Experimental Determination of Ionization Potentials of Organic Amines, β-Carotene and Chlorophyll a

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Ionization potentials(I_p's) of several organic compounds have been determined by the method of photo-current measurements in gas and organic solvents. It has been found that the vapor-phase I_p's, calculated from those determined from the onsets of the photo-currents in solutions by using Born equation for the solvation energies of the cations and a common term for the energy of the electron in solution, agree well with those measured in the vapor phase. Based on this result, the I_p's of molecules in the gas phase can be derived from those measured in the solution. This method is useful for the determination of I_p's of large molecules which cannot be obtained in the gas phase. Some of the I_p's obtained are: 5.6 for 1,1,4,4-tetrakis(dimethylamino)butadiene, 5.7 for 3,3'-dimethyl-2,2'-bibenzothiazolinylidene, 6.4 for β-carotene, 6.1 for chlorophyll a, 6.3 for dihydridobis(π-cyclopentadienyl)tungsten (eV unit). The conditions of lowering the I_p's of organic molecules are discussed.

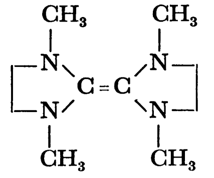
Recently, we found that tetraaminoethylenes have ionization potentials (I_p's) of *ca.* 5.4 eV,[1] which are, to our knowledge, the lowest I_p's of organic compounds reported so far, even comparable with that of the lithium atom. These interesting results stimulated us to search for other organic compounds with still lower I_p's. In this paper, some of the results of our trials along this direction are reported.

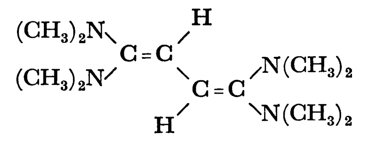
All previous methods to obtain the I_p's of molecules are applicable only to compounds with enough vapor pressures.[2,3] For example, no measurements of the I_p's of large molecules, such as chlorophylls, and carotenes, have yet been made. For such molecules, only the photo-electric work functions in the solid phase were reported.[4]

We have studied the photo-ionization of molecules not only in the gas phase but also in solutions, and found a simple relation between the gas phase I_p's and the photo-current threshold in the solution.[5] Based on this relation, it is possible to calculate the gas phase I_p's of large molecules from the photo-current thresholds in the solutions. This new method has been applied in this work to the determinations of the I_p's of some large molecules.

Experimental

The preparation and handling of tetrakis(dimethylamino)ethylene, (TMAE), and 1,1',3,3'-tetramethyl-2,2'-biimidazolidinylidene, (TMBI), were described previously.[1,5] 1,1,4,4-tetrakis(dimethylamino)butadiene, (TMAB),[6] and 3,3'-dimethyl-2,2'-bibenzothiazolinylidene, (DMBT),[7] were prepared according to the literature. Dihydridobis(π-cyclopentadienyl)tungsten, $(C^p)_2WH_2$, and dispiro[2.2.2.2]deca-4,9-diene were offered from Nakamura and Otsuka,[8] and Tsuji and Nishida,[9] respectively. A Merck reagent dimethylphenylphosphine was used. All these compounds except dispiro[2.2.2.2]deca-4,9-diene are highly reactive with atmospheric oxygen and were treated in the similar way as TMAE and TMBI.[1,5] Chlorophyll a was prepared from fresh spinach and purified by column chromatography according to the literature.[10] β-Carotene, a Wako GR grade reagent, was used without further purification. A Merck NMR grade tetramethylsilane (TMS) and a Wako spectroquality isooctane were dried with Na–K mirrors in ampoules connected to a vacuum line just before use.


TMBI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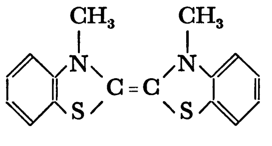
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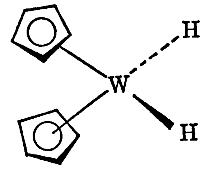
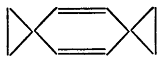

$(C_p)_2WH_2$


dispiro[2.2.2.2]deca-4,9-diene

Absorption spectra and photo-ionization curves in the vacuum ultraviolet region were measured with a Nalumi vacuum monochromator. Photo-currents in solutions were measured by using a quartz cell equipped with two parallel platinum plate electrodes. The details of the experimental apparatus and procedure were described elsewhere.[1,5]

Results

The Photo-ionization in the Gas-phase. Figure 1 shows the photo-ionization curve for 1,1,4,4-tetrakis(dimethylamino)butadiene, (TMAB). σ_i^{rel} is the relative photo-ionization cross section, which is calculated by using the equation, $\sigma_i^{rel}=\sigma\cdot i/(I_0-I)$, where σ, i and I_0-I are the relative absorption cross section, the photo-current and the relative light intensity absorbed by the sample vapor, respectively. As in the previous work,[1] the point of appearance of σ_i^{rel} is taken as an upper limit for the first adiabatic ionization potential (I_p), and the maximum of $d\sigma_i^{rel}/dE$, the first derivative of σ_i^{rel}, as the vertical I_p. Because of the relatively low vapor pressure of TMAB, the slit-width of the monochromator had to be broadened, resulting in a somewhat large error.

The photo-ionization curves for dimethylphenylphosphine and dispiro[2.2.2.2]deca-4,9-diene were also measured. In these cases, however, only the adiabatic

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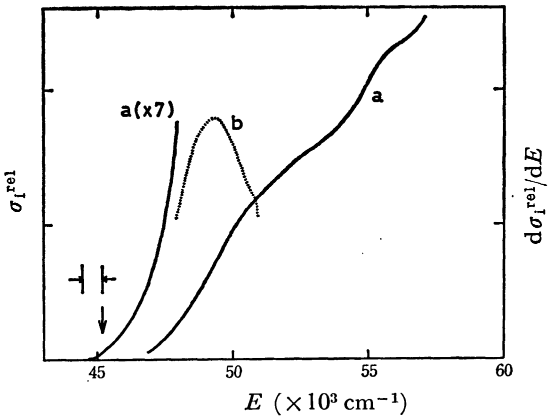


Fig. 1. Gas-phase photo-ionization of TMAB; curve a shows σ_I^{rel} *vs* E and curve b $d\sigma_I^{rel}/dE$ *vs* E. The photoionization threshold is shown by an arrow. The energy spread of the photon beam at the threshold is also indicated.

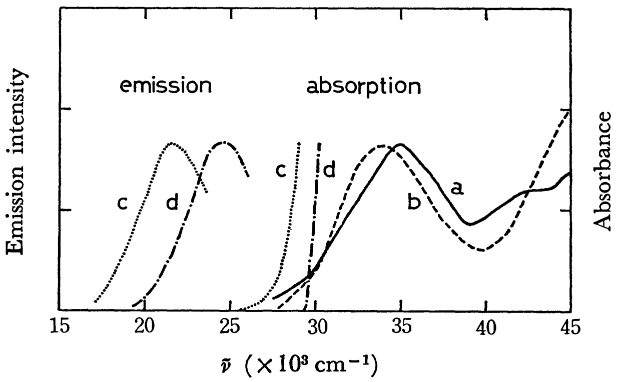


Fig. 2. Absorption and emission spectra of TMAB; curve a for the vapor, curve b for the tetramethylsilane solution at 25°C, curve c for the concentrated 3-methylpentane solution at 25°C, and curve d for the same one at 77 K.

Table 1. Gas-phase ionization potentials (eV)

Compounds	Adiabatic ionization potential	Vertical ionization potential
TMAB	5.6±0.10	6.14±0.10
Dimethylphenyl-phosphine	7.58±0.05	——
Dispiro[2.2.2.2]-deca-4,9-diene	7.33±0.05	——

I_p's could be determined since these compounds had relatively high I_p's, near the limit of our experimental apparatus. The observed I_p's are summarized in Table 1.

Figure 2 shows the absorption and emission spectra of TMAB. Both the absorption spectra in the range of 25000—30000 cm^{-1} and the emission spectra are blue-shifted by change from the vapor phase to the liquid solution, and further to the solid solution. These behaviors are quite the same as those of the first absorption band and the emission band of TMAE, which were assigned to the transition between the first Rydberg state and the ground state.[1,5] It can, therefore, be concluded that the first excited singlet state of TMAB is of Rydberg character.

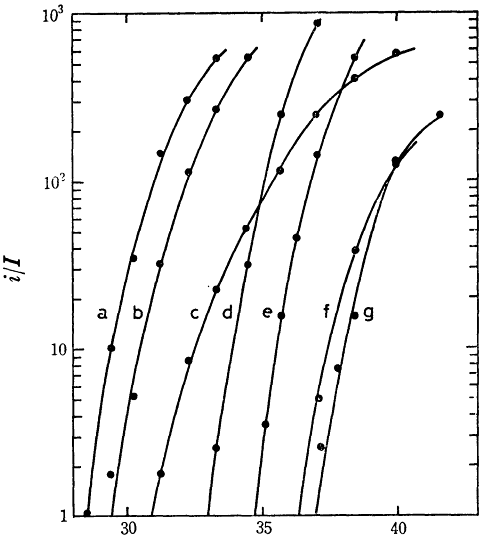


Fig. 3. Photo-ionization curves of various organic compounds in tetramethylsilane; a: TMAE, b: TMBI, c: TMAB, d: DMBT, e: $(C_p)_2WH_2$, f: chlorophyll a. g: β-carotene. All solutions are deaerated. Applied field is 400 V/cm. The half-width of the light of illumination is 10 nm.

The Photo-ionization in Organic Solutions. The photo-currents measured for several organic compounds in tetramethylsilane (TMS) are shown as functions of photon energy in Fig. 3, where the ordinate shows the photo-current (i) divided by the intensity of illumination (I). It should be noted that even the photo-currents of large molecules, such as chlorophyll a and β-carotene, can be measured easily in the solutions. The photo-currents in isooctane show similar behavior.

The photo-current threshold in a solution of a molecule, M, E_{th}(M), is related with the gas-phase I_p, I_g(M), as follows.[5]

$$E_{th}(M) = I_g(M) + S(M) - S(M^+) + E(e) \qquad (1)$$

where S(M) is the solvation energy for M and $S(M^+)$ that for the cation, M$^+$, and E(e) the energy of the electron photoejected into the solvent. E(e) can be taken as the energy of an electron at the bottom of the conduction band of the solvent relative to the vacuum level, which is expressed by E_s^0(e) in Ref. 5 or by V_0 in Ref's. 11 and 12.

$S(M^+)$ can be divided into two parts,

$$S(M^+) = S_B(M^+) + S'(M^+) \qquad (2)$$

where $S_B(M^+)$ is the part of the solvation energy relevant only to the mono-positive charge on the cation, M$^+$, approximated by the Born equation,[13] and $S'(M^+)$ the remaining part of the solvation energy.

$$S_B(M^+) = (e^2/2a)(1-1/\varepsilon_{op}) \qquad (3)$$

where a is the radius of the sphere for the cation, M$^+$, and ε_{op} the optical dielectric constant of the solvent ($\varepsilon_{op}=n^2$, n is the refractive index). The method of calculation of the radius a for the cation, M$^+$, is given in the Appendix.

Table 2. The values of E(e) calculated from observed ionization energies in the vapor and solutions (eV unit)

Compound	I_g	E_{th} in TMS	E_{th} in *iso*-octane	a(Å)	E(e) in TMS	E(e) in *iso*-octane
TMAE	$5.36\pm0.02^{b)}$	3.54 ± 0.11	——	3.21	−0.79	——
TMBI	$5.41\pm0.02^{b)}$	3.65 ± 0.11	4.02 ± 0.13	3.25	−0.74	−0.32
TMAB	5.60 ± 0.10	3.83 ± 0.13	4.28 ± 0.15	3.23	−0.75	−0.24
TMPD[a)]	$6.20\pm0.02^{c)}$	$4.40^{d)}$	——	3.24	−0.78	——

a) *N,N,N′,N′*-Tetramethyl-*p*-phenylenediamine. b) See Ref. 1. c) See Ref. 14. d) S. S. Takeda, N. E. Houser, and R. C. Jarnagin, *J. Chem. Phys.*, **54**, 3195 (1971); R. A. Holroyd, *ibid.*, **57**, 3007 (1972).

Table 3. Gas-phase ionization potentials calculated from observed photo-current thresholds in solutions (eV unit)

Compound	E_{th} in TMS	E_{th} in isooctane	a(Å)	I_g[a)] calcd from E_{th} in TMS	I_g[a)] calcd from E_{th} in isooctane
DMBT	4.09 ± 0.14	4.43 ± 0.16	3.70	5.8	5.7
$(C_p)_2WH_2$	4.30 ± 0.15	4.64 ± 0.18	2.50	$6.4^{b)}$	$6.3^{b)}$
Chlorophyll a	4.50 ± 0.17	——	3.82	6.1	—
β-carotene	4.59 ± 0.18	5.02 ± 0.22	3.30	6.4	6.4

a) The error estimated will be 0.2 eV at most. b) The value obtained from the CT absorption bands is 6.3 eV; Ref. 8.

Under the approximation that $S'(M^+)$ is nearly equal to $S(M)$, Eq. (1) is expressed as

$$E_{th}(M) = I_g(M) - S_B(M^+) + E(e) \qquad (4)$$

From the data for the four compounds shown in Table 2, where the ionization potentials both in the gas phase and in the solutions are determined experimentally, E(e) can be calculated by using Eq's. (3) and (4). The results are shown in Table 2, together with the radius a used. It is found that the values of E(e) are nearly constant for each solvent, as expected from the definition. This shows that the Eq's (3) and (4) are fairly good approximations.

Now, based on the values of E(e) obtained above and the Eq's (3) and (4), it is possible to calculate $I_g(M)$ from $E_{th}(M)$. The results are given in Table 3. As expected, the values of $I_g(M)$ calculated from $E_{th}(M)$ in tetramethylsilane (TMS) are in good agreement with those from $E_{th}(M)$ in isooctane.

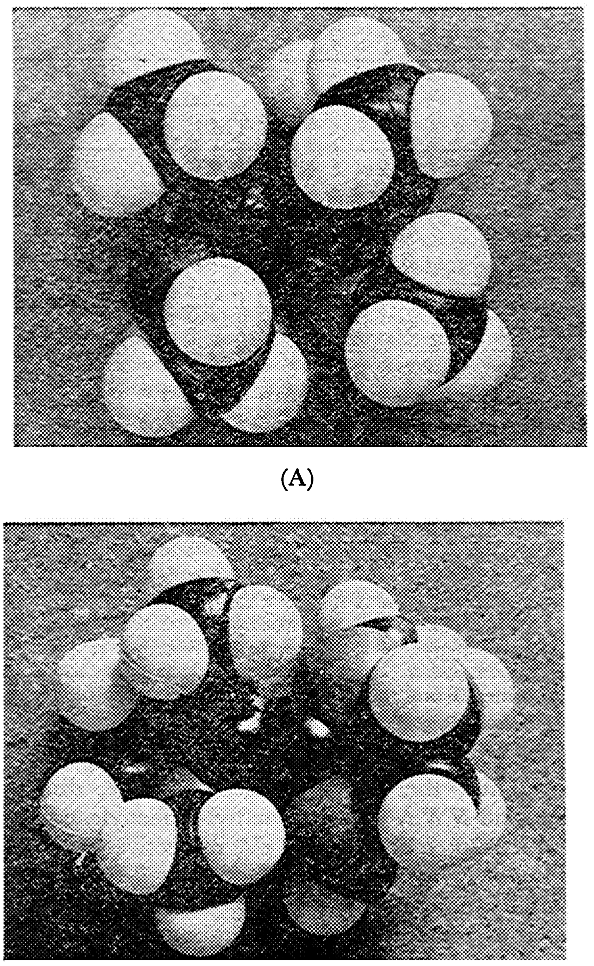
Discussion

As TMAE and TMBI have very interesting properties, both chemically and physically, it seemed to be a challenging problem to seek for organic molecules having still lower ionization potentials. As the results show, this trial has failed so far: All molecules dealt with in this paper have I_p's higher than that of TMAE. Here, we wish to give some criteria for the conditions which can lower the I_p of a molecule based on the present results, as well as those already obtained.

It is well known that, for aromatics and conjugated polyenes, the I_p's become lower with the length of conjugated chain. It is also known that the I_p gets lower, the more amino groups, or preferably dimethylamino groups, are substituted in the conjugated molecules. Thus, the I_p's of benzene, aniline, dimethylaniline, and *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine are 9.24, 7.70, 7.14 and 6.20 eV, respectively.[1,14)] The lowering of I_p by conjugation is attributed to an increased stabilization of the cations. The effect of amino group is of course due to the non-bonding electrons in the nitrogen atom having itself a low I_p. The effect of methyl substitution, more generally speaking, alkyl substitution, has been attributed to the inductive, or hyperconjugative effect of the substituent. However, we propose another view that the steric repulsion of an alkyl group toward the nitrogen non-bonding electrons might be a reason.

In the case of TMAE, as an example, the four dimethylamino groups are believed to lie nearly perpendicular to the $N_2C{=}CN_2$ plane of the molecule.[1)] In this molecule, therefore, the nitrogen lone pairs can hardly conjugate with the π-electrons of the ethylene bond. In TMBI, on the other hand, the nitrogen lone pair orbitals are thought to be nearly parallel to the latter. From these facts, it can be asserted that the conjugational effect will lower the I_p of TMBI compared to TMAE. The fact that the I_p of TMAE is quite low, even lower than that of TMBI seems to be attributable to the large steric repulsion of methyl electrons toward the nitrogen lone pair; in other words, due to the extremely large crowding of the methyl groups aronnd each N atom as is seen clearly from the structure model of TMAE (Fig. 4). These steric repulsions certainly destabilize the nitrogen lone pair electrons in the molecule, leading to the lowering of I_p. On the other hand, the less steric repulsion and the more conjugational effect cansel each other in TMBI, leading to an I_p accidentally almost equal to that of TMAE.

In the present results, the I_p of TMAB (tetrakis-(dimethylamino)butadiene) is found to be slightly



(A)

(B)

Fig. 4. The molecular models of TMAE (A) and TMBI (B).

higher than that of TMAE ($I_p^{\text{adiabatic}}$ 5.36, I_p^{vertical} 6.11 eV). This can also be explained in a similar way: Increased conjugated chain length and less crowding around N atoms. In TMAE, the direct repulsion between the N lone pairs might also be responsible for lowering the I_p.$^{1)}$

The sulfur atom included in a conjugated system is also regarded to be a factor to lower the I_p, because of its non-bonding pair with a relatively low I_p. It is significant that DMBT has an I_p comparable to that of TMAE.

Unexpectedly low I_p's for both dispiro[2.2.2.2]deca-4,9-diene and $(C_p)_2WH_2$ are obtained. The I_p of $(C_p)_2WH_2$ was reported to be $\sim$7000 cm^{-1} lower than that of dimethylaniline from their charge transfer absorption bands with several olefins as the common acceptors, being $\sim$6.3 eV, which is in good agreement with the value obtained in this work.

The I_p of dimethylphenylphosphine is higher than that of dimethylaniline(7.14 eV). It was also reported that the I_p of triphenylphosphine was higher than that of triphenylamine.$^{14)}$ From these results, it seems that the substitution of the N atom of amino compounds by the P atom is generally ineffective to lower the I_p's.

The I_p's of chlorophyll a and β-carotene obtained here are probably the first reliable ones ever observed. The present method can be applied to other biologically important compounds. The main error seems to originate from the calculation of $S_B(M^+)$ by the use of the Born equation. It seems likely that the Born equation is a good approximation in non-polar solvents, but the calculation of radius a for the solute molecule is somewhat erroneous because of its non-spherical shape(see Appendix). It should, however, be noted that as the radius becomes larger, $S_B(M^+)$ becomes smaller and so does the error. For example, the values of $S_B(M^+)$ are 1.2, 1.0 and 0.9 eV at a=3, 3.5 and 4 Å, respectively. Therefore, the error estimated seems to be 0.2 eV at most.

Appendix

To apply Born equation to a non-spherical molecular ion, an appropriate average radius must be given from the molecular geometry. Let us consider tetramethyl-p-phenylenediamine (TMPD) as an example. The molecular shape is approximated as illustrated in Fig. 5. The average radius a was calculated by using the following equation,

$$1/a = \sum_i (1/r_i) \cdot (\Delta S_i \cdot \cos\theta_i / 4\pi r_i^2) \tag{5}$$

where ΔS_i is, as shown in Fig. 5, a fraction of the surface of the molecule, taken appropriately so that the distance between the center of the molecule, 0, and any point on that fraction of the surface does not change largely from an average distance r_i set up for each of the fractions ΔS_i, and θ_i is the angle between r_i and the normal to the plane of ΔS_i. The summation is made over all the surface area. The calculations of a for other compounds have been made in a similar way.

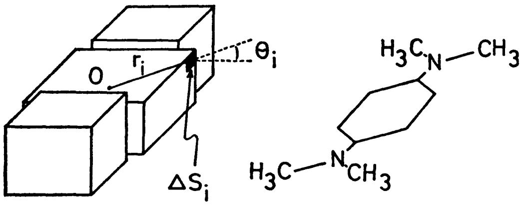


Fig. 5. The molecular shape of TMPD used to calculate the radius a.

The above method can be rationalized by the following argument: Let us consider a non-spherical molecular ion with a center of symmetry, existing in a dielectric medium. By taking dS a planar element of molecular surface, r the distance between the surface element and the center of the molecule and θ the angle between r and the normal to the plane of dS, the element of solid angle, dΩ, is given as follows.

$$d\Omega = dS \cdot \cos\theta / r^2 \tag{6}$$

Under the assumption that the electric charge of the molecular ion, e, is located at its center, the ion-medium electrostatic interaction energy within the region of this elemental solid angle can be expressed as

$$(e^2/2r) \cdot (1 - 1/\varepsilon) \cdot (d\Omega/4\pi)$$

where ε is the dielectric constant of the medium. The total interaction energy is obtained by integrating the above expression,

$$(e^2/2) \cdot (1 - 1/\varepsilon) \cdot \int (1/r)(d\Omega/4\pi) \tag{7}$$

Equation 5 can be regarded as approximating the integral part of Eq. 7 by a summation, and taking it to be $1/a$ so as to make the energy expressed by the Born equation.

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