

complex, it is barely discernible in the *p*-methoxy compound. This suggests that the acetonitrile complex is of *cis* symmetry, while the *p*-methoxybenzonitrile complex is *trans*. The low intensity absorption which does appear at 303  $\text{cm}^{-1}$  in the latter compound may be due to a small amount of the *cis* isomer or to lattice effects which remove slightly the selection rule restriction. This evidence regarding the geometry of the *p*-methoxybenzonitrile complex parallels the results of dielectric constant measurements of benzene solutions of benzonitrile and tin(IV) chloride,<sup>1</sup> although the evidence in both instances is weak. The much lower solubility of the acetonitrile complex in benzene may also be ascribed to its *cis* geometry.

**The Nitrile Intensity.**—The intensities of the complexed nitrile absorptions relate closely to the points just mentioned. The variation in the nitrile absorption intensity with substituent has been treated previously.<sup>4</sup> The same considerations apply to the complexed nitriles, with the exception that the lowering of the  $\pi^*$  level of the nitrile group upon addition compound formation results in an increased intensity. The intensity increase is much larger for the benzonitriles substituted with electron releasing substituents, a result which is consistent with the observed frequency variations, as discussed.

It is interesting that the square root of the complexed nitrile intensity correlates with the electrophilic substituent constants just as the free nitrile intensities<sup>4</sup>; the slope of the correlation line is, however, steeper. The extent to which the slope changes in this correlation as the Lewis acid is varied should provide an interesting measure of acid strength.

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## Appendix

The vibrational system to be considered is the linear

$$\begin{matrix} F_1 & F_2 & F_3 \\ M_1-M_2-M_3-M_4 \end{matrix}$$

where  $M_1$  equals 15 ( $\text{CH}_3$ ) or 100 ( $p\text{-CH}_3\text{OC}_6\text{H}_4$ ),  $M_2=12$  (C),  $M_3=14$  (N)  $M_4=\infty$  ( $\text{SnCl}_4$ ). The axial vibrations only are considered. In a more precise treatment one would need to consider the interaction which leads to the symmetric-asymmetric Sn-N frequency difference in the 2:1 complexes. In the present case the frequency of the tin-nitrogen mode is taken as the mean of the two frequencies which are assigned to the symmetric and asymmetric tin-nitrogen vibrations. If the assignment of these two frequencies is correct the approximation is good, since the central group possesses a large mass. If the assignment is incorrect and only the higher frequency, for example, is a tin-nitrogen vibration, the results are not qualitatively changed. Only the value for the tin-nitrogen force constant,  $F_3$ , would be affected to any extent. Table III contains the requisite experimental information, as well as the results of the

TABLE III

RESULTS OF NORMAL COÖRDINATE ANALYSIS OF NITRILE-TIN VIBRATIONS IN TIN(IV) CHLORIDE-NITRILE ADDITION COMPOUNDS

Compound	$\nu_1^a$	$\nu_2$	$\nu_3$	$F_1^b$	$F_2^b$	$F_3^b$
$\text{CH}_3\text{CN}$	2248 <sup>c</sup>	920 <sup>d</sup>	..	5.2	17.4	0
$\text{SnCl}_4 \cdot 2\text{CH}_3\text{CN}$	2303 <sup>e</sup>	940 <sup>d</sup>	322 <sup>e</sup>	5.2	17.6	3.1
$p\text{-CH}_3\text{OC}_6\text{H}_4\text{CN}$	2227 <sup>e</sup>	..	..	5.5	17.1	0
$\text{SnCl}_4 \cdot 2p\text{-CH}_3\text{OC}_6\text{H}_4\text{CN}$	2249 <sup>f</sup>	..	320 <sup>e</sup>	5.5	16.9	3.1

<sup>a</sup> Frequencies in  $\text{cm}^{-1}$ . <sup>b</sup> Force constants in units of  $\text{mdynes}/\text{Å}$ . <sup>c</sup> Ref. 8; spectrum in benzene solution. <sup>d</sup> Ref. 9; spectrum of solid. <sup>e</sup> Present work; spectrum of solid as Nujol mull. <sup>f</sup> Present work; spectrum in benzene solution. This is essentially the nitrile frequency for the 1:1 complex, which differs very little, if at all, from that for the 2:1.

calculations. The values for  $F_1$  were assumed. The results of interest, the values for  $F_2$  and the change in  $F_2$  on addition compound formation, are not sensitive to the choice of  $F_1$ . No interaction force constants were employed. A trial calculation was made with an interaction force constant  $F_{23}$  of  $+0.5$   $\text{mdyne}/\text{Å}$ . The result was slightly higher value for  $F_2$  (about 0.2  $\text{mdyne}/\text{Å}$ . higher) and a slightly lower value for  $F_3$ . It thus remains true that the force constant of the nitrile group in the addition compounds is lower for *p*-methoxybenzonitriles than for acetonitrile.

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## On the Electronic Spectra of Some Substituted Benzenes

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Conjugative and inductive effects in styrene, phenylacetylene, benzaldehyde and benzonitrile are determined by means of second order perturbation method based on the molecular orbital theory including electron interaction and neglecting overlap. It is shown that mixing of locally excited states and the electron transfer states arising from the transfer of electron from the benzene to the substituent and from the substituent to the benzene is of importance in determining the energies of lower electronic states of substituted benzenes. Inductive parameters for phenylacetylene, benzaldehyde and benzonitrile are also determined.

The electronic spectrum of a composite alternant hydrocarbon R-S was theoretically discussed by Longuet-Higgins and Murrell<sup>1</sup> in relation to the excited electronic states of the separate fragments RH and SH. It was shown that the mixing of

(1) H. C. Longuet-Higgins and J. N. Murrell, *Proc. Phys. Soc.*, **68A**, 601 (1955).

the locally excited states and the electron transfer states plays an important role in the electron migration effect. In their calculations on the electronic spectra of composite hydrocarbons only one-electron transfer configurations were considered but interactions with two-electron transfer configurations are not negligible. It was shown by

I'Haya<sup>2</sup> that mixing of singly and doubly excited states of hydrocarbon and the one- and two-electron transfer states plays an important role in both the conjugative and inductive effects. The object of this paper is to evaluate the four main singlet-singlet transitions of some substituted benzenes with substituents possessing unsaturation, corresponding to the  $L_b$ ,  $L_a$ ,  $B_b$  and  $B_a$  bands of benzene making use of the second order perturbation theory and the configuration interaction. The inductive parameters are also determined from the observed ionization potentials and the calculated electron affinities. In the present calculation all possible one- and two-electron transfer states were considered except those which arise from the excitations  $\psi_b \rightarrow \psi_6$  and  $\psi_1 \rightarrow \psi_a$  where  $\psi_b$ ,  $\psi_a$  are the bonding and antibonding orbitals of the substituent molecule and  $\psi_1$ ,  $\psi_6$  are the lowest filled and the highest vacant orbitals of benzene. The six molecular orbitals of benzene are taken in the same real form as described in the reference.<sup>3</sup>

**Energies of Electron Transfer States.**—The energies of the possible one- and two-electron transfer states in styrene, phenylacetylene, benzonitrile and benzaldehyde are determined by the semi-empirical method discussed by I'Haya.<sup>2</sup> According to that method the ionization potentials and the electron affinities of the two conjugated systems are needed. The observed  $\pi$ -ionization potentials<sup>4-6</sup> of benzene, ethylene, acetylene, hydrogen cyanide and the formaldehyde are 9.24, 10.51, 11.41, 13.91 and 11.80 eV., respectively, and the electron affinity of benzene is  $-0.54$  eV.<sup>7</sup> In absence of the experimental values of the electron affinities of ethylene and acetylene, the latter quantities are taken as  $-2.04$  and  $-2.94$  eV., respectively, which are obtained from the theorem of Pople and Hush<sup>7</sup> that  $I+A$  is constant for alternating hydrocarbons. For the molecules hydrogen cyanide and formaldehyde the s.c.f.-m.o. treatment of Pople<sup>8</sup> or Hideo Kon<sup>9</sup> which introduces the semi-empirical features into the Roothan formulations, was chosen for the calculation of the ionization potentials and electron affinities. In determining the s.c.f.-m.o.'s for the  $\pi$  electrons, the lone pair orbitals and the  $\pi$  orbitals normal to the  $\pi$  orbitals that are conjugated with the benzene ring along with the  $\sigma$  orbitals are not treated explicitly but are treated as part of the core. This approximation does not appear to be too bad if certain core parameters are adjusted accordingly. Moreover no attempt has been made in this paper to determine the  $n \rightarrow \pi$  transition energies. Besides this approximation, the simplifying assumption of zero differential overlap is employed in common with Pople and Pariser and Parr. The SCF equations for the  $\pi$  orbitals of hydrogen cyanide and the formaldehyde were solved iteratively. The values

of  $\beta_{CN}$  and  $\beta_{CO}$  for hydrogen cyanide and formaldehyde were chosen to be  $-2.7$  and  $-3.0$  eV., respectively, which give the best agreement between the observed  $\pi$ -ionization potentials and the energies of the bonding orbital of those molecules. The results of the calculations are shown in the Table I and the energies of the bonding orbitals are compared with the observed ionization potentials. The calculated energies of the bonding and antibonding orbitals of hydrogen cyanide and formaldehyde are employed in the evaluation of the energies of the electron-transfer states in benzonitrile and benzaldehyde. The electronic repulsion integrals over the atomic orbitals are evaluated using the uniformly charged sphere approximation<sup>10</sup> and assuming all the bonds in the benzene ring and the bond joining the two conjugated systems to have lengths 1.39 and 1.44 Å., respectively, while the observed bond lengths are chosen for the bonds in the substituent molecule.

TABLE I  
ORBITAL ENERGIES AND MOLECULAR ORBITALS OF  
HYDROGEN CYANIDE AND FORMALDEHYDE

Molecules	$\pi$ -orbitals	Energy, eV.	Observed $\pi$ -ionization potential
Hydrogen cyanide	$\psi_b = 0.5985 \phi_c + 0.8212 \phi_N$	-14.01	13.91 eV. <sup>8</sup>
	$\psi_a = .8012 \phi_c - .5985 \phi_N$	-0.22	.....
Formaldehyde	$\psi_b = .6489 \phi_c + .7611 \phi_O$	-11.99	11.80 eV. <sup>8</sup>
	$\psi_a = .7611 \phi_c - .6489 \phi_O$	+2.58	.....

**Inductive Effect and Determination of Inductive Parameters.**—The inductive effect may be ascribed to the fact that the substituent modifies the potential field acting on the  $\pi$  electrons of hydrocarbon. In the present work we will consider the perturbation on a single electron at the atom attached to the substituent. The perturbations on the other atoms are neglected. The coulomb integral contribution  $\delta_\gamma$  on the carbon atom  $\gamma$  adjacent to the substituent due to the perturbing potential  $H_1'$  acting on the  $i$ 'th electron at atom  $\gamma$  is defined as

$$\delta_\gamma \int \phi_\gamma(i) H_1' \phi_\gamma(i) d\nu(i)$$

where  $\phi_\gamma$  is the atomic orbital of the atom  $\gamma$ . This inductive parameter  $\delta$  can be determined by the following formula<sup>2</sup> obtained from the second order perturbation theory and taking into account the electron interaction

$$I - I_B = \frac{1}{2} \left\{ \delta/3 + 0.0037\delta^2 + \frac{H_{3b}^2}{I_S - I_B} + \frac{H_{3a}^2}{A_S - I_B} \right\} \dots (1)$$

where  $I$  and  $I_B$  are the ionization potentials of the substituted benzene and benzene, respectively, while  $I_S$  and  $A_S$  are the ionization potential and electron affinity of the substituent molecule.  $H_{3b}$  and  $H_{3a}$  are the matrix elements between benzene orbital  $\psi_3$  and the bonding and antibonding orbitals  $\psi_b$  and  $\psi_a$  of the substituent, respectively. The matrix elements  $H_{3b}$  and  $H_{3a}$  are expressed in terms of the exchange integral  $\gamma$  of the C-C bond joining the two conjugated systems. On com-

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 (3) Y. I'Haya, *ibid.*, **81**, 6120 (1959).  
 (4) K. Watanabe, *J. Chem. Phys.*, **26**, 512 (1957).  
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 (7) J. A. Pople and N. S. Hush, *ibid.*, **51**, 600 (1955).  
 (8) J. A. Pople, *ibid.*, **49**, 1375 (1953).  
 (9) H. Kon, *Bull. Chem. Soc., Japan*, **28**, 275 (1955).

(10) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953).

TABLE II  
 ASSIGNMENTS<sup>a</sup> AND ENERGIES OF THE ELECTRON TRANSFER STATES IN STYRENE, PHENYLACETYLENE, BENZALDEHYDE AND BENZONITRILE

Assignments	Energy (eV.)			Assignment	Benzonitrile		
	Styrene	Phenylacetylene	Benzaldehyde		Energy (eV.)	Assignment	Energy (eV.)
$1/\sqrt{2} (\psi_b^4 \pm \psi_a^4)$	6.98	8.09	8.00	$\psi_b^4$	10.68	$\psi_{b_3^{54}}(A)$	15.05
$1/\sqrt{2} (\psi_b^5 \pm \psi_a^5)$	6.63	7.70	7.60	$\psi_a^5$	10.27	$\psi_{b_2^{54}}(A)$	15.82
$1/\sqrt{2} (\psi_{b_2^{55}} \pm \psi_{a_3^{54}})$	11.45	12.63	12.52	$\psi_a^a$	4.42	$\psi_{b_3^{54}}(B)$	17.67
$1/\sqrt{2} (\psi_{b_3^{55}} \pm \psi_{a_3^{55}})$	12.43	13.51	13.40	$\psi_a^a$	4.86	$\psi_{b_2^{54}}(B)$	16.24
$1/\sqrt{2} (\psi_{b_3^{54}}(A) \pm \psi_{a_2^{55}}(A))$	11.62	12.71	12.61	$\psi_{b_2^{55}}$	15.17	$\psi_{a_2^{54}}(A)$	10.28
$1/\sqrt{2} (\psi_{b_3^{54}}(B) \pm \psi_{a_2^{55}}(B))$	10.23	15.09	14.98	$\psi_{b_3^{55}}$	16.07	$\psi_{a_2^{54}}(B)$	10.38
$1/\sqrt{2} (\psi_{b_2^{54}}(A) \pm \psi_{a_2^{54}}(A))$	12.33	13.41	13.31	$\psi_{a_3^{54}}$	9.29	$\psi_{a_3^{54}}(A)$	9.70
$1/\sqrt{2} (\psi_{b_2^{54}}(B) \pm \psi_{a_2^{54}}(B))$	10.60	13.67	13.57	$\psi_{a_3^{55}}$	10.22	$\psi_{a_2^{54}}(B)$	11.84

<sup>a</sup> For explanation of notations see text and ref. 2.

TABLE III  
 CALCULATED MAGNITUDES OF THE RESONANCE AND INDUCTIVE EFFECTS RELATIVE TO THAT OF THE GROUND STATE (IN eV. UNITS)

	Styrene		Phenylacetylene		Benzaldehyde		Benzonitrile	
	Resonance effect	Inductive effect	Resonance effect	Inductive effect	Resonance effect	Inductive effect	Resonance effect	Inductive effect
L <sub>b</sub>	-0.3094	...	-0.1106	-0.0097	-0.1120	-0.3028	+0.8719	-1.2280
L <sub>a</sub>	-.7614	...	-.4431	+ .0056	-.4573	+ .1735	+ .1429	+ .7071
B <sub>b</sub>	-.9138	...	-.5273	+ .0048	-.6891	+ .1483	+ .2458	+ .6044
B <sub>a</sub>	+ .8478	...	-.4753	+ .0022	-.8851	+ .0693	+ .1921	+ .2821

TABLE IV  
 INDUCTIVE PARAMETERS AND COMPARISON OF THE CALCULATED AND OBSERVED SPECTRA (IN eV. UNITS)

	Styrene		Phenylacetylene		Benzaldehyde		Benzonitrile	
	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.
$\delta$	..	...	-0.377	...	-2.116	...	-4.279	...
I	8.96	8.86 <sup>a</sup>	9.15	9.15 <sup>a</sup>	9.51	9.51 <sup>e</sup>	9.95	9.95 <sup>f</sup>
L <sub>b</sub>	4.58	4.42 <sup>b</sup>	4.77	4.51 <sup>c</sup>	4.47	4.43 <sup>d</sup>	4.53	4.53 <sup>g</sup>
L <sub>a</sub>	5.38	5.03 <sup>b</sup>	5.70	5.27 <sup>d</sup>	5.86	5.08 <sup>d</sup>	6.99	5.54 <sup>d</sup>
B <sub>b</sub>	5.84	6.10 <sup>b</sup>	6.23	...	6.21	...	7.60	...
B <sub>a</sub>	7.60	7.19 <sup>b</sup>	6.28	...	5.93	...	7.22	...

<sup>a</sup> J. D. Morrison and A. J. C. Nicholson, *J. Chem. Phys.*, **20**, 1021 (1952). <sup>b</sup> H. B. Kleven and J. R. Platt, "Technical Report of the Laboratory of Molecular Structure and Spectra," University of Chicago (1954). <sup>c</sup> J. F. Music and F. A. Matsen, *J. Am. Chem. Soc.*, **72**, 5256 (1950). <sup>d</sup> Assumed from the data in solution, A. E. Gillam and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry," Edward Arnold (Publishers) Ltd. (1957). <sup>e</sup> See ref. 4. <sup>f</sup> See ref. 5. <sup>g</sup> B. D. Joshi, *J. Sci. Res. (Banaras Hindu University)*, **6**, 266 (1956).

paring the exchange integral of the C-C bond in benzene where it is -2.39 eV. (Parriser and Parr),  $\gamma$  in the present treatment is taken as -2.199 eV. Using this value of  $\gamma$  and the values of ionization potentials and the electron affinities estimated either experimentally or by the methods discussed in the earlier section,  $\delta$  for phenylacetylene, benzaldehyde and benzonitrile are determined and recorded in the Table IV. The inductive effect due to vinyl group in styrene has been neglected, and this seems to be justified because the carbon atoms in the two conjugated systems are in the same state of hybridization. Moreover the ionization potential of styrene calculated from the equation 1 neglecting  $\delta$  is found to agree fairly well with the observed value (Table IV). The second order energy shifts arising from the inductive interactions with the various singly and doubly excited states of benzene can be expressed in units of  $\delta^2$  and they were taken from I'Haya's paper.<sup>2</sup>

### Results

The energies and the assignments of the possible electron transfer states in styrene, phenylacetylene, benzaldehyde and benzonitrile are recorded in the Table II. To apply the second order

perturbation theory, the matrix elements of the resonance interactions between lower electronic states of benzene and the electron transfer states of the substituted benzenes are needed, and they are evaluated by the standard formulas<sup>2,11</sup> after neglecting the differential overlap. The observed energies and the assignments of the locally excited states of benzene corresponding to the L<sub>b</sub> L<sub>a</sub> B<sub>b</sub> and B<sub>a</sub> bands are taken from the reference.<sup>2</sup> Calculated resonance effect and the inductive effect of the lower electronic states relative to that of the ground state are recorded in the Table III. It is to be noted, however, that the magnitudes of the resonance interactions in some cases where the energies of the two interacting states involved are almost equal are obtained from solution of the second order determinant.

### Discussion

Table IV shows that agreement between the calculated and observed spectra is fairly satisfactory except for the L<sub>a</sub> bands of the benzaldehyde and benzonitrile. The agreement can be expected to be better if the electron transfer states arising

(11) J. N. Murrell and K. L. McEwen, *J. Chem. Phys.*, **24**, 1143 (1956).

from the excitations  $\psi_b \rightarrow \psi_6$  and  $\psi_1 \rightarrow \psi_a$  are allowed for. It would not be surprising if the predicted  $B_b$  and  $B_a$  bands of benzaldehyde and benzonitrile (Table IV) deviate appreciably from the observed spectra. Any deviation of the calculated result from the observed data should be attributed to the use of second order perturbation theory and to the assumption that  $\delta$  and  $\gamma$  are fixed in all interactions. Moreover, we have assumed the inductive perturbations only on the atom attached to the substituent. In view of large values of  $\delta$  for the nitrile and aldehyde groups, perturbations should be extended to the other atoms.

Now some comments should be made on the large values of  $\delta$  for the nitrile and aldehyde groups. The  $\pi$ -ionization potentials of a substituted benzene is increased due to the inductive effect of an electron attracting substituent and decreased by the conjugative effect of the substituent. These two opposing effects should therefore be considered in the determination of the  $\pi$ -ionization potentials of substituted benzenes. In view of higher observed ionization potentials of benzonitrile and benzaldehyde than that of benzene, large values of

$\delta$  in these two cases are therefore not surprising. Although large values of  $\delta$  in benzonitrile and benzaldehyde compared to that in chlorobenzene and phenol<sup>2</sup> seem to be incompatible with the empirical evidence conventionally quoted, some support of these results may be had from the discussions of dipole moments. It should be mentioned in this connection that the values of  $\delta$  as are shown in Table IV may involve appreciable error since they are very much sensitive to any error in the observed ionization potentials of the substituted benzenes.

Several works<sup>1,12</sup> have been done on the spectra of substituted benzenes. They have chosen to deal with this problem either using perturbation method or by the straightforward solution of the secular determinant but not including higher order configuration interaction in either case. It should be noted that the present paper and the references<sup>2,11</sup> show that two electron excited configurations play the important role in the spectra of substituted benzenes.

(12) L. Goodman and H. Shull, *J. Chem. Phys.*, **27**, 1388 (1957), and L. Goodman, I. G. Ross and H. Shull, *ibid.*, **26**, 474 (1957).

[CONTRIBUTION FROM ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS]

## Evidence for Exchangeable Hydrogen in Chlorophyll<sup>1</sup>

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Both chlorophylls a and b undergo slow exchange of hydrogen with methanol in carbon tetrachloride solution. Both compounds possess one enolizable (or exchangeable) hydrogen atom and exist predominantly in the keto form.

### Introduction

Whether chlorophyll possesses any labile or readily exchangeable hydrogen has long been the subject of discussion. From the structural formula it can be anticipated that the hydrogen atom at position 10 is in a favorable position for enolization and should, therefore, be both labile and exchangeable. Fischer and Goebel<sup>2</sup> observed that ethyl chlorophyllide has one hydrogen atom that reacts with Grignard reagent and showed that this reaction occurs at carbon 10; these experiments were carried out in pyridine solution. Direct attempts to observe hydrogen exchange in chlorophyll, however, have in the past been uniformly unsuccessful. The early experiments of Norris, Ruben and Allen<sup>3</sup> indicated less than 5% exchange with a mixture of chlorophylls a and b in aqueous-ethanol solution in a 30 minute period; these workers concluded that no hydrogen exchange occurs. Weigl and Livingston<sup>4</sup> made a detailed search for exchangeable hydrogen in chlorophyll. No detectable hydrogen-deuterium exchange was observed in neutral organic solvents containing an

excess of deuterium oxide; a reaction time of about 2 hr. was usually employed. Although in one experiment the exchange observed in 24 hr. was about 0.2 atom per molecule of chlorophyll, nevertheless, Weigl and Livingston concluded that no exchangeable hydrogen was present in chlorophyll. More recently, Kutyurin,<sup>5</sup> in connection with a study of possible photochemical exchange of hydrogen in chlorophyll, found a small amount of hydrogen exchange between chlorophyll and aqueous acetone in a 3-hr. period. Kutyurin did not exclude the possibility that chlorophyll does in fact have a labile hydrogen atom.

Our interest in the subject originated in observations we have made of the infrared spectra of ordinary and fully deuteriated (hereafter referred to as deuterio-) chlorophylls a and b.<sup>6</sup> Holt and Jacobs,<sup>7</sup> who have made the most detailed study of the infrared spectra of chlorophylls a and b, interpreted the absorption peaks in the 1600–1700  $\text{cm}^{-1}$  region to indicate that chlorophyll a exists as the enol, but that chlorophyll b is in the keto-form. The hydrogen at carbon atom 10 was assumed to be the enolized hydrogen atom in chlorophyll a. The reasons for the existence of chlorophyll a as the enol while

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

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