Aromatic Nucleophilic Substitution. VII.[1] Electronic Structure of 1,1-Disubstituted 2,4-Dinitronaphthalene Meisenheimer Complexes

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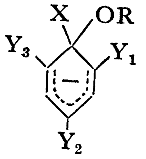
The electronic structures of 1,1-disubstituted 2,4-dinitronaphthalene Meisenheimer complexes were studied by UV-visible and infrared spectrometry and compared with the results calculated by a semiempirical SCF-MO-CI method. The electronic transitions in the complexes were assigned to those of π-π^*. Calculated transition energies and intensities agree well with the observed values. The infrared spectra of the complex indicated that the complex is not a charge transfer complex or a radical anion, but an anionic σ complex.

Many Meisenheimer complexes such as I (hereinafter referred to as anionic σ complex) have been prepared by nucleophilic attack on polynitro aromatic compounds. These reactions have been extensively studied and the results are reviewed in detail.[2] Simple MO treatments of aromatic nucleophilic substitution have been attempted by several workers.[3] Abe[3g] has explained with the Hückel MO method the result that in the longer wavelength region one and two absorption bands are observed for di- and trinitrocyclohexadienate



I

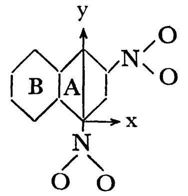
X=H, OR, halogen

(I, $X=OCH_3$, $R=CH_3$, $Y_1=Y_2=NO_2$, and $Y_3=H$; $X=OCH_3$, $Y_1=Y_2=Y_3=NO_2$), although the characters of the electronic transitions were not explained. Furthermore, Caveng *et al.*[3d] have reported with the aid of the HMO treatment that π-electrons in I ($X=OCH_3$, $R=CH_3$, $Y_1=Y_2=Y_3=NO_2$) are attracted by the three nitro groups such that the ring becomes positively charged. Criticizing the work of Abe and Caveng *et al.*, Hosoya *et al.*[3f] have indicated that nitro compounds are something beyond the limit of the HMO treatment, and they have performed the Pariser-Parr-Pople type SCF-MO-CI calculation for 1,3,5-trinitrocyclohexadienate (I, $Y_1=Y_2=Y_3=NO_2$, neglecting the effect of X and OR groups), indicating that the lower electronic transitions in this complex are assigned as due to charge transfer from the pentadienyl group to the nitro group. However, no SCF-MO-CI calculation has been performed for naphthalene anionic σ complexes. This paper will report the electronic transitions in 1,1-disubstituted 2,4-dinitronaphthalene anionic σ complexes with the aid of a semiempirical SCF-MO-CI calculation.

Method of Calculation

The π electronic structures of 1,1-disubstituted 2,4-dinitronaphthalene Meisenheimer complexes were studied by the variable β, γ procedure of semiempirical SCF-MO method combining with singly excited CI calculation. The parameters were taken as proposed by Nishimoto and Forster.[4] One-center repulsion integrals $\gamma_{\mu\mu}$ were estimated from the corresponding valence state ionization potentials (I_μ) and electron affinities (A_μ) by the Pariser-Parr approximation,[5] I_μ and A_μ being determined from spectroscopic data using the promotion energies of Hinze and Jaffé.[6] Two-center electron repulsion integrals $\gamma_{\mu\nu}$ were estimated by use of the Mataga-Nishimoto approximation.[7] Two-center core resonance integrals $\beta_{\mu\nu}$ were evaluated by the Nishimoto-Forster approximation.[4]

The geometry of the complex (II) was assumed as follows:



II

The C–C bond lengths and all bond angles were assumed to be 1.39 Å and 120°, respectively. The C–N and N–O bond lengths were assumed to be 1.486 and 1.210 Å, respectively. The computation was carried out with a HITAC 8800 located at the Computer Center of the University of Tokyo

Experimental

Materials. 1-Ethoxy-(III) and 1-methoxy-2,4-dinitronaphthalene (IV) were prepared by the action of $NaOC_2H_5$ on an ethanolic solution of 1-chloro-2,4-dinitronaphthalene (CDNN), mp 91—92 °C (lit, 93 °C[8] and 90—91 °C[9]) and 97—98 °C (lit. 97 °C[10] and 97.5—98 °C[11]). 1-Piperidino-(V) or 1-dimethylamino-2,4-dinitronaphthalene (VI) were prepared by the action of the corresponding amine on CDNN in DMSO according to the method of Orvik and Bunnett.[8] Recrystallization from 95% ethanol gave an analytical sample: V, yield 80%, mp 136—137 °C (Found: C, 60.05; H, 5.21; N, 14.23. Calcd for $C_{15}H_{15}N_3O_4$: C, 59.79; H, 5.02; N, 13.95%) and VI, yield 45%, mp 88—89 °C (Found: C, 55.39; H, 4,40; N, 16.30. Calcd for $C_{12}H_{11}N_3O_4$: C, 55.17; H, 4.24; N, 16.09%).

IR Spectra of the Reactions System of VI with $NaOCH_3$ in DMSO. 0.035 ml of methanolic $NaOCH_3$ (4.18 M) was added to a DMSO solution (0.15 ml) of VI (1.48×10^{-4} mol), in which the molar ratio VI to $NaOCH_3$ was one, and the spectra of the mixture were taken.

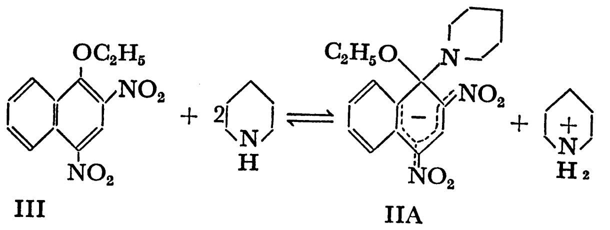
Results and Discussion

Absorption Spectra of the Reaction of 1-Ethoxy-2,4-dinitronaphthalene (III) with Piperidine and the Reaction of

Table 1. Calculated and observed transition energies, transition moments and oscillator strength of Meisenheimer complex (II)

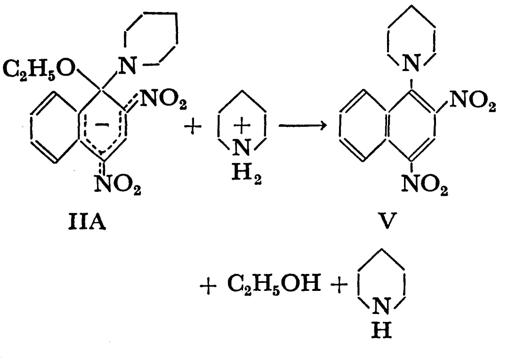
	Transition energy (eV)			Transition moment		Oscillator strength		
	E_{calcd}	E_{obsd}				f_{calcd}	f_{obsd}	
		IIA	IIB	X	Y		IIA	IIB
S_1	2.815	2.372	2.376	1.282	1.322	0.835	0.30	0.33
S_2	3.729	3.388	3.308	−0.638	0.936	0.419	0.16	0.20
S_3	3.878	—	—	0.220	0.289	0.028	—	—
S_4	4.908	—	—	−0.175	−0.502	0.121	—	—

1-Methoxy-2,4-dinitronaphthalene(IV) with Dimethylamine in DMSO. Addition of excess piperidine to a DMSO solution of III at room temperature (III 2.60×10^{-5} M, piperidine 1.01 M) yielded a red solution, indicating the formation of an anionic σ complex as follows:[8,12,13]



(1)

The complex IIA was catalyzed with piperidinium ion to form the replaced product V as shown in Eq. 2.[8] The absorption spectrum measured immediately after mixing is shown in Fig. 1, in which the positions and intensities are typical of 1,1-disubstituted 2,4-dinitronaphalene anionic σ complexes.[13–15] In the case of the reaction of IV with dimethyl amine, a similar spectrum to that in Fig. 1 was obtained. The absorption spectra of IIA and IIB (1-methoxy-1-dimethylamino-2,4-dinitronaphthalene anionic σ complex) comprise two allowed transitions, Band I (ε 2.4×10^4 at 522 nm) and Band II (ε 1.7×10^4 at 357 nm) for IIA, and Band I (ε 2.7×10^4 at 519 nm) and Band II (ε 1.6×10^4 at 364 nm) for IIB, respectively.



(2)

The calculated and observed transition energies, transition moments, and oscillator strengths of the anionic σ complex are listed in Table 1. The calculated transition energies are smaller than those of the observed values, because the complex in the excited state, S_1 or S_2, is more stabilized in DMSO, a comparatively polar solvent, than that in the ground state, S_0, as can be seen from the result that the dipole moment in the excited state is about twice larger than that in the ground state.

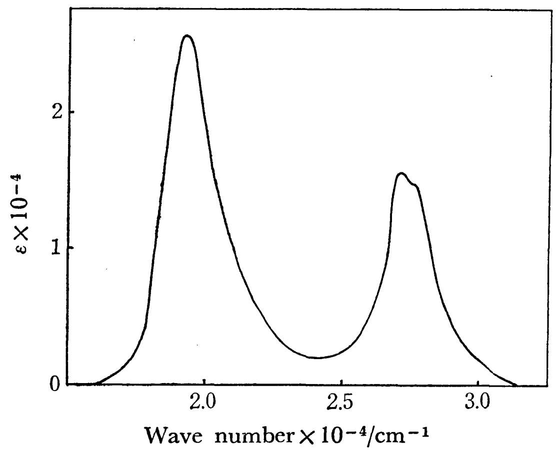


Fig. 1. Absorption spectrum relevant to the reaction of 2,4-dinitro-1-naphthylmethyl ether(IV, 3.30×10^{-5} M) with piperidine(2.00×10^{-1} M).

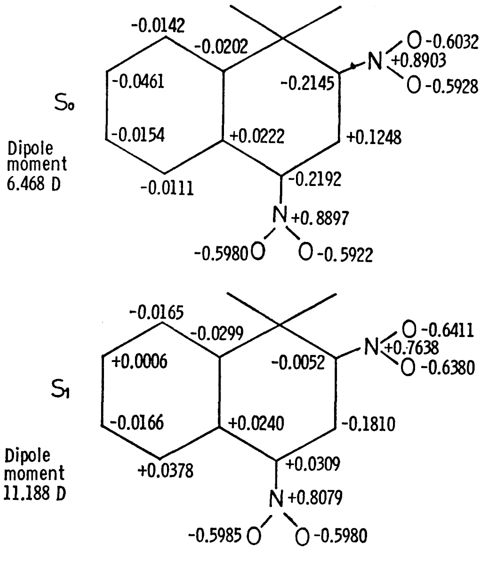
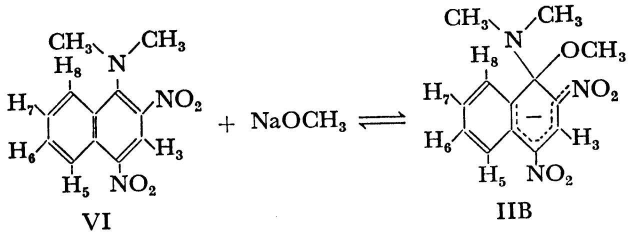


Fig. 2. π formal charge of the complex in the S_0 and S_1 states.

The π formal charges of the complex in the S_0 and S_1 states are shown in Fig. 2. In the S_0 state, the negative charge donated by a nucleophile to the π system is distributed on the two nitro groups to a large extent (*ca.* 60%). In the S_1 state, *ca.* 90% of one negative charge is distributed on the two nitro groups, where the charge distribution on the nitro group attached to C_1 is larger in comparison with that on the nitro group attached to C_3 and *ca.* 10% of it distributed on the B ring. These facts indicate that Band I corresponds to that of an intramolecular CT. From the analysis of charge distribution in the complex, one can understand how the two nitro groups are responsible for electron acceptors resulting in the stability of II.

Naturally, the fact that the absorption spectra of IIA and IIB agree well with the result of SCF-MO-CI calculation of II based on the assumption of an 18 π-electron closed system indicates that IIA and IIB are not anion radicals but anionic σ complexes. Similar results have been obtained on 1,1-disubstituted tri- and dinitrocyclohexadienates by Hosoya *et al.*[3f)]

IR spectra of the Reaction of N,N-*Dimethyl-2,4-dinitro-1-naphthylamine (VI) with Methanolic NaOCH$_3$ in DMSO.* We have recently found that VI reacts with $NaOCH_3$ in DMSO at room temperature to produce the same anionic σ complex as IIB,[9b)] which is stable enough for a long time to be observed by IR measurement, different from IIB obtained in the similar way to Eqs. 1 and 2, as follows:[14)]



(3)

The IR spectra of the reaction system in Eq. 3 are shown in Fig. 3. Ohsawa[15)] has stated that the strong and broad band characteristic of the ketal-like structure $>C<^{OR}_{NH_2}$ in Meisenheimer complexes appears at 1020—1040 cm^{-1}. The band appeared at 1040 cm^{-1}, therefore, is clearly attributable to the structure of $>C<^{OR}_{N<}$ bond, which indicates that the hybrid orbital of C_1 changes from sp^2 to sp^3 in conversion of V to IIB. Furthermore, in conversion of V to IIB, H_3 and H_8 resonance signals are shifted downfield, and H_5, H_6, and H_7 ones upfield, the shifts of which are characteristic of an anionic σ complex.[14)] All these results show that IIB is an anionic σ complex.

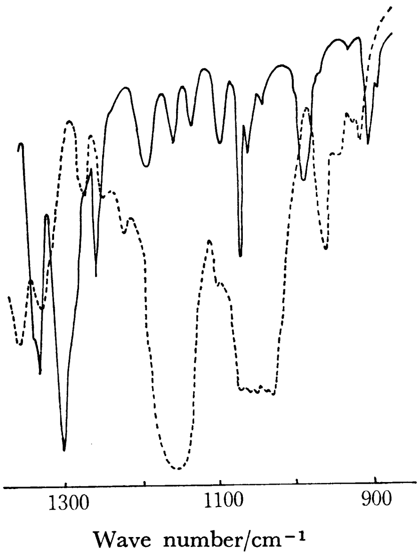


Fig. 3. Infrared spectra relevant to the reaction of *N,N*-dimethyl-2,4-dinitronaphthylamine(VI) with methanolic $NaOCH_3$ in DMSO.
——: VI, ----: IIB.

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