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Physicochemical Study on Leuco Triarylmethane Dyes; Comparisons of the Electronic Structures by CNDO/S-CI Calculation of Propensity to Photoionization of Phthalide and 3,4-Dihydro-1(2*H*)-phthalazinone

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It was shown that CNDO/S-CI calculation is capable of distinguishing the electronic structures of the excited singlet state of two ring systems; phthalide (**3**) and 3,4-dihydro-1(2*H*)-phthalazinone (**4**). In the excited state calculations by the CNDO/S-CI method, the computed transition energies of **3** and **4** to the lowest π-π^* excited singlet state were found to be in reasonable agreement with the observed and reduced values for **3** and **4**.

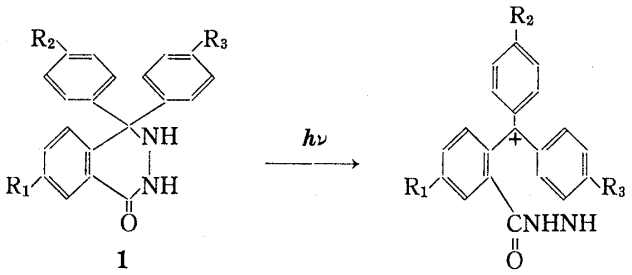
The wavelengths of the maximum extinction coefficient of **3** and **4**, which can be assigned to the lowest π-π^* singlet state, were deduced from the difference ultraviolet (UV) absorption spectrum of malachite green lactone (MGL) and malachite green hydrazide (MGH) against bis-(*p*-dimethylanilino)-methane, respectively.

Inspection of the configuration mixing in the CI states disclosed that the lowest π-π^* excited singlet state is mainly composed of the HOMO-LUMO transition in both compounds, though the mixing ratios are different. However, the HOMO polarizations are quite different from each other; the HOMO coefficient of the N_3-atom in the hydrazino moiety of **4** is much larger than that of the O_2-atom of **3**. Thus, the excitation of **4** to the lowest excited singlet state results in a substantial intramolecular charge transfer of π-electrons from the N_3–C_4-group to the benzoyl moiety based on the variation of the atomic electron densities. The n-π^* excitation and the lowest π-π^* excited triplet state of **4** did not show similar propensities. These findings may be associated with the heterolytic cleavage of the C_4–N_3 bond in the lowest excited singlet state.

Keywords——MO calculation; CNDO/S-CI; intramolecular charge transfer; difference UV spectrum; photoionization; phthalide; 3,4-dihydro-1(2*H*)-phthalazinone; malachite green lactone; malachite green hydrazide

In a previous paper,[1] we reported that a solution of 5% EtOH-dichloroethane containing 4,4-bis-(*p*-dimethylaminophenyl)-7-dimethylamino-3,4-dihydro-1(2*H*)-phthalazinone (**1a**) [crystal violet hydrazide (CVH)] of 4,4-bis-(*p*-dimethylaminophenyl)-3,4-dihydro-1(2*H*)-phthalazinone (**1b**) [malachite green hydrazide (MGH)] underwent a rapid photolytic coloration upon ultraviolet (UV) irradiation, and the colored dye formed was identified as the triarylmethane dye cation based on the absorption wavelength, which is nearly identical with that of crystal violet (CV) or malachite green (MG), respectively. It was also shown that the solvent has a pronounced effect upon the coloration efficiency.

This process, however, cannot be rationalized in a simple manner, such as in terms of the great stability of the carbocation formed, since crystal violet lactone (CVL) (**2a**) and malachite



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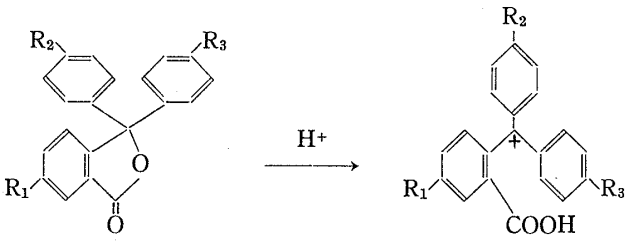
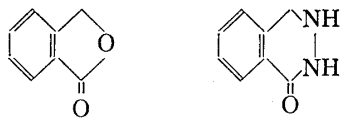


2

a: $R_1=R_2=R_3=N(Me)_2$
b: $R_1=H$, $R_2=R_3=N(Me)_2$

Chart 1



3 4

Chart 2

green lactone (MGL) (**2b**) are not photolabile upon UV irradiation though they are labile to weak acid to form the dye cation. Thus, the difference in the efficiency of coloration seems to stem from the difference in the structures and the electronic states intrinsic to the two ring systems, phthalide (**3**) and 3,4-dihydrophthalazinone (**4**).

Photocolorations are known in many other systems and the mechanisms have been extensively discussed. However, the electronic details of the mechanisms are not fully understood, particularly as regards the structure–solvent polarity–coloration relationship. Prior to further detailed experimental work which we intend to perform on the present system, we have studied the electronic structure of the excited states of **3** and **4** as calculated by the CNDO/S-CI method, to obtain insight into the reasons for the difference in the efficiency of coloration.

Calculation

The method employed in this study is the all-valence-electrons CNDO/S-CI procedure first proposed by Del Bene and Jaffé,[2] in which the parameters of the approximate SCF-LCAO-MO scheme are chosen to reproduce the spectroscopic properties of low-lying electronic transitions in organic molecules rather than accurate ground state energies. This method has been applied successfully to predict the excited states of a number of organic compounds. It involves readjustment of two sets of Pople's original CNDO parameters. One readjustment of the two is in the electron repulsion integrals, γ_{AB}. One-center Coulomb integrals are evaluated semiempirically from the ionization potentials and electron affinities.[3] The numerical values used in this work are given in Table I.[4] As was pointed out later[4,5] in connection with the evaluation of the two-center integrals of benzene-based compounds, the Mataga–Nishimoto interpolation formula[6] is preferable to the method of Pariser[7] employed in the original CNDO/S method,[2] so we evaluated the γ_{AB} according to the Mataga–Nishimoto formula, given by

$$\gamma_{AB}=14.395(\text{eV})\times\left(R_{AB}(\text{Å})+\frac{28.79(\text{Å/eV})}{\gamma_{AA}+\gamma_{BB}}\right)^{-1}$$

TABLE I. One-Center Coulomb Integrals (eV)

	H	C	N	O
γ_{AA}	12.85	10.93	11.88	15.13

The other reparametrization relates to resonance integrals, and is the same as in the original CNDO/S method.[2]

In CI (configuration interaction) calculations, the number of configurations to be included was the 20 lowest singly excited states.

The geometries of phthalide and 3,4-dihydrophthalazinone with C_s symmetry were taken, in which the geometry of the benzene rings was approximated as regular hexagons with C–C bond distances equal to 1.40 Å,

and C–H bond distances equal to 1.80 Å. For other internal coordinates, standard bond lengths and bond angles were used.[8] We believe that these approximations, in principle, do not significantly influence the main features of the computed electronic structures.

All calculations were carried out on a FACOM M-200 computer at the Computation Center of Nagoya University.

Results and Discussion

Malachite green lactone (MGL) (**2b**) and malachite green hydrazide (MGH) (**1b**) possess essentially two types of independent π-chromophore; one involving a benzoyl moiety and one involving a dimethylaniline moiety. Both chromophores are benzene-based ones and thus the π-π^* transition energies are fairly close to each other.

The difference UV absorption spectra **2b** and **1b** against equimolar bis-(*p*-dimethylanilino)-methane can be approximated to the UV absorption spectra **3** and **4**, respectively. Fig. 1 and Fig. 2 show such difference UV absorption spectra, as well as UV absorption spectra of **3** and **1b** measured in ethanol[9] with a Hitachi 323 spectrophotometer.

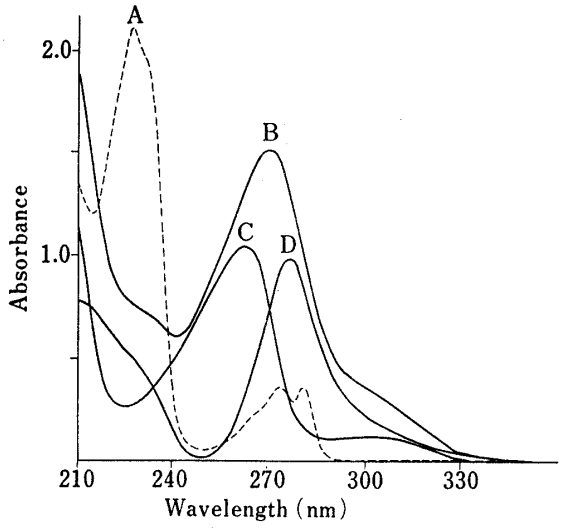


Fig. 1. UV Absorption Spectra and the Difference Spectrum in Ethanol

A, phthalide (**3**); B, MGL (**2b**); C, bis-(*p*-dimethylanilino)-methane; D, difference spectrum of B against C.
The concentration of A was 2.1×10^{-4} M and those of B and C were 4.2×10^{-5} M.

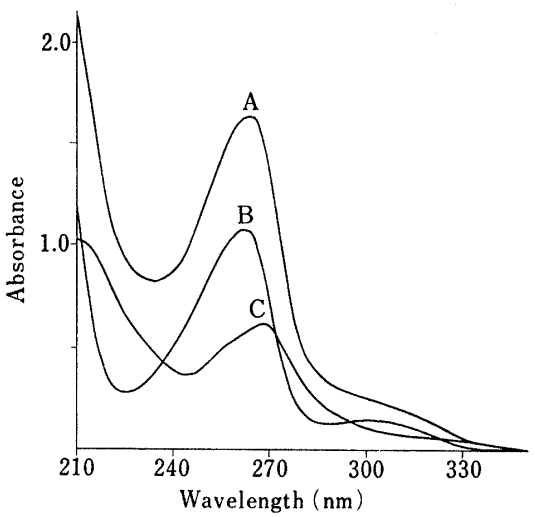


Fig. 2. UV Absorption Spectra and the Difference Spectrum in Ethanol

A, MGH (**1b**); B, bis-(*p*-dimethylanilino)-methane; C, difference spectrum of A against B.
The concentrations of A and B were 4.2×10^{-5} M.

As can be seen in Fig. 1, the λ_{max} 275 nm[assigned to the lowest excited singlet state (B-band)] of the difference UV absorption spectrum for **3** agrees fairly well (though it is hyperchromic) with λ_{max} 273 nm of phthalide (**3**), although an intense, fine-structured band of **3** appeared at 280 nm (ε 1750).

3,4-Dihydrophthalazinone (**4**) is not readily available. Thus, we similarly deduced λ_{max} of the B-band from the difference UV spectrum of MGH (**1b**) and bis-(*p*-dimoethylanilin)-methane as shown in Fig. 2. The lowest π-π^* excited singlet state (B-band) at λ_{max} 269 nm was observed from this difference UV spectrum. This value can be regarded as an experimental transition energy and can thus be used as a criterion of the validity of the present computational method as applied to **4**.

The lowest computed singlet and triplet excited state energies and other quantities associated with excited states of phthalide (**3**) and 3,4-dihydrophthalazinone (**4**) are listed in Tables II and III. Inspection of Tables II and III shows that the four triplet states lie under the first π-π^* singlet state (S_2), and the computed wavelength of singlet excited states for **3** and **4** acceptably reproduce the observed wavelength of **3** and λ_{max} derived from the difference UV spectra of MGH (**1b**), respectively.

TABLE II. Computed Electronic Features for Excited States of **3**

Singlet states							Triplet states	
Type of transition	Transition energies		Oscillator strength	Polarization[a]			Type of transition	Transition energies
	eV	nm		x	y	z		
$S_1^{n\to\pi^*}$	4.5121	275	0.0012	0.001	−0.003	1.000	$T_1^{\pi\to\pi^*}$	3.0530
$S_2^{\pi\to\pi^*}$	4.6241	268(273)[b]	0.0289	−0.336	0.942	0.000	$T_2^{\pi\to\pi^*}$	3.7113
$S_3^{\pi\to\pi^*}$	5.6786	218	0.1595	0.858	−0.513	0.000	$T_3^{\pi\to\pi^*}$	3.8612
$S_4^{\pi\to\pi^*}$	6.0454	205	0.0002	0.041	0.031	0.999	$T_4^{\pi\to\pi^*}$	4.5120

a) The coordinate axes are shown in Fig. 3.
b) The observed wavelength.

TABLE III. Computed electronic features for excited states of **4**

Singlet states							Triplet states	
Type of transition	Transition energies		Oscillator strength	Polarization[a]			Type of transition	Transition energies(eV)
	eV	nm		x	y	z		
$S_1^{n\to\pi^*}$	4.4973	276	0.0023	0.000	0.000	1.000	$T_1^{\pi\to\pi^*}$	3.0153
$S_2^{\pi\to\pi^*}$	4.5643	272(269)[b]	0.0251	−0.075	0.997	0.000	$T_2^{\pi\to\pi^*}$	3.6683
$S_3^{\pi\to\pi^*}$	5.4425	228	0.1052	0.751	−0.660	0.000	$T_3^{\pi\to\pi^*}$	3.8198
$S_4^{\pi\to\pi^*}$	5.8932	210	0.0411	0.915	−0.404	0.000	$T_4^{\pi\to\pi^*}$	4.4973

a) The coordinate axes are shown in Fig. 4.
b) The wavelength deduced from the difference UV spectrum.

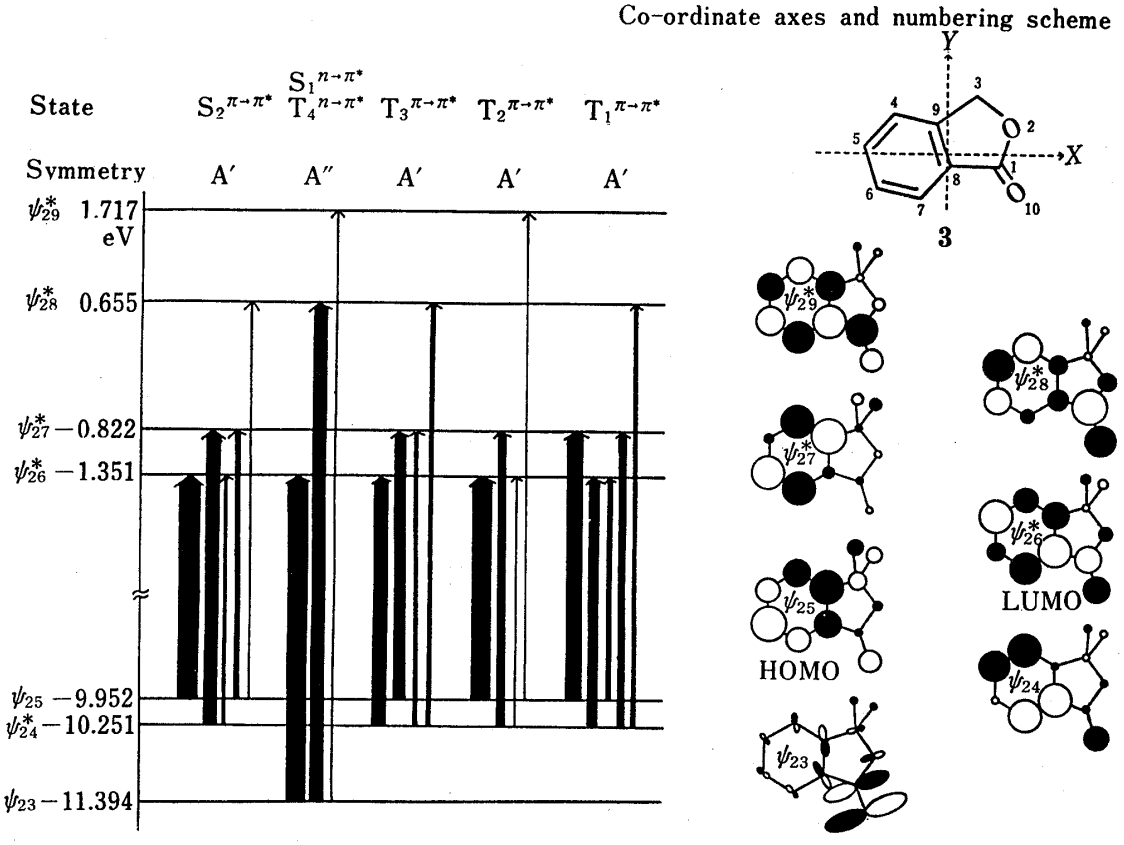


Fig. 3. Configuration Mixing involved in CI States of Low-lying Excited States of **3** and the Relevant Molecular Orbitals

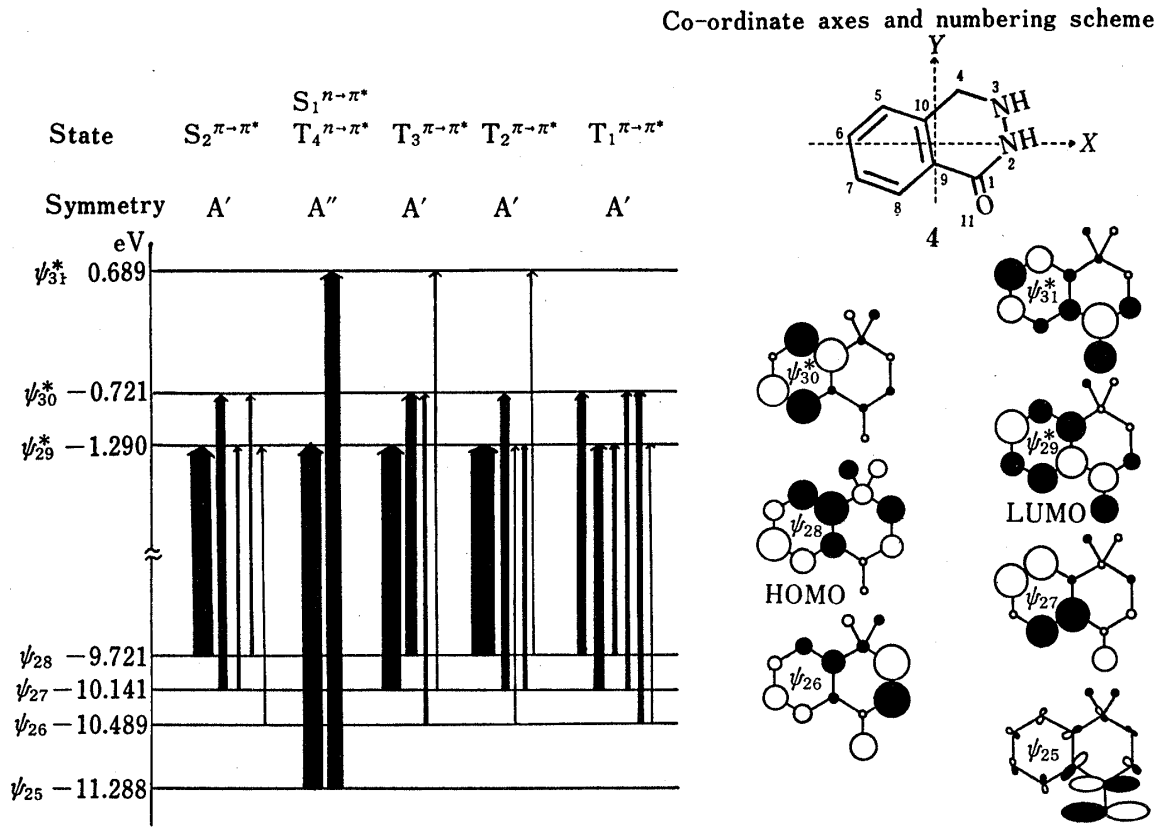


Fig. 4. Configuration Mixing involved in CI States of Lowlying Excited States of **4** and the Relevant Molecular Orbitals

The CI states with more than 5% mixing configurations responsible for each excited state are shown together with the coefficient distributions and nodal properties of the relevant molecular orbital in Fig. 3 for phthalide (**3**) and in Fig. 4 for 3,4-dihydrophthalazinone (**4**). These figures are idealized and oversimplified, but embody several interesting features. The computed T_3 state and T_2 state would be transient states to the T_1 state and may not play important roles in the photodissociation processes, so these states are not further discussed. The π-π^* transition of both compounds, **3** and **4**, is related to the excited state of A′ symmetry under the point group of symmetry C_s.

First, examination of Fig. 3 revealed that the lowest π-π^* excited singlet state (S_2) mainly consisted of two configurations; ϕ_{25}(HOMO)-ϕ^*_{26}(LUMO) and ϕ_{24}(NHOMO)-ϕ^*_{27}(NLUMO) transitions, whereas the lowest π-π^* excited triplet state (T_1) consisted of an admixture of many configurations. The coefficient distributions of all the molecular orbitals responsible for low-lying excited states, however, are largely polarized to the aromatic and/or carbonyl moiety as shown. Thus, any excitation of phthalide (**3**) would result in a rather local excitation on the aromatic moiety. Furthermore, the n-π^* excited state (S_1 or T_4) consisted largely of two configurations; ϕ_{23}—ϕ_{26} and ϕ_{23}—ϕ^*_{28}. However, these transitions contribute only to the polarization toward the z-direction over the benzoyl moiety. Thus, there is no indication that any excited state can lead effectively to the photolytic cleavage of the lactone ring of **3** upon UV irradiation.

On the other hand, Fig. 4 shows that, although each CI state of 3,4-dihydrophthalazinone (**4**) consists of configurations similar to those of the former compound, there is a noticeable difference in the configuration mixing ratio the lowest π-π^* excited singlet state (S_2) and the lowest excited triplet state (T_1); the ϕ_{28}(HOMO)-ϕ^*_{29}(LUMO) transition contributes to S_2 on 3,4-dihydrophthalazinone (**4**) to a greater extent than S_2 on phthalide (**3**), whereas the T_1 state

of 3,4-dihydrophthalazinone (**4**) consisted of a complex mixture of configurations. The most noteworthy feature of Fig. 4 is in the distribution of the HOMO coefficients; the ψ_{28}(HOMO) in **4** has a rather large coefficient at N_3 and C_4, although ψ_{26} is much more polarized to the hydrazine moiety of **4** as shown. Thus, the excitation to the lowest excited singlet state, whose main configuration is ψ_{28}(HOMO)-ψ_{29}(LUMO) transition, results in an intramolecular charge transfer of π-electron from the -N_3-C_4-group to the remaining part of the molecule, mainly over the benzoyl moiety. In this regard, the transition from ψ_{26} can be expected to be very effective for intramolecular charge transfer, but the contribution of ψ_{26} to each excited state is negligible. Likewise, the distribution of coefficients of all the relevant orbitals indicates that α-cleavage with respect to the carbonyl group upon excitation, which is quite general in photochemical reactions, may not occur in either of the present ring systems.

These electronic modifications upon excitation clearly reflect the marked variation of the distribution of electron densities at the site of bond cleavage of **4** between the ground state and the excited state, as summarized in Tables IV and V, together with those of **3**.

Table IV. Atomic Electron Densities of **4**

States	Type of electron density (Q)	Atom number										
		C_1	N_2	N_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	O_{11}
S_0	Q_{total}	3.6317	5.1932	5.2599	3.9499	4.0531	4.0064	4.0431	3.9908	3.9982	3.9554	6.4608
	Q_π	0.7197	1.8962	1.9944	1.0295	1.0513	0.9491	1.0297	0.9266	1.0847	0.9279	1.4403
S_1	Q_{total}	3.7237	5.1439	5.2485	3.9336	4.0691	4.2233	4.0827	4.0380	4.0234	3.9910	6.1102
	Q_π	0.9207	1.9160	1.9946	1.0302	1.1063	1.1803	1.0909	1.0132	1.2330	1.0129	1.5490
S_2	Q_{total}	3.7126	5.1749	5.2078	3.9321	4.0283	4.0787	3.9518	4.0653	3.9920	3.9313	6.4918
	Q_π	0.7961	1.8651	1.9221	1.0103	1.0111	1.0213	0.9680	0.9748	1.0819	0.9519	1.4722
T_1	Q_{total}	3.6921	5.1560	5.1907	3.9347	4.0766	3.9929	4.0410	4.0734	3.9125	4.0254	6.4661
	Q_π	0.7783	1.8568	1.9204	1.0140	1.0473	0.9515	1.0351	0.9893	1.0321	1.0062	1.4462

Table V. Atomic Electron Densities of **3**

States	Type of electron density (Q)	Atom number									
		C_1	O_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	O_{10}
S_0	Q_{total}	3.5932	6.2352	3.9203	4.0479	4.0060	4.0376	3.9928	4.0078	3.9712	6.4433
	Q_π	0.7264	1.9096	1.0321	1.0465	0.9548	1.0258	0.9453	1.0668	0.9287	1.4170
S_1	Q_{total}	3.7745	6.2102	3.9134	4.0593	4.1236	4.0370	4.0829	3.9528	3.9684	6.1800
	Q_π	0.9272	1.9254	1.0325	1.1306	1.1793	1.0746	1.0495	1.2122	0.9913	1.5271
S_2	Q_{total}	3.6637	6.2406	3.9088	4.0103	4.0546	3.9575	4.0347	3.9872	3.9590	6.4523
	Q_π	0.7957	1.9154	1.0206	1.0090	1.0036	0.9451	0.9880	1.0463	0.9163	1.4260
T_1	Q_{total}	3.6531	6.2392	3.9113	4.0084	4.0001	4.0283	4.0201	3.9418	4.0225	6.4393
	Q_π	0.7853	1.9143	1.0231	1.0069	0.9484	1.0171	0.9727	0.9996	0.9807	1.4132

By inspection of the atomic electron densities listed in Table IV, it is apparent that an intramolecular charge transfer of 0.0723 π-electron (1.9944—1.9221) of N_3-atom, whose charge magnitude is the largest among all the atoms, and 0.0192 π-electron (1.0295—1.0103) of C_4 to the rest of the molecule takes place as a result of the transition to the lowest π-π^* excited singlet state of **4**; S_0-S_2 excitation. Having lost this quantity of π-electron, the atoms forming the -N_3-C_4-group, particularly the N_3-atom, subsequently attract some of the σ-bonding electrons. A charge separation must occur at some point along the excited state surface to lead to an ionic product, and the variation of these electron densities is presumably associated with the

heterolytic cleavage of C_4-N_3 in **1** with the assistance of the solvent polarity and the strongly electron-donating dimethylanilino groups at the C_4-position.

The electron densities of the atoms relevant to α-cleavage with respect to the carbonyl group were more or less invariant. Furthermore, the mixing ratio of configurations involving the HOMO is rather small in the lowest excited triplet state (T_1). Consequently, the T_1 state may not be an effective state for photodissociation of **4**.

On the other hand, inspection of Table V showed that intramolecular transfer from the -O_2-C_3- atoms of **3** (this bond undergoes facile heterolytic cleavage on exposure to weak acid) does not occur upon any excitation, as expected from the foregoing discussion (*vide supra*), and noticeable modification of the electron densities occurs only over the aromatic and carbonyl moieties at each excited state.

CVL (**2a**) and MGL (**2b**) undergo coloration in acidic media, where the O_2-atom bonding to triarylmethane carbon will lead to electron deficiency. The present calculation by the CNDO/S-CI method demonstrated that the similar electronic state in **4**, where N_3-atom bonding to triarylmethane carbon tends to produce electron deficiency, was generated upon excitation to the lowest singlet state.

Thus, we can consider the difference in the efficiency of coloration upon irradiation between **3** and **4** in terms of the difference in the variation of the electron densities on the atoms relevant to the photodissociation.

However, the dimethylaniline also has a UV absorption wavelength similar to that of **4**, so that a different mechanism can be conceived. If the coloration process of **1** is initiated by excitation of the dimethylanilino group, the excited dimethylanilino group would generate the cation radical. Thus, it is possible that the coloration process involves intermolecular electron transfer between the cation radical of the dimethylanilino group and the hydrazino group of **1**.

A more definitive treatment of this coloration mechanism must await both further detailed experimental studies and more precise descriptions of the excited states of the molecule.

References and Notes

1) M. Kuzuya, T. Usui, F. Miyake, K. Kamiya and T. Okuda, *Chem. Pharm. Bull.*, **30**, 708 (1982).
2) J. Del Bene and H.H. Jaffé, *J. Chem. Phys.*, **48**, 1807 (1968); *idem*, *ibid.*, **48**, 4050 (1968); *idem*, *ibid.*, **49**, 1221 (1968); *idem*, *ibid.*, **50**, 1126 (1969); J. Del Bene, H.H. Jaffé, R.L. Ellis and G. Kuehnlenz, *QCPE*, **11**, 174 (1970).
3) J. Hinze and H.H. Jaffé, *J. Am. Chem. Soc.*, **84**, 540 (1962).
4) R.L. Ellis, G. Kuehnlenz and H.H. Jaffé, *Theoret. Chim. Acta* (Berl.), **26**, 131 (1972).
5) N.O. Lipari and C.B. Duke, *J. Chem. Phys.*, **63**, 1748 (1975).
6) N. Mataga and K. Nishimoto, *Z. Phys. Chem.* (Frankfurt and Main), **13**, 140 (1957).
7) R. Pariser and R.G. Parr, *J. Chem. Phys.*, **21**, 767 (1953).
8) J.A. Pople and D.L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, 1970.
9) MGH (**1b**) is very difficult to dissolve in nonpolar solvents. Thus, we measured the UV spectra in ethanol.