

## Application of Self-Consistent HMO Theory to Heteroconjugated Molecules

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Substantial improvement of the self-consistent HMO theory, as recently developed by one of us, is made in the parametrization for heterobonds. The theory is extensively applied to a large scale of heteroconjugated molecules including rather complicated ones which are biologically important. The calculated molecular geometries and the wavelengths of optical absorption spectra are found to be in good agreement with experimental values. Examining the effect of inclusion of the  $\omega$ -technique to this theory, we find that the calculated values of molecular geometries, electronic spectra and ionization potentials are little affected for most molecules. Dependences of the absorption wavelength and the adiabatic potential on the molecular geometry are also investigated.

**Key words:** Heteroconjugated molecules – Self-consistent HMO theory

### 1. Introduction

One of the main objects in many earlier theories of conjugated molecules [1, 2] was to obtain the electronic structures of these molecules using the experimental molecular geometries. However, recently some investigators have intended to obtain the electronic structure and the molecular geometry at the same time by minimizing the total energy of the molecule [3–5] or by self-consistently satisfying the empirical relation between bond order and bond length [6–16]. Such studies are very valuable when a molecular geometry is not known, and these are useful for the calculations of the adiabatic potential surfaces, in cases such as *cis-trans* isomerizations of carotenoids [10]. Indeed, it is a theoretically important problem to know whether or not a small change in the bond length or in the torsional angle of the bond would significantly affect electronic properties of conjugated molecules.

The self-consistent HMO theory is one of the simplest methods for calculating molecular geometries and electronic spectra and other properties of conjugated molecules in some detail. In this method, the resonance integral is varied according to the bond length, and a relation between bond order and length satisfied self-consistently. Many investigators tried to improve the parametrization involved, and they obtained a considerably good agreement between the calculated values and experiment for molecular geometries [4, 10–12], electronic spectra [4, 10–13], other electronic properties [10, 11, 13–16], and vibronic spectra [17]. Among them, the method of Golebiewski and Nowakowski who used a considerably steeper function of the bond length than would be expected from the IR spectra of butadiene was very good to be applied for polyenes [10]. The method of Kakitani who included the effect of the electron-electron interaction in the resonance integral was also applicable for most conjugated hydrocarbons. This method was devised so that the molecular geometry, electronic spectra and vibronic spectra might be calculated simultaneously.

In this paper, we examine the scope of the utility of our self-consistent HMO theory by extensively applying our theory to heteroconjugated molecules. For this purpose, we substantially refine the parametrization in the pseudoresonance integrals and the skeletal potentials for C–C, C–N and C–O bonds.

## 2. Outline of the Self-Consistent HMO Theory and Refinement of Parametrization

In our self-consistent HMO theory, the total energy (to say exactly, the adiabatic potential)  $E^T$  of a conjugated molecule is expressed by [4]

$$E^T = \sum_a q_a \alpha_a + 2 \sum_{(ab)} p_{ab} \beta_{ab}^* + \sum_{(ab)} f_{ab}(R_{ab}), \quad (1)$$

where  $q_a$ ,  $\alpha_a$ ,  $p_{ab}$ ,  $f_{ab}$  and  $R_{ab}$  are the electron density, Coulomb integral, a bond order, a skeletal potential due to a  $\sigma$ -bond and a bond length, respectively. The pseudoresonance integral  $\beta_{ab}^*$  is defined by

$$\beta_{ab}^* = \{ \beta_{ab}(R_{ab}) - \zeta (2p_{ab} - \sum_{(cd)}^{\text{neigh.}} p_{cd} |\cos \theta_{cd}|) \} \cdot |\cos \theta_{ab}|, \quad (2)$$

where  $\theta_{ab}$  is a torsional angle around the bond  $ab$ . In this paper, we treat it as a given parameter for simplicity. This method is rather different from that of Golebiewski and Parczewski [12] where the torsional angle was also determined from the minimization of the energy. In Eq. (2), we consider that  $\beta_{ab}(R_{ab})$  includes the effect of the Coulomb repulsion between  $\pi$ -electrons to some extent [4], so that the  $|\cos \theta_{ab}|$ -dependence of this term may be an approximate one. The term with  $\zeta$  represents the bond order-bond order correlation which originates essentially from the three-center integral of the type  $(ab|bc)$  [4], so that the  $|\cos \theta_{ab} \cdot \cos \theta_{cd}|$ -dependence in this correlation term will be reasonable. The summation over  $cd$  should be made for the neighboring bonds of  $ab$ .

The functions  $\beta_{ab}(R_{ab})$  and  $f_{ab}(R_{ab})$  are expanded by a small quantity  $\Delta R_{ab} = R_{ab}^s - R_{ab}$  as follows:

$$\beta_{ab}(R_{ab}) = A_{ab} + B_{ab} \Delta R_{ab} + \frac{1}{2} C_{ab} (\Delta R_{ab})^2 + \frac{1}{6} D_{ab} (\Delta R_{ab})^3 + \dots, \quad (3)$$

$$f_{ab}(R_{ab}) = \frac{1}{2} K_{ab}^s (\Delta R_{ab})^2 + \frac{1}{6} L_{ab}^1 (\Delta R_{ab})^3 + \frac{1}{24} L_{ab}^2 (\Delta R_{ab})^4 + \dots, \quad (4)$$

where  $R_{ab}^s$  is a  $sp^2$ - $sp^2$  single-bond length. According to the result of our parametrization, it is found that the second and third powers in  $\beta_{ab}(R_{ab})$  and the third and fourth powers in  $f_{ab}(R_{ab})$  are rather small except near the double-bond length. However, these terms become important when the derivatives of Eqs. (3) and (4) are taken. Especially, the anharmonic terms in  $f_{ab}(R_{ab})$  were found to be indispensable to the calculation of the force constant [17].

The molecular orbital coefficients  $C_{ia}$  in the LCAO approximation and orbital energies  $e_i$  are obtained from the condition  $(\partial E^T / \partial C_{ia}) = 0$  as follows:

$$C_{ia}(\alpha_a - e_i) + \sum_b^{\text{n.a.}} C_{ib} \beta_{ab}^* = 0, \quad (5)$$

where the summation over  $b$  should be made for the neighboring atoms of  $a$ .

At an equilibrium conformation of a molecule,  $(\partial E^T / \partial R_{ab})_0 = 0$  holds. Then, we obtain the following bond order-bond length relation:

$$2p_{ab} |\cos \theta_{ab}| = - \frac{K_{ab}^s \Delta R_{ab}^0 + L_{ab}^1 (\Delta R_{ab}^0)^2 / 2 + L_{ab}^2 (\Delta R_{ab}^0)^3 / 6}{B_{ab} + C_{ab} \Delta R_{ab}^0 + D_{ab} (\Delta R_{ab}^0)^2 / 2}. \quad (6)$$

**Table 1.** Conditions for parametrization. Units of  $R$ ,  $F$ , and  $\beta(r)$  are Å,  $10^5$  dyn/cm and eV, respectively

$p$	C-C			C-N			C-O		
	$R$	$F$	$\beta(R)$	$R$	$F$	$\beta(R)$	$R$	$F$	$\beta(R)$
0	1.520 <sup>a</sup>	4.40 <sup>e</sup>	—	1.475 <sup>i</sup>	5.0 <sup>k</sup>	—	1.437 <sup>l</sup>	5.0 <sup>k</sup>	—
0.350	1.455 <sup>b</sup>	—	—	1.397 <sup>b</sup>	—	—	1.346 <sup>b</sup>	—	—
0.667	1.397 <sup>c</sup>	7.6 <sup>f</sup>	-2.95 <sup>h</sup>	1.327 <sup>j</sup>	8.2 <sup>l</sup>	—	1.261 <sup>b</sup>	9.0 <sup>b</sup>	—
1	1.337 <sup>d</sup>	10.95 <sup>g</sup>	—	1.260 <sup>i</sup>	11.5 <sup>b</sup>	-3.35 <sup>b</sup>	1.180 <sup>m</sup>	13.0 <sup>a</sup>	-3.50 <sup>b</sup>

<sup>a</sup> Assumed  $sp^2$ - $sp^2$  single bond.

<sup>b</sup> Arbitrary. These values are chosen so that the calculated values of bond lengths and absorption wavelengths of various conjugated molecules may best fit the experimental values.

<sup>c</sup> Bond length of benzene.

<sup>d</sup> Bond length of ethylene.

<sup>e</sup> From vibrational frequency of the C-C stretching mode of ethane.

<sup>f</sup> From vibrational frequency of the breathing mode of benzene.

<sup>g</sup> From vibrational frequency of the C-C stretching mode of ethylene. See Ref. [17].

<sup>h</sup> Assumed from the ionization potential of benzene. See Ref. [17].

<sup>i</sup> Mean value of experimental data of C-N or C-O containing molecules. See Refs. [18-21].

<sup>j</sup> Estimated from the bond length of  $s$ -triazine.

<sup>k</sup> From Ref. [21].

<sup>l</sup> Estimated from the vibrational frequency of the totally symmetric mode of  $s$ -triazine.

<sup>m</sup> Estimated from the bond length of carbonyl group.

<sup>n</sup> Estimated from the vibrational frequency of carbonyl group.

	C-C	C-N	C-O
$R^s$ (Å)	1.520	1.475	1.437
$A$ (eV)	-2.554	-2.316	-1.900
$B$ (eV/Å)	-2.555	-3.250	-3.573
$C$ (eV/Å <sup>2</sup> )	-3.405	-9.575	-16.81
$D$ (eV/Å <sup>3</sup> )	-176.4	-68.55	-44.57
$K^s$ (eV/Å <sup>2</sup> )	27.46	31.21	31.21
$L^1$ (eV/Å <sup>3</sup> )	68.17	87.05	143.0
$L^2$ (eV/Å <sup>4</sup> )	5962.0	3051.8	2113.4

**Table 2.** Values of  $R^s$  and expansion coefficients

The bond lengths and the electronic states are solved self-consistently by satisfying Eqs. (5) and (6) with use of Eq. (2).

From the second derivative  $(\partial^2 E^T / \partial R_{ab}^2)_0$ , we obtain a localized force constant  $F_{ab}$  as follows:

$$F_{ab} = K_{ab}^s + L_{ab}^1 \Delta R_{ab}^0 + \frac{1}{2} L_{ab}^2 (\Delta R_{ab}^0)^2 + 2p_{ab}^0 (C_{ab} + D_{ab} \Delta R_{ab}^0) |\cos \theta_{ab}^0|. \quad (7)$$

Substituting  $p_{ab}$  of Eq. (6) into Eq. (7), we obtain  $F_{ab}$  as a function of the bond length.

Now, we are going to determine the expansion coefficients of  $f_{ab}(R_{ab})$  and  $\beta_{ab}(R_{ab})$ . We choose the conditions listed in Table 1. Using Eqs. (3), (6) and (7), the expansion coefficients are determined as listed in Table 2.

The obtained relations of the bond order and the bond length (6) are considerably smooth ones. The curve for the C-N bond is in considerably good agreement with those which were empirically obtained by Cox and Jefferey [18], Lofthus [19] and Häfelinger [20] in the HMO scheme. The curve for the C-O bond is in good agreement with that obtained by Häfelinger in the HMO scheme [21].

In Table 3, we compared our resonance integral  $\beta(R)$  with that of the usual HMO theory using the parameter  $k_{C-X}$  defined by

$$\beta_{C-X}(R) = k_{C-X} \beta_0, \quad (8)$$

where  $\beta_0$  is the resonance integral of benzene. From this, it is found that our  $\beta(R)$  is similar to that of the HMO theory.

	SC-HMO	HMO <sup>a</sup>
$k_{C-C}$	0.87	0.9
$k_{C=C}$	1.11	1.1
$k_{C=N}$	0.79	0.8
$k_{C=N}$	1.14	—
$k_{C-O}$	0.64	0.8
$k_{C=O}$	1.19	1.0

**Table 3.** Comparison of resonance integrals between the self-consistent HMO theory and the HMO theory

<sup>a</sup> Ref. [22].

**Table 4.** Values of Coulomb integrals of some atoms in the self-consistent HMO theory and comparison with accepted values in the HMO theory

Atom	SC-HMO		HMO $h_x$
	(eV)	$h_x$	
	-6.30 <sup>b</sup>	0	0
	-7.53 <sup>b</sup>	0.42	0.5
	-8.82 <sup>b</sup>	0.86	1.0
	-10.0 <sup>c</sup>	1.25	1.5
	-11.5 <sup>c</sup>	1.76	2.0
	-10.7 <sup>c</sup>	1.49	(2.0)
	-9.0 <sup>c</sup>	0.91	—

<sup>a</sup> Protonated cation.

<sup>b</sup> See Ref. [4].

<sup>c</sup> These values are obtained by fitting experimental values of the bond length and optical absorption wavelength in many conjugated molecules.

<sup>d</sup> Ref. [22].

In Table 4, our chosen values of the Coulomb integrals are listed and compared with those in the HMO theory using the parameter  $h_x$  defined by

$$\alpha_x = \alpha_0 + h_x \beta_0, \quad (9)$$

where  $\alpha_0$  is the Coulomb integral of the carbon atom. It is found that our values are a little smaller than those in the HMO theory.

The value of  $\zeta$  is determined so that the calculated absorption wavelengths of planar polyenes may agree with the experimental values. As a result, we obtain  $\zeta = 0.35$  eV, which is a little larger than the previous value 0.33 eV [4].

### 3. Molecular Geometries

In this study, the self-consistent HMO theory was applied to about 200 conjugated molecules. Among them, the calculated results of 44 heteroconjugated molecules which are typical or biologically important are reported in this paper. The results were compared with experimental values when available. Some molecular geometries are given in Fig. 1. It is found that the calculated results are in good agreement with the experimental results for most molecules. The calculated result of ionic molecules such as lumiflavine cations (XXV), tropolonate (XI) and protonated Schiff-base of retinal (XXIX) are also in fairly good agreement with the experimental values. The calculated values of the twisted bonds in retinal, its Schiff base and canthaxanthin (XXX) are in relatively good agreement with experiment for  $\theta_{ab} \lesssim 50^\circ$ , but they become considerably larger than the experiments for  $\theta_{ab} \gtrsim 50^\circ$ . From this, it may be said that our theory might be

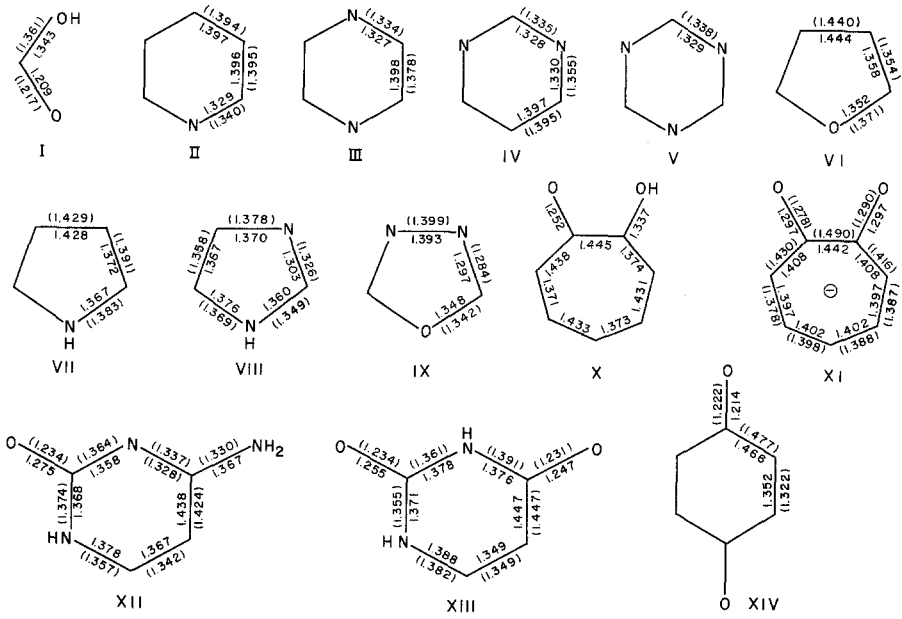


Fig. 1 (1)

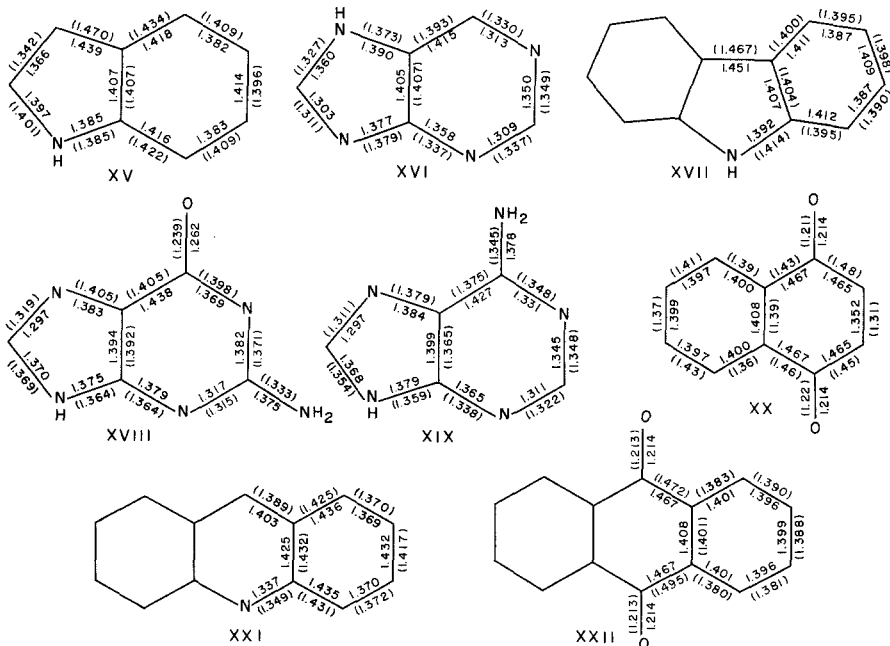


Fig. 1 (2)

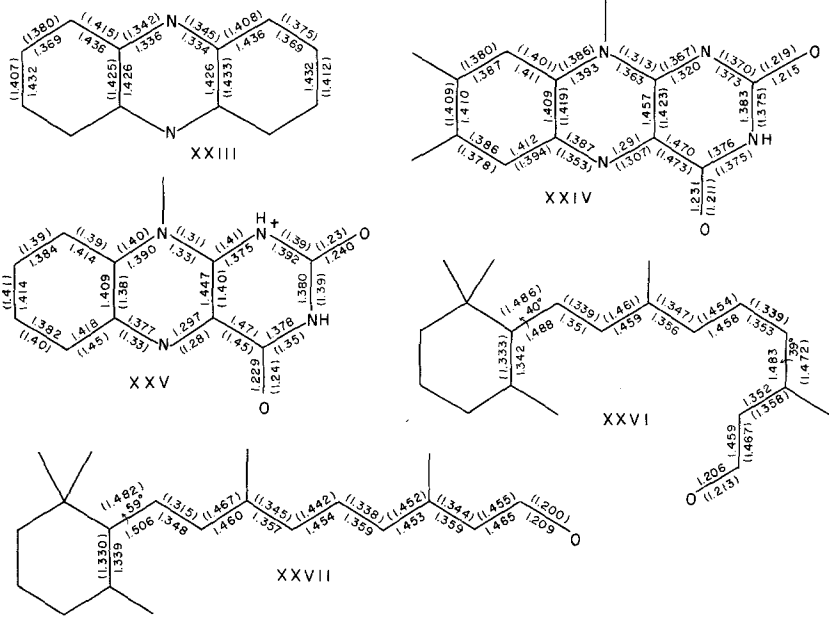


Fig. 1. (3)

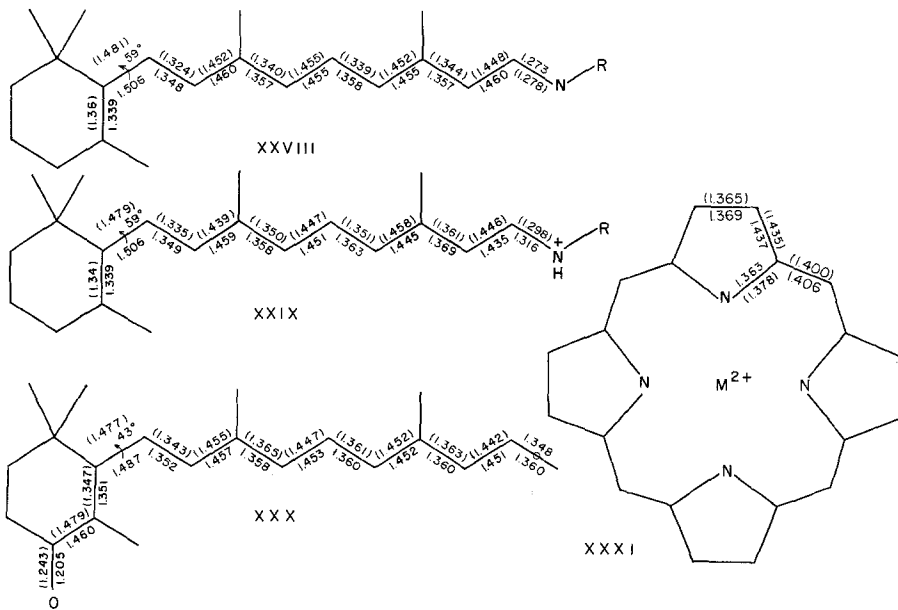


Fig 1 (4)

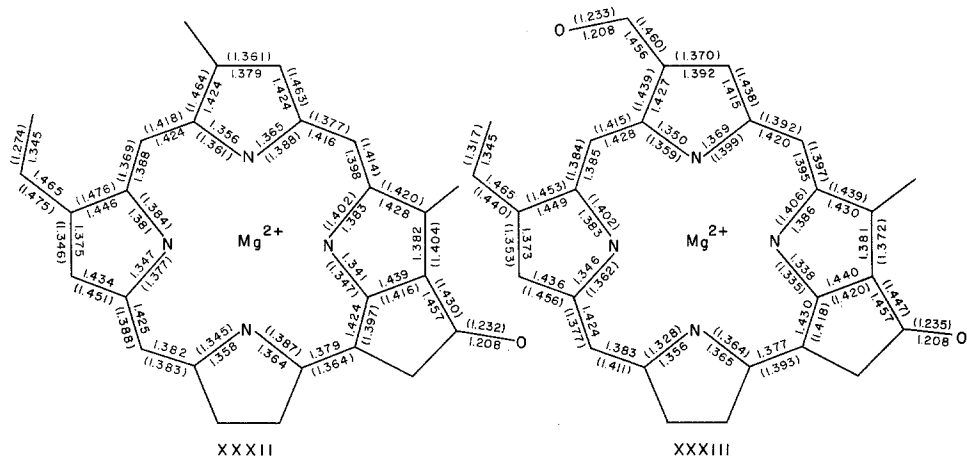


Fig. 1 (5)

**Fig. 1.** Calculated molecular geometries of heteroconjugated molecules. The values in the parentheses are experimental. Names and references to the experimental are listed in Table 5. Most of the experimental values are the averaged ones among the corresponding bonds. The torsional angles around the C<sub>6</sub>-C<sub>7</sub> bond of retinal (XXVI, XXVII), its Schiff-base (XXVIII, XXIX) and canthaxanthin (XXX) are given in the figure. The open circle in the molecular structure of canthaxanthin denotes the inversion symmetry

safely applicable to molecules with twisted angles less than 50°. The standard deviations of all the calculated values from the experimental values are 0.013 Å for the C-C bond, 0.015 Å for the C-N bond and 0.017 Å for the C-O bond. If we consider that some of the experimentally obtained structures are considerably distorted due to the crystal fields, we find that the above standard deviations are small.

As our theory is considerably successful for the molecules whose bond lengths are experimentally known, it is expected that we can predict a molecular geometry experimentally unknown, and that we can make a systematic investigation of a relation among molecular geometries of similar molecules with much accuracy, because the theoretical results for each molecule are more coherent than the experimental results are. For example, comparing the calculated results of lumiflavine and its cation, we find that the dominant effect of the protonation is to change the bond lengths in the region of N-C-N-C-O very much. In the experimental results, such a systematic change is not so evident. We think this is because the experimental errors are involved rather independently in determining the two molecular geometries. The similar situation is also seen in the molecular geometries of tropolone and tropolonate and of chlorophyll a and chlorophyll b. It will be a theoretically important task to investigate a correlation among the molecular geometries together with the electronic structures of many conjugated molecules.



#### 4. Wavelength of Optical Absorption and Oscillator Strength

We consider the optical absorption due to the transition from the ground state  $|0\rangle$  to the first excited state  $|1\rangle$ . In our theory, the absorption wavelength  $\lambda$  is expressed by

$$\lambda_{01} = 1240 / (e_{N/2+1} - e_{N/2}) \text{ m}\mu, \quad (10)$$

where  $e_{N/2+1}$  and  $e_{N/2}$  are the energies (in eV) of the lowest unoccupied and the highest occupied molecular orbitals, respectively. The calculated wavelengths of optical absorption between these states are listed and compared with the experimental values in Table 5. In the table, the oscillator strength  $f_{01}$  is also listed. The theoretical value of it is obtained using the dipole velocity formalism. The experimental value of it is obtained from a formula [58]

$$f_{01} = 7.65 \times 10^{-2} (\varepsilon_{\max} \Gamma / \lambda_{\max}^2), \quad (11)$$

by assuming the absorption curve as a Gaussian form as follows

$$\varepsilon(\lambda) = \varepsilon_{\max} \exp [ -(\lambda - \lambda_{\max})^2 / \Gamma^2 ], \quad (12)$$

where  $\varepsilon$ ,  $\varepsilon_{\max}$ ,  $\lambda_{\max}$  and  $\Gamma$  are an extinction coefficient, that of the maximum absorption, the wavelength of the maximum absorption, and the half width of the absorption curve, respectively, and  $\Gamma$  and  $\lambda_{\max}$  are in units of  $\text{m}\mu$ .

For the molecules marked by asterisks, the energy level of HOMO and LUMO are degenerate or nearly degenerate. Then, the lower excited levels are expected to be split by configuration mixing. As we do not adopt the CI method in this theory, we compare our calculated wavelengths to the experimental values of the  $p$ -band for aromatics and the  $Q$ -band for porphyrins.

From Table 5, we see that the calculated values of absorption wavelengths agree well with the experimental values although we have not taken into account the solvent effect which would be considerably larger for these heteroconjugated molecules. The calculated oscillator strengths are not in good agreement with the experimental values. The situation will be considerably improved for some molecules if we adopt the CI method [65]. However, at present, satisfactory results have not been obtained for many molecules even in the detailed calculation [66].

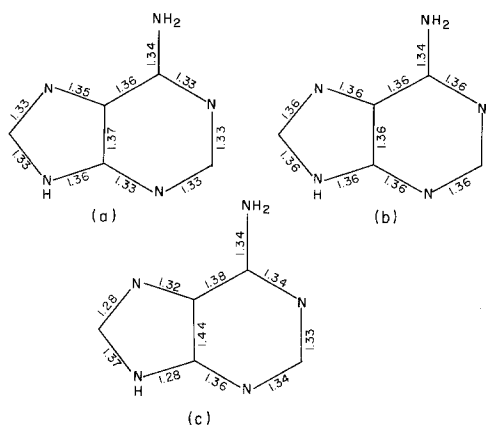
#### 5. Relation among Molecular Geometry, Electronic Structure and Adiabatic Potential Surface

In this section, we examine the relation between the molecular geometry and the electronic structure in some detail, using two typical molecules, adenine and all-*trans* retinal. The accurate molecular geometry of adenine was not obtained until recently. Therefore, many calculations so far were made using some assumed geometries or the former experimental one. In Fig. 2, three tentative molecular

**Table 5.** Molecular structures, wavelengths of the optical absorption  $\lambda_{01}$ 's and oscillator strengths  $f_{01}$ 's

Molecules <sup>a,b</sup>	Mol. str.		$\lambda_{01}$ (m $\mu$ )		$f_{01}$	
	No.	Ref.	calc.	exp. <sup>c</sup>	calc.	exp. <sup>h</sup>
urea			196	< 220(NaOH) <sup>d</sup>	0.244	—
formic acid	I	[23]	172	205 <sup>d</sup>	0.252	—
phenol*			228	211(W)*	0.342	0.15
pyridine*	II	[24]	226	251(H)*	0.294	0.04
pyrazine*	III	[25]	243	260(CH)*	0.302	0.10
pyrimidine*	IV	[26]	225	244(CH)*	0.298	0.04
<i>s</i> -triazine*	V	[27]	207	216(H)*	0.442	0.003
furan	VI	[28]	218	207(CH)	0.186	—
pyrrole	VII	[29]	212	208(H)	0.212	—
imidazole	VIII	[30]	208	206(ASP)	0.200	—
1,3,4-oxadiazole	IX	[31]	203		0.173	
tropolone	X		347	353(E)	0.422	—
tropolonate	XI	[32]	418	398(KOH)	0.223	0.15
cytosine	XII	[33]	287	267(W)	0.194	0.14
thymine	XIII	[34]	276	264(W)	0.316	0.18
<i>p</i> -benzoquinone*	XIV	[35]	325	278(H)*	0.646	0.009
benzoic acid			260	272(E)	0.418	0.02
quinoline			288	281(M)	0.229	0.17
1-naphthol			300	295(M)	0.257	0.13
1-naphthylamine			327	320(E)	0.256	0.14
indole	XV	[36]	268	263(M)	0.212	—
purine	XVI	[37]	268	263(M)	0.396	0.29
carbazole	XVII	[38]	296	324(E)	0.130	0.07
guanine	XVIII	[39]	315	275(W)	0.312	0.17
adenine	XXIX	[40]	280	262(W)	0.359	0.30
<i>p</i> -naphthaquinone	XX	[41]	345	332(M)	0.343	0.06
acridine	XXI	[42]	387	351(E)	0.204	0.14
acridinylium			412	400(ACI)	0.152	0.07
9-aminoacridinylium			391	407(ACI)	0.281	0.14
anthraquinone*	XXII	[43]	335	321(CH)*	0.496	0.09
$\alpha$ -phenazine	XXIII	[44]	397	362(M)	0.180	0.19
lumiflavine	XXIV	[45]	443	445(W)	0.441	—
lumiflavine cation	XXV	[45]	368	399(ACI)	0.507	0.40
fluorenone			360	379(E)	0.068	0.006
PPF			345	326(CH)	0.663	0.75
PPD			318	285(CH)	0.632	0.92
11- <i>cis</i> retinal	XXVI	[46]	347	369(EPA) <sup>e</sup>	0.329	0.65
all- <i>trans</i> retinal	XXVII	[47]	382	373(EPA) <sup>e</sup>	0.877	1.2
all- <i>trans</i> RSB	XXVIII	[48]	365	365(W) <sup>e</sup>	0.941	1.2
all- <i>trans</i> PRSB	XXIX	[48]	442	438(HCl) <sup>f</sup>	0.802	1.0
canthaxanthin	XXX	[49]	464	480(B) <sup>g</sup>	1.35	2.0
metalloporphyrin**	XXXI	[50]	622	637(D)**	0.526	0.03
chlorophyll a**	XXXII	[51]	697	660(DE)**	0.691	0.4
chlorophyll b**	XXXIII	[52]	670	642(DE)**	0.626	0.2

<sup>a</sup> RSB and PRSB are abbreviations of unprotonated and protonated Schiff-bases of retinal, respectively. For the N–N bond in 1, 3, 4-oxadiazole, the resonance integral is calculated using the function of C–N bond. The Coulomb integrals of the four nitrogen atoms in porphyrins are chosen as  $-9.0$  eV.



**Fig. 2.** Tentative molecular geometries of adenine. (a) is the one proposed by Spencer [67], (b) is the one used by Tanaka and Nagakura [68], and (c) is the one obtained by Broomhead [69]

geometries of adenine are drawn. Structure (a) is the one proposed by Spencer [67], who used some experimental data of similar molecules, structure (b) is the one used by Tanaka and Nagakura in the calculation of the electronic structure of this molecule [68], and the structure (c) is one which was experimentally obtained by Broomhead for the hydrochloride in the earlier time [69]. These structures are able to become good representatives in our study. We denote molecular geometries of ours, of the experiment by Stewart and Jensen, of Spencer, of Tanaka and Nagakura, and of Broomhead as T, E, A, B and C, respectively. In Fig. 3a, we plotted the calculated and the adiabatic potentials  $E_g$  and  $E_e$  of the ground and the excited states, and the transition energy  $\Delta E$  by changing the molecular geometry along the path which connects the two points among T, E, A, B and C in the multi-dimensional space of internal coordinates. From this, we find that the absorption wavelength obtained in our geometry is the smallest and that the wavelength obtained in the geometry of Tanaka and Nagakura is the largest. The difference of the two wavelengths is 19  $m\mu$  and this is about 7% of our calculated value. It is also seen from this graph that the variation of  $E_e$  is relatively smaller than that of  $E_g$ ; and that  $\Delta E$  is likely to be small when  $E_g$  is large although there are some exceptions. This property appears to hold true for many conjugated molecules.

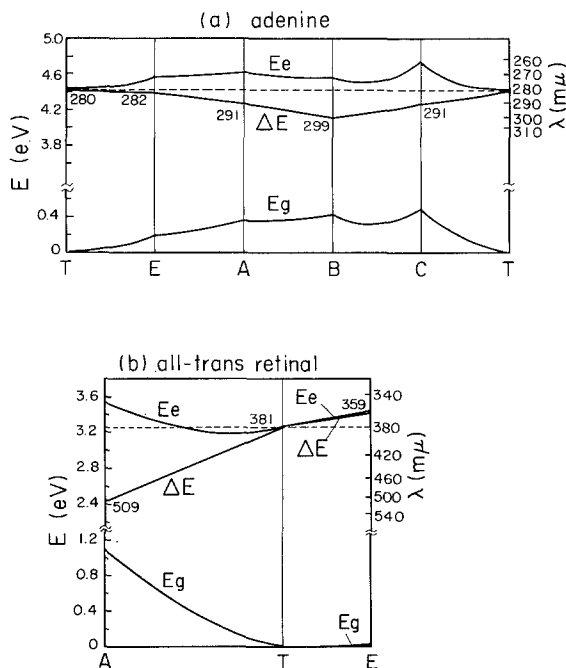
In Fig. 3b, we also plotted the similar diagram of all-*trans* retinal. Points T, A and E correspond to the geometry obtained by our calculation, the one assumed in the

<sup>b</sup> For adenine, the structure of 9-methyladenine is used. For indole, the structure of scatole is used. For metalloporphyrin, the structure of dichloro-octaethylprophatinotin is used.

<sup>c</sup> All the values are for the first absorption, but those marked by \* refer to the *p*-band, and those marked by \*\* are for the *Q*-band. Unless otherwise noted, data are from Ref. [53]. Letters in parentheses denote solvents. H: hexane, CH: cyclohexane, ASP: aqueous  $\text{Na}_2\text{HPO}_4$ , E: ethanol, W: water, M: methanol, ACl: aqueous HCl, EPA: ether-isopentane-alcohol, B: benzene, D: dioxane, DE: diethyl ether.

<sup>d</sup> Ref. [54]. <sup>e</sup> Ref. [55]. <sup>f</sup> Ref. [56]. <sup>g</sup> Ref. [57].

<sup>h</sup> The bar — denotes that it is impossible to obtain an experimental value because of an overlap of some spectral curves or broad band.



**Fig. 3.** Graphs of the adiabatic potentials  $E_g$  and  $E_e$  of the ground and excited states, respectively, and of the transition energy  $\Delta E$  along the path connecting the typical points in the multidimensional space of internal coordinates. In all these calculations, the self-consistent HMO theory is used so that the self-consistency may be satisfied for the bond order in  $\beta_{ab}^*$ . In adenine, points T, E, A, B and C denote the molecular geometries of our calculation, of the experiment by Stewart and Jensen, of (a), (b) and (c) in Fig. 2, respectively. In all-*trans* retinal, points T, E and A are molecular geometries of our calculation, of the experiment by Hamanaka *et al.*, and of the usual Hückel approximation, respectively. Numbers in the figure denote the wavelength

usual HMO theory (that is, all the C–C bond lengths are 1.40 Å and C–O bond length 1.20 Å), and the experiment by Hamanaka *et al.*, respectively. In this case, the difference of the absorption wavelengths between T and A is 128 m $\mu$ , and it is 34% of our calculated value. These properties are also seen in many other conjugated molecules. From these results, it is found that the electronic structure is considerably sensitive to the molecular geometry. The following rule holds true for the path between T and A of all-*trans* retinal as before. The variation of  $E_e$  is smaller than that of  $E_g$ , and  $\Delta E$  becomes small when  $E_g$  is large. However, this does not apply for the path between T and E. That is,  $E_g$  scarcely varies and  $E_e$  increases considerably for the path T  $\rightarrow$  E. So that, the adiabatic potential surface of retinal will be considerably specific. We see that this is chiefly due to the large bond alternation near the minimum point of  $E_g$  and relatively small bond alternation near the minimum point of  $E_e$  [70, 71]. In the ground state, the adiabatic potential is very steep along the path corresponding to the bond alternation due to the cooperative force of electrons to enhance the bond alternation [4] and it

becomes very flat along the other paths. These properties apply for the other carotenoids. We have already obtained the peculiar force constants for these molecules [17].

## 6. Effect of Inclusion of the $\omega$ -Technique

In the self-consistent HMO theory up to this point, the Coulomb integral  $\alpha_a$  is taken as a constant for simplicity. However, it is a natural idea that  $\alpha_a$  should be changed according to the charge density on each atom. To examine this effect, we apply the  $\omega$ -technique to our self-consistent HMO theory as follows [72];

$$\alpha'_a = \alpha_a + \omega\beta_0(n_a - q_a), \quad (13)$$

where  $\omega$  and  $n_a$  are a constant which we choose as 1.0 in this paper, and the charge density for  $\pi$ -electrons, respectively. Applying this method to 44 heteroconjugated molecules in Table 5, we find that the difference between molecular geometries calculated with and without using the  $\omega$ -technique is very small (about 0.01 Å in many bonds) except for cytosine and some ionic molecules. However, there seems to be a systematic tendency that C–O and C–N bonds projecting from an aromatic ring become smaller in the calculation with the  $\omega$ -technique and closer to experiment. For example, the calculated value of the C–O bond in guanine is 1.220 Å for  $\omega = 1.0$  and 1.262 Å for  $\omega = 0$ , respectively.

In Table 6, the calculated results of the absorption wavelength, the oscillator strength, the ionization potential and the dipole moment for  $\omega = 1$  and  $\omega = 0$  are shown. In these, the ionization potential is equated to the negative of the highest occupied molecular orbital energy. The dipole moment is calculated by the use of an equation

$$\mathbf{d} = \sum_a \mathbf{R}_a(n_a - q_a), \quad (14)$$

where  $\mathbf{R}_a$  is a position vector of atom  $a$ . This equation can be applied only to neutral molecules.

Comparing Table 5 with Table 6, we find that  $\lambda_{01}$  and  $f_{01}$  differ very little in most molecules between the two calculations. In the ionic molecules, considerable differences are seen. The ionization also differs very little between the two calculations and the calculated values are relatively in good agreement with the experiments. In the dipole moment, it is evident that the calculated values with the  $\omega$ -technique are much smaller than those without the  $\omega$ -technique. The experimental values are considerably different from those of the two calculations. This may be due to our neglect of the effects of hydrogen atoms and methyl groups where considerable amounts of the charge are expected to be stored and the effects of core electrons of conjugated regions [22]. From this table, it is estimated that the contributions of the above effects to the dipole moment would be comparable to the one which we calculated for the heteroconjugated molecules. Then we must wait to determine which calculation is better for the dipole moment until we can estimate the magnitude of the above effects accurately.

**Table 6.** Wavelengths of optical absorption  $\lambda_{01}$ , oscillator strengths  $f_{01}$ , ionization potentials  $I$  and dipole moments  $d$  calculated with and without using the  $\omega$ -technique

Molecules	$\lambda_{01}(\text{m}\mu)^{\text{a}}$ $\omega = 1.0$	$f_{01}^{\text{a}}$ $\omega = 1.0$	$I(\text{eV})$			$d(\text{D})$		
			$\omega = 0$	$\omega = 1.0$	exp. <sup>b</sup>	$\omega = 0$	$\omega = 1.0$	exp. <sup>f</sup>
urea	204	0.272	10.0	10.36		5.49	3.24	4.56 <sup>g</sup>
phenol	226	0.265	8.78	8.79	8.51	0.71	0.64	1.55
pyridine	221	0.295	9.26	9.32	9.3	0.91	0.68	2.19 <sup>g</sup>
pyrimidine	221	0.297	9.45	9.51	9.42 <sup>c</sup>	0.88	0.67	
furan	218	0.182	8.79	8.74	8.89	1.61	1.24	0.69
pyrrole	214	0.205	8.54	8.48	8.20	2.93	2.19	1.84
imidazole	211	0.197	8.76	8.74		3.69	2.67	
tropolone	337	0.152	8.12	8.02		6.04	2.99	
tropolonate	395	0.233	7.58	8.10		—	—	
cytosine	310	0.233	8.38	7.99	8.90 <sup>c</sup>	8.96	4.88	
thymine	270	0.290	8.51	8.42	9.43 <sup>c</sup>	5.54	3.00	
<i>p</i> -benzoquinone	331	0.665	9.40	9.17	9.95 <sup>d</sup>	0	0	
quinoline	287	0.233	8.66	8.64	8.62 <sup>e</sup>	1.01	0.70	2.29 <sup>g</sup>
indole	263	0.383	8.29	8.30		1.27	1.01	
purine	262	0.421	8.74	8.80		5.03	3.62	
guanine	321	0.315	7.76	7.57		9.22	5.78	
adenine	277	0.356	8.18	8.23	8.91 <sup>c</sup>	2.77	2.14	
lumiflavine	421	0.405	8.00	7.92		8.15	3.65	
11- <i>cis</i> retinal	343	0.305	8.26	8.25		2.80	1.68	10.3 ± 5.6 <sup>h</sup>
all- <i>trans</i> retinal	375	0.886	8.16	8.15		3.72	2.19	3.5 ± 3.3 <sup>h</sup>
all- <i>trans</i> RSB	364	0.945	8.11	8.10		1.84	1.12	1.3 ± 0.7 <sup>h</sup>
all- <i>trans</i> PRSB	426	0.776	8.23	8.20		—	—	
canthaxanthin	462	1.36	7.67	7.67		0	0	

<sup>a</sup> Values for  $\omega = 0$  are listed in Table 5.

<sup>b</sup> Unless otherwise noted, the experimental values are taken from Ref. [59].

<sup>c</sup> Ref. [60]. <sup>d</sup> Ref. [61]. <sup>e</sup> Ref. [62].

<sup>f</sup> Unless otherwise noted, the experimental values are taken from Ref. [63].

<sup>g</sup> Ref. [59]. <sup>h</sup> Ref. [64].

To conclude this section, it may be said that the  $\omega$ -technique would not be necessary for most molecules in the calculation of the molecular geometry and the electronic structure so far as the calculation is made self-consistently for the bond length.

## 7. Conclusion and Discussion

It was shown that the self-consistent HMO theory is very useful for the investigation of the molecular geometry, the electronic spectra, the ionization potential and so on for heteroconjugated molecules. It is also proved that the electronic structure is considerably sensitive to the molecular geometry and that the inclusion of the  $\omega$ -technique is generally not so important for the molecular geometry and the electronic spectrum.

In our formalism, all the force constants are easily calculated by differentiating  $E^T$  given in Eq. (1) by bond lengths and torsional angles. Extensive application of this theory for the analysis of the molecular vibration is now in progress. This theory can be also applied for the calculation of the molecular structure in the excited state and the fluorescence spectra [71].

It is satisfying to find that a good quantitative agreement was obtained, for many molecular properties, between experiment and the results of such a simple theory. It will be a theoretically important task to investigate its reason. The self-consistent HMO theory is essentially based on the one-body approximation for a many- $\pi$ -electrons system. In this theory, the most important contribution from the two-center electron repulsion integrals is taken into account by means of the variable resonance integral  $\beta(R)$  [4], and the electron-electron correlation is taken into account by the adoption of a correlation between the bond orders. This correlation term affects the electronic structure and the molecular geometry considerably through the variable resonance integral by satisfying the condition of the self-consistency. From these, it may be said that the self-consistency is an important key to consider the reason why the present theory is phenomenologically so successful. The form of Eq. (2) is similar to the form of the  $\omega$ -technique of Eq. (13). Therefore, we may call our method as a  $\zeta$ -technique.

When we want to obtain the triplet state by the self-consistent HMO theory, we should use another function of  $\beta(R)$  and another value of  $\zeta$  which are suitable for the triplet state. It is because the effect of the exchange interaction which enters into our  $\beta(R)$  and  $\zeta$  differs for the singlet and the triplet states. This situation is much different from that of the usual HMO theory where the triplet state is not obtainable.

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## References

1. Pariser, R., Parr, R. G.: *J. Chem. Phys.* **21**, 446, 767 (1953); Pople, J. A.: *Trans. Faraday Soc.* **49**, 1375 (1953)
2. Pople, J. A., Santry, D. P., Segal, G. A.: *J. Chem. Phys.* **43**, s129 (1965); Pople, J. A., Segal, G. A.: *J. Chem. Phys.* **43**, s136 (1965), **44**, 3289 (1966)
3. Warshel, A., Karplus, M.: *J. Am. Chem. Soc.* **94**, 5612 (1972), **96**, 5677 (1974)
4. Kakitani, T.: *Progr. Theoret. Phys.* **52**, 1721 (1974)
5. Bingham, R. C., Dewar, M. J. S., Lo, D. H.: *J. Am. Chem. Soc.* **97**, 1285, 1294, 1302, 1307 (1975); Dewar, M. J. S., Lo, D. H., Ramsden, C. A.: *J. Am. Chem. Soc.* **97**, 1311 (1975)
6. Dewar, M. J. S., Gleicher, G. J.: *J. Am. Chem. Soc.* **87**, 685 (1965); Dewar, M. J. S., Morita, T.: *J. Am. Chem. Soc.* **91**, 796, 802 (1969)
7. Lo, D. H., Whitehead, M. A.: *Can. J. Chem.* **46**, 2027, 2041 (1968)
8. Yamaguchi, H., Nakajima, T., Kunii, T. L.: *Theoret. Chim. Acta (Berl.)* **12**, 349 (1968); Nakajima, T., Toyota, A.: *Chem. Phys. Letters* **3**, 272 (1969); Fujimura, Y., Yamaguchi, H., Nakajima, T.: *Bull. Chem. Soc. Japan* **45**, 384 (1972)

9. Suzuki, H., Takizawa, N., Komatsu, T.: *Suppl. Prog. Theoret. Phys.* **46**, 16 (1970); Suzuki, H., Takizawa, N., Komatsu, T.: *J. Phys. Soc. Japan* **31**, 895 (1971)
10. Golebiewski, A., Nowakowski, J.: *Acta Phys. Polon.* **25**, 647 (1964)
11. Parczewski, A.: *Tetrahedron* **26**, 3539 (1970)
12. Golebiewski, A., Parczewski, A.: *Acta Physica Polon.* **A37**, 879 (1970)
13. Evleth, Jr. E. M., Berson, J. A., Manatt, S. L.: *J. Am. Chem. Soc.* **87**, 2908 (1965)
14. Berson, J. A., Evleth, Jr. E. M., Hamlet, Z.: *J. Am. Chem. Soc.* **87**, 2887 (1965)
15. Figeys, H. P.: *Tetrahedron* **26**, 4615 (1970)
16. Caldow, G. L.: *Mol. Phys.* **18**, 383 (1970)
17. Kakitani, T.: *Prog. Theoret. Phys.* **51**, 656 (1974)
18. Cox, E. G., Jeffrey, G. A.: *Proc. Roy. Soc.* **A207**, 110 (1951)
19. Lofthus, A.: *Mol. Phys.* **2**, 367 (1959)
20. Häfelinger, G.: *Chem. Ber.* **103**, 2902 (1970)
21. Häfelinger, G.: *Chem. Ber.* **103**, 2922 (1970)
22. Streitwieser, A., Jr.: *Molecular orbital theory for organic chemists*, Chapt. 5. New York-London: John Wiley 1961
23. Almenningen, A., Bastiansen, O., Motzfeldt, T.: *Acta Chem. Scand.* **23**, 2848 (1969)
24. Bak, B., Hansen-Nygaard, L., Rastrup-Anderson, J.: *J. Mol. Spectry.* **2**, 361 (1958)
25. Wheatley, P. J.: *Acta Cryst.* **10**, 182 (1957)
26. Wheatley, P. J.: *Acta Cryst.* **13**, 80 (1960)
27. Lancaster, E. B., Stoicheff, B. P.: *Can. J. Phys.* **34**, 1016 (1956)
28. Bak, B., Hansen, L., Rastrup-Anderson, J.: *Disc. Faraday Soc.* **19**, 30 (1955)
29. Bak, B., Christensen, D., Hansen, L., Rastrup-Anderson, J.: *J. Chem. Phys.* **24**, 720 (1956)
30. Carrera, S. M.: *Acta Cryst.* **20**, 783 (1966)
31. Nygaard, L., Hansen, R. L., Nielsen, J. T., Rastrup-Anderson, J., Sørensen, G. O., Steiner, P. A.: *J. Mol. Struct.* **12**, 59 (1972)
32. Shiono, R.: *Acta Crysta.* **14**, 42 (1961)
33. Barker, D. L., Marsh, R. E.: *Acta Cryst.* **17**, 1581 (1964)
34. Gerdil, R.: *Acta Cryst.* **14**, 333 (1961)
35. Trotter, J.: *Acta Cryst.* **13**, 86 (1960)
36. Hanson, A. W.: *Acta Cryst.* **17**, 559 (1964)
37. Watson, D. G.: *Acta Cryst.* **19**, 573 (1965)
38. Lahiri, B. N.: *Acta Cryst.* **A25**, s127 (1964)
39. Thewalt, U., Bugg, C. E., Marsh, R.: *Acta Cryst.* **B27**, 2358 (1971)
40. Stewart, R. F., Jensen, L. H.: *J. Chem. Phys.* **15**, 2071 (1964)
41. Gaultier, J., Hauw, C.: *Acta Cryst.* **18**, 179 (1965)
42. Phillips, D. C., Ahmed, F. R., Barnes, W. H.: *Acta Cryst.* **13**, 365 (1960)
43. Prakash, A.: *Acta Cryst.* **22**, 439 (1967)
44. Herbststein, F. H., Schmidt, G. M. J.: *Acta Cryst.* **8**, 406 (1955)
45. Kierkegaard, P., Norrestam, R., Werner, P., Csöregi, I., Von Glehn, M., Karlson, R., Leijonmarck, M., Rönnquist, O., Stensland, B., Trillberg, O., Torbjörnsson, L.: *Flavins and flavoproteins*, Kamin, H. ed., p. 1. Butterworths, University Park Press 1971
46. Gilardi, R. D., Karle, I. L., Karle, J.: *Acta Cryst.* **B28**, 2605, (1972)
47. Hamanaka, T., Mitsui, T.: *Acta Cryst.* **28**, 214 (1972)
48. Hamanaka, T., Mitsui, T., Azuma, K.: Report of 12th annual meeting of Biophysical Society of Japan, p. 81, 1973 (in Japanese)
49. Bart, J. C. J., MacGillavry, C. H.: *Acta Cryst.* **B24**, 1587 (1968)
50. Cullen, D. L., Meyer, Jr., E. F.: *Chem. Commun.* 616 (1971)
51. Chow, H. C., Serlin, R. C., Strouse, C. E.: *J. Am. Chem. Soc.* **97**, 7230 (1975)
52. Serlin, R., Chow, H. C., Strouse, C. E.: *J. Am. Chem. Soc.* **97**, 7237 (1975)
53. *UV Atlas of organic compounds*, Perkampus, H. H., et al. eds., Vol. I 1966, Vol. II 1966, Vol. III 1967, Vol. IV 1968, Vol. V 1971, London: Butterworths
54. Grasselli, J. G., Ritchey, W. H.: *Atlas of spectral data and physical constants for organic compounds*. CRC 1975
55. Sperling, W., Rafferty, C. N.: *Nature* **224**, 591 (1969)



56. Pitt, G. A., Collins, F. D., Morton, R. A., Stok, P.: *Biochem. J.* **59**, 122 (1955)
57. Zechmeister, L.: *Cis-trans isomeric carotenoids, vitamin A, and arylpolyenes*. Wien: Springer-Verlag 1962
58. Burke, M. J., Pratt, D. C., Faulkner, T. R., Moscovitz, A.: *Exp. Eye Res.* **17**, 557 (1973)
59. Weast, R. C.: *Handbook of chemistry and physics*, 52nd edition. The Chemical Rubber Co. 1971-1972
60. Bergmann, E. D., Feilchenfeld, H. W., Lifshitz, C.: *Jerusalem Symp.* **1**, 72 (1969)
61. Dewar, M. J. S., Worley, S. D.: *J. Chem. Phys.* **50**, 654 (1969)
62. Dewar, M. J. S., Worley, S. D.: *J. Chem. Phys.* **51**, 263 (1969)
63. McClellan, A. L.: *Tables of experimental dipole moments*. San Francisco: Freeman 1963
64. Mathies, R., Stryer, L.: *Proc. Natl. Acad. Sci.* **73**, 2169 (1976)
65. Nagata, C., Imamura, A., Fujita, H.: *Advan. Biophys.* **4**, 1 (1973)
66. Benard, M., Julg, A.: *Intern. J. Quantum Chem.* **7**, 945 (1973)
67. Spencer, M.: *Acta Cryst.* **12**, 59 (1959)
68. Tanaka, M., Nagakura, S.: *Theoret. Chim. Acta (Berl.)* **6**, 320 (1966)
69. Broomhead, J. M.: *Acta Cryst.* **1**, 324 (1948)
70. Kakitani, T.: *Prog. Theoret. Phys.* **49**, 1 (1973)
71. Kakitani, T., Kakitani, H.: *J. Phys. Soc. Japan* **42**, 1287 (1977)
72. Streitwieser, A., Jr.: *J. Am. Chem. Soc.* **82**, 4123 (1960)

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