

Dichroism and Configuration Analysis of 2-Ethylthio-1,3-Diazaazulene

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Electronic absorption spectrum of 2-ethylthio-1,3-diazaazulene (ESDA) is investigated by means of dichroism analysis using the stretched PVA film. Seven π - π^* bands and an allowed n - π^* band are assigned. The experimental assignment of π - π^* bands is in good agreement with the theoretical result using the PPP calculation. The effect of substituent groups on 1,3-diazaazulene (DA) is discussed by making use of a correlation diagram of SCF MO's of ESDA, 2-ethoxy-1,3-diazaazulene (EODA), DA, and the substituent groups. Configuration analysis of wave functions for ESDA and EODA is carried out, and the substituent effects of the ethylthio and ethoxyl groups are compared. The result shows that the ethylthio group perturbs the electronic structure of DA more strongly than the ethoxyl group.

To date we have investigated the electronic spectra, including n - π^* transition bands, of 1,3-diazaazulene (abbreviation, DA) and its derivatives, such as 2-ethoxy-1,3-diazaazulene (EODA).¹⁻³⁾ We have determined that they have five π - π^* transition bands above 220 nm, which are correspondent to each other concerning the transition direction, the position, and the relative intensity. These bands also correspond in nature to the respective ones of azulene. The only difference is that all bands of DA (and EODA) are at shorter wavelengths than the corresponding bands of azulene.

In this series of study on the 1,3-diazaazulenes, we expected that 2-ethylthio-1,3-diazaazulene (ESDA) would also reveal a spectrum similar to EODA, but found that the ESDA spectrum does not always correspond to those of EODA and DA. This fact has already been noticed by Nozoe *et al.*,⁴⁾ they have pointed out that the absorption spectrum of 2-methylthio-1,3-diazaazulene as well as that of the 2-dimethylamino derivative does not resemble that of DA. The only difference in the chemical structure between EODA and ESDA is in the substituent group: ethoxyl and ethylthio. For that reason, their spectral characteristics must be attributed to the difference of the substituent effect between the ethoxyl and the ethylthio groups.

We will first analyze the absorption spectrum of ESDA theoretically and experimentally. Then, in order to clarify the distinction between the ethylthio and the ethoxyl groups for the substituent effect on the MO levels of DA, we will examine the correlation diagram of their MO levels, and also analyze the state wave functions of ESDA and EODA by means of the configuration analysis proposed by Baba *et al.*⁵⁾

Experimental and Calculation

2-Ethylthio-1,3-diazaazulene (ESDA) was provided by the Sankyo Company Ltd. It was recrystallized from cyclohexane solution. The analytical values in percent were as follows:

Found: C, 63.28; H, 5.50; N, 14.80; S, 17.00%. Calcd for $C_{10}H_{10}N_2S$: C, 63.15; H, 5.30; N, 14.73; S, 16.72%.

The measurement of the solution spectrum was carried out by using a Shimadzu MPS-50L recording spectrophotometer. The details of measurement and analysis of the dichroic spectra are given in the previous paper.^{1,3)} In the figure of the dichroic spectra, D_{\parallel} and D_{\perp} indicate the absorbance for the plane polarized light whose electric vector

is respectively parallel (\parallel) and perpendicular (\perp) to the stretched direction of the film. The dichroic ratio R_d is defined as D_{\parallel}/D_{\perp} . R_s is the stretching ratio of the film.

We followed the Pariser-Parr-Pople method modified by the Nishimoto-Mataga approximation⁶⁾ including CI. The CI calculation was limited to all the singly excited configurations. The one-center Coulomb repulsion integral was set equal to the valence state ionization potential (I_p) minus the valence state electron affinity (E_a) after Pariser and Parr.⁷⁾ The two-center repulsion was estimated by the Nishimoto-Mataga formula.⁶⁾ The core resonance integral ($\beta_{\mu\nu}$) was constant. Parameters used are listed in Table 1.

TABLE 1. PARAMETER VALUES USED

	C	S	N	O
Ionization potential (eV)	11.16	22.2	14.12	33.00
Electron affinity (eV)	0.03	9.15	1.78	11.47
	C-C	C-S	C-N	C-O
Core resonance integral (eV)	-2.32	-1.16	-2.38	-2.30

The molecular geometry of the diazaazulene skeleton used was the same as before.²⁾ The bond lengths of carbon-carbon and carbon-nitrogen were taken as 1.40Å, and those of carbon-oxygen and carbon-sulfur as 1.37Å and 1.70Å, respectively.

Assignment

The calculated result for ESDA is given in Table 2 and is compared with the absorption spectrum determined in cyclohexane solution in Fig. 1. It has already been shown that both 1,3-diazaazulene (DA) and 2-ethoxy-1,3-diazaazulene (EODA) have five electronic transitions (bands) in the region below 50000 cm^{-1} .¹⁾ In the case of ESDA, however, eight transitions are computed in the same region.

From the comparison of the calculated result and the observed spectrum shown in Fig. 1, the following assignment is obtained. The shoulder in the region of 23000—25000 cm^{-1} corresponds to the first π - π^* transition (Y-polarization), the intense band with the double peak in the region of 26000—30000 cm^{-1} to the second transition (X), and the two peaks in 30000—34000 cm^{-1} to the third transition (Y). The intense bands at about 37000 and 41000 cm^{-1} are respectively correspondent to the fourth (X) and the sixth (X) transitions. An absorp-

TABLE 2. CALCULATED RESULTS AND ASSIGNMENT FOR 2-ETHYLTHIO-1,3-DIAZAAZULENE (ESDA)

Number of Transition	Transition energy		Oscillator strength		Polarization ^{d)}	
	calcd	obsd ^{a)}	calcd	obsd ^{e)}	calcd	obsd ^{e)}
1	22480 cm ⁻¹ (445 nm)	23800 cm ⁻¹ ^{b)} (420 nm)	0.007	0.001	Y	Y
2	26660 (375)	26500 (378)	0.323	0.267	X	X
3	31890 (314)	31500 (318)	0.154	0.099	Y	Y
4	35020 (286)	36630 (273)	0.279	0.263	X	X
5	40090 (249)		0.002		Y	Y
6	40900 (245)	41320 (242)	1.187	0.387	X	X
7	47030 (213)		0.565		Y	Y
8	48760 (205)		0.004		X	

a) Observed in cyclohexane solution. b) Shoulder. c) Estimated by the following equation using the component spectra obtained in the dichroism analysis: $f = 4.32 \times 10^{-9} \times \epsilon_{\max} \times (\Delta\nu)_{1/2}$, where $(\Delta\nu)_{1/2}$ is the half value width in cm⁻¹ units and for the extinction coefficient, ϵ_{\max} , the value in ethanol is used instead of that in PVA film. Band shapes of IV and VI are determined by the optional way. d) X and Y are molecular long and short axes, respectively. e) Results of dichroism analysis using a stretched PVA film.

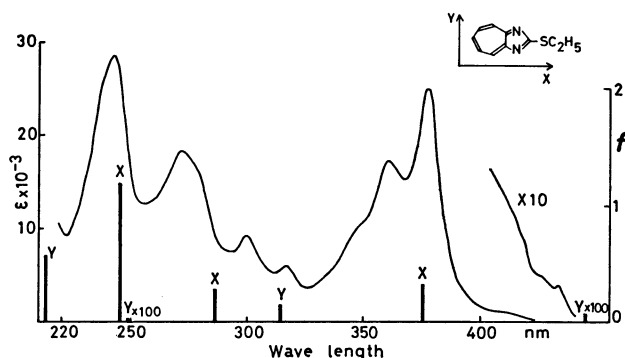


Fig. 1. Absorption spectrum of 2-ethylthio-1,3-diazaazulene (ESDA) in cyclohexane solution and the calculated result.

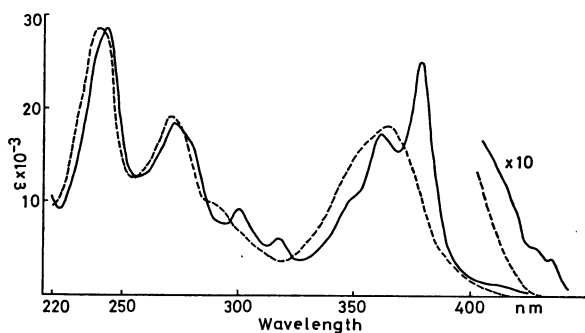


Fig. 2. Absorption spectra of 2-ethylthio-1,3-diazaazulene (ESDA) in cyclohexane (—) and ethanol solution (---).

tion band due to the fifth transition (Y) which is computed to be of very low intensity (see Table 2) should be hidden in the intense band which has been attributed

to the sixth transition. The assignment thus deduced is tabulated in Table 2.

Figure 2 illustrates a solvent effect on the absorption spectrum of ESDA. The spectrum in ethanol solution loses its structure and undergoes a blue shift in comparison with that in cyclohexane solution. A similar situation is also observed for the spectrum in PVA film.

As above, we could characterize the absorption bands from the point of view of transition energy and intensity. However, in order to accomplish the assignment, it is desirable to examine the polarizations of the bands.

Dichroism Analysis

Since the symmetry of the π electron system of the ESDA molecule belongs to the point group C_{2v} , the possible π - π^* transitions must be along the long (X) or the short axis (Y) in the molecular plane. According to the dichroism-measurement using stretched PVA film, this is simply decided by the fact that the dichroic ratio ($R_d = D_{//}/D_{\perp}$) of a band polarized along the long axis of the molecule is larger than that along the short axis, because the orientation of the molecule by stretching is preferential in its longitudinal direction. Concerning the band polarizations in the quantitative sense, the dichroism analysis can provide the orientation angles of bands: the angles between an orientation axis of a molecule and the transition moments of bands. Since an orientation axis of a molecule must be a common axis to all the band polarizations which will determine orientation angles, the angle between any two band polarizations can be obtained by taking the sum or difference of the two experimental orientation angles, provided that the orientation axis and the two polarizations are in the same plane. In this case, when the two bands are both due to the transitions to the pure

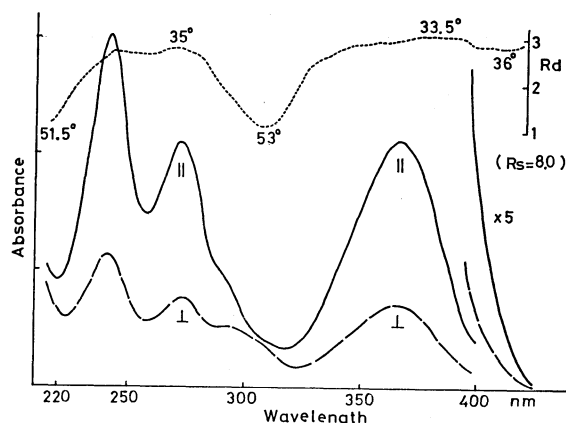


Fig. 3. Dichroic spectra and R_d curve of 2-ethylthio-1,3-diazaazulene (ESDA). $R_s=8.0$.

electronic excited states, the sum of the orientation angles must be equal to 90° or the difference to 0° according to whether two band polarizations are orthogonal or parallel to each other, respectively. But it is rarely the case that the orthogonal-parallel relation is rigorously obtained under actual conditions, because there is often some mixing of other kinds of transitions and overlapping of other kinds of absorption bands with the band under consideration.

Figure 3 shows the dichroic spectra of ESDA in the stretched PVA film. The figures indicated along the R_d curve represent the orientation angles of the bands at the respective wavelengths. According to Fig. 3, the absorption band in the region 330–420 nm seems to be a single band. However, the R_d curve for the absorption above 400 nm falls slightly, indicating that a weak absorption is hidden. The presence of this weak absorption (the first band) is obvious from the absorption below 25000 cm^{-1} in Fig. 1.

The R_d value at 380 nm of the second band is the highest in the whole region observed (Fig. 3). It can be said, therefore, that the polarization of the second band is along the molecular long axis (X) and the first band which is hidden in the long wavelength tail of the second band must be polarized to the short axis (Y). The polarizations of other bands can be qualitatively discussed in the same way.

Incidentally, it should be noticed that the R_d curve is somewhat depressed (260 nm) between the strong fourth and sixth bands of X-polarization. This suggests the presence of a weak (fifth) band with Y-polarization.

In order to discuss in detail the polarization, in the next section, we will resolve the spectrum into the X- and Y-components.

Component Spectra of ESDA. The absorption spectrum of ESDA determined in a non-stretched PVA film could be decomposed into X- and Y-component spectra¹⁾ using the R_d value in Fig. 3, assuming that the absorption at 380 nm, which shows the highest R_d value, has the pure X-polarization. The result is shown in Fig. 4.

From a comparison of the component spectra in Fig. 4 and the calculated results in Table 2, the absorption

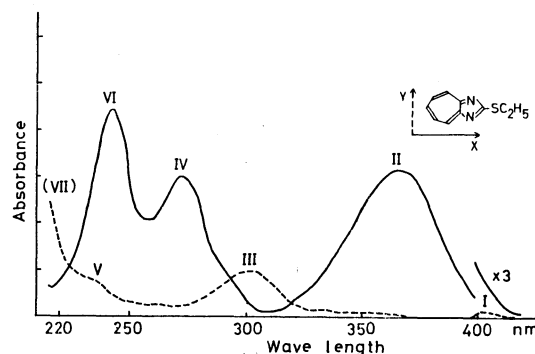


Fig. 4. Component spectra of 2-ethylthio-1,3-diazaazulene (ESDA). X(—) and Y(---) mean the components whose polarizations are along the molecular long and short axes, respectively.

spectrum of ESDA in the PVA film is characterized in the following way. The second, fourth, and sixth bands which are polarized along the long axis (X) of the molecule can be attributed respectively to the second, fourth, and sixth transitions with X-polarizations. In addition, the observed bands and the calculated transitions correspond well to one another with respect to the relative intensities as well as the transition energies. Concerning the Y-component spectrum, the first, third, fifth, and seventh bands can be attributed to the first, third, fifth, and seventh transitions, respectively. In this assignment, however, the calculated oscillator strength of the fifth transition (Table 2) seems to be extremely small compared with the observed intensity of the fifth band (Fig. 4). Furthermore, the component spectra of Fig. 4 show that the shoulder due to the fifth band (Y) is at a shorter wavelength than the maximum of the sixth band (X). Therefore, the numbering of the order of the fifth (Y) and sixth (X) transitions by calculation must be reversed.

An extra weak absorption appears in the Y-component spectrum of Fig. 4, which extends from 320 to 365 nm. This is also suggested by the behavior of the R_d curve in Fig. 3, that is, the R_d curve shows some depression in that region. This extra band may be assigned to the forbidden character of the second $\pi\text{-}\pi^*$ transition band and/or $n\text{-}\pi^*$ transition band. However, since similar extra bands have been found in the Y-component spectrum of DA (1,3-diazaazulene) and EODA (2-ethoxy-1,3-diazaazulene) and have reasonably been assigned to allowed $n\text{-}\pi^*$ transition bands polarized normal to the molecular plane (Z axis),¹⁾ we may take the latter assignment here. (In the dichroism analysis, it must be noted that the Z- and Y-components cannot be distinguished from each other.^{1,3)})

Substituent Effect

Correlation Diagram of Molecular Orbitals. It has already been pointed out that the absorption spectrum of ESDA does not resemble that of DA, while that of EODA does.⁴⁾ That is to say, while all the bands observed for EODA keep the one-to-one correspondence to those of DA, in the case of ESDA, there appears an extra fourth and fifth band. The reason is to be

found in the difference of the substituent effect of the ethoxyl and ethylthio groups. In such a case, we can explain the substituent effect from the point of view of a one-electron molecular orbital. This is carried out by expanding the j -th SCF MO wave function ϕ_j of EODA (or ESDA) into the SCF MO wave functions ϕ^o 's of DA and the ethoxyl (or ethylthio) group. Thus we have

$$\phi_j(\text{EODA}) = \sum_m C_m^j \phi_m^o(\text{DA}) + C_o^j \phi_o^o(\text{O}). \quad (1)$$

Using the expansion coefficients, we can make a correlation among the SCF MO wave functions of EODA (or ESDA), DA, and the substituent. A correlation diagram of energy levels is shown in Fig. 5. The diagram consists of five sets of levels: from left to right, the energy levels for the MO's of substituent sulfur (S), ESDA, DA, EODA, and substituent oxygen (O). The levels are drawn by full and dotted lines which represent the symmetry species a_2 and b_1 , respectively. For both ESDA and EODA, the occupied orbitals consist of four b_1 and two a_2 orbitals. DA has three b_1 and two a_2 occupied orbitals and three b_1 and two a_2 unoccupied ones. The substituents S and O have only one occupied orbital of b_1 symmetry, to which the substituents belong in the molecules.

Now, as is known from the symmetry consideration in the case of ESDA, for instance, the orbital of S cannot couple with a_2 type orbitals but only with b_1 type orbit-

als of DA. Actually, all four full lines (a_2) of ESDA or EODA keep nearly the same levels as the corresponding ones of DA. Furthermore, from the comparison of the unoccupied orbitals of ESDA (or EODA) and those of DA, it is recognized that even the b_1 orbitals are not perturbed by the substituent orbital. For that reason, in the correlation diagram, we can restrict the discussion to the relation between the substituent orbital and the occupied b_1 orbitals of DA.

The figures indicated on the correlation lines of Fig. 5 show the square values of the coefficients of Eq. 1 and represent the extent of the contribution from each of the wave functions. The highest occupied b_1 MO of ESDA, for instance, receives contributions of 65% and 31% from the MO of substituent S and the highest occupied b_1 MO of DA, respectively.

As the correlation diagram shows, the orbital of substituent S lies at around the highest occupied b_1 MO of DA, while the MO level of substituent O is much lower than that of the DA orbital. Consequently, the S MO couples strongly with the highest b_1 MO of DA to make two b_1 MO's of ESDA, while the O MO in EODA interacts more or less with all the occupied b_1 MO's of DA, but its interaction with the highest b_1 MO is especially weak (14%). This difference in the extent of interactions of the S and O orbitals with the DA orbitals could produce such differences in the spectra of ESDA and EODA as were described before; in comparison with the spectrum of DA, an extra band (either fourth or fifth band) is found in that of ESDA.

CA for Wave Functions of ESDA and EODA. The substituent effect can also be discussed from a point of view of CA (configuration analysis).⁵⁾ Making use of the CA method, any of the state wave functions of EODA or ESDA can be explained in terms of the wave functions of DA and the charge-transfer configurations which represent transitions from the π -orbital of the substituent to unoccupied molecular orbitals of DA. In short, we can write down the i -th state wavefunction Ψ_i (EODA) or Ψ_i (ESDA) by the reference configurations Ψ^o 's as follows:

$$\Psi_i(\text{EODA}) = \sum_k C_k^i \Psi_k^o(\text{DA}) + \sum_l C_{ct_l}^i \Psi_{ct_l}^o, \quad (2)$$

where $\Psi_k^o(\text{DA})$ stands for the k -th wave functions of DA and $\Psi_{ct_l}^o$ stands for the l -th charge transfer configuration (electron excitation to the l -th molecular orbital of DA from the orbital of the substituent).

By squaring the coefficients C_k^i and $C_{ct_l}^i$, we can obtain the relative contribution of the respective configurations Ψ_k^o and $\Psi_{ct_l}^o$ to the state wave function Ψ_i (EODA) or Ψ_i (ESDA). The difference of the substituent effect of the ethoxyl and ethylthio groups can therefore be estimated by comparing the absolute values of $C_{ct_l}^i$ of Ψ_i (EODA) and Ψ_i (ESDA).

Figure 6 shows the results of CA. The square values of the expansion coefficients are represented by circles which are drawn in such a way that their areas are proportional to the square values. Circles of values below 1% are omitted in Fig. 6. State wave functions (Ψ_i) are put on the tops of the columns and the reference configurations ($\Psi_k^o, \Psi_{ct_l}^o$) are arranged in the left column. Total weights are listed at the bottom of the columns.

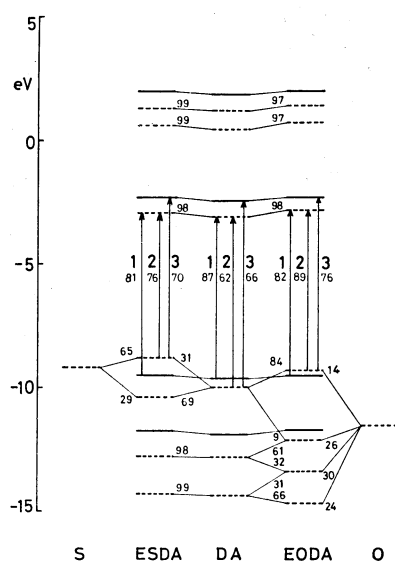


Fig. 5. Correlation diagram for SCF MO. From left to right, SCF MO's for sulfur, ESDA (2-ethylthio-1,3-diazaazulene), DA (1,3-diazaazulene), EODA (2-ethoxy-1,3-diazaazulene) and oxygen are arranged. a_2 and b_1 type SCF MO's are represented by the horizontal full and dotted lines, respectively. The figures along the joining fine lines are contribution weight from the MO's of sulfur, DA, oxygen to the MO's of ESDA and EODA. Each transition, being numbered by Roman numerals along the vertical arrow, is represented by the configuration which contains the two MO's connected with arrow and whose contribution weight is shown as the figure beneath the transition number.

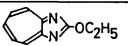
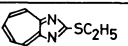
															
		Ψ_0	Ψ_1	Ψ_2	Ψ_3	Ψ_4	Ψ_5	Ψ_0	Ψ_1	Ψ_2	Ψ_3	Ψ_4	Ψ_5	Ψ_6	Ψ_7
DA	Ψ_0^0	(87)						(92)							
	Ψ_1^0	(88)						(92)							
	Ψ_2^0		(77)						(4)						
	Ψ_3^0			(78)						(51)		(50)			
	Ψ_4^0				(79)							(4)			
	Ψ_5^0					(78)							(80)		
CT	Ψ_{CT7}	°		°		°		°	(47)						
	Ψ_{CT8}		°		°		°		°	(49)		(42)		°	
Total(%)		91	89	88	88	87	88	96	94	92	93	90	92	91	92

Fig. 6. The result of Configuration Analysis (CA). Top of each column is the state wave function of EODA and ESDA. Left hand side of each row is the reference configuration.

Since the total weight of the respective columns is nearly 90%, we may safely discuss the substituent effect without taking into account other wave functions such as doubly excited configurations. We can read any column in accordance with Eq. 2; for example, the ground (Ψ_0) and the first excited (Ψ_1) state wave functions of ESDA are as follows:

$$\Psi_0(\text{ESDA}) = (0.923)^{1/2}\Psi_0^0(\text{DA}) + \dots + (0.033)^{1/2}\Psi_{CT7}^0, \quad (3)$$

$$\Psi_1(\text{ESDA}) = (0.917)^{1/2}\Psi_1^0(\text{DA}) + \dots - (0.020)^{1/2}\Psi_{CT8}^0, \quad (4)$$

where Ψ_0^0 (DA) and Ψ_1^0 (DA) are the wave functions of the ground and first excited configurations of DA, respectively, and Ψ_{CT7}^0 and Ψ_{CT8}^0 mean respectively the transitions to the unoccupied DA orbitals 7th and 8th from the substituent orbital. In Eqs. 3 and 4, the absolute values of the coefficients of Ψ_0^0 (DA) and Ψ_1^0 (DA) are the largest and all the other coefficients are small enough to be neglected. In the first approximation, therefore, we can correlate Ψ_0 (ESDA) and Ψ_1 (ESDA) to Ψ_0^0 (DA) and Ψ_1^0 (DA), respectively.

Any wave functions for ESDA and EODA in Fig. 6 can be read in the same manner as above. As shown

in Fig. 6, all wave functions from Ψ_0 to Ψ_5 of EODA are approximately equivalent to those from Ψ_0^0 to Ψ_5^0 of DA, respectively. As for ESDA, however, there is no one-to-one correspondence except for the pairs of Ψ_0 - Ψ_0^0 and Ψ_1 - Ψ_1^0 . In fact, all four wave functions, Ψ_2 to Ψ_5 , of ESDA involve two kinds of predominant configurations: localized and charge transfer ones. Conversely, Ψ_2^0 of DA are distributed to Ψ_2 and Ψ_4 of ESDA, and Ψ_3^0 (DA) to Ψ_3 (ESDA) and Ψ_5 (ESDA). Therefore, the wave functions Ψ_2 to Ψ_5 of ESDA cannot be correlated by a one-to-one correspondence to Ψ_2^0 or Ψ_3^0 of DA. However, Ψ_6 and Ψ_7 of ESDA correspond well to Ψ_4^0 and Ψ_5^0 of DA.

From the above discussion, we can conclude as follows. The five transition bands of EODA correspond to each of the respective five bands of DA. Direct correspondence of the transition bands of ESDA and EODA exists between both of the first bands, between the sixth (ESDA) and fourth (EODA) bands and between the seventh (ESDA) and fifth (EODA) bands. But the second, third, fourth, and fifth bands of ESDA do not correspond directly to any single transition band of EODA.

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