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Electronic Spectra and Electronic Structures of α- and β-Nitronaphthalenes and 1, 8-Dinitronaphthalene

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The absorption spectra of α-, β-nitronaphthalenes and 1, 8-dinitronaphthalene were measured in the near and vacuum ultraviolet regions. The peak wavelengths are as follows: α-nitronaphthalene, 213, 243 and 326.5 mμ; β-nitronaphthalene, 210.5, 259.5, 303 and 342 mμ; 1, 8-dinitronaphthalene, 199.5, 229.5 and 303 mμ. The transition energies and oscillator strengths were calculated with these three molecules by considering the configurational interaction among the ground, locally-excited and charge-transfer configurations. By combining the theoretical results with the observed peak wavelengths and the oscillator strengths, the nature of the electronic excitations corresponding to the observed absorption bands was clarified. Concerning 1, 8-dinitro-naphthalene, the twisting angle between the nitro groups and the naphthalene ring was estimated to be 60—70° by comparing the observed peak wavelengths and intensities with the calculated values. The effect of solvents on the absorption spectrum of 1, 8-dinitronaphthalene was found to be explained by the energy change in the charge-transfer configurations caused by the polarity of solvents. By considering the contribution of the charge-transfer configurations in the ground state, the increment in the dipole moment due to the delocalization of π-electrons was estimated for α- and β-nitronaphthalenes and 1, 8-dinitronaphthalene. The estimated dipole moment could explain the fact that the observed dipole moment of β-nitronaphthalene is greater than that of α-nitronaphthalene.

In previous papers,[1,2] we studied the electronic spectra and the electronic structures of nitrobenzene, nitromesitylene and 1, 5-dinitronaphthalene from both experimental and theoretical points of view. Concerning nitrobenzene,[1] a new band characteristic of the charge-transfer interaction between the benzene ring as an electron donor and the nitro group as an electron acceptor was observed at 240 mμ. This band almost completely disappeared in nitromesitylene, in which the nitro group is twisted from the benzene ring plane and in which, therefore, the resonance interaction is largely prohibited. In addition to this, the theoretical consideration based on the configurational interaction calculation and the direction of the transition moment measured by Labhart[3] lead to the conclusion that the 240 mμ band of nitrobenzene is an intramolecular charge-transfer absorption. A similar study has also been made with 1, 5-dinitronaphthalene.[2]

In the present study, we have undertaken to study the electronic spectra and electronic structures of α- and β-nitronaphthalenes and 1, 8-dinitronaphthalene by measuring the absorption spectra in the near and vacuum ultraviolet regions. Particularly, concerning 1, 8-dinitronaphthalene, the relation between the electronic spectra and the twisting angle of the nitro groups from the naphthalene ring plane was investigated, with the result that the twisting angle is 60—70° in solution.

Experimental

Materials.—Commercial 1, 8-dinitronaphthalene was purified by repeating recrystallizations from methanol and ethanol (m. p. 167°C).

Purified samples of α- and β-nitronaphthalenes were kindly presented by Mr. Akira Ishitani.* The *n*-heptane and methanol used as solvents were purified by the method described in the literature.[4,5] Commercial acetonitrile (OK type Special Grade, manufactured by the Asahi Chemical Industry, Ltd.) was first refluxed over calcium hydride for ten hours and then roughly distilled. The distillate was refluxed again over phosphorus pentoxide for half an hour and distilled. Finally it was distilled again from calcium hydride.

Measurements.—The absorption spectra of mono-nitro- and dinitronaphthalenes in the wavelength region of 190—500 mμ were measured with a Cary recording spectrophotometer, model 14. The absorption measurements of the acetonitrile solutions in the 180—200 mμ region were made with a vacuum ultraviolet spectrophotometer constructed in our

1) S. Nagakura, M. Kojima and Y. Maruyama, *J. Mol. Spect.*, **13**, 174 (1964).
2) M. Kojima and S. Nagakura, *Theoret. Chim. Acta*, **3**, 432 (1965).
3) H. Labhart, *Tetrahedron*, **19**, Suppl., 2, 223 (1963).

* We should like to express our hearty thanks to Mr. Ishitani for his kindness in providing us with the purified samples.

4) H. Yada, J. Tanaka and S. Nagakura, This Bulletin, **33**, 1660 (1960).
5) S. Nagakura, *Mol. Phys.*, **3**, 152 (1960).

TABLE I. THE ABSORPTION PEAK WAVELENGTHS AND INTENSITIES OF α-NITRONAPHTHALENE

Absorption peak wavelength, mμ	Molar extinction coefficient	Transition energy eV. Obs.	Transition energy eV. Calcd.	Oscillator strength Obs.	Oscillator strength Calcd.	Transition
326.5	4200	3.79	3.99	0.17	0.01	$W_0 \rightarrow W_1$
			4.14		0.17	$W_0 \rightarrow W_2$
243	10600	5.10	4.96	~0.22	0.01	$W_0 \rightarrow W_3$
			5.37		0.21	$W_0 \rightarrow W_4$
213 (long tail at the shorter wavelength side)	52900	5.83	5.67	~1.41	0.01	$W_0 \rightarrow W_5$
			5.86		0.45	$W_0 \rightarrow W_6$
			6.14		0.16	$W_0 \rightarrow W_7$
			6.19		0.06	$W_0 \rightarrow W_8$
			6.51		0.79	$W_0 \rightarrow W_9$

The experimental values were observed in the *n*-heptane solution.

TABLE II. THE ABSORPTION PEAK WAVELENGTH AND INTENSITIES OF β-NITRONAPHTHALENE

Absorption peak wavelength, mμ	Molar extinction coefficient	Transition energy eV. Obs.	Transition energy eV. Calcd.	Oscillator strength Obs.	Oscillator strength Calcd.	Transition
342	2500	3.62	3.95	0.04	0.03	$W_0' \rightarrow W_1'$
303	8100	4.09	4.45	0.13	0.12	$W_0' \rightarrow W_2'$
259.5	33400	4.78	5.23	0.59	0.48	$W_0' \rightarrow W_3'$
210.5 (long tail at the shorter wavelength side)	41400	5.89	5.77	~1.14	0.08	$W_0' \rightarrow W_4'$
			5.77		0.46	$W_0' \rightarrow W_5'$
			6.17		0.29	$W_0' \rightarrow W_6'$
			6.33		0.07	$W_0' \rightarrow W_7'$
			6.45		0.01	$W_0' \rightarrow W_8'$
			6.64		0.50	$W_0' \rightarrow W_9'$

The experimental values were observed in the *n*-heptane solution.

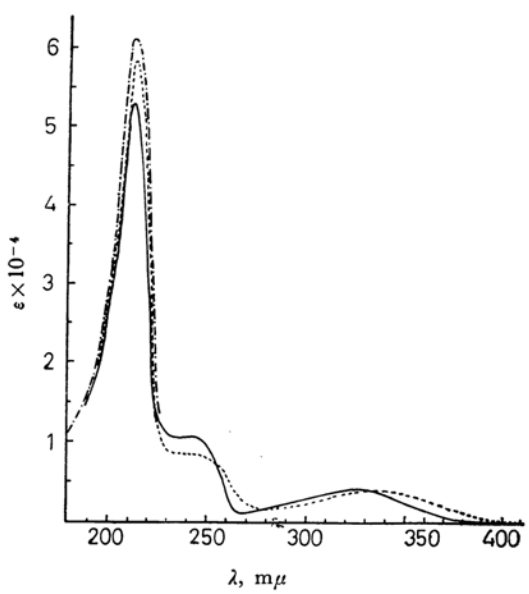

Fig. 1. The absorption spectrum of α-nitronaphthalene in several solvents.
—— *n*-heptane, ····· methanol,
-·-· acetonitrile

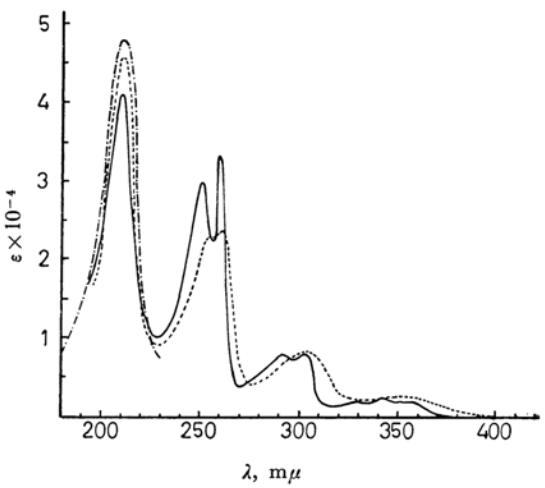

Fig. 2. The absorption spectrum of β-nitronaphthalene in several solvents.
—— *n*-heptane, ····· methanol,
-·-· acetonitrile

laboratory,**,6) an absorption cell with a path length of 0.1 mm. and with quartz windows being used.

Results.—The absorption spectra of mononitro- and dinitronaphthalenes are shown in Figs. 1—3. Furthermore, the peak wavelengths and molar extinction coefficients in their spectra are given in Tables I—III. In these tables the observed oscillator strength

** Our thanks are due to Mr. Koji Kaya and Mr. Masashi Tanaka for their kindness in measuring the vacuum ultraviolet absorption spectra.

6) H. Tsubomura, K. Kimura, K. Kaya, J. Tanaka and S. Nagakura, This Bulletin, **37**, 417 (1964).

Table III. The absoprtion peak wavelengths and intensities of 1, 8-dinitronaphthalene

Absorption peak wavelength, mμ	Molar extinction coefficient*1	Transition energy eV. Obs.	Transition energy eV. Calcd.*2	Oscillator strength Obs.	Oscillator strength Calcd.*2	Transition*3
303	6600	4.09	4.15	0.19	0.19	$W_0'' \rightarrow W_2''$
			4.46		0.02	$W_0'' \rightarrow W_3''$
229.5	35800	5.40	5.49	0.60	0.40	$W_0'' \rightarrow W_6''$
			5.69		0.02	$W_0'' \rightarrow W_7''$
199.5	38400	6.21	6.16	0.91	0.62	$W_0'' \rightarrow W_{10}''$
			6.18		0.09	$W_0'' \rightarrow W_{11}''$
			6.85		0.73	$W_0'' \rightarrow W_{12}''$

The experimental values were observed in the *n*-heptane solution.

*1 Since 1, 8-dinitronaphthalene is hardly soluble in *n*-heptane and the concentration of the *n*-heptane solution could not be determined accurately, all the molar extinction coefficient values are adjusted on the assumption that the values of the peak molar extinction coefficient of the longest wavelength band in the *n*-heptane solution coincides with that observed with the methanol solution. This may cause the errors of the order of 10%.

*2 Values calculated with $\theta=60°$.

*3 The other transitions are all forbidden.

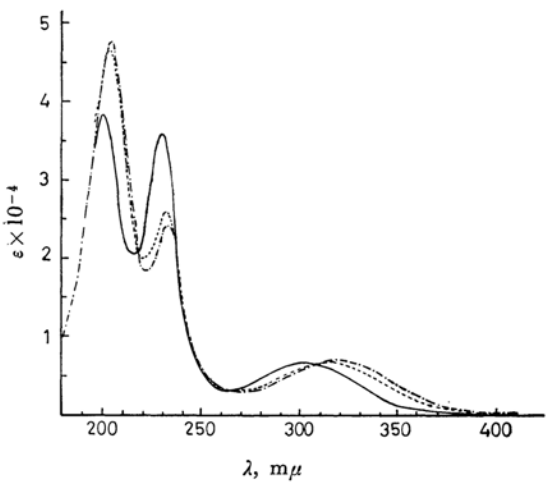

Fig. 3. The absorption spectrum of 1,8-dinitronaphthalene in several solvents.
—— *n*-heptane, ····· methanol,
–·–· acetonitrile

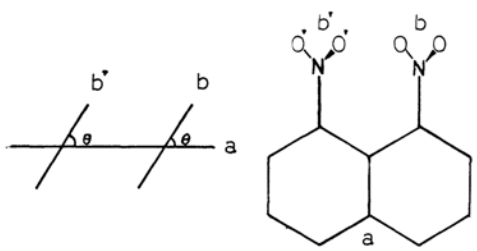

Fig. 4. 1,8-dinitronaphthalene with a hypothetical molecular symmetry C_2.
a: naphthalene ring plane
b, b': nitro group plane
θ: twisting angle

(f) values are also tabulated. In some cases, several bands overlap with each other and so we can not determine the oscillator strength value separately for each band. In these cases, the sums of the oscillator strengths for the overlapped bands are shown.

Theoretical

The π-electron structures of α- and β-nitronaphthalene and 1, 8-dinitronaphthalene were studied theoretically by the method used in the cases of 1, 5-dinitronaphthalene,[2] nitrobenzene and nitromesitylene.[1] That is to say, the respective nitronaphthalene molecules were separated into the naphthalene ring and the nitro groups, and the molecular orbitals of the components were evaluated by combining the results of the MO calculations with the experimental data of the electronic spectra. Thereafter, the interaction between the components was considered in terms of the configurational interaction among the ground, locally excited and charge-transfer configurations.

Concerning the geometrical configurations of the three molecules under consideration, no experimental data were found, so we assumed them to be follows: in β-nitronaphthalene, the nitro group is coplanar with the naphthalene ring plane; on the other hand, in α-nitronaphthalene, the nitro group is twisted from the aromatic ring plane by 49°, as in the case of 1, 5-dinitronaphthalene[7]; in 1, 8-dinitronaphthalene, the angle between the nitro group and the naphthalene ring plane may be assumed to change from 90° to 49° with a molecular symmetry (C_2) (see Fig. 4) and the calculation of the electronic structure was made with four values of the angle (49°, 60°, 70°, 80°). The other data necessary for the calculations were taken to be equal to the experimental data observed with 1, 5-dinitronaphthalene.[7] The C–N, N–O and C–C bond lengths were taken to be equal to 1.486 Å, 1.207 Å and 1.405 Å respectively, the C–C bond length being an averaged value for the ring

7) J. Trotter, *Acta Cryst.*, **13**, 95 (1960).

Table IV. The diagonal matrix elements used for the calculation of α-, β-nitronaphthalene and 1, 8-dinitronaphthalene

Configuration (No.)	Energy, eV.	Wave function	Wavelenghth of corresponding band, mμ[b]
Ground (I)[c,d]	0	Ψ_G	—
Locally excited (II)[c,d]	4.45	$\Psi_{B^+_{2u}}$	278.5[i]
Locally excited (III)[c,d]	5.73	$\Psi_{A^-_{1g}}$	—
Locally excited (IV)[c,d]	5.99	$\Psi_{B^-_{1g}}$	—
Locally excited (V)[c,d]	5.51	$\Psi_{B^+_{1g}}$	—
Locally excited (VI)[c,d]	3.97	$\Psi_{B^-_{3u}}$	312[i]
Locally excited (VII)[c,d]	5.89	$\Psi_{B^+_{3u}}$	210.5
Locally excited (VIII)[c]	6.62	Ψ_{NO_2}	198[j]
Charge-transfer (IX)[c]	4.56[e], 4.79[f]	Ψ_{CT_5}	
Charge-transfer (X)[c]	5.52[e], 5.76[f]	Ψ_{CT_4}	
Locally-excited (XI)[d]	6.32[g], 5.22[h]	$(\Psi_{NO_2}-\Psi_{NO_2'})/\sqrt{2}$	198[j]
Charge transfer (XII)[d]	4.56[g], 4.41[h]	$(\Psi_{CT_5}+\Psi_{CT_5'})/\sqrt{2}$	—
Charge-transfer (XIII)[d]	5.52[g], 5.57[h]	$(\Psi_{CT_4}-\Psi_{CT_4'})/\sqrt{2}$	—
Locally excited (XIV)[d]	6.20[g], 7.30[h]	$(\Psi_{NO_2}+\Psi_{NO_2'})/\sqrt{2}$	198[j]
Charge-transfer (XV)[d]	4.56[g], 4.41[h]	$(\Psi_{CT_5}-\Psi_{CT_5'})/\sqrt{2}$	—
Charge-transfer (XVI)[d]	5.52[g], 5.57[h]	$(\Psi_{CT_4}+\Psi_{CT_4'})/\sqrt{2}$	—

a) The exact forms of the locally excited configurations are given in Refs. 11 and 12.
b) Data from the spectra observed in the gaseous states.
c) Used for the calculation of α- and β-nitronaphthalenes.
d) Used for the calculation of 1, 8-dinitronaphthalene.
e) Values for α-nitronaphthalene.
f) Values for β-nitronaphthalene.
g) Values at $\theta=49°$.
h) Values at $\theta=90°$.
i) Taken from Ref. 13.
j) Taken from Ref. 5.

Table V. The off-diagonal matrix elements used for the calculation of α-nitronaphthalene

$H_{I\cdot IX}=-0.4214\beta'_{CN}$
$H_{I\cdot X}=0.0120\beta'_{CN}$
$H_{II\cdot VIII}=0.1051$ eV.
$H_{II\cdot IX}=0.2882\beta'_{CN}$
$H_{II\cdot X}=0.0064\beta'_{CN}$
$H_{III\cdot IX}=0.0910\beta'_{CN}$
$H_{III\cdot X}=0.1660\beta'_{CN}$
$H_{IV\cdot IX}=-0.1969\beta'_{CN}$
$H_{IV\cdot X}=0.0097\beta'_{CN}$
$H_{V\cdot VIII}=0.1109$ eV.
$H_{V\cdot IX}=-0.1978\beta'_{CN}$
$H_{V\cdot X}=0.0060\beta'_{CN}$
$H_{VI\cdot IX}=-0.0179\alpha'_{CN}$
$H_{VI\cdot X}=0.2055\beta'_{CN}$
$H_{VII\cdot VIII}=-0.2288$ eV.
$H_{VII\cdot IX}=0.0309\beta'_{CN}$
$H_{VII\cdot X}=0.2010\beta'_{CN}$
$H_{IX\cdot X}=0.0997$ eV.

($\beta'_{CN}=-1.57$ eV.)

The other off-diagonal matrix elements are zero.

Table VI. The off-diagonal matrix elements used for the calculation of β-nitronaphthalene

$H_{I\cdot IX}=-0.2595\beta_{CN}$
$H_{I\cdot X}=0.3988\beta_{CN}$
$H_{II\cdot VIII}=0.1190$eV.
$H_{II\cdot IX}=-0.1782\beta_{CN}$
$H_{II\cdot X}=0.0705\beta_{CN}$
$H_{III\cdot IX}=-0.1017\beta_{CN}$
$H_{III\cdot X}=-0.0921\beta_{CN}$
$H_{IV\cdot IX}=0.0855\beta_{CN}$
$H_{IV\cdot X}=-0.0158\beta_{CN}$
$H_{V\cdot VIII}=-0.1080$ eV.
$H_{V\cdot IX}=0.0859\beta_{CN}$
$H_{V\cdot X}=-0.0097\beta_{CN}$
$H_{VI\cdot IX}=-0.1836\beta_{CN}$
$H_{VI\cdot X}=-0.1270\beta_{CN}$
$H_{VII\cdot VIII}=-0.1334$ eV.
$H_{VII\cdot IX}=0.1693\beta_{CN}$
$H_{VII\cdot X}=-0.1243\beta_{CN}$
$H_{IX\cdot X}=0.2211$ eV.

($\beta_{CN}=-2.4$ eV.)

The other off-diagonal matrix elements are zero.

C–C bonds.

We took the energy of the ground configuration as the standard. Beside this, several locally excited configurations and the two types of charge-transfer configurations were taken into account.

The diagonal and off-diagonal matrix elements of the total electronic Hamiltonian were evaluated according to the methods presented by Pariser and Parr,[8] by Longuet-Higgins and Murrell[9] and by Pople[10]. They are shown in Tables IV—VII. The secular equations were solved by the aid of an electronic computer, FACOM 202, located at the Institute for Solid State Physics.

The finally-obtained energy levels and wave functions are shown in Tables VIII—X.

Discussion

α-Nitronaphthalene.—It is seen from Fig. 1 that the absorption spectrum of α-nitronaphthalene consists of three bands in the observed wavelength region. They appear at 213, 243 and 326.5,

8) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953).
9) H. C. Longuet-Higgins and J. N. Murrell, *Proc. Phys. Soc.*, **A68**, 601 (1955).
10) J. A. Pople, ibid., **A68**, 81 (1955).

Table VII. The off-diagonal matrix elements used for the calculation of 1, 8-dinitronaphthalene

$H_{I\cdot XII}=-0.5959\beta''_{CN}$ $H_{II\cdot XIII}=0.0090\beta''_{CN}$ $H_{IV\cdot XV}=-0.2785\beta''_{CN}$ $H_{V\cdot XVI}=0.0085\beta''_{CN}$ $H_{VII\cdot XV}=0.0436''_{CN}$

$H_{I\cdot XIII}=0.0170\beta''_{CN}$ $H_{III\cdot XII}=0.1287\beta''_{CN}$ $H_{IV\cdot XVI}=0.0138\beta''_{CN}$ $H_{VI\cdot XV}=-0.0253\beta''_{CN}$ $H_{VII\cdot XVI}=0.2843\beta''_{CN}$

$H_{II\cdot XI}=0.1486$(49°)—0 eV.(90°) $H_{III\cdot XIII}=0.2348\beta''_{CN}$ $H_{V\cdot XIV}=0.1568$(49°)—0 eV.(90°) $H_{VI\cdot XVI}=0.2906\beta''_{CN}$ $H_{XV\cdot XVI}=0.0996$ eV.

$H_{II\cdot XII}=0.4076\beta''_{CN}$ $H_{XII\cdot XIII}=0.0996$ eV. $H_{V\cdot XV}=-0.2797\beta''_{CN}$ $H_{VII\cdot XIV}=-0.3236$(49°)—0 eV.(90°)

$\beta''_{CN}(\theta)=\beta_{CN}(0°)\cos\theta$ (θ: 49°—90°); $\beta_{CN}(0°)=-2.4$eV.

The other off-diagonal matrix elements are zero.

Table VIII. Calculated energy levels and wave functions of α-nitronaphthalene

Energy, eV.	Wave function									
	Ψ_G	$\Psi_{A_{1g}^-}$	$\Psi_{B_{1g}^-}$	$\Psi_{B_{1g}^+}$	$\Psi_{B_{3u}^-}$	$\Psi_{B_{2u}^+}$	$\Psi_{B_{3u}^+}$	Ψ_{CT_5}	Ψ_{CT_4}	Ψ_{NO_2}
$W_9=$ 6.42	$\Psi_9=$ 0.0044	−0.0920	0.0274	0.1154	−0.0278	0.0319	−0.4922	0.0487	0.2149	0.8274
$W_8=$ 6.09	$\Psi_8=$ 0.0269	−0.3626	0.6927	0.0685	−0.0518	−0.0946	−0.2527	0.2578	0.3627	−0.3309
$W_7=$ 6.04	$\Psi_7=$ 0.0121	0.3208	0.6480	0.1333	0.0697	−0.0033	0.3779	0.0981	−0.4384	0.3309
$W_6=$ 5.77	$\Psi_6=$ 0.0110	−0.7187	−0.1348	0.2145	−0.0070	−0.0156	0.5947	0.0977	0.0478	0.2305
$W_5=$ 5.58	$\Psi_5=$ 0.0310	0.2016	−0.1988	0.8937	0.0097	−0.1196	−0.1051	0.2600	−0.0258	−0.1621
$W_4=$ 5.27	$\Psi_4=-$0.0047	0.4334	0.0235	0.0061	−0.1895	0.0121	0.4286	−0.0163	0.7628	0.0974
$W_3=$ 4.86	$\Psi_3=$ 0.0857	0.0912	−0.1734	−0.3169	0.0345	−0.6708	0.0352	0.6268	−0.0408	0.0813
$W_2=$ 4.04	$\Psi_2=$ 0.1050	0.0566	−0.1019	−0.1339	0.1850	0.7155	0.0162	0.6403	0.0150	−0.0255
$W_1=$ 3.90	$\Psi_1=-$0.0253	0.0184	0.0227	0.0283	0.9592	−0.1142	0.0302	−0.1428	0.2076	0.0066
$W_0=-$0.10	$\Psi_0=$ 0.9894	−0.0032	0.0073	0.0079	0.0014	−0.0143	−0.0008	−0.1437	0.0057	0.0000

Table IX. Calculated energy levels and wave functions of β-nitronaphthalene

Energy, eV.	Wave function									
	Ψ_G	$\Psi_{A_{1g}^-}$	$\Psi_{B_{1g}^-}$	$\Psi_{B_{1g}^+}$	$\Psi_{B_{3u}^-}$	$\Psi_{B_{2u}^+}$	$\Psi_{B_{3u}^+}$	Ψ_{CT_5}	Ψ_{CT_4}	Ψ_{NO_2}
$W_9'=$ 6.40	$\Psi_9'=$ 0.0705	−0.0629	−0.1112	−0.1321	−0.0183	0.1099	−0.5278	0.1550	−0.3705	0.7133
$W_8'=$ 6.21	$\Psi_8'=-$0.0940	0.3544	0.0300	−0.0902	0.1087	−0.0044	0.2718	0.0904	0.6691	0.5611
$W_7'=$ 6.09	$\Psi_7'=-$0.0133	−0.3681	0.6901	0.0670	−0.1014	−0.0584	0.3109	−0.3722	−0.1599	0.3242
$W_6'=$ 5.93	$\Psi_6'=-$0.0037	−0.3898	−0.6951	0.0375	−0.0642	−0.0291	0.5016	−0.2079	−0.1122	0.2254
$W_5'=$ 5.53	$\Psi_5'=$ 0.0857	0.7129	0.0112	−0.0885	−0.1277	0.0605	0.3888	−0.0759	−0.5450	0.0482
$W_4'=$ 5.53	$\Psi_4'=-$0.0211	0.1888	−0.0741	0.9431	−0.0423	−0.0535	−0.1526	−0.1617	0.0171	0.1202
$W_3'=$ 4.98	$\Psi_3'=$ 0.1011	−0.1829	0.1334	0.2553	0.2406	0.5479	0.3215	0.6319	−0.1155	0.0039
$W_2'=$ 4.21	$\Psi_2'=-$0.0949	0.0339	−0.0453	−0.0649	−0.4309	0.7851	−0.1239	−0.3591	0.1838	−0.0569
$W_1'=$ 3.71	$\Psi_1'=-$0.0559	0.0659	−0.0394	−0.0517	0.8436	0.2449	−0.0747	−0.4524	−0.0773	−0.0175
$W_0'=-$0.24	$\Psi_0'=$ 0.9776	−0.0003	−0.0053	−0.0053	0.0020	0.0178	−0.0166	−0.1314	0.1620	−0.0007

TABLE X. CALCULATED ENERGY LEVELS AND WAVE FUNCTIONS OF 1, 8-DINITRONAPHTHALENE ($\theta=60°$)

Energy, eV.		Symmetric wave function					
		Ψ_G	$\Psi_{A_{1g}^-}$	$\Psi_{B_{2u}^+}$	$\frac{(\Psi_{CT_5}-\Psi_{CT_5'})}{\sqrt{2}}$	$\frac{(\Psi_{CT_4}+\Psi_{CT_4'})}{\sqrt{2}}$	$\frac{(\Psi_{NO_2}-\Psi_{NO_2'})}{\sqrt{2}}$
$W_9''=$ 5.96	$\Psi_9''=$	−0.0164	0.8009	0.0591	−0.1535	−0.5707	0.0728
$W_8''=$ 5.88	$\Psi_8''=$	−0.0025	−0.0669	0.0818	−0.0197	0.0467	0.9930
$W_5''=$ 5.34	$\Psi_5''=$	−0.0047	0.5787	−0.0030	−0.0123	0.8153	0.0006
$W_4''=$ 5.00	$\Psi_4''=$	0.1064	0.1268	−0.6388	0.7426	−0.0807	0.0800
$W_2''=$ 4.04	$\Psi_2''=$	0.1121	0.0536	0.7624	0.6328	−0.0249	−0.0451
$W_0''=$ −0.11	$\Psi_0''=$	0.9878	−0.0037	−0.0165	−0.1545	0.0060	0.0003

Energy, eV.		Antisymmetric wave function						
		$\Psi_{B_{1g}^-}$	$\Psi_{B_{1g}^+}$	$\Psi_{B_{3u}^-}$	$\Psi_{B_{3u}^+}$	$\frac{(\Psi_{CT_5}+\Psi_{CT_5'})}{\sqrt{2}}$	$\frac{(\Psi_{CT_4}-CT_4')}{\sqrt{2}}$	$\frac{(\Psi_{NO_2}+\Psi_{NO_2'})}{\sqrt{2}}$
$W_{12}''=$6.74	$\Psi_{12}''=$	0.0098	0.0939	−0.0113	−0.3107	0.0269	0.0925	0.9407
$W_{11}''=$6.07	$\Psi_{11}''=$	0.8848	0.1082	−0.0327	−0.2838	0.2368	0.2175	−0.1424
$W_{10}''=$6.05	$\Psi_{10}''=$	0.3763	0.0954	0.0894	0.6973	0.0465	−0.5296	0.2687
$W_7''=$5.58	$\Psi_7''=$	−0.1955	0.9420	−0.0119	0.0539	0.2401	0.0759	−0.0886
$W_6''=$5.37	$\Psi_6''=$	0.0112	−0.0893	−0.1932	0.5760	0.0180	0.7798	0.1194
$W_3''=$4.35	$\Psi_3''=$	−0.1914	−0.2729	0.1138	0.0249	0.9344	−0.0427	0.0162
$W_1''=$3.89	$\Psi_1''=$	0.0175	0.0217	0.9697	0.0349	−0.0991	0.2186	0.0022

TABLE XI. THE SOLVENT EFFECT ON THE ABSORPTION BANDS OF 1, 8-DINITRONAPHTHALENE

Solvent	Absorption maxima and molar extinction coefficients		
n-Heptane	303.0 mμ (6600)	229.4 mμ (35800)	199.6 mμ (38400)
Methanol	313.5 mμ (6600)	231.2 mμ (25800)	201.9 mμ (46600)
Acetonitrile	318.8 mμ (7000)	232.9 mμ (24000)	203.5 mμ (47800)

TABLE XII. DEPENDENCE OF TRANSITION ENERGIES AND OSCILLATOR STRENGTHS UPON THE CHARGE-TRANSFER CONFIGURATIONS (Calculated for $\theta=60°$)

Case	1	2	3	4	5
H_{CT_5}	4.52 eV.	4.32 eV.	4.12 eV.	3.92 eV.	3.72 eV.
H_{CT_4}	5.54 eV.	5.34 eV.	5.14 eV.	4.94 eV.	4.74 eV.
Energy(I)*	4.18 eV.	4.09 eV.	3.98 eV.	3.84 eV.	3.70 eV.
f(I)**	0.21	0.21	0.20	0.19	0.21
Energy(II)*	5.50 eV.	5.36 eV.	5.21 eV.	5.15 eV.	4.99 eV.
f(II)**	0.42	0.28	0.19	0.15	0.10
Energy(III)*	6.51 eV.	6.45 eV.	6.41 eV.	6.40 eV.	6.38 eV.
f(III)**	1.44	1.58	1.66	1.71	1.75

* Mean values weighted by calculated oscillator strengths for all the transitions assigned to a band.
** Sum of the calculated oscillator strength values classified to the same observed band.
(The numbers in bracket correspond to the 303.0 mμ band 229.4 mμ band and 199.6 mμ band (observed with the *n*-heptane solution), respectively.)

mμ. From a comparison of the observed absorption spectrum with the theoretical results, the broad 326.5 mμ band may be considered to include the two overlapped bands corresponding to the $W_0\rightarrow W_1$ and $W_0\rightarrow W_2$ transitions. The wave functions, Ψ_1 and Ψ_2, given in Table VIII show that the former corresponds to the $A_{1g}^-\rightarrow B_{3u}^-$ transition of naphthalene, while the latter contains the $A_{1g}^-\rightarrow B_{2u}^-$ transition of naphthalene and the CT_5-type charge-transfer transition in almost equal proportions. As is revealed by the calculated oscillator strengths given in Table I, the $W_0\rightarrow W_1$ transition is weaker than the $W_0\rightarrow W_2$ transition.

The 243 mμ band may be ascribed to the $W_0\rightarrow W_3$ and $W_0\rightarrow W_4$ transitions. In view of the calculated oscillator strength values given in Table I, this band may be assigned substantially to the W_0—W_4 transition, which results mainly from the CT_4-type charge-transfer transition.

The strong band at 213 mμ seems to include various transitions, transitions from the ground state, W_0, to the W_5, W_6, W_7, W_8 and W_9 states. An inspection of the calculated oscillator strengths given in Table I reveals that the $W_0\rightarrow W_5$ and $W_0\rightarrow$

W_8 transition bands are weak and may be covered by the other transition bands. The $W_0 \rightarrow W_6$ transition is mainly composed of the $A_{1g}^- \rightarrow B_{3u}^+$ and $A_{1g}^- \rightarrow A_{1g}^+$ transitions. The $W_0 \rightarrow W_7$ transition has a complicated character and comes from the $A_{1g}^- \rightarrow B_{1g}^-$, $A_{1g}^- \rightarrow B_{3u}^+$ and $A_{1g}^- \rightarrow A_{1g}^-$ transitions, besides the local transition within the nitro group and CT_4-type charge-transfer transitions. The $W_0 \rightarrow W_9$ transition results largely from the local excitation within the nitro group. The tail at the shorter wavelength side of the 213 mμ band might be due to this transition.

β-Nitronaphthalene.—The absorption spectrum of β-nitronaphthalene shown in Fig. 2 consists of four bands in near and vacuum ultraviolet regions down to 180 mμ. They appear at 210.5, 259.5, 303 and 342 mμ.

The 342 mμ band may safely be assigned to the $W_0' \rightarrow W_1'$ transition. The wave function, Ψ_1', given in Table IX shows that the band may be regarded as the shifted band of the $A_{1g}^- \rightarrow B_{3u}^-$ transition band of naphthalene.

The 303 mμ band can be assigned to the $W_0' \rightarrow W_2'$ transition. Its character is, for the most part, that of the shifted band of the $A_{1g}^- \rightarrow B_{2u}^+$ transition of naphthalene, though it also includes, to some extent, the $A_{1g}^- \rightarrow B_{3u}^-$ and CT_5-type charge-transfer transitions.

The $W_0' \rightarrow W_1'$ and $W_0' \rightarrow W_2'$ transitions of β-nitronaphthalene are similar to, respectively, the $W_0 \rightarrow W_1$ and $W_0 \rightarrow W_2$ transitions of α-nitronaphthalene in their nature. Therefore, it may be said that the overlapping bands at 326.5 mμ in α-nitronaphthalene appear separately at 342 and 303 mμ in β-nitronaphthalene. This difference can be explained satisfactorily by the present theoretical treatment. That is to say, the B_{2u}^+ locally excited configuration is stabilized by the contribution of the charge-transfer configurations to a greater extent in the W_1' state of β-nitronaphthalene than in the W_1 state of α-nitronaphthalene; the reverse is the case for the W_2 and W_2' states.

The 259.5 mμ band is undoubtedly due to the $W_0' \rightarrow W_3'$ transition. From the wave function, Ψ_3', given in Table IX, this transition is known to result mainly from the $A_{1g}^- \rightarrow B_{2u}^+$ and CT_5-type transitions. This transition corresponds to the $W_0 \rightarrow W_3$ transition of α-nitronaphthalene, whose transition probability is very small.

The 210.5 mμ band may be regarded as overlapping bands corresponding to the $W_0' \rightarrow W_4'$, $W_0' \rightarrow W_5'$, $W_0' \rightarrow W_6'$, $W_0' \rightarrow W_7'$ and $W_0' \rightarrow W_8'$ transitions. An inspection of the calculated oscillator strength values given in Table IX shows that this band consists substantially of the $W_0' \rightarrow W_5'$ and $W_0' \rightarrow W_6'$ transitions. The $W_0' \rightarrow W_4'$, $W_0' \rightarrow W_7'$ and $W_0' \rightarrow W_8'$ transitions are very weak in intensity. Roughly speaking, the $W_0' \rightarrow W_5'$ and $W_0' \rightarrow W_6'$ transitions of β-nitronaphthalene correspond to the $A_{1g}^- \rightarrow A_{1g}^-$ and $A_{1g}^- \rightarrow B_{1g}^-$ transitions of naphthalene respectively, though the $A_{1g}^- \rightarrow B_{3u}^+$ transition of naphthalene also contributes considerably to these two transitions. The tail at the shorter wavelength side of the 210.5 mμ band might be due to the $W_0' \rightarrow W_9'$ transition. Table IX shows that the upper state of this transition is mainly composed of the local excitation within the nitro group (50%) and of the local excitation ($A_{1g}^- \rightarrow B_{3u}^+$) within the naphthalene ring (25%).

1, 8-Dinitronaphthalene. — As is shown in Fig. 3, the absorption spectrum of 1, 8-dinitronaphthalene consists of three bands in the observed wavelength region. They appear at 199.5, 229.5 and 303 mμ.

The Determination of the Angle between the Naphthalene Ring and the Nitro Groups.—In order to evaluate the twisting angle between the nitro groups and the naphthalene ring, we calculated the transition energies and oscillator strengths for the four angles of 49°, 60°, 70° and 80°. Each of the observed bands consists of multiple transitions. Therefore, the mean value of the calculated transition energies, weighted by the calculated oscillator strengths, was evaluated for each observed band. Consequently, the deviation, δw_i, between the observed and calculated transition energies could be obtained for each band. The minimum sum of the $|\delta w_i|$ values for the three observed bands was found to be that for the angle of 70°. From the comparison between the calculated and observed oscillator strengths, the most suitable value of the angle was determined to be 60°. Therefore, it is most probable that the angle between the naphthalene ring plane and the nitro groups in 1, 8-dinitronaphthalene is 60°—70° in solution. This value seems reasonable in view of the fact that the nitro groups are twisted by 49° from the naphthalene ring in 1, 5-dinitronaphthalene.[7]

The Assignment of the Absorption Bands.—The 303 mμ band may safely be assigned to the $W_0'' \rightarrow W_2''$ and $W_0'' \rightarrow W_3''$ transitions. Judging from the calculated oscillator strengths, the latter transition band may be considered to be hidden under the former. The latter mainly consists of the CT_5-type charge-transfer transition. An inspection of Ψ_2'' given in Table X shows that the $W_0'' \rightarrow W_2''$ transition is a mixture of the $A_{1g}^- \rightarrow B_{2u}^+$ transition of naphthalene and the charge-transfer (CT_5-type) transition.

In view of the oscillator strength values of the $W_0'' \rightarrow W_6''$ and $W_0'' \rightarrow W_7''$ transitions, the character of the 229.5 mμ band comes mostly from the former. The latter is composed of the shifted $A_{1g}^- \rightarrow B_{1g}^+$ transition. The $W_0'' \rightarrow W_6''$ transition consists mainly of the CT_4-type charge-transfer

11) J. Tanaka, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zassi*), **78**, 1643 (1957).
12) R. Pariser, *J. Chem. Phys.*, **24**, 250 (1956).
13) G. D. Nordheim and H. S. Sponer, *Discussions Faraday Soc.*, **9**, 19 (1950).

band, although it also includes the $A_{1g}^{-} \rightarrow B_{3u}^{+}$ transition to some extent. The 199.5 mμ band may owe its character chiefly to the $W_0'' \rightarrow W_{10}''$, $W_0'' \rightarrow W_{11}''$ and $W_0'' \rightarrow W_{12}''$ transitions. The $W_0'' \rightarrow W_{11}''$ transition is very weak in comparison with the other two. The $W_0'' \rightarrow W_{10}''$ transition may be regarded as a mixture of the $A_{1g}^{-} \rightarrow B_{3u}^{+}$ and CT_4-type transitions. The $W_0'' \rightarrow W_{12}''$ transition corresponds to the local excitation of the NO_2 groups.

The Solvent Effect on the Absorption Bands.—Figure 3 shows that the 199.5 mμ and 229.5 mμ bands of 1, 8-dinitronaphthalene are sensitive to the polarity of the solvent; these bands change not only in the peak wavelength but also in the intensity with the polarity of the solvent. These tendencies are tabulated in Table XI. In order to explain the solvent effect, we calculated the energy levels and wave functions, changing the energy values of the two types of charge-transfer configurations, H_{CT_5} and H_{CT_4}. The results are shown in Table XII. It is seen that the decrease in the energies of the two types of charge-transfer configurations brings about a decrease in the transition energies (mean values) corresponding to the three absorption bands at 199.5, 229.5 and 303 mμ, and that it causes a decrease and an increase in the oscillator strength values of the 229.5 mμ and 199.5 mμ bands respectively. On the other hand, the oscillator strength of the 303 mμ band is insensitive to the solvent. These theoretical results satisfactorily explain the observed solvent effects shown in Table XI. Thus the absorption spectrum of 1, 8-dinitronaphthalene may be regarded as a typical example showing conspicuous solvent effects through the energy change of the charge-transfer configurations.

Dipole Moments of α- and β- Nitronaphthalenes.—According to the present theoretical consideration, the contributions of the charge-transfer configurations in the ground state are 2.1% and 4.4% for α- and β- nitronaphthalenes respectively. From this it may be expected that the dipole moments due to π-electrons would be greater in β-nitronaphthalene than in α-nitronaphthalene. In fact, the dipole moments of α- and β-nitronaphthalenes were observed to be 3.62—3.88D and 4.36—4.4D respectively.[14] In order to treat the problem more quantitatively, we calculated the dipole moments of these compounds by considering the additional moment due to the contribution of the charge-transfer configurations.[15] Consequently, the dipole moments of α- and β-nitronaphthalenes were calculated to be 3.52 and 4.10D respectively. Therefore, it may be said that the present theoretical treatment can explain quantitatively, or at least semi-quantitatively, the difference in the dipole moment between α- and β-nitronaphthalenes. A similar calculation was made for the dipole moment of 1, 8-dinitronaphthalene, with the result of 6.77D. This value also coincides well with the observed value, 7.1—7.87D.[14]

14) L. G. Wesson, "Tables of Electric Dipole Moments," The Technology Press, Massachusetts Institute of Technology, Cambridge, Massachusetts (1948), pp. 13, 45.

15) The dipole moments of the charge-transfer configurations were evaluated to be as follows from the π-electron distribution of each CT configuration:

α-Nitronaphthalene CT_4, CT_5; 16.40D

β-Nitronaphthalene CT_4, CT_5; 20.74D

From these values and the contribution of each charge-transfer configuration in the ground state, the additional dipole moments due to resonance interaction are evaluated to be 0.36 and 0.92 D for α- and β-nitronaphthalenes respectively. By combining these additional dipole moments with the observed dipole moment of nitromethane, 3.2D, the dipole moments of α- and β-nitronaphthalenes were evaluated to be 3.52 and 4.10D respectively.