

silane (5.0 g, 28 mmol) was dissolved in ether (200 mL). Triethylamine (5.7 g, 56 mmol) and methanol (1.8 g, 56 mmol) in ether (25 mL) were added in a dropwise manner to the chlorosilane solution. After stirring for 12 h the salts and solvent were removed leaving **12** as a colorless oil: yield 4.7 g (97%);  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  4.16 (s, 1 H), 3.45 (s, 3 H), 1.04 (s, 18 H); mass spectrum  $m/e$  (%) 174 (13), 117 (46), 89 (100). Exact mass determination: calcd for  $\text{C}_9\text{H}_{22}\text{OSi}$ , 174.1440, measured, 174.1423.

**Synthesis of Bis(*tert*-butylamino)di-*tert*-butoxysilane (**14**).** To a solution of *tert*-butylamine (30.9 g, 422 mmol) and triethylamine (42.7 g, 422 mmol) in diethyl ether (300 mL) was added di-*tert*-butoxydichlorosilane (15.0 g, 70.3 mmol). After addition was complete, the mixture was warmed to reflux and stirred overnight. Removal of the salts by filtration and stripping of the solvent and excess amines by rotary evaporation afforded di-*tert*-butoxy-*tert*-butylaminochlorosilane, which was further purified by distillation at reduced pressure [ $56^\circ\text{C}$  (0.1 torr)]: yield 18.2 g (92%) as a colorless liquid;  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  1.38 (s, 18 H), 1.20 (s, 9 H); mass spectrum  $m/e$  (%) 266 (21,  $\text{M}^+ - \text{CH}_3$ ), 210 (12), 154 (47). Exact mass determination (for  $\text{M}^+ - \text{CH}_3$ ): calcd for  $\text{C}_{11}\text{H}_{25}\text{ClNO}_2\text{Si}$ , 266.1343; measured, 266.1338.

Further treatment of the chlorosilane with *tert*-butylamine failed to give the desired product. It was necessary to use the corresponding lithium amide. *tert*-Butylamine (0.52 g, 7.09 mmol) in ethyl ether (25 mL) was treated with *n*-BuLi (2.5 M in hexane, 2.8 mL) to give lithium *tert*-butylamide. The amide solution was added to the chlorosilane prepared above (2.00 g, 7.09 mmol) in ether (25 mL); after approximately 1 h a precipitate began to form. The solution was allowed to stir overnight. Removal of the solvent and salts afforded **14** in 95% purity (2.10 g, 93%). Further purification was effected by preparative GC:  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  1.39 (s, 18 H), 1.30 (s, 18 H), 0.76 (br s, 2 H); mass spectrum  $m/e$  (%) 318 (1), 303 (100), 287 (4), 247 (42). Exact mass determination: calcd for  $\text{C}_{16}\text{H}_{38}\text{N}_2\text{O}_2\text{Si}$ , 318.2702; measured, 318.2703. Anal. calcd for  $\text{C}_{16}\text{H}_{38}\text{N}_2\text{O}_2\text{Si}$ : C, 60.32; N, 12.02; H, 8.79. Found: C, 60.11; N, 11.98; H, 9.48.

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## Electronic Structure of Dicyanobarrelenes Studied by Integration of Photoelectron Spectroscopy, Cyclic Voltammetry, Electronic Spectroscopy, Molecular Orbital Theory, and Composite Molecule Theory

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**Abstract:** The photoelectron spectra, electronic absorption spectra, and reduction potentials of 2,3-dicyanobarrelene (DCB) and its 5,6,7,8-tetramethyl derivative were measured. On the basis of these experimental data, the electronic and orbital structure of these compounds in the ground and electronically excited states was discussed from the standpoints of MO theory and composite molecule (molecules-in-molecule) theory, the group orbital concept being adopted as the common basis throughout the discussion. Special attention was paid to intramolecular 3D orbital interactions. It was established that the first LU- $\pi$ -MO of each compound is almost completely localized on the maleonitrile (MN) type moiety from the reduction potential data. The first singlet-singlet electronic transition of each compound is an almost pure LUMO  $\leftarrow$  HOMO transition with the character of an intramolecular charge-transfer (CT) transition accompanied by the electron migration from the cyclohexadiene (CHD) type moiety  $b_2$  HO- $\pi$ -O to the MN type group  $a_2$  LU- $\pi$ -O and provides a typical example of an unusual type of CT transition, a CT transition between the orbitals CT interaction forbidden. From the photoelectron and electronic absorption spectral standpoints independently the mixing coefficients for the component basis HO- $\pi$ -Os of the CHD-like moiety and the MN-like one were evaluated for each compound consistently with each other. The mutual consistency of the results of the mixing coefficients estimated from the two standpoints independently substantiates strongly the validity of the intensity-borrowing model that the first electronic transition of each compound owes its intensity to the allowed LU- $\pi$ -O  $\leftarrow$  HO- $\pi$ -O type electronic transition of the MN-like moiety. This is also supported by a kind of composite molecule type approach. This is the first experimental substantiation of intensity borrowing by intramolecular CT transitions from local excitations.

The concept of orbital interaction is now recognized to be fundamentally important in various fields of chemistry, for example, physical organic, physical inorganic, and theoretical chemistry, and even for materials science. Among orbital interactions three-dimensional (3D) intramolecular orbital interactions between equivalent or inequivalent orbitals are particularly attractive. In order to study these types of interactions, 2,3-di-

cyanobarrelene (bicyclo[2.2.2]octa-2,5,7-triene-2,3-dicarbonitrile, DCB) and its 5,6,7,8-tetramethyl derivative (TMDCB) have been adopted as model systems in this paper (Figure 1). The reasons why these systems are chosen are as follows: First, as these compounds are simple-structured and of rather high symmetry, that is, are of  $C_{2v}$  symmetry, a straightforward clear-cut discussion is expected to be possible in the analysis of 3D orbital interactions. Second, each compound is regarded to contain two electron-donor (D) type groups and one electron-acceptor (A) type one in the same molecular framework in a unique configuration, which is almost inaccessible in intermolecular cases. In addition, generally

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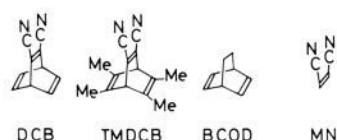


Figure 1. Molecular structural formulas.

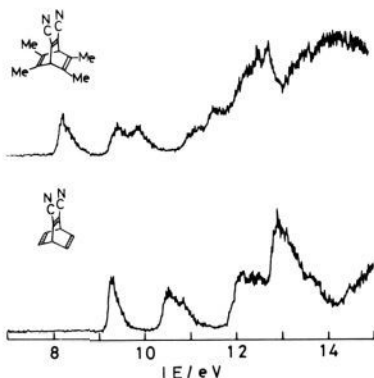


Figure 2. Photoelectron spectra of DCB and TMDCB.

Table I. Experimental Vertical Ionization Energy (VIE) Data

compd	VIE/eV		
	DCB	9.30	10.49
TMDCB	8.28	9.47	9.89
BCOD <sup>a</sup>	8.87	9.45	10.42
ethylene <sup>b</sup>	10.51	12.85	
(Z)-2-butene <sup>c</sup>	9.12		
MN <sup>d</sup>	11.15	12.77	

<sup>a</sup> Reference 2. <sup>b</sup> Reference 3. <sup>c</sup> Reference 4. <sup>d</sup> Reference 5.

speaking, in intramolecular D-A type cases, relative spatial and symmetry relationships between D and A type groups can often be rigidly fixed; this is the case in the present systems. Therefore, D-A type molecules such as treated here should be quite adequate for the deeper understanding of electron D-A type or charge-transfer (CT) type phenomena.

In the following the electronic and orbital structure of DCB and TMDCB in the ground and electronically excited states is studied in detail by the combination of photoelectron and electronic absorption spectroscopies, cyclic voltammetry, and quantum theoretical approaches, the group orbital (GO) concept being adopted as the common basis throughout the discussion. Special attention will be paid to the intramolecular orbital interactions mentioned above.

## Results and Discussion

**Photoelectron Spectroscopy.** At first let us discuss the electronic and orbital structure of DCB and TMDCB from the standpoint of photoelectron (PE) spectroscopy. The gas-phase He I PE spectra of these compounds are shown in Figure 2. The ionization energy (IE) values of these compounds obtained from these spectra are summarized in Table I with those of related compounds.<sup>2-5</sup> Compounds DCB and TMDCB show their first three PE spectral bands in the low-IE region, well separated from the following bands.

Each compound contains two double-bond groups (D type groups) and one maleonitrile (MN) type group (an A type group) but can also be regarded, roughly speaking, to be composed of a cyclohexadiene- (CHD-) like moiety and an MN-like one

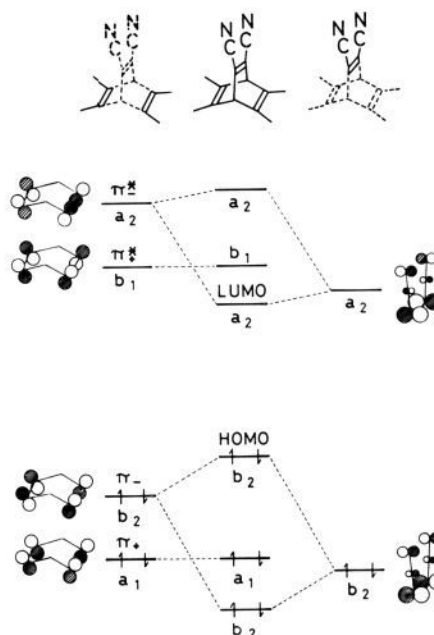


Figure 3. Schematic drawing of basis group orbital interaction diagram for DCB and TMDCB.

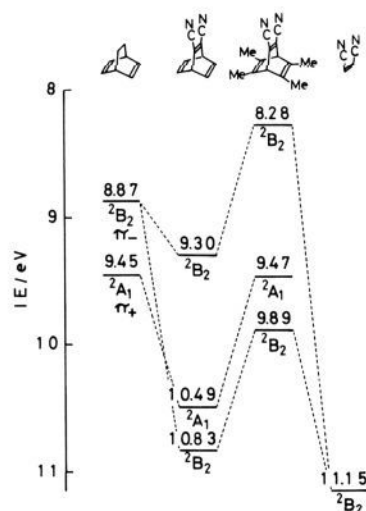


Figure 4. Doublet radical-cation state correlation diagram.

bridged by two CC single bonds (Figure 3). In the following the stress will be put on the discussion on the interactions between these two types of symmetry-adapted moieties and those between their GOs.

The first three PE spectral bands of each compound correspond to the ionization from the three MOs formed mainly by the interactions between the two highest occupied  $\pi$  group orbitals (HO- $\pi$ -GOs) of the CHD-like part and HO- $\pi$ -GO of the MN-like one. The  $\pi$  system of the CHD-like part can be regarded to be very close to that of bicyclooctadiene (BCOD) and the first and second HOMOs of BCOD itself are, roughly speaking, the MO formed by the antibonding (out-of-phase) type of combination between the two double-bond group HO- $\pi$ -GOs and the MO formed by their bonding (in-phase) type of combination, respectively.<sup>2</sup> These MOs are designated as  $\pi_-$  and  $\pi_+$ , respectively, and belong to the  $b_2$  and  $a_1$  irreducible representations of the  $C_{2v}$  point group, respectively.

From the vertical IEs of BCOD<sup>2</sup> and MN,<sup>5</sup> the second band of DCB or TMDCB is regarded to correspond to the  $a_1 \pi_+$  band, that is, to be correlated with the second band of BCOD. The corresponding  $a_1 \pi_+$  type MO is mainly localized on the CHD-like moiety, and the contribution from the MN-like group  $\pi$  orbitals

(2) (a) Bischof, P.; Hashmall, J. A.; Heilbronner, E.; Hornung, V. *Helv. Chim. Acta* **1969**, *52*, 1745. (b) Haselbach, E.; Heilbronner, E.; Schröder, G. *Ibid.* **1971**, *54*, 153.

(3) Brundle, C. R.; Robin, M. B.; Kuebler, N. A.; Basch, H. *J. Am. Chem. Soc.* **1972**, *94*, 1451.

(4) Masclat, P.; Grosjean, D.; Mouvrier, G.; Dubois, J. *J. Electron Spectrosc. Relat. Phenom.* **1973**, *2*, 225.

(5) Stafast, H.; Bock, H. *Tetrahedron* **1976**, *32*, 855.

to this MO is absent because of the orbital symmetry. The first and third bands of DCB or TMDCB are regarded to correspond to the ionization from the HO- $\pi$ -MO formed mainly by the antibonding type of combination of the HO- $\pi$ -GO of the CHD-like moiety and that of the MN-like one and from the third HO- $\pi$ -MO formed mainly by their bonding type of combination, respectively. That is, the first and third bands are associated with the  $b_2$  MOs delocalized over the molecule while the second band is associated with the  $a_1$  MO localized on the CHD-like moiety. Now the cation state correlation diagram may be drawn as shown in Figure 4.

Although the second and third bands of DCB or TMDCB are rather closely located to each other, the cross correlation of the second and third bands of DCB with those of TMDCB is not adequate; that is, the band ordering of DCB is not changed by tetramethylation as for the first three bands. This is supported by the fact that the spectral shape of the first three-band region of DCB is close to that of TMDCB. In addition, the methyl substituent effect for the third VIE of DCB is the smallest among those for the first three bands, and this fact supports the assignment of the third band as the  $b_2$  MO primarily contributed from the MN-like moiety HO- $\pi$ -GO.

**Orbital Mixing Assessed by Photoelectron Spectroscopy.** Let us estimate approximately the mixing coefficients of the component  $b_2$  type HO- $\pi$ -GOs in the first and third HOMOs of DCB or TMDCB on the basis of the PE spectral data. We treat the case of DCB. Let us assume that the magnitude of the interaction between the two ethylene-like moieties HO- $\pi$ -GOs in DCB before going into the interaction with the MN type group  $\pi$  orbital is almost the same as that in BCOD. We can then estimate the basis orbital (BO) energy of the  $b_2$  type  $\pi$  orbital of the CHD-like group in DCB as -9.91 eV before the orbital interaction with the MN-like moiety  $b_2$  HO- $\pi$ -GO on the assumption that the energy of the  $a_1$  type second HO- $\pi$ -GO of the CHD-like moiety is the same as that of the second HO- $\pi$ -MO of DCB. When this value and the first and third vertical IE values of DCB are used, the interaction term between the  $b_2$  type BO of the CHD-like moiety and that of the MN-like one can be estimated to be -0.749 eV and, at the same time, the mixing coefficients of the component  $b_2$  type BOs of the CHD-like and MN-like groups in the HOMO as +0.775 and -0.631, respectively, if we take the two-BGO model.

By the tetramethylation of DCB, because of the delocalization of the  $\pi$  orbitals of the ethylene-like groups over the methyl groups, the interaction term between the two component BGOs is decreased in the absolute value. This interaction term in TMDCB can be evaluated as -0.692 eV by using the interaction term in DCB and the AO coefficients of the HOMO of (Z)-2-butene<sup>6</sup> calculated by a modified CNDO method proposed formerly.<sup>7</sup> By the combination of this value and the observed first and third vertical IEs of TMDCB, we can estimate the mixing coefficients of the two component  $b_2$  type BOs of the tetramethyl CHD-like and MN-like groups in the HOMO as +0.869 and -0.494 and their energy values as -8.67 and -9.50 eV, respectively, in the two-BGO model. That is, by the tetramethylation of DCB, the delocalization of the HOMO or the third HOMO is decreased. This suppression effect is almost completely due to the destabilization of the CHD-like group  $b_2$  type BO from -9.91 to -8.67 eV and not because of the slight decrease in the interaction term (cross-term) value between the two component BGOs from 0.749 to 0.692 eV in the absolute values. Thus, we could estimate the mixing coefficients of the component BOs in the HOMOs and the third HOMOs of DCB and TMDCB, though approximately, by photoelectron spectroscopy. These results will later be discussed in conjunction with the results from electronic absorption spectroscopy again.

**Cyclic Voltammetry.** As the reduction potential (RP) is relevant almost directly to the vacant MO energy, the RP values of DCB and TMDCB were also measured by cyclic voltammetry. The first RP (vs SCE) of DCB, -1.46 V, is changed to -1.55 V by

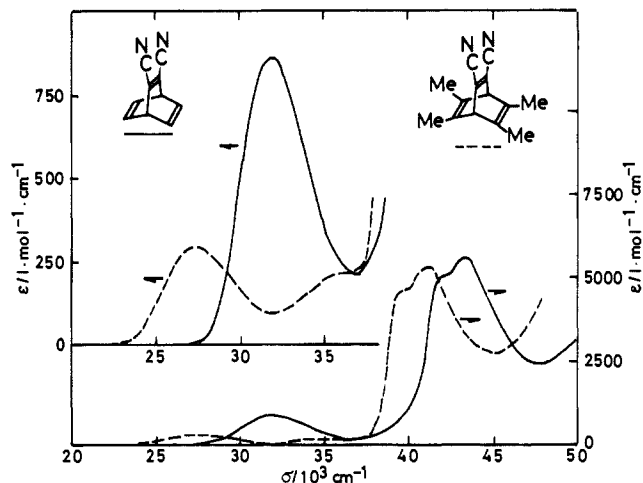


Figure 5. Electronic absorption spectra of DCB and TMDCB in ethanol.

Table II. Observed Electronic Absorption Spectral Band Characteristics in Ethanol

compd	$\lambda_{\max}^a$ /nm	$\log(\epsilon_{\max} \cdot \text{M} \cdot \text{cm})$	$\sigma_{\max}/\text{cm}^{-1}$	$f$
DCB	314	2.94	31 800	0.019 <sup>1</sup>
	260 <sup>b</sup>	2.64	38 500	<i>c</i>
	231	3.75	43 300	0.141
TMDCB	365	2.47	27 400	0.006 <sup>8</sup>
	274 <sup>b</sup>	2.35	36 500	0.003 <sup>0</sup>
	243.5	3.73	41 100	0.121

<sup>a</sup> Apparent band maximum. <sup>b</sup> Shoulder. <sup>c</sup> It is difficult to assess the  $f$  value of this band because of the heavy overlap of this band with the following strong one.

Table III. Calculated Electronic Transitions of TMDCB with Observed Ones

sym	$E/\text{eV}$	$f$	calcd		obsd	
			main CI component <sup>a</sup>	$E/\text{eV}$	$f$	
<sup>1</sup> B <sub>1</sub>	3.953	0.086	1L ← 1H	0.910	3.40	0.006 <sup>8</sup>
<sup>1</sup> A <sub>2</sub>	4.716	0	2L ← 1H	0.417	4.53	0.003 <sup>0</sup>
			1L ← 2H	0.795		
<sup>1</sup> A <sub>2</sub>	4.981	0	2L ← 1H	0.773	5.09	0.121
			1L ← 2H	-0.388		
<sup>1</sup> B <sub>1</sub>	5.056	0.068	1L ← 1H	0.350	5.09	0.121
			1L ← 3H	-0.862		
<sup>1</sup> B <sub>2</sub>	5.652	0.001	1L ← 6H	0.572	5.09	0.121
			1L ← 8H	0.530		
			6L ← 5H	0.393		

<sup>a</sup> Transition, indicated as  $j \leftarrow i$ , refers to a one-electron excitation from orbital  $i$  to virtual orbital  $j$ . The second column gives the CI coefficient of the configuration  $j \leftarrow i$ ,  $nH$  and  $mL$  denoting the  $n$ th HOMO and  $m$ th LUMO, respectively.

tetramethylation; that is, the first RP of DCB is only slightly (by -0.09 V) affected by the tetramethylation on the CHD-like group moiety, or the methyl substituent effect on the RP is -0.02<sup>3</sup> V per methyl group. This effect is only one-tenth of the methyl substituent effect on the first three IE values of DCB (see Table I). This means that the contribution of the lowest unoccupied  $\pi$  group orbital (LU- $\pi$ -GO) of the CHD-like moiety to the LU- $\pi$ -MO is quite small and is consistent with the CNDO type MO calculations of DCB and TMDCB, which predict that the LU- $\pi$ -MOs of these compounds are almost completely localized on the MN-like groups. This conclusion will be quite useful for the analysis of the electronic absorption spectra in the later section.

**Electronic Absorption Spectroscopy.** The electronic and orbital structure of DCB and TMDCB is discussed from the standpoint of electronic absorption (EA) spectroscopy. The EA spectra of these compounds are shown in Figure 5. The EA spectral band characteristics of these compounds are summarized in Table II. The EA spectral data of TMDCB were formerly reported by Cookson et al.<sup>8</sup> also.

(6) (a) Kobayashi, T.; Yoshida, Z.; Asako, Y.; Miki, S.; Kato, S. *J. Am. Chem. Soc.* **1987**, *109*, 5103. (b) *Chem. Phys. Lett.* **1986**, *125*, 586.

(7) Kobayashi, T. *J. Electron Spectrosc. Relat. Phenom.* **1976**, *9*, 381.

In order to make clear the characters of the EA bands, configuration interaction (CI) calculations were carried out with the SCF-MOs obtained by the modified CNDO method. As an example, the calculated electronic transitions for TMDCB are given in Table III with the observed ones. According to the calculations, the first singlet-singlet (*s-s*) electronic transition of each compound responsible for the first weak band is a transition contributed almost completely from the LUMO ← HOMO excitation configuration. From the calculations the LUMO of each compound is a  $\pi$  MO almost completely localized on the MN-like moiety, and this has already been supported by the RP data as discussed in the preceding section. On the other hand, as discussed in the former sections relevant to the PE spectra, the HOMO of DCB or TMDCB is a  $\pi$  MO delocalized over the three  $\pi$  systems with the weight on the CHD-like part. Therefore, the first *s-s* transition of each compound can be called as the intramolecular CT transition accompanied by the electron migration from the CHD-like moiety  $b_2$  HO- $\pi$ -GO to the MN-like moiety  $a_2$  LU- $\pi$ -GO. Here, it should be remarked that there are no CT interactions between these two types of component BGOs in the ground state because of the orbital symmetry; that is, the first *s-s* transition of each compound provides a typical example of an unusual type of CT transition, a CT transition between the orbitals CT interaction forbidden in the ground state (for another example and detailed discussion on this type of transitions, see ref 9). The degree of the CT character will be discussed in the next section.

According to the calculations, the strong band of each compound observed around 5 eV is assigned as the transition mainly contributed from the LUMO ← third HOMO excitation configuration and slightly from the LUMO ← HOMO one. That is, the strong band around 5 eV of each compound is regarded to be originating from the local excitation of the MN type group.

The 4.53-eV weak second band of TMDCB is regarded to be associated with either or both of the calculated two  $^1A_2$  transitions, which are symmetry-forbidden and contributed from the LUMO ← second HOMO and second LUMO ← HOMO excitation configurations. Roughly speaking, the calculated 4.716-eV transition of TMDCB is a CT transition, and the 4.981-eV one, a local excitation in the CHD-like group in nature. The band assignments of BCD are the same as in the case of TMDCB.

**Orbital Mixing Assessed by Electronic Absorption Spectroscopy.** As we have shown in our previous paper,<sup>6a</sup> it is possible to evaluate the mixing coefficients of the component BGOs in the HOMOs of these compounds by using the EA band intensity data. The basic formalism is as follows: The oscillator strength (*f*) for an electronic transition can be expressed by the relation in eq 1.

$$f \propto \sigma |\langle \Phi_f | \mu | \Phi_i \rangle|^2 \quad (1)$$

Here,  $\sigma$  denotes the wavenumber corresponding to the energy of a certain electronic transition,  $\Phi_i$  and  $\Phi_f$  mean the total wave functions of the initial and final states, and  $\mu$  denotes the dipole moment operator for the system. We get the expression in eq 2

$$(f/\sigma)^{1/2} \propto |\langle \Phi_f | \mu | \Phi_i \rangle| \quad (2)$$

by transforming the above relationship. In the case of the first and fourth (calculated) electronic excitations of DCB and TMDCB, the right-hand side can approximately be reduced to the MO level representation (as we can almost completely neglect configuration interactions according to the CI calculations) given in eq 3 where  $\phi_{AII}$  and  $\phi_{AIH}$  denote the LU- $\pi$ -GO and HO- $\pi$ -GO

$$(f/\sigma)^{1/2} \propto |\langle \phi_{AII} | f_1 | C_{AIH} \phi_{AIH} + C_{DIH} \phi_{DIH} \rangle| \quad (3)$$

of the MN-like moiety (an A type group), respectively, and  $\phi_{DIH}$

**Table IV.** Component Basis Group Orbital Coefficients in HOMOs Evaluated from Photoelectron Spectra (PES) and Electronic Absorption Spectra (EAS)

compd	method	$C_{DIH}^a$	$C_{AIH}^a$
DCB	PES	0.775	-0.631
	EAS	0.919	-0.395
TMDCB	PES	0.869	-0.494
	EAS	0.960	-0.279

<sup>a</sup> For the definitions of  $C_{DIH}$  and  $C_{AIH}$ , see text.

denotes the HO- $\pi$ -GO of the CHD-like one (a D type group),  $C$ 's denote the BGO coefficients, and  $r_1$  denotes the position operator of an electron. The above formula can further be reduced as in eq 4 within the zero-differential overlap approximation.

$$(f/\sigma)^{1/2} \propto |C_{AIH}| \quad (4)$$

Therefore, when the oscillator strength values of the observed bands corresponding to the first and fourth calculated electronic transitions are used, it is possible to evaluate the  $C_{DIH}$  and  $C_{AIH}$  values for the first and third HOMOs approximately within the two-BGO model of these HOMOs.

According to the above formalism and by using the observed oscillator strength values of the first band and the strong band around 5 eV of each compound given in Table II, the BGO mixing coefficients  $C$ 's were evaluated as summarized in Table IV with the results from the PE spectral data.

As is seen in Table IV, the mixing coefficients of the component BGOs in the HOMOs of these compounds estimated from the EA spectral band intensity data are qualitatively consistent with those estimated from the PE spectral data in the former section. Thus, the HOMO of DCB is mainly contributed from the D type group HO- $\pi$ -O, and this contribution is enhanced by the tetramethylation of DCB; that is, the localization of the HOMO on the D type group is enhanced by the tetramethylation, this enhanced localization being caused by the destabilization of the HO- $\pi$ -GO of the CHD-like moiety by the tetramethylation relative to the HO- $\pi$ -GO of the MN-like one as discussed in the former section on the basis of the PE spectral data. The fact that these principal features of the results have commonly been obtained by the two independent methods, one based on the PE spectral data and the other one based on the EA spectral data, supports the assumptions included in these two methods. From the above data the CT characters of the first bands of DCB and TMDCB are estimated to be around 0.85 and 0.9, respectively. The increase in the CT character of the first band of DCB by the tetramethylation is due to the enhanced localization of the HOMO of DCB mentioned above.

**Molecular Orbital Theoretical View of Intensity Borrowing among Electronic Transitions.** The first band of each compound has the character of the CT band associated with the electron migration from the D type group HO- $\pi$ -O to the A type group LU- $\pi$ -O as discussed already. If the HOMO and LUMO relevant to this CT band of each compound were completely localized on the D type group and the A type one, respectively, the *f* value for the LUMO ← HOMO transition should become zero as easily understood from relation 3 (if we neglect CI). However, in reality, the first band of each compound has relatively strong intensity for a forbidden band, and the mixing coefficients evaluated on the basis of these intensity data are consistent with those estimated independently by using the PE spectral data as seen in the preceding section. This fact means that the first band intensity of each compound is caused by the mixing in of the HO- $\pi$ -O of the A type group into the HO- $\pi$ -MO; that is, the first band intensity is caused by the intensity borrowing by the first band from the A type group local LUGO ← HOGO excitation. The above argument strongly supports the intensity-borrowing model for the first band intensity of each compound. Formerly, Cookson et al.<sup>8a</sup> regarded the first band of TMDCB as a CT band borrowing intensity from the A type group local excitation without any detailed examination. However, this picture has now clearly been substantiated in the present work on the basis of the combined study of the PE and EA spectra of DCB and TMDCB.

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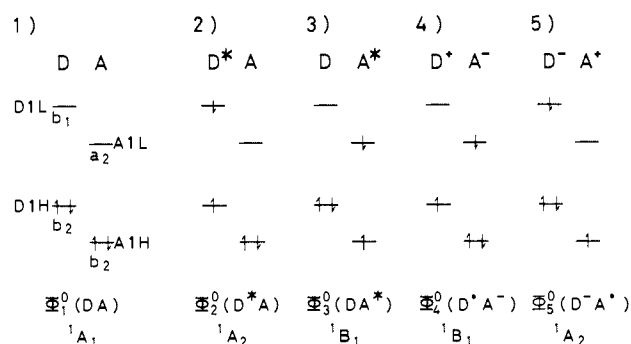


Figure 6. Basis electron configurations taken into account in the composite molecule type model consideration for DCB and TMDCB (for the notation, see text).

**Composite Molecule Theoretical View of Intensity Borrowing among Electronic Transitions.** Murrell<sup>10</sup> discussed formerly the CT band intensity of molecular complexes generally by a kind of composite molecule (CM) or molecules-in-molecule type approach. Now let us discuss the CT band intensity of the present systems from the standpoint of a CM type model like that by Murrell. For simplicity, we take into account explicitly frontier GOs only, that is, the LU- $\pi$ -GO and HO- $\pi$ -GO of a D type group (D1L and D1H), those of an A type group (A1L and A1H), and four  $\pi$  electrons. The ground and singly excited singlet electronic configurations relevant to these four BGOs are schematically drawn in Figure 6 with the symmetry notation for the  $C_{2v}$  point group. In Figure 6,  $\Phi_1^0$ (DA) denotes the ground no-bond configuration function (CF),  $\Phi_2^0$ (D\*A), the D-excited one,  $\Phi_3^0$ (DA\*), the A-excited one,  $\Phi_4^0$ (D\*A<sup>-</sup>), the normal CT one with the complete one-electron migration from the D type group to the A type one, and  $\Phi_5^0$ (D<sup>-</sup>A\*), the back CT one with the complete one-electron migration from the A type group to the D type one. By using these CFs as the basis functions, the electronic state wave functions are expressed approximately as in eq 5. However, in

$$\Phi_i = \sum_{j=1}^5 C_{ij} \Phi_j^0 \quad i = 1-5 \quad (5)$$

reality, within the five-CF approximation described above and in our present  $C_{2v}$  systems, DCB and TMDCB, the ground-state wave function,  $\Phi_1$ , and the normal CT state one,  $\Phi_4$ , become quite simple in their forms because of the molecular symmetry as in eq 6 and 7. That is,  $\Phi_1$  and  $\Phi_4$  are expressed simply by one and two CFs only, respectively. Here coefficient  $C_{44}$  is greater than  $C_{43}$  in the absolute values.

$$\Phi_1 = \Phi_1^0(\text{DA}) \quad (6)$$

$$\Phi_4 = C_{44} \Phi_4^0(\text{D}^+ \text{A}^-) + C_{43} \Phi_3^0(\text{DA}^*) \quad (7)$$

As discussed above the first observed band of DCB or TMDCB is a CT band and the transition moment relevant to such a CT band is now given as in eq 8. Here the first integral is the CT

$$\langle \Phi_1 | \mu | \Phi_4 \rangle = \langle \Phi_1^0(\text{DA}) | \mu | C_{44} \Phi_4^0(\text{D}^+ \text{A}^-) + C_{43} \Phi_3^0(\text{DA}^*) \rangle = C_{44} \langle \Phi_1^0(\text{DA}) | \mu | \Phi_4^0(\text{D}^+ \text{A}^-) \rangle + C_{43} \langle \Phi_1^0(\text{DA}) | \mu | \Phi_3^0(\text{DA}^*) \rangle \quad (8)$$

transition moment for the one-electron migration from the D type group to the A type one, and the second integral is the transition moment for the local excitation in the A type group before CI, respectively. If we take the zero-differential overlap approximation, the first integral can be neglected (eq 9). This formula

$$\langle \Phi_1 | \mu | \Phi_4 \rangle = C_{43} \langle \Phi_1^0(\text{DA}) | \mu | \Phi_3^0(\text{DA}^*) \rangle \quad (9)$$

means that the CT band owes its intensity to the local excitation in the A type one; that is, the intensity-borrowing model for the

Table V. Numerical Data for the Evaluation of the Magnitude of the CT Transition Moment for DCB Relative to That for TMDCB<sup>a</sup>

compd	$s_{\text{D1H,A1H}}$ (rel)	$\frac{H_{44} - H_{33}}{H_{33}/\text{cm}^{-1}}$	$ C_{43} $ (rel)	$(f/\sigma)^{1/2}$ (rel)
DCB	0.7071	-11 500	1.2 <sup>9</sup>	1.5 <sup>6</sup>
TMDCB	0.6533	-13 700	1	1

<sup>a</sup> For the notation, see text.

CT bands of the present systems has now been supported by the CM type formal theory also.

In order to check the validity of the above formalism further, let us try to compare theory with experiment numerically. According to the perturbation theory,  $C_{43}$  is given as in eq 10–12 approximately.

$$C_{43} \approx (H_{43} - S_{43}H_{44}) / (H_{44} - H_{33}) \quad (10)$$

$$H_{ij} = \langle \Phi_i^0 | H | \Phi_j^0 \rangle \quad (11)$$

$$S_{ij} = \langle \Phi_i^0 | \Phi_j^0 \rangle \quad (12)$$

Here  $H$  is the total Hamiltonian for a four- $\pi$ -electron system. In the present systems,  $S_{43}$  can approximately be reduced as follows as in eq 13 and 14; that is,  $s_{\text{D1H,A1H}}$  is the overlap integral between

$$S_{43} \approx s_{\text{D1H,A1H}} \quad (13)$$

$$s_{\text{D1H,A1H}} = \langle \phi_{\text{D1H}} | \phi_{\text{A1H}} \rangle \quad (14)$$

the HO- $\pi$ -GOs of the D and A type groups. As we are taking the zero-differential overlap approximation,  $C_{43}$  is given as eq 15. If we take the Mulliken approximation,<sup>11</sup> eq 16 applies where  $k$  is a constant. Therefore,  $C_{43}$  is given as eq 17.

$$C_{43} \approx H_{43} / (H_{44} - H_{33}) \quad (15)$$

$$H_{43} \approx kS_{43} \quad (16)$$

$$C_{43} \approx kS_{43} / (H_{44} - H_{33}) \approx k s_{\text{D1H,A1H}} / (H_{44} - H_{33}) \quad (17)$$

By using this formula let us estimate the magnitude of the CT transition moment for DCB relative to that for TMDCB. The relevant data are summarized in Table V. The relative  $s_{\text{D1H,A1H}}$  values were evaluated from the AO coefficients of the HO- $\pi$ -MO for ethylene and those for (Z)-2-butene calculated by the modified CNDO type MO method. The denominator of formula 17, the energy difference between the D<sup>+</sup>A<sup>-</sup> and DA\* configurations, was approximately estimated by taking the energy difference between the observed CT band and the strong band around 5 eV of DCB or TMDCB. Both the  $k$  and the transition moment for the local excitation in the A type group before CI were assumed to be common for DCB and TMDCB. The magnitude of the CT transition moment of DCB relative to that of TMDCB is now estimated to be 1.2<sup>9</sup> as given in Table V. The corresponding relative value can independently be estimated from the experimental  $(f/\sigma)^{1/2}$  values also, on the basis of relation 2 in our former section, the value for DCB relative to that for TMDCB being estimated to be 1.5<sup>6</sup>. That is, the theoretically roughly estimated relative value is consistent with the experimental relative value for the CT transition moments. This substantiates the validity of the above formalism and discussion based on it.

From the multiphased discussion given above and in the preceding section it is now evident that the first observed CT band of DCB or TMDCB is borrowing intensity from the local excitation in the A type group. It should be remarked here that quite rare are the cases of the CT bands, which are definitely known borrowing intensity from local excitations. The present study is the first experimental substantiation of intensity borrowing by intramolecular CT bands from local excitations based upon electronic spectral intensity data relevant to CT transitions, as

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far as we know (for intermolecular phenomena, see ref 12, for example).

**Molecular Design.** Finally, we call the readers' attention to the molecular-design-oriented aspect of this work. In principle, in intramolecular D-A type molecules, relative spatial and symmetry relationships between (among) D and A type groups can be designed and realized much more easily than in intermolecular cases. Moreover, this is also the case for the energetics. For example, by choosing the combination of D and A type groups rather freely it is easy intramolecularly to locate CT bands well separated from local excitation bands so as to make assessments of CT transition moments experimentally with reasonable accuracy. From these standpoints, such D-A type molecules as treated here are quite attractive and fundamentally important for model studies of CT phenomena.

### Conclusions

The electronic and orbital structure of DCB and TMDCB has been discussed from various standpoints, the group orbital concept being used as the common basis throughout the discussion. It has been established that the first LU- $\pi$ -MOs of DCB and TMDCB are almost completely localized on the MN-like moieties from the RP data. The first s-s electronic transition of each compound is an intramolecular CT transition mainly associated with the electron migration from the CHD-like moiety  $b_2$  HO- $\pi$ -GO to the MN-like moiety  $a_2$  LU- $\pi$ -GO and provides a typical example of an unusual type of CT transition, a CT transition between the orbitals CT interaction forbidden in the ground state. The mixing coefficients of the component BGOs in the HOMOs of DCB and TMDCB have been evaluated from the PE spectral data and the EA spectral band intensity data, independently from and consistently with each other. The consistency of the mixing coefficients evaluated from the two different standpoints strongly supports the validity of the used models and substantiates the intensity-borrowing model of the first band of each compound from the local allowed  $\pi^*-\pi$  electronic excitation of the A type group. This conclusion has further been supported by a CM type model consideration for the CT transition moments. This is the first experimental substantiation of intensity borrowing by intramo-

lecular CT bands from local excitations. The CT character of the first band of DCB is enhanced by tetramethylation, and this is mainly ascribed to the destabilization of the basis HO- $\pi$ -GO of the D type group relative to that of the A type one, therefore, to the enhanced localization of the HOMO onto the D type group by the tetramethylation of DCB. The integration of PE spectroscopy, cyclic voltammetry, EA spectroscopy, and quantum theoretical approaches is very powerful for the multiphased study of molecular electronic structure, in particular, when combined with well molecular-designed model systems as demonstrated in this work.

### Experimental and Computational Methods

**Materials.** 2,3-Dicyanobarrelene (DCB)<sup>13</sup> and its 5,6,7,8-tetramethyl derivative (TMDCB)<sup>8,13</sup> were synthesized according to the methods described in the literature indicated.

**Measurements.** The gas-phase He I photoelectron spectra of DCB and TMDCB were measured with the instrument described formerly.<sup>14,15</sup> The sample inlet and target chamber systems were heated and kept at 121 °C during the measurements.

The reduction potentials were measured with a Yanaco polarographic analyzer P-1100, Pt wires being used as working and counter electrodes. The solutions contained 0.1 M Et<sub>4</sub>NClO<sub>4</sub> supporting electrolyte. The potentials were determined under nitrogen atmosphere at room temperature relative to a saturated calomel electrode (SCE) connected with a salt bridge.

The electronic absorption spectra were measured on a Hitachi 340 recording spectrophotometer.

**Computational Details.** The CNDO type SCF-MO-CI calculations of DCB and TMDCB were carried out on a FACOM M380 computer at The Institute of Physical and Chemical Research with the method described formerly.<sup>7</sup> All the singly excited configurations between 10 HOMOs and 10 LUMOs were taken into account in the CI calculations. The molecular geometrical structural parameters assumed in the calculations are based on the X-ray diffraction analysis data for TMDCB.<sup>16</sup>

**Registry No.** DCB, 18341-68-9; TMDCB, 19004-90-1.

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## Isomerization of the Dimethyl Sulfoxide Radical Cation and the Possible Analogies to the Neutral Species

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**Abstract:** The interconvertibility of the dimethyl sulfoxide (DMSO) radical cation, its proton tautomeric *aci*-DMSO, and methyl methanesulfonate isomers, respectively, has been investigated by application of collision activation mass spectrometry and metastable ion studies. The isomerization reactions are discussed based on isotopic labeling studies as well as thermodynamical considerations. The interconvertibility of the radical cations of DMSO and *aci*-DMSO as well as the isomerization of the methyl methanesulfonate radical cation into the radical cation of DMSO could be concluded, whereas no unambiguous evidence concerning the possible operation of the DMSO to methyl methanesulfonate isomerization was obtained. Low-pressure gas-phase pyrolysis studies have been applied to elucidate the possible analogies to the corresponding neutral species.

In connection with our continuing interest in isomerization reactions in the gas phase, we recently reported a study on the isomerizations of the nitromethane radical cation in the gas phase<sup>1</sup> as a part of our search for the neutral *aci*-nitromethane. In order

to disclose the possible existence of such *aci* tautomers we are currently studying systems containing " $\text{CH}_3=\text{X}=\text{O}$ " moieties (X = N, P, S), which potentially are able to rearrange into the corresponding *aci* tautomers " $\text{H}_2\text{C}=\text{X}-\text{OH}$ ". These studies involve neutral species as well as radical cations.

The present paper describes our studies of the dimethyl sulfoxide system, involving three different structures, which are dimethyl

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