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The Electronic Spectrum and Electronic Structure of 1,5 Dinitronaphthalene

By

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The electronic absorption spectra of the *n*-heptane and ethanol solutions and the polarized absorption spectrum of the single crystal were measured with 1,5-dinitronaphthalene. 1,5-Dinitronaphthalene shows three absorption bands at 198.7, 230 and 323 m μ . The 230 m μ and 323 m μ bands are polarized almost parallel with the long and short axes of the naphthalene ring respectively. The assignment of the bands has been made by combining the observed results with the theoretical consideration.

Das UV-Absorptionsspektrum von 1,5-Dinitronaphthalin in Lösung von *n*-Heptan und Äthanol und das Polarisationsabsorptionsspektrum des Einkristalls wurde aufgenommen. Es zeigt drei Banden bei 198,7, 230 und 323 m μ , wobei die Polarisationsrichtungen der beiden letzteren nahezu parallel zur langen und kurzen Achse des Naphthalinringes liegen. Die Zuordnung der Banden wurde auf Grund einer Kombination experimenteller und theoretischer Gegebenheiten vorgenommen.

Le spectre électronique d'absorption du 1,5-dinitronaphthalène a été mesuré dans l'éthanol, le *n*-heptane et dans le monocristal. Des bandes à 198,7, 230 et 323 m μ la deuxième (troisième) est polarisée presque parallèle à l'axe longue (courte) du noyau naphthalénique. La comparaison aux résultats théoriques permet l'interprétation des bandes.

1. Introduction

In our previous paper [4], we studied the absorption spectra of nitrobenzene and nitromesitylene from both theoretical and experimental points of view, and succeeded in interpreting quantitatively the absorption bands of nitrobenzene in near and vacuum ultraviolet regions. The results show that the intramolecular charge-transfer band characteristic of the electron donor-acceptor interaction appears at 240 m μ for nitrobenzene. In the present paper, we have undertaken to extend a similar study to 1,5-dinitronaphthalene. The assignment of the absorption bands of 1,5-dinitronaphthalene could be made by comparing the observed transition energies and intensities with the theoretical values. According to Trotter's X-ray crystal analysis data [10], the nitro group and the naphthalene ring in 1,5-dinitronaphthalene make an angle of 49°. In theoretical consideration, the effect of the non-coplanarity upon the electronic spectrum was taken into account. In addition to the measurement of ultraviolet absorption spectra in solution, we have measured the polarized ultraviolet absorption of the single crystal, for the purpose of determining the direction of transition moments.

2. Experimental

Materials. — The commercial 1,5-dinitronaphthalene was purified by repeating recrystallization more than three times from methanol and ethanol (m. p. 213° C).

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Purified *n*-heptane and ethanol [12] were used as solvents for the measurements of electronic absorption spectra.

Measurements. — The absorption spectrum of 1,5-dinitronaphthalene in the wavelength region (190 ~ 500 m μ) was measured with a Cary recording spectrophotometer Model 14. Furthermore, the polarized electronic absorption spectrum

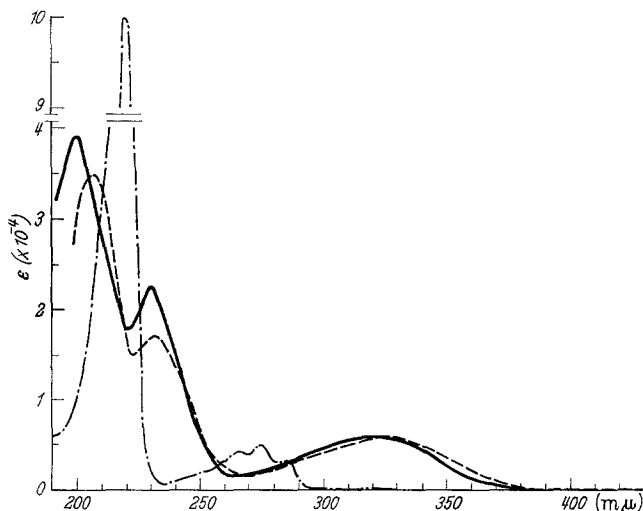


Fig.1. The ultraviolet absorption spectra of 1,5-dinitronaphthalene and naphthalene in *n*-heptane and ethanol solutions. ————— 1,5-dinitronaphthalene in *n*-heptane solution, - - - - - 1,5-dinitronaphthalene in ethanol solution, - · - · - naphthalene in *n*-heptane solution

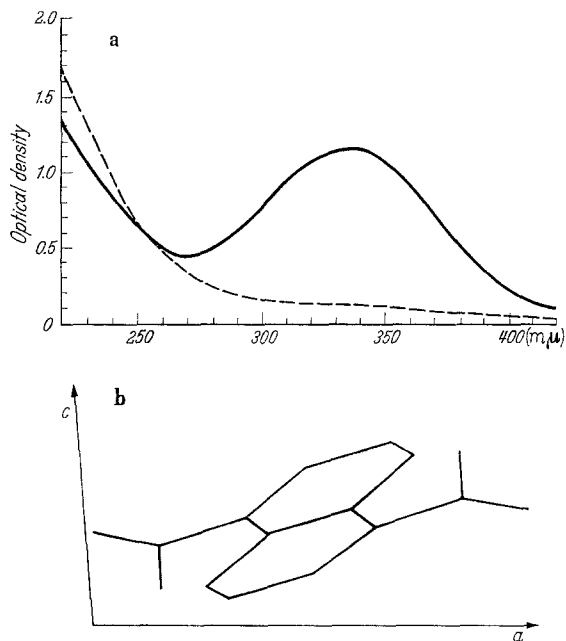


Fig. 2. a The polarized ultraviolet absorption spectrum of the 1,5-dinitronaphthalene crystal. Solid line: perpendicular to the *c* axis. Broken line: parallel to the *c* axis. b Projection of the 1,5-dinitronaphthalene molecules to the (010) plane

of the single crystal of 1,5-dinitronaphthalene was measured in the wavelength region of 220 to 420 m μ with a ultraviolet microspectrophotometer [8].

The absorption spectrum of 1,5-dinitronaphthalene in *n*-heptane is shown in Fig. 1. The polarized electronic absorption spectrum measured with the single crystal is shown in Fig. 2.

The peak wavelengths and molar extinction coefficients in their spectra are given in Tab. 1. In this table are also tabulated the observed oscillator strength (*f*) values which were obtained by the usual equation $f = 4.32 \times 10^{-9} \int \epsilon_r dv$. In some cases, several bands overlap with each another and we could not determine separately the oscillator strength for each band. In these cases, the sum of the oscillator strengths for overlapped bands is given in Tab. 1.

Table 1. Observed and Calculated Transition Energies and Absorption Intensities

Experimental ^{a)}		Transition energy (eV)		Oscillator strength		Transition ^{d)}
Peak wavelength (m μ)	Peak molar extinction ^{b)} coefficient	obs.	calc.	obs.	calc. ^{c)}	
323 (327.1)	6000 (6000)	3.84	3.99 4.08	0.16	0.09 0.15	$W_0 \rightarrow W_1$ $W_0 \rightarrow W_2$
230 (231.8)	23000 (17000)	5.39	5.32 5.47	0.50	0.04 0.43	$W_0 \rightarrow W_4$ $W_0 \rightarrow W_6$
198.7 (205)	39000 (35000)	6.26	6.23 6.73	1.05	0.22 1.19	$W_0 \rightarrow W_9$ $W_0 \rightarrow W_{12}$

a) The values observed with the *n*-heptane and ethanol solutions are shown. The latter values are given in parentheses.

b) Since 1,5-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 so that the molar extinction coefficients of the longest wavelength band observed with the *n*-heptane and ethanol solutions are coincident with each other. The error caused by this procedure may conceivably be less than 10%.

c) The transition moments corresponding to the $W_0 \rightarrow W_1$, $W_0 \rightarrow W_2$, $W_0 \rightarrow W_4$ and $W_0 \rightarrow W_6$ transitions are given as follows:

$$Q_{01} = -e (0.056 x + 0.501 y + 0.019 z)$$

$$Q_{02} = -e (0.217 x + 0.616 y + 0.178 z)$$

$$Q_{04} = -e (0.239 x + 0.123 y - 0.063 z)$$

$$Q_{06} = -e (0.945 x + 0.014 y - 0.120 z)$$

d) Only the allowed transitions are taken in this table.

3. Theoretical

We calculated the electronic structure of 1,5-dinitronaphthalene according to the " π -electron approximation" considering only singlet states. 1,5-Dinitronaphthalene was divided into the three component groups; the naphthyl and two nitro groups. The interaction among the component groups was evaluated by considering the configuration interaction among several electron configurations, such as ground (taken as the standard), locally excited and electron- (or charge-) transfer configurations. Some of the energy values of the locally excited configurations (if available) were set equal to the corresponding excitation energies taken from the electronic absorption bands of each component [5, 3]. As for the orbital

wave functions of the locally excited configurations of naphthalene, we adopted those calculated by PARISER [6].

With regard to the locally excited configuration of the nitro group, we used the orbital wave functions calculated by one of the present authors based on the self-consistent field molecular orbital method [9].

We took two types of charge-transfer configurations into account for each nitro group. They correspond to electron transfer from the highest occupied (φ_5) and the second highest occupied (φ_4) orbitals of the naphthyl group to the vacant orbital of the nitro group (φ_{NO_2}). The wave functions (ψ_{CT_5} , ψ_{CT_4}) and energy values (E_{CT_5} , E_{CT_4}) of these two charge-transfer configurations are given by the following equation.

$$\begin{aligned}\psi_{CT_5} &= \varphi_5^{-1} \varphi_{\text{NO}_2}, \\ E_{CT_5} &= I_5 - A_{\text{NO}_2} - \Delta_5, \\ \psi_{CT_4} &= \varphi_4^{-1} \varphi_{\text{NO}_2}, \\ E_{CT_4} &= I_4 - A_{\text{NO}_2} - \Delta_4.\end{aligned}$$

A_{NO_2} is the electron affinity of the nitro group and was estimated to be 0.4 eV. This value is the same as used in the calculations of the nitromethyl anion [3], nitrobenzene [4], nitramide and ethyl nitrate [1]. The value of I_5 , the first ionization potential of naphthalene, was determined by WATANABE to be 8.12 eV from the photoionization experiment [11]. I_4 , the second ionization potential, was estimated to be 9.14 eV in the following way;

$$I_4 = I_4(\text{calc}) - I_5(\text{calc}) + I_5(\text{exp}).$$

$I_5(\text{calc})$ and $I_4(\text{calc})$ were evaluated according to the following equation:

$$I_n = -H_n + \sum_j^5 (2J_{nj} - K_{nj})$$

where H_n , J_{nj} and K_{nj} are core, coulomb and exchange integrals, respectively, over the molecular orbitals φ_n or φ_n and φ_j . The data necessary for the evaluation were cited from the literature [6]. Thus we evaluated the value of $I_4(\text{calc}) - I_5(\text{calc})$ as 1.02 eV.

Δ_5 and Δ_4 are the electrostatic repulsion (or attraction) terms between the naphthyl and the nitro groups in each charge-transfer configuration. Δ_4 and Δ_5 contain the two center repulsion integrals of the type ($pp|qq$) which were evaluated by the uniformly charged sphere model [7], taking the non-coplanarity of the molecule into consideration. The X-ray crystal analysis data by TROTTER [10] show that in 1,5-dinitronaphthalene the nitro group is twisted by 49° out of the naphthalene ring plane. The molecular geometry of 1,5-dinitronaphthalene is given in Fig. 3.

The off-diagonal matrix elements of the total electron Hamiltonian $H_{m,n}$

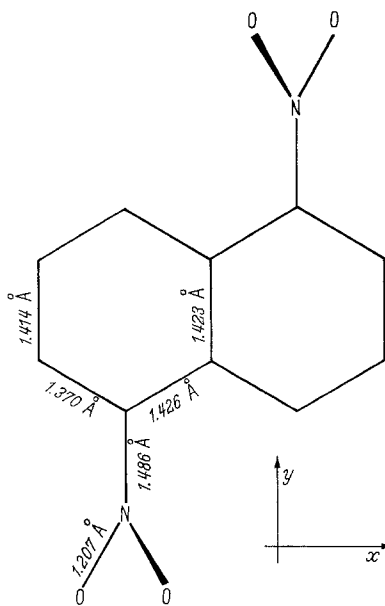


Fig. 3. The geometrical configuration of the 1,5-dinitronaphthalene molecule as determined by the aid of the X-ray crystal analysis technique

were calculated according to the method of LONGUET-HIGGINS and MURRELL [2]. The energies and wave functions of the electron configurations under consideration and off-diagonal matrix elements used for the present calculation are given in

Table 2. *The Diagonal Matrix Elements used for the Calculation of 1,5-Dinitronaphthalene*

Configuration ^{a)} (No.)	Energy* (eV)	Wave function	Symmetry ^{b)}	Wavelength of corresponding ^{c)} band (m μ)
Ground (I)	0	G	S (sym.)	—
Locally excited (II)	5.73	$\psi_{A_{1g}}^-$	S	—
Locally excited (III)	5.99	$\psi_{B_{1g}}^-$	S	—
Locally excited (IV)	5.51	$\psi_{B_{1g}}^+$	S	—
Locally excited (V)	6.23	$(\psi_{NO_2} + \psi_{NO_2}')/\sqrt{2}$	S	198 (3) ^{d)}
Charge-transfer (VI)	4.56	$(\psi_{CT_5} + \psi_{CT_5}')/\sqrt{2}$	S	—
Charge-transfer (VII)	5.52	$(\psi_{CT_4} + \psi_{CT_4}')/\sqrt{2}$	S	—
Locally excited (VIII)	3.97	$\psi_{B_{3u}}^-$	A (antisym.)	312 (5)
Locally excited (IX)	4.45	$\psi_{B_{2u}}^+$	A	278.5 (5)
Locally excited (X)	5.89	$\psi_{B_{3u}}^+$	A	210.5
Locally excited (XI)	6.29	$(\psi_{NO_2} - \psi_{NO_2}')/\sqrt{2}$	A	198 (3) ^{d)}
Charge-transfer (XII)	4.56	$(\psi_{CT_5} - \psi_{CT_5}')/\sqrt{2}$	A	—
Charge-transfer (XIII)	5.52	$(\psi_{CT_4} - \psi_{CT_4}')/\sqrt{2}$	A	—

a) The real forms of the locally excited configurations are given in the literatures [6] and [9]

b) Symmetry with reference to the inversion.

c) The data taken from the spectra observed in the gaseous state.

d) The two locally excited configurations V and XI are brought about by the interaction between the two electron configurations ψ_{NO_2} and ψ_{NO_2}' which correspond to the local excitation within each nitro group. As is shown in the table, their energies are a little different from each other.

Table 3. *The Off-Diagonal Matrix Elements used for the Calculation of 1,5-Dinitro Naphthalene*

$H_{I . VI} = 0.9385 \beta'_{CN}$	$H_{VIII . XII} = -0.0252 \beta'_{CN}$
$H_{I . VII} = 0.0170 \beta'_{CN}$	$H_{VIII . XIII} = 0.2905 \beta'_{CN}$
$H_{II . VI} = 0.1287 \beta'_{CN}$	$H_{IX . XI} = 0.1486$ (eV)
$H_{II . VII} = 0.2348 \beta'_{CN}$	$H_{IX . XII} = 0.4076 \beta'_{CN}$
$H_{III . VI} = -0.2784 \beta'_{CN}$	$H_{IX . XIII} = 0.0089 \beta'_{CN}$
$H_{III . VII} = 0.0137 \beta'_{CN}$	$H_{X . XI} = -0.3236$ (eV)
$H_{IV . V} = 0.1568$ (eV)	$H_{X . XII} = 0.0436 \beta'_{CN}$
$H_{IV . VI} = -0.2796 \beta'_{CN}$	$H_{X . XIII} = 0.2843 \beta'_{CN}$
$H_{IV . VII} = 0.0084 \beta'_{CN}$	$H_{XII . XIII} = 0.0997$ (eV)
$H_{VI . VII} = 0.0997$ (eV)	
$(\beta'_{CN} = -1.57$ eV)	

The other off-diagonal matrix elements are zero.

Tab. 2 and 3. In Tab. 3, β'_{CN} denoting the core resonance integral between the adjacent carbon and nitrogen atoms was estimated on the assumption of $\beta_{CN}' = \beta_{CN}S'/S$, where β_{CN} (determined to be -2.4 eV) is the core resonance integral used in the calculation of nitrobenzene [4]. S and S' are the overlap integrals

between the adjacent carbon and nitrogen atoms of nitrobenzene and of 1,5-dinitronaphthalene respectively, and $S' = S \cos \theta$ (θ is the angle between the nitro group and the naphthalene ring plane).

The finally obtained energy levels and wave functions are shown in Tab. 4. We can calculate oscillator strengths (f_{ih}) for the transitions of 1,5-dinitronaphthalene by the aid of the wave functions given in Tab. 4 and the following equation;

$$f_{ih} = 1.085 \times 10^{11} \times \nu_{ih} \times Q_{ih}^2,$$

where ν_{ih} and Q_{ih} are the transition energy (in cm^{-1}) and the transition moment (in cm units) for the transition $i \rightarrow h$, respectively. The calculated transition energies and oscillator strengths are shown in Tab. 1.

4. Results and Discussion

From Fig. 1, it is seen that the absorption spectrum of 1,5-dinitronaphthalene consists of three bands in the observed wavelength region. They appear at 198.7 $\text{m}\mu$, 230 $\text{m}\mu$, 323 $\text{m}\mu$. As is easily seen from Fig. 1, the absorption spectrum of 1,5-dinitronaphthalene differs from that of naphthalene to a considerable extent.

From the comparison of the observed transition energy and oscillator strength with the theoretical results (see Tab. 1), the 323 $\text{m}\mu$ band can be assigned to the two transitions $W_0 \rightarrow W_1$ and $W_0 \rightarrow W_2$. Inspection of the wave functions Ψ_1 and Ψ_2 given in Tab. 4 shows that the former corresponds mainly to the $A_{1g}^- \rightarrow B_{3u}^-$ transition of naphthalene, although it includes to some extent the $A_{1g}^- \rightarrow B_{2u}^+$ transition and CT_5 type charge-transfer transition. On the other hand, the latter transition includes the above-mentioned three transitions in almost equal proportions.

Table 4. Calculated Energy Levels and Wave Functions of 1,5-Dinitronaphthalene

Energy (eV)	Symmetric Wave Function						
	ψ_C	$\psi_{A_{1g}^-}$	$\psi_{B_{1g}^-}$	$\psi_{E_{1g}^+}$	$\psi_{CT_5} + \psi_{CT_5'}$	$\psi_{CT_4} + \psi_{CT_4'}$	$\psi_{NO_2} + \psi_{NO_2'}$
					$\sqrt{2}$	$\sqrt{2}$	$\sqrt{2}$
$W_0 = -0.1888$	$\psi_0 = 0.9801$	-0.0063	0.0140	0.0153	-0.1970	0.0077	-0.0004
$W_3 = 4.4194$	$\psi_3 = 0.1854$	0.1230	-0.2446	-0.3579	0.8717	-0.0422	0.0310
$W_5 = 5.2416$	$\psi_5 = -0.0059$	0.6001	0.0293	0.0631	-0.0104	0.7968	-0.0100
$W_7 = 5.5993$	$\psi_7 = 0.0439$	0.0763	-0.3006	0.8976	0.2589	-0.1152	-0.2187
$W_8 = 6.0155$	$\psi_8 = 0.0030$	0.7072	0.4438	0.0144	0.0038	-0.5501	-0.0105
$W_{10} = 6.1670$	$\psi_{10} = 0.0496$	-0.3316	0.7741	0.1365	0.3318	0.2109	-0.3394
$W_{11} = 6.2770$	$\psi_{11} = 0.0230$	-0.0943	0.2292	0.2741	0.1554	0.0546	0.9142

Energy (eV)	Antisymmetric Wave Function					
	$\psi_{B_{3u}^-}$	$\psi_{B_{2u}^+}$	$\psi_{E_{3u}^+}$	$\psi_{CT_5} - \psi_{CT_5'}$	$\psi_{CT_4} - \psi_{CT_4'}$	$\psi_{NO_2} - \psi_{NO_2'}$
				$\sqrt{2}$	$\sqrt{2}$	$\sqrt{2}$
$W_1 = 3.8039$	$\psi_1 = 0.7425$	-0.4426	0.0397	-0.4438	0.2304	0.0317
$W_2 = 3.8853$	$\psi_2 = 0.6054$	0.5891	0.0476	0.5086	0.1563	-0.0300
$W_4 = 5.1296$	$\psi_4 = 0.0517$	-0.6660	0.0717	0.7299	-0.0672	0.1055
$W_6 = 5.2829$	$\psi_6 = -0.2463$	0.0179	0.6317	0.0078	0.7068	0.2005
$W_9 = 6.0366$	$\psi_9 = 0.1276$	0.1037	0.5138	-0.1050	-0.5853	0.5960
$W_{12} = 6.5404$	$\psi_{12} = -0.0487$	0.0476	-0.5726	0.0173	0.2571	0.7690

The above assignment is supported by the result of the polarized ultraviolet spectrum of 1,5-dinitronaphthalene in the wavelength region of 220 $m\mu$ to 420 $m\mu$. The polarized ultraviolet absorption spectrum measured with the (010) plane of 1,5-dinitronaphthalene is given in Fig. 2. From the observed dichroism of the spectrum and the X-ray crystal analysis data, it is deduced that the 323 $m\mu$ band is polarized almost parallel to the short axis. From the theoretical consideration, the $W_0 \rightarrow W_1$ and $W_0 \rightarrow W_2$ transitions may be expected to be polarized approximately parallel to the short axis of the naphthalene ring (see Tab. 1). Therefore, it may be said that the observed polarization of the 323 $m\mu$ band well satisfies this expectation.

The 230 $m\mu$ band may safely be assigned to the superposed band corresponding to the $W_0 \rightarrow W_4$ and $W_0 \rightarrow W_6$ transitions. The former transition consists of the $A_{1g}^- \rightarrow B_{2u}^+$ transition of naphthalene and the charge-transfer transition (CT_5 type), and the latter of the $A_{1g}^- \rightarrow B_{3u}^+$ transition and the charge-transfer transition (CT_4 type). The calculated oscillator strength value given in Tab. 1 shows that the $W_0 \rightarrow W_6$ transition band is ten times stronger than the $W_0 \rightarrow W_4$ transition band. Therefore, the $W_0 \rightarrow W_4$ transition band is supposed to be hidden under the $W_0 \rightarrow W_6$ transition band. This assignment may also be justified by the comparison of the direction of calculated transition moment (Q_{06} in Tab. 1) with the observed polarized ultraviolet absorption spectrum. That is to say, the 230 $m\mu$ band was observed to be almost parallel with the long axis of the naphthalene ring, in accordance with the theoretical expectation.

The 198.7 $m\mu$ band may reasonably be assigned to the $W_0 \rightarrow W_9$ and $W_0 \rightarrow W_{12}$ transitions. The oscillator strength of the $W_0 \rightarrow W_9$ transition, which contains the $A_{1g}^- \rightarrow B_{3u}^+$ transition of naphthalene, the locally excitation in the nitro groups and the CT_4 type charge-transfer transition, is smaller (calculated f_{09} value: 0.22) than that of the $W_0 \rightarrow W_{12}$ transition. Therefore this transition band may be covered by the following $W_0 \rightarrow W_{12}$ transition band. The $W_0 \rightarrow W_{12}$ transition is a mixed one of the $A_{1g}^- \rightarrow B_{3u}^+$ transition and the local excitation in the nitro groups.

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