. However, the "*cis*-alkyl substituent effect" was reported to be accounted for by the hyperconjugative model[9] rather than the inductive model.[11]

The hyperconjugative model is inadequate for compounds having the *cis*, *s-cis*, *cis*-hexa-2,4-diene type unsaturated system, such as the compound (**26**), because two pseudo atoms must be located in space unrealistically close to each other. Thus, the hetero-atom model was used in this investigation. The numerical values of the valence state ionization potential and the one-center repulsion integral of the hetero-atom have been presented by Párkányi *et al.*[26] and others.[36] The calculated π-π^* transition energies of fourteen methylated polyenes, (**8**—**21**), using the values given by Párkányi *et al.*, I_r=24.79 eV and $(rr|rr)$=11.67 eV, were found to coincide very satisfactorily with the observed energies (Table IV). Therefore, it is considered that these values can be used in the calculation of transition energies of alkylated polyenes.

TABLE IV. π-π^* Transition Energies of Methylated Polyenes

Compound No.	Observed[a] [cm^{-1}, (log ε)]	Calculated [cm^{-1}, (f)]
8	44640(4.42)	44630(0.84)
9	44840(4.41)	45640(0.81)
10	43860(4.34)	45430(0.83)
11	44150(4.38)	43240(0.79)
12	42740(4.36)	42900(0.75)
13	43860(—)	44290(0.82)
14	43010(4.36)	43630(0.77)
15	41840(4.44)	41550(0.65)
16	40980(4.38)	41020(0.70)
17	36760(4.56)	36470(1.12)
18	33200(4.77)	32660(1.47)
19	30250(5.03)	30110(1.78)
20	28060(5.09)	28450(2.10)
21	26400(5.13)	27160(2.38)

a) No. **8**—**14**, **16**: reference 37, in cyclohexane. No. **15**: reference 37, in *n*-hexane. No. **17**: T.S. Sorensen, *Can. J. Chem.*, **42**, 2781 (1964), in 2,2,4-trimethylpentane. No. **18**—**21**: reference 13, in 2,2,4-trimethylpentane.

TABLE V. π-π^* Transition Energies of Steroid Polyenes

Compound No.	Observed [cm^{-1}, (log ε)]	Calculated [cm^{-1}, (f)]
22	35460(4.08)[a]	35450(0.20)
23	42550(4.29)[a]	42600(0.73)
24	39530(4.23)[a]	41060(0.66)
25	41150(4.21)[a]	42290(0.71)
26	32570(4.20)[b]	32270(0.41)
27	35340(4.52)[a]	35400(0.85)
28	30770(4.11)[a]	31300(0.25)
29	31650(4.28)[a]	31870(0.41)
30	36230(4.64)[c]	36030(1.05)
31	32570(4.81)[d]	32240(1.36)
32	27400(4.75)[e]	28030(1.06)
33	25000(4.98)[e]	26200(1.21)

a) L. Dorfman, *Chem. Rev.*, **53**, 47 (1953), in ethanol.
b) In reference 1, one of the three absorption peaks of this compound in ethanol was misprinted as 315 nm; it should be 307 nm.
c) $\lambda_{\max}^{n\text{-heptane}}$ nm (ε): 266 (33270), 276 (43300), 289 (29600).
d) $\lambda_{\max}^{n\text{-heptane}}$ nm (ε): 294 (46700), 307 (64900), 322 (50600).
e) Reference 1, in *n*-heptane.

π-π^* Transition energies of twelve steroid polyenes, **22**—**33**, were calculated by using the aforementioned numerical values of parameters, κ, I_r and $(rr|rr)$. The results, shown in Table V, show excellent agreement between the calculated energies and the experimental ones. In this comparison the experimental values measured in both ethanol and *n*-heptane were used, and values measured in ethanol were used without any correction for the solvent effect, because it is known that absorption bands of conjugated dienes and polyenes are not displaced significantly by solvents,[3] and actually, the differences between the wavelengths of absorption maxima of compounds (**1**,[37] **2**,[38] **3**[38]) and methylated butadienes[37] measured in ethanol and those measured in non-polar solvents[34,35,37] are 1—2 nm at most.

π-π^* Transition Energies of Polyenyl Cations

The polyenyl cation formed by the addition of a proton to the terminal carbon atom of polyene C_nH_{n+2} (n: even) has $(n\text{-}2)\pi$ electrons delocalized on $(n\text{-}1)$ carbon atoms. Moreover, the electronic spectra of polyenyl cations are measured in strong acids. Therefore, the empirical parameter κ selected in the calculation of π-π^* transition energies of polyenes is considered not to be applicable to the case of polyenyl cations.

TABLE VI. π-π^* Transition Energies of Polyenyl Cations

Compound No.	Observed [cm^{-1}, (log ε)]	Calculated [cm^{-1}, (f)]
34	25250(4.70)	24920(0.93)
35	21160(5.04)	20720(1.35)
36	18190(5.18)	17750(1.72)
37	15990(>5.23)	15500(2.03)
38	14250(—)	13760(2.30)
39	25320(4.67)	25610(0.86)
40	21280(5.45)	21090(1.25)

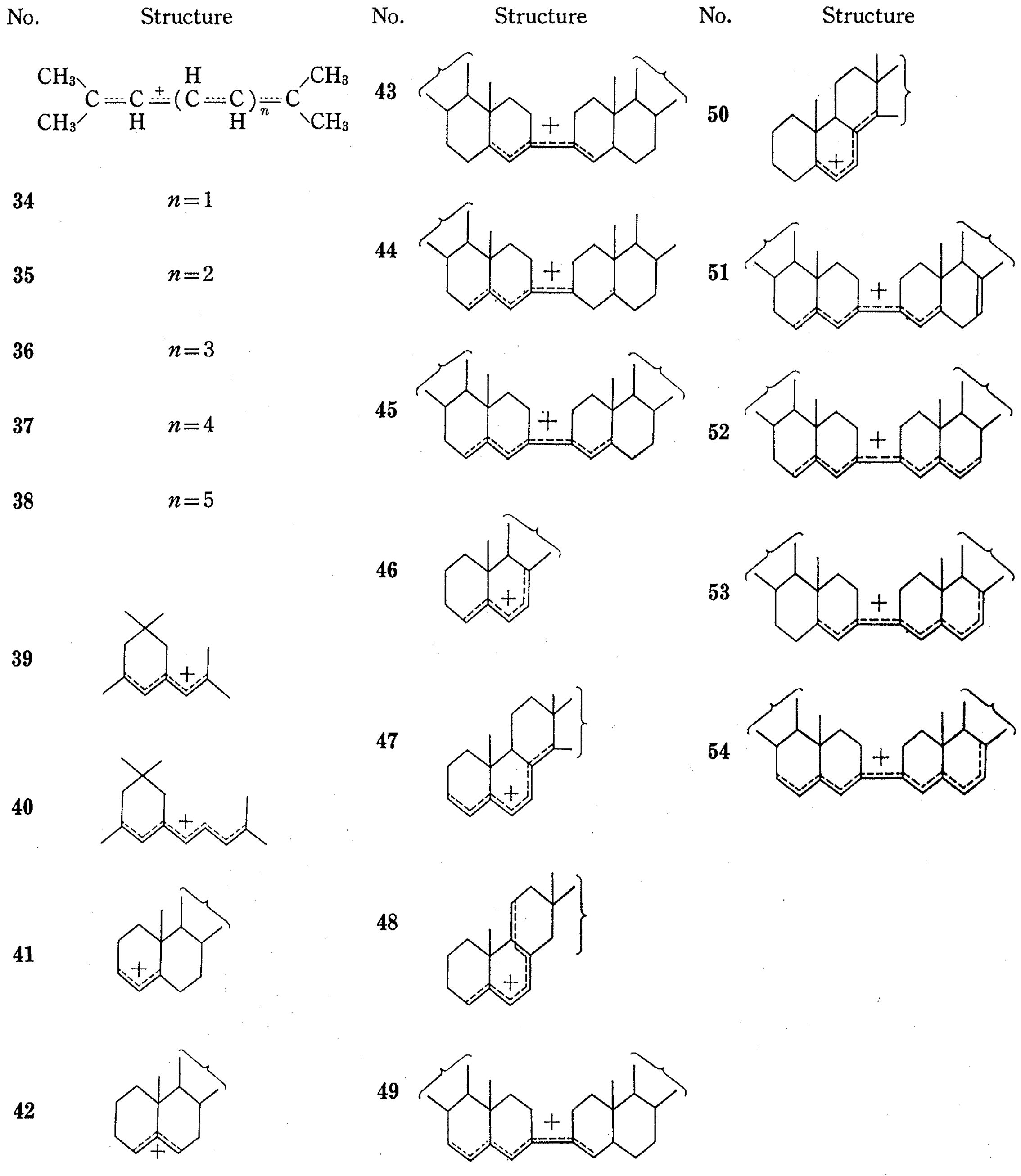

Chart 1

Absorption spectra of polyenyl cations have not been reported, so the absorption maxima of five methylated polyenyl cations, **34**—**38**, measured in H_2SO_4 or 80% H_2SO_4[13] were used in the assignment of the empirical parameter κ. In this investigation, methyl groups were treated by the hetero-atom model using the same values of I_r and $(rr|rr)$ as those used in the calculation of methylated polyenes. A value of 0.80 was found to give satisfactory results, as shown in Table VI. Although only two results on methylated polyenyl cations (**39**)[39] and (**40**)[40] other than those mentioned above are available, their absorption maxima were found to be predicted very satisfactorily by the present method (Table VI).

The structures of all cations referred to in the discussion are shown in Chart 1.

Examination of the Propriety of the Chemical Structures of Steroid Polyenyl Cations assumed in the Previous Paper[1]

An H_2SO_4 solution of cholest-3,5-diene (**23**) was found to show an absorption band having a maximum at 320 nm (31250 cm^{-1}), and the cation responsible for the maximum was assumed to be either cholest-3-en-5-yl cation (**41**) or cholest-4-en-6-yl cation (**42**). π-π^* Transition energies of these cations were calculated to be at 33000 cm^{-1} (303 nm) and 30950 cm^{-1} (323 nm), respectively. Therefore, the latter cation (**42**) must be responsible for the maximum at 320 nm.

Both a trifluoroacetic acid (TFA) solution and an H_2SO_4 solution of (3,3′-bicholest)-3,3′,5-triene (**30**) were found to show intense absorption bands having maxima at 413 nm (24210 cm^{-1}) and 408 nm (24510 cm^{-1}), respectively, and the cation responsible for these maxima was assumed to be (3,3′-bicholest)-3,3′-dien-5-yl cation (**43**). The polyene has two kinds of terminal carbon atoms in its unsaturated system, $C_{(6)}$ and $C_{(4')}$, therefore, the addition of a proton to a terminal carbon atom gives two kinds of cations, (**43**) and (3,3′-bicholest)-3,5-dien-3′-yl cation (**44**). π-π^* Transition energies of these cations were calculated to be at 25190 cm^{-1} (397 nm) and 23640 cm^{-1} (423 nm), respectively. Since the empirical parameter κ was assigned to reproduce observed π-π^* transition energies of cations measured in H_2SO_4, these values must be compared with the maximum of the H_2SO_4 solution. The results show that the observed value is closer to the calculated value of the cation (**43**) than that of the cation (**44**).

Both a TFA solution and an H_2SO_4 solution of 3,3′-bi(cholest-3,5-diene) (**31**) were found to show intense absorption bands having maxima at 491 nm (20370 cm^{-1}) and 494 nm (20240 cm^{-1}), respectively, and the cation responsible for these maxima was assumed to be (3,3′-bicholest)-3,3′,5-trien-5′-yl cation (**45**). The polyene has only one kind of terminal carbon atom in its unsaturated system, $C_{(6)}$ or $C_{(6')}$. Therefore, the π-π^* transition energy of only the above-mentioned cation was calculated, and it corresponded to 20440 cm^{-1} (489 nm). The result supports the assumption made in the previous paper.

Both a TFA solution and an 80% H_2SO_4 solution of ergost-3,5,7,22-tetraene (**29**) were found to show intense absorption bands having maxima at 453 nm (22080 cm^{-1}) and 454 nm (22030 cm^{-1}), respectively. Ergost-4,6,8(14),22-tetraene (**27**) also gave identical spectra. The cation responsible for these maxima was assumed to be ergost-4,6,22-trien-8-yl cation (**46**). Since two polyenes having different unsaturated systems give the same cation, the cation must have a structure derivable from both polyenes. The structure assumed in the previous paper is the sole structure which fulfils this requirement, therefore, its π-π^* transition energy was calculated. The calculated value of 22160 cm^{-1} (451 nm) coincides well with the observed value, so the assumption made in the previous paper can be considered to be proper.

It was shown in the previous paper that the above-mentioned absorption maxima at 454 nm of 80% H_2SO_4 solutions of both **29** and **27** were lost on standing and the solutions began to show intense absorption bands having maxima at 502 nm (19920 cm^{-1}). The cations responsible for these maxima were proved to be protonated species of the monomeric molecules and were assumed to be species such as ergost-3,5,7,22-tetraen-14-yl cation (**47**) and ergost-4,6,8(9),22-tetraen-11-yl cation (**48**). The calculated π-π^* transition energies of these cations were 19440 cm^{-1} (514 nm) and 18450 cm^{-1} (542 nm), respectively. The results indicate that the cation (**47**) is more likely to be the cation responsible for the maximum at 502 nm.

As was reported in the previous paper, the wavelength of absorption maximum of a steroid polyene measured in H_2SO_4 is different from that measured in TFA. A similar phenomenone was also observed with methylated polyenyl cations.[13] The empirical parameter κ was adjusted to reproduce the observed π-π^* transition energies of cations measured in H_2SO_4. Therefore, the wavelengths of absorption maxima of cations measured in TFA must be converted into the values expected to be observable in H_2SO_4. In order to carry out the conversion, the wavelengths of absorption maxima of polyenyl cations measured in TFA and those measured in H_2SO_4 must be known. However, no useful data are available in the literature. Moreover, chemical conversions and dimerizations of monomeric molecules were found to take place much faster in H_2SO_4 than in TFA in the previous paper. Accordingly, our previous investigation can afford only three sets of absorption maxima, each of which can be considered to be due to the same cation. These data were already given in the preceding part of this paper. In order to obtain another set of data, the substance formed by dissolution of **29** in H_2SO_4 was isolated and its absorption spectrum was measured again in both H_2SO_4 and TFA. The H_2SO_4 solution showed a spectrum identical with that of the H_2SO_4 solution of **29**. This result indicates that the substance isolated is simply that initially formed, and it is therefore fairly stable in H_2SO_4. The TFA solution showed an absorption spectrum having a shape quite similar to that of the H_2SO_4 solution, but its maximum was observed at 497.5 nm (20100 cm^{-1}) instead of the maximum of the H_2SO_4 solution at 502 nm (19920 cm^{-1}). The above-mentioned four sets of data give the following correlation equation ($r=0.9997$):

$$\text{(wave number in } H_2SO_4) = 1.111 \times \text{(wave number in TFA)} - 2420 \qquad (3)$$

A TFA solution of (3,3′-bicholest)-3,3′,5-triene (**30**) was found to show at first an intense absorption band having a maximum at 413 nm as mentioned before. Thereafter, the solution lost this maximum on standing and developed an intense absorption band having two maxima at 464 and 491 nm. These maxima were proved spectrometrically to be due to two different cations, and the cation responsible for the maximum at 464 nm (21550 cm^{-1}) was assumed to be the (3,3′-bicholest)-3,3′,5-trien-7-yl cation (**49**). The π-π^* transition energy of this cation was calculated to be 21990 cm^{-1} (455 nm). This value is very close to the value of 21520 cm^{-1} (465 nm) converted into the value in H_2SO_4 by means of equation (3). Therefore, the assumption made in the previous paper is supported.

A TFA solution of 3α, 5-cyclo-5α-ergost-6,8 (14), 22-triene was found to show an absorption band having a maximum at 504 nm (19840 cm^{-1}), and the cation responsible for this maximum was assumed to be the ergost-5,7-dien-14-yl cation (**50**). The π-π^* transition energy of this cation was calculated to be 21460 cm^{-1} (466 nm). This value does not coincide with the value of 19620 cm^{-1} (510 nm) converted into the value in H_2SO_4, and dose not support the assumption made in the previous paper.

A TFA solution of (3,3′-biergost)-28′-nor-3,3′,5,5′,7,22-hexaene (**32**) was found to show three absorption bands having maxima at 490 nm (20410 cm^{-1}), 580 nm (17240 cm^{-1}) and 631 nm (15850 cm^{-1}), and cations responsible for these maxima were assumed to be (3,3′-biergost)-28′-nor-3,3′,5′,7,22-pentaen-5-yl cation (**51**), (3,3′-biergost)-28′-nor-3,3′,5,5′,22-pentaen-7-yl cation (**52**) and (3,3′-biergost)-28′-nor-3,3′,5,7,22-pentaen-5′-yl cation (**53**), respectively. π-π^* Transition energies of these cations were calculated to be 20440 cm^{-1} (489 nm), 18330 cm^{-1} (546 nm) and 16480 cm^{-1} (607 nm), respectively. Among them, the value of 20440 cm^{-1} is very close to 20260 cm^{-1} (494 nm), converted from 20410 cm^{-1} into the value in H_2SO_4. Therefore, the present result supports the assumption made in the previous paper. On the contrary, the other two values do not coincide well with 16730 cm^{-1} (598 nm) and 15190 cm^{-1} (658 nm), converted from 17240 and 15850 cm^{-1} into the values in H_2SO_4, respectively.

An H_2SO_4 solution of 3,3'-bi (ergost-3,5,7,22-tetraene) (**33**) was found to show an absorption band having two maxima at 672 nm (14880 cm^{-1}) and 765 nm (13070 cm^{-1}), and the cation responsible for the latter maximum was assumed to be the (3,3'-biergost)-3,3',5,5',7,-22,22'-heptaen-7'-yl cation (**54**). The π-π^* transition energy of this cation was calculated to be 15140 cm^{-1} (661 nm). The calculated value does not coincide with the observed value.

The results described above indicate that the present method is not suitable for the calculation of π-π^* transition energies of steroid polyenyl cations having π electrons delocalized on more than nine carbon atoms.

References and Notes

1) T. Niiya, Y. Goto, Y. Ono, and Y. Ueda, *Chem. Pharm. Bull.*, **28**, 1747 (1980).
2) R.B. Woodward, *J. Am. Chem. Soc.*, **64**, 72, 76 (1942).
3) L.F. Fieser and M. Fieser, "Steroids," Reinhold, pub. Corp., New York, 1959.
4) N.L. Allinger and M.A. Miller, *J. Am. Chem. Soc.*, **86**, 2811 (1964).
5) J.R. Andrews and B.S. Hudson, *Chem. Phys. Lett.*, **60**, 380 (1979).
6) N.L. Allinger and J.C. Tai, *J. Am. Chem. Soc.*, **87**, 2081 (1965).
7) N.L. Allinger, J.C. Tai, and T.W. Stuart, *Theoret. Chim. Acta* (Berl.), **8**, 101 (1967).
8) T.W. Stuart and N.L. Allinger, *Theoret. Chim. Acta* (Berl.), **10**, 247 (1968).
9) T. Fueno and K. Yamaguchi, *J. Am. Chem. Soc.*, **94**, 1119 (1972).
10) B. Honig, A.D. Greenberg, U. Dinur, and T.G. Ebrey, *Biochemistry*, **15**, 4593 (1976).
11) N.L. Allinger and J.C. Tai, *J. Am. Chem. Soc.*, **99**, 4256 (1977).
12) U. Dinur and B. Honig, *J. Am. Chem. Soc.*, **101**, 4453 (1979).
13) T.S. Sorensen, *J. Am. Chem. Soc.*, **87**, 5075 (1965).
14) K. Hafner and H. Pelster, *Angew. Chem.*, **73**, 342 (1961).
15) D. Oseen, R.B. Flewivelling, and W.G. Laidlaw, *J. Am. Chem. Soc.*, **90**, 4209 (1968).
16) H.V. Navangul and P.E. Blatz, *J. Am. Chem. Soc.*, **95**, 1508 (1973).
17) R. Pariser and R.G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953).
18) J.A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).
19) K. Kuchitsu, T. Fukuyama, and Y. Morino, *J. Mol. Structure*, **1**, 463 (1967—68).
20) J.C. Tai and N.L. Allinger, *J. Am. Chem. Soc.*, **98**, 7928 (1976).
21) M. Traetteberg, *Acta Chem. Scand.*, **22**, 628 (1968).
22) R.R. Birge and B.M. Pierce, *J. Chem. Phys.*, **70**, 165 (1979).
23) S.E. Hull and M.M. Woolfson, *Acta Cryst.*, **B32**, 2370 (1976).
24) *cf.* E. Charney, H. Ziffer, and U. Weiss, *Tetrahedron*, **21**, 3121 (1965).
25) J. Hinze and H.H. Jaffé, *J. Am. Chem. Soc.*, **84**, 540 (1962).
26) C. Párkányi and L.S. Levitt, *Z. Naturforsch.*, **32b**, 1160 (1977).
27) M. Wolfsberg and L. Helmholtz, *J. Chem. Phys.*, **20**, 837 (1952).
28) R. Pariser, *J. Chem. Phys.*, **21**, 568 (1953).
29) K. Nishimoto and N. Mataga, *Z. Phys. Chem.* (Frankfurt am Main), **12**, 335 (1957).
30) M.J.S. Dewar and G.T. Gleicher, *J. Chem. Phys.*, **44**, 759 (1966).
31) J.A. Pople and D.L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, 1970.
32) B. Honig, private communication.
33) The interpretation of the many experimental olefin spectra is still ambiguous.[6] In the present work, depending on the shapes of the absorption bands, we have chosen either the position of the peak next to that at the longest wavelength of the vibronically structured spectrum or the position of the maximum absorption of the unresolved spectrum as the experimental transition energy.
34) A. Smakula, *Angew. Chem.*, **47**, 657 (1934).
35) F. Sondheimer, D.A. Ben-Efraim, and R. Wolovsky, *J. Am. Chem. Soc.*, **83**, 1675 (1961).
36) *e.g.* B. Tinland, *Tetrahedron Lett.*, **1968**, 1789; J. Fabian, *Tetrahedron*, **29**, 2449 (1973).
37) W.F. Forbes, R. Shilton, and A. Balasubramanian, *J. Org. Chem.*, **29**, 3527 (1964).
38) K. Hirayama, *J. Am. Chem. Soc.*, **77**, 373 (1955).
39) N.C. Deno and C.U. Pittman, Jr., *J. Am. Chem. Soc.*, **86**, 1871 (1964).
40) N.C. Deno, C.U. Pittman, Jr., and J.O. Turner, *J. Am. Chem. Soc.*, **87**, 2153 (1965).