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Electronic Structures of Dicyanobicycloalkadienes

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Abstract: Photoelectron spectra, electronic absorption spectra, and reduction potentials of 2,3-dicyanobicyclo[2.2.n]alka-2,5-dienes (n = 1, 2, and 3) and their 5,6-dimethyl derivatives were measured, and the ground- and excited-state electronic structures of these compounds including their cationic and anionic states were discussed based on these data combined with MO calculations. On the basis of the ionization energy data it was established that the first and second a′ HO-π-MO levels or the ground and first excited ${}^2A'$ cation states of these series of compounds avoid mutual crossings between n = 2 and 3. From the reduction potential data it was also concluded that the a″ LU-π-MO levels or the ${}^2A''$ anion ground states of these compounds suffer avoided crossings with the counter levels between n = 2 and 3. The mixings between the two apparently spatially separated π systems in these series of compounds were evaluated using the spectral data, and the charge-transfer characters of the electronic absorption bands were also discussed. This work provides a typical example which demonstrates the effectiveness of the combination of photoelectron spectroscopy, reduction potential measurements, and electronic spectroscopy for the study of molecular electronic structures.

Orbital interactions are quite attractive themselves and are becoming much more important from the standpoints of chemical reactivities and material science also. For the study of orbital interactions, photoelectron spectroscopy is a very powerful tool because it gives almost directly orbital energy diagrams, though approximately, if we follow Koopmans' theorem.[2] In this paper we study three-dimensional intramolecular orbital interactions between two unsaturated groups inequivalent to and spatially separated from each other by photoelectron spectroscopy in combination with electronic absorption spectroscopy, reduction potential measurements, and molecular orbital (MO) calculations.

For this purpose, we adopted two series of compounds, 2,3-dicyanobicyclo[2.2.n]alka-2,5-dienes (I(n): n = 1, 2, and 3) and their 5,6-dimethyl derivatives (II(n): n = 1, 2, and 3) as model systems (Figure 1). Each molecule of the I(n) and II(n) series contains in itself an electron-donating-type (D-type) and an electron-accepting-type (A-type) group apparently separated from each other spatially by a saturated aliphatic framework. The interaction mechanisms between these D- and A-type groups in the same molecules are quite attractive. The electronic structures of the bicyclo[2.2.n]alka-2,5-diene series (III(n)), closely related to the I(n) and II(n) series, are also often referred to for the sake of comparison.

Results and Discussion

Photoelectron Spectra. Gas-phase He I photoelectron spectra of the I(n) and II(n) series of compounds are shown in Figures 2 and 3, respectively. The vertical ionization energies (IE) of these compounds obtained from these spectra are summarized in Table I with those of related compounds.[3-7]

Table I. Experimental Vertical Ionization Energies (IE_v)

compd	IE_v, eV		
I(1)	9.60	10.40	11.90
I(2)	9.81	10.34	11.33
I(3)	9.74	10.04	11.41
II(1)	9.00	9.98	11.74
II(2)	9.03	9.93	10.94
II(3)	9.00	9.73	11.11
III(1)[a]	8.69	9.55	11.26
III(2)[a]	8.87	9.45	10.42
III(3)[b]	9.00	9.18	10.03
ethylene[c]	10.51	12.85	
cis-2-butene[d]	9.12		
maleonitrile[e]	11.15	12.77	

[a] Reference 3. [b] Reference 4. [c] Reference 5. [d] Reference 6. [e] Reference 7.

Compound I(1), I(2), or I(3) shows two bands well separated from the following bands in the energy region from 9.0 to 11.0 eV. As the IEs of the HO-π-MOs of ethylene and maleonitrile are 10.51[5] and 11.15 eV,[7] the first two bands of each compound of the I(n) series are safely regarded to correspond to the ionizations from the two HO-π-MOs composed mainly of the HO-π-O of the ethylene-type (a D-type) group and that of the maleonitrile-type (an A-type) group. The contributions of the HO-π-O of the D-type group should be larger than that of the A-type group in the HO-π-MO, and the situation should be reversed in the case of the second HO-π-MO. Dimethyl substitutions on the D-type groups in the I(n) series of compounds cause the shifts of the first two bands to the lower IE side. The fact that these shifts are greater for the first bands than for the second supports the above assignments.

The problems are the phases of the combinations between the two main component orbitals. As reported briefly in our preliminary paper,[8] we can conclude that the HOMO of I(1) or I(2) corresponds to the antibonding (out-of-phase) type of combination of the two main component basis orbitals and the second HOMO to the bonding (in-phase) type of combination (these resultant MOs being designated as the π_- and π_+ MOs, respectively); that is, the ordering of the two HOMOs is natural, while in the case of I(3) the situation is reversed. As compounds I(1), I(2), and I(3) belong (approximately) to the C_s point group, the two HOMOs belong to the same a′ irreducible representation. Therefore, by changing n from 2 to 3, the two HOMO levels cannot cross but are forced to avoid mutual level crossing according to the Neumann-Wigner noncrossing rule,[9] in spite of the phase inversion. Briefly, the reasoning is as follows. With an increase in n, the dihedral angle between the A-type group skeletal plane and the D-type one (θ) is increased as in the case of the III(n) series,[4,10] and, therefore, the overlap integral between the HO-π-Os

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(1) (a) Institute of Physical and Chemical Research. (b) Kyoto University.

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(8) Kobayashi, T.; Yoshida, Z.; Asako, Y.; Miki, S.; Kato, S. *Chem. Phys. Lett.* **1986**, *125*, 586.

(9) (a) v. Neumann, J.; Wigner, E. P. *Phys. Z.* **1929**, *30*, 467. (b) See also: Longuett-Higgins, H. C. *Proc. R. Soc. London, Ser. A* **1975**, *344*, 147.

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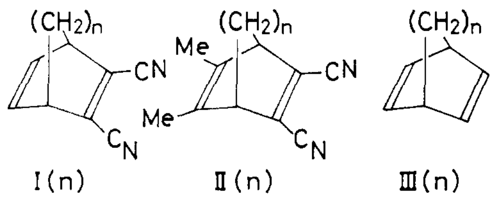

Figure 1. Molecular structural formulas.

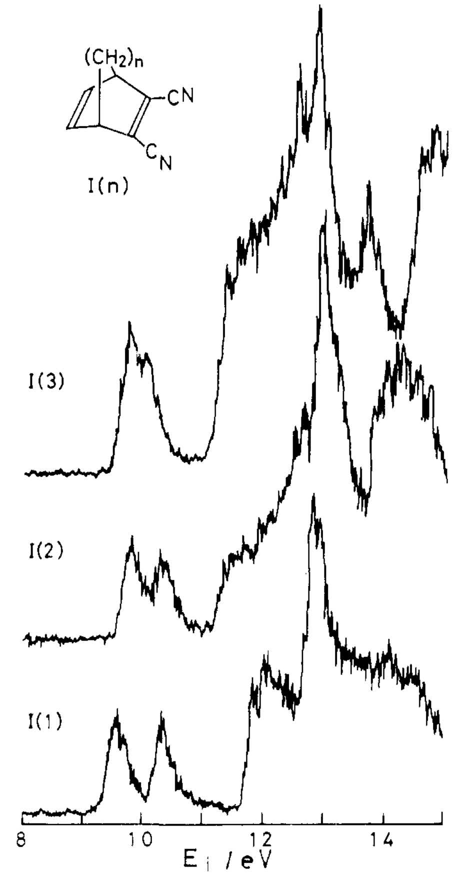

Figure 2. Photoelectron spectra of the I(n) series.

of these two unsaturated groups is decreased. That is, the first IE is expected to increase with n. In reality by increasing n from 1 to 2, the first vertical IE is observed to increase as expected. However, by increasing n from 2 to 3 the first vertical IE is unexpectedly decreased. This anomaly is ascribed to the destabilization of the π_+ orbital caused by the aliphatic bridge part σ orbital mixing-in. That is, with an increase in n the direct overlap interaction between the two component basis orbitals is decreased and the splitting between the two resultant HOMOs is decreased, while with an increase in n the mixing of the a′ σ orbitals of the aliphatic bridge part into the π_+ orbital is enhanced because of the effectively increasing overlap between the π_+ and a′ σ orbitals with the increase in θ. If the latter "through-bond interaction"[11] overwhelms the former "through-space interaction",[11] the π_+ orbital becomes the HOMO and the π_- one, the second HOMO. The anomaly observed about the first vertical IEs is ascribed to the overwhelming through-bond interaction over the through-space interaction.

In the case of the III(n) series of (approximately) C_{2v} symmetry, the two HOMO levels are known to cross just between $n = 2$ and 3.[4,10] As the I(n) and III(n) series are structurally very close to each other, the two HOMOs of the I(n) series are naturally expected to avoid mutual crossing just between $n = 2$ and 3 as discussed above.

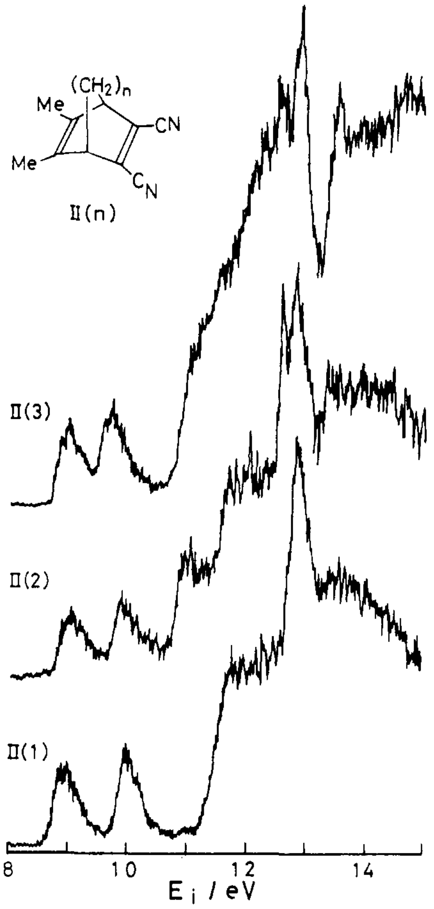

Figure 3. Photoelectron spectra of the II(n) series.

In order to get further supporting evidence we have carried out SCF–MO calculations with a modified CNDO method proposed formerly.[12] For the computations 1,2-dicyanocyclohexa-1,4-diene was adopted as a model compound for the I(n) series and cyclohexa-1,4-diene for the III(n) series. As shown in Figure 4, the computations suggest that the I(n) series should show the avoided crossing mentioned above just at the same dihedral angle where the III(n) series shows orbital energy level crossing. This is perfectly consistent with the discussion described above.

From the above argument it has become certain that in the case of the I(n) series the two HO-π-MO levels avoid mutual crossing between $n = 2$ and 3 while in the case of the III(n) series the two HO-π-MOs cross just between $n = 2$ and 3. In order to ascertain this point further, model calculations were also carried out for I(3) and III(3) by changing θ. As is seen in Figure 5 the two HOMOs of I(3) avoid mutual level crossing just at the same dihedral angle where the two HOMOs of III(3) cross. This computational result also strongly supports the above argument.

Now let us examine the dimethyl substituent effects from the standpoint of the avoided-crossing mentioned above. The dimethyl substituent effects on the first vertical IEs of the I(n) series are −0.60 eV for $n = 1$, −0.78 eV for $n = 2$, and −0.74 eV for $n = 3$. With an increase in n the direct overlap interaction between the two main-component basis HO-π-Os becomes smaller, and the contribution of the D-type group HO-π-O to the HO-π-MO should become larger so long as we neglect the σ orbital mixing-in. In this case the methyl substituent effect should become larger (in the absolute value) with an increase in n. This is the tendency observed for the methyl substituent effect on the first vertical IEs with an increase in n from 1 to 2. However, with an increase in n from 2 to 3, the observed dimethyl substituent effect (in the absolute value) becomes smaller. This tendency is abnormal so long as we neglect the contribution of the σ orbitals. In reality as discussed above, it is now certain that the phase inversion from

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[10] Heilbronner, E. *Isr. J. Chem.* **1972**, *10*, 143.

[11] Hoffmann, R.; Imamura, A.; Hehre, W. J. *J. Am. Chem. Soc.* **1968**, *90*, 1499.

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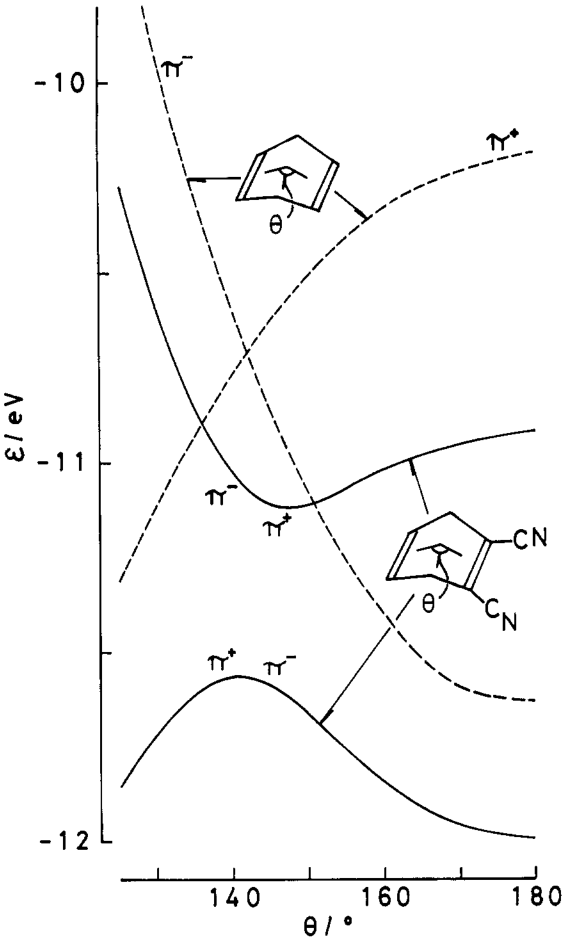

Figure 4. Dihedral angle (θ) dependence of the first and second HOMO energies (ϵ) of cyclohexa-1,4-diene and 1,2-dicyanocyclohexa-1,4-diene calculated by the modified CNDO method.

π_- to π_+ for the HO-π-MO occurs between $n = 2$ and 3. The above anomaly as for the dimethyl substituent effect observed between $n = 2$ and 3 should be ascribed to the phase inversion caused by the dominant σ-orbital mixing into the π_+ orbital. The σ-orbital mixing into the π_+ orbital dilutes the contribution of the π component orbitals. This is the reason why the dimethyl substituent effect on the first vertical IE is decreased (in the absolute value) by changing n from 2 to 3. From the above discussion it is concluded that the two HO-π-MO levels of the I(n) and II(n) series avoid mutual crossing between $n = 2$ and 3 where the two HO-π-MO levels of the III(n) series cross mutually.

Before closing this section let us estimate roughly the order of the mixing of the two main-component HO-π-Os in the two HOMOs in the typical cases. In the case of I(1) the pure π–π resonance integral between the two component HO-π-Os is estimated to be −0.540 eV from the π–π overlap integral, basis orbital coefficients of the HO-π-MO of maleonitrile, and the carbon 2pπ–2pπ bonding parameter evaluated formerly.[13] If we assume the energy difference between the two component basis orbitals as 0.64 eV on the basis of the first vertical IEs of ethylene and maleonitrile, the coefficients of the mixing of the two component HO-π-Os in the HOMO are evaluated to be 0.869 and −0.494 for the D-type group HO-π-O and the A-type group one, respectively. The expected orbital energy difference is 1.255 eV and the observed one is 0.80 eV. Therefore, the destabilization energy difference for the two HOMOs by the through-bond interaction is 0.46 eV, that is, around 0.5 eV. This value is comparable in the magnitude with the destabilization energy of the e′ MOs in barrelene, 0.6 eV, by the through-bond interaction.[13] In the case of II(1) the pure π–π resonance integral is evaluated to be −0.497 eV by using the resonance integral value for I(1) and the AO coefficients of the HO-π-MO of *cis*-2-butene calculated by the CNDO method.[12] By estimating the basis orbital energy difference of the component HO-π-Os as 2.03 eV based on the vertical IE of the HO-π-MO of *cis*-2-butene, 9.12 eV,[6] and that of maleonitrile, 11.15 eV,[7] the expected two HOMO energy difference is 2.260 eV. On the other hand, the observed splitting between the first two bands is 0.98 eV. Therefore, the destabilization energy difference of the two HOMOs by the through-bond interaction is estimated to be 1.28 eV. The mixing coefficient in the HOMO is evaluated to be 0.974 and −0.226 for the D- and A-type group HO-π-Os, respectively. The increase in the group orbital (GO) coefficient of the D-type group HO-π-O by the dimethylation is ascribed to the destabilization of the basis HO-π-O of the D-type group relative to that of the A-type group.

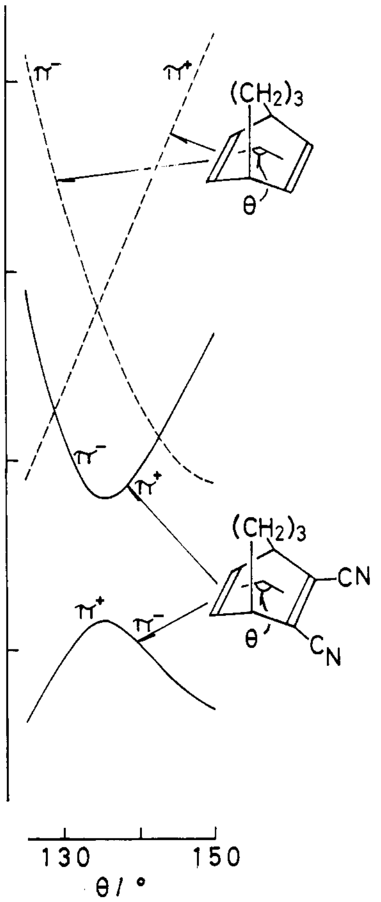

Figure 5. Dihedral angle (θ) dependence of the first and second HOMO energies (ϵ) of I(3) and III(3) calculated by the modified CNDO method.

Table II. Reduction Potentials (V_{red})

compd	V_{red},[a] V	compd	V_{red},[a] V
I(1)	−1.50	II(1)	−1.65
I(2)	−1.72	II(2)	−1.75
I(3)	−1.72	II(3)	−1.85

[a] Potentials *vs.* Ag/AgCl.

Reduction Potentials. Reduction potentials of these compounds were measured with cyclic voltammetry, though oxidation potentials of the I(n) series could not be determined. The measured reduction potential values for the I(n) and II(n) series are given in Table II.[14] These values reflect almost directly the vacant orbital energies. In the case of the I(n) series the LUMO and the second LUMO are regarded to be mainly composed of the LU-π-O of the D-type group and that of the A-type group. As in the case of the HOMOs of these compounds the LUMO energy is expected to be increased by increasing n from 1 to 2 so long

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(13) Kobayashi, T.; Kubota, T.; Ezumi, K. *J. Am. Chem. Soc.* **1983**, *105*, 2172.

(14) For the electron affinity data of III(1), see: Jordan, K. D.; Michejda, J. A.; Burrow, P. D. *Chem. Phys. Lett.* **1976**, *42*, 227.

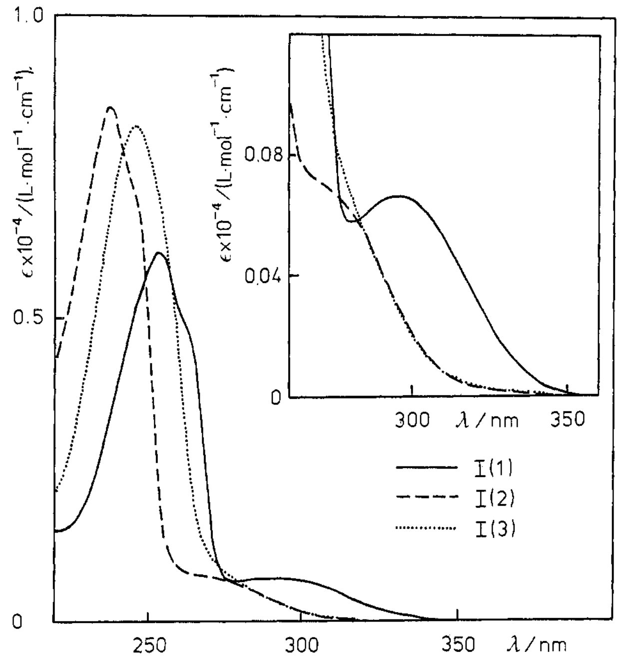

Figure 6. Electronic absorption spectra of the I(*n*) series in acetonitrile. The inset spectra are on an expanded scale.

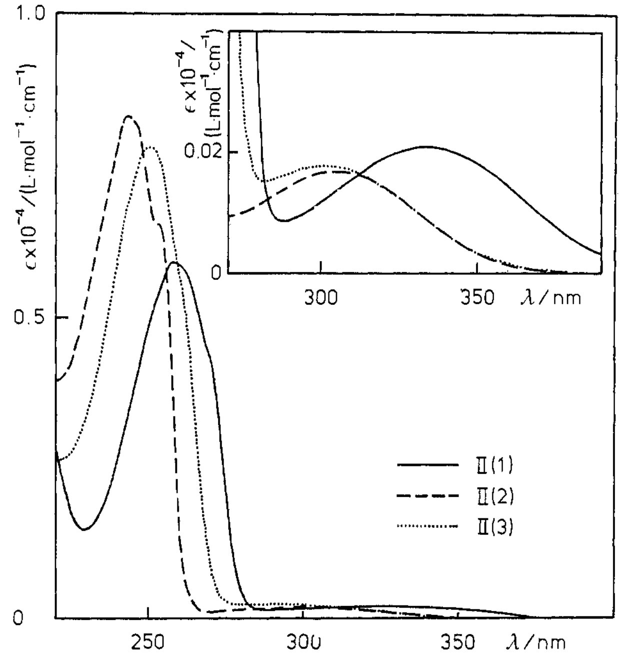

Figure 7. Electronic absorption spectra of the II(*n*) series in acetonitrile. The inset spectra are on an expanded scale.

as we take the through-space interaction model. And this is the tendency observed as for the reduction potentials experimentally. However, by increasing *n* from 2 to 3, the reduction potential is unexpectedly not changed and, therefore, the LUMO energy level is not affected by the change in *n*. This is peculiar so long as we follow the through-space-interaction-only model. That is, again, in this case also, this anomaly suggests that the LUMO level has been changed from the π_+^* to π_-^* between $n = 2$ and 3 because of the overwhelming through-bond interaction over the through-space interaction just as in the case of the HOMO levels. This point can further be supported by the dimethyl substituent effects.

The dimethyl substituent effects on the reduction potentials are −0.15 V for I(1) and −0.03 V for I(2), and this tendency is reasonable from the standpoint of the through-space interaction model. The contribution of the ethylene-type group LU-π-O to the LU-π-MO becomes smaller by changing *n* from 1 to 2; therefore, the destabilization of the LU-π-MO by the dimethyl substitution is diminished. However, by changing *n* from 2 to 3 this reasonable tendency is destroyed and the dimethyl substitution effect becomes −0.13 V again. This abnormal tendency is regarded to reflect the overwhelming through-bond interaction over the through-space interaction. The modified CNDO-type MO calculations also support the above argument as in the case of the HOMOs. In summary the LU-π-MO is the in-phase type combination of the two main-component LU-π-Os in the case of I(1), I(2), II(1), or II(2) and the out-of-phase-type combination of them in the case of I(3) or II(3); these phase inversions between $n = 2$ and 3 are ascribed to the avoided level crossings with the counter levels. It can also be said simultaneously that the $^2A''$ anion ground states of these compounds suffer the avoided crossings between $n = 2$ and 3.

Here at the end of this section we would like to add a few words. The phase inversions in the vacant π orbitals are closely relevant to the avoided crossings between the LUMOs discussed in this section just as in the case of the avoided crossings between the HOMOs. We think that, apart from avoided crossings, phase inversions in vacant orbitals themselves, may not necessarily be so rare phenomena generally. In reality a few other cases have recently been reported, by Balaji et al.,[15] for example.

Electronic Spectra. Now let us discuss the electronic structures of these series of compounds based on their electronic spectra, shown in Figures 6 and 7. The electronic spectral characteristics are summarized in Table III. The electronic absorption spectral data of I(1) and I(2) have formerly been reported by Cookson et al.[16] As is seen in Figures 6 and 7 these compounds show two

Table III. Observed Electronic Absorption Spectral Characteristics in Acetonitrile

compd	λ_{max}, nm[a]	ϵ_{max}, L/(mol·cm)[a]	σ_{max}, kcm^{-1} [b]	$f \times 10^3$ [b]
I(1)	293	662	33.5	12.2
	252	6020	39.6	108
I(2)	280	620[c]	35.8	7.1
	236	8480	42.0	128
I(3)	280	700[c]	35.8	7.8
	246	8110	40.8	138
II(1)	334	212	29.7	5.1
	256	5990	39.0	109
II(2)	303	172	32.7	4.2
	240	8330	41.8	126
II(3)	300	178	32.8	4.4
	248	7870	40.3	140

[a] Apparent spectral characteristics. [b] Spectral characteristics after the deconvolutions with Guassian-type functions. [c] Shoulder.

Table IV. Calculated Electronic Transitions of II(1) with Observed Ones

calcd					obsd	
			main CI component[a]			
sym	*E*, eV	*f*			*E*, eV	*f*
$^1A''$	4.08	0.092	1L ← 1H	0.914	3.68	0.005^1
$^1A''$	4.95	0.145	1L ← 2H	0.887	4.84	0.109
$^1A''$	5.69	0.381	1L ← 4H	0.629		
			2L ← 1H	0.543		
			1L ← 2H	−0.305		
$^1A''$	5.80	0.281	2L ← 1H	−0.686		
			1L ← 4H	0.533		
$^3A''$	2.89	0	1L ← 1H	0.791		
			1L ← 2H	−0.539		
$^3A''$	3.40	0	2L ← 1H	0.796		
			1L ← 2H	−0.410		
			2L ← 2H	0.387		

[a] Transition, indicated as *j* ← *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* ← *i*, *n*H means the *n*th HOMO, and *n*L the *n*th LUMO.

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[15] Balaji, V.; Jordan, K. D.; Gleiter, R.; Jähne, G.; Müller, G. *J. Am. Chem. Soc.* **1985**, *107*, 7321.

bands in the longer wavelength region, the first bands being weak and the second one strong. To interpret these spectra we have carried out CNDO-type SCF-CI calculations with the method described formerly.[12]

As an example, the calculated electronic transitions for II(1) are given in Table IV with the observed ones. Based on the calculations the first bands of these compounds are ascribed to the transitions mainly contributed from the LU-π-MO ← HO-π-MO excitation configurations, and the second bands are assigned to the excitations mainly contributed from the LU-π-MO ← second HO-π-MO excitation configurations. According to the calculations the a″ LU-π-MOs are almost completely localized on the maleonitrile-type groups. This is supported by the fact that the reduction potentials are only slightly affected by dimethylations in the I(n) series as seen in Table II. On the other hand, as discussed in the section of photoelectron spectra, the first two HOMOs of each compound are mainly composed of the HO-π-Os of the component D-type and A-type groups, and in the case of the HOMO the contribution of the former component is predominant and in the case of the second HOMO the contribution of the latter component is. Therefore, the first bands can be called intramolecular charge-transfer (CT) transitions accompanied by the electron migration from the D-type group to the A-type one. Cookson et al.[16] assigned formerly the first bands of I(1) and I(2) as the CT bands from qualitative discussion.

The oscillator strength of an electronic transition is given as follows:

$$f \propto \nu|\langle \Phi_f|\mu|\Phi_i\rangle|^2$$

where ν denotes the frequency corresponding to the energy of a certain electronic transition, Φ_i and Φ_f mean electronic wave functions of initial and final states, and μ denotes the dipole moment operator for the system. By reformulating the above relationship, we get the following:

$$\sqrt{f/\nu} \propto |\langle \Phi_f|\mu|\Phi_i\rangle|$$

In the present case and especially in the case of the first and second electronic absorption bands of the I(n) or II(n) series, the right-hand side can approximately be reduced to the MO level representation as follows, as we can almost neglect configuration interactions:

$$\sqrt{f/\nu} \propto |\langle \phi_{A1L}|\boldsymbol{r}_1|C_{A1H}\phi_{A1H} + C_{D1H}\phi_{D1H}\rangle|$$

Here the ϕ_{A1L} and ϕ_{A1H} denote the LU-π-O and HO-π-O of the maleonitrile-type group (an A-type group), respectively, and the ϕ_{D1H} denotes the HO-π-O of the D-type group; the C's denote the basis GO coefficients, and $\boldsymbol{r}_1$ denotes the position operator of an electron. If we adopt the zero-differential overlap approximation, the above formula can further be simplified as follows:

$$\sqrt{f/\nu} \propto |C_{A1H}|$$

Therefore, by using the observed oscillator strength values of the first and second electronic absorption bands, we can evaluate C_{D1H} and C_{A1H} values for the two HOMOs approximately within the two-component basis orbital model of the HOMOs.

In order to evaluate the oscillator strength values the first and second bands of the electronic absorption spectrum of each compound were deconvoluted on the assumption that this two-band region can be expressed by a linear combination of three Gaussian-type functions, two of which were assigned for the second band region. The resolved spectral data are summarized in Table III. The mixing coefficients in the HOMOs of these compounds estimated using these resolved spectral data are summarized in Table V. These values of the mixing coefficients for I(1) and II(1) are close to those roughly estimated from the IE data as described before in the section on photoelectron spectra, and, therefore, the estimated values summarized in Table V seem to be reasonable for tendency. The signs of the coefficients are based on results from the photoelectron spectra. In the case of the second HOMOs the absolute values of the basis GO coefficients, C_{D1H} and C_{A1H}, are reversed compared to those for the HOMOs. The contribution of the A-type group HO-π-O to the HOMO decreases by changing n from 1 to 2 in both the I(n) and II(n) series. This tendency is reasonable and consistent with the discussion described in the section on photoelectron spectra. From the above data it is concluded that the charge-transfer characters of the first and second bands are around 90 and ~10–5%, respectively. The charge-transfer characters of the first bands are slightly increased by dimethylations. This is because of the destabilizations of the component HO-π-Os of the D-type groups by the dimethylations relative to those of the A-type groups as mentioned before in the section on photoelectron spectra.

Table V. Component Basis Group Orbital Coefficients in HOMOs Evaluated from Electronic Absorption Band Intensities

compd	C_{D1H}[a]	C_{A1H}[a]	compd	C_{D1H}[a]	C_{A1H}[a]
I(1)	0.939	−0.344	II(1)	0.971	−0.241
I(2)	0.968	−0.251	II(2)	0.980	−0.200
I(3)	0.969	0.247	II(3)	0.981	0.192

[a] For the definitions of C_{D1H} and C_{A1H}, see text.

Solvent effects on the absorption spectral bands are also consistent with the above results as for the mixing coefficients and the conclusion that the first bands are CT bands. That is, the first bands of I(1), II(1), II(2), and II(3) suffer red shift with the increase in the solvent dielectric constant while the second strong bands suffer almost no shifts. For example, the shifts of the first bands of the II(n) series are ca. 0.2 eV to the longer wavelength side by changing the solvent from heptane to acetonitrile and are twice as large as that in the case of I(1), 0.10 eV. This is consistent with the tendency shown for the basis group orbital coefficients in Table V.

Conclusion

Photoelectron spectra of the I(n) and II(n) series have revealed that in these systems the HOMO and second HOMO levels avoid mutual level crossings between $n = 2$ and 3 while the HOMO and second HOMO levels of the III(n) series cross just between $n = 2$ and 3. This situation is simultaneously also the case for the ground and first excited $^2A'$ cation states of the I(n) and II(n) series. These avoided crossings are caused by the overwhelming through-bond interaction between the two component basis HO-π-Os of the two inequivalent olefin groups over the through-space interaction between $n = 2$ and 3. On the basis of the reduction potential data it was also revealed that the a″ LU-π-MO levels or the $^2A''$ anion ground-state levels of the I(n) and II(n) series suffer avoided crossings with the counter levels just between $n = 2$ and 3. From the electronic absorption spectral intensities of these compounds the CT character of these bands could be evaluated, the first bands being assigned to the charge-transfer bands accompanied by electron migration of 0.9 unit. Combination of photoelectron spectroscopy, reduction potential measurements, and electronic spectroscopy is very powerful for the study of molecular electronic structures as demonstrated in this work.

Experimental and Computational Section

General and Measurements. Melting points were determined with a YANACO micro-melting point apparatus and are uncorrected. Proton and ^{13}C NMR spectra were recorded on a JEOL FX-90Q spectrometer with tetramethylsilane as internal standard. Infrared spectra were obtained with a JASCO A-102 diffraction grating infrared spectrophotometer and only the diagnostic peaks are reported. Mass spectra were obtained with a JEOL JMS-DX300 spectrometer. Electronic absorption spectra were measured on a Hitachi 340 recording spectrophotometer.

The gas-phase He I photoelectron spectra of the I(n) and II(n) series were measured with the instrument described formerly.[13,17] The sample inlet and target chamber systems were heated and kept at 85 °C for I(1),

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110 °C for I(2), 151 °C for I(3), 134 °C for II(1) and II(3), and 115 °C for II(2).

Reduction potentials were detrmined by a YANACO cyclic voltammetric analyzer, Model P-1000. The voltammetric cell was composed of Pt wire working and counter electrodes; an Ag/AgCl couple was used as a reference electrode. Measurements were carried out under nitrogen atmosphere in methylene dichloride freshly distilled from CaH_2, employing n-Bu_4NClO_4 as a supporting electrolyte of 0.1 M concentration. The salt was recrystallized from ethyl acetate and was dried thoroughly in a vacuum oven before use.

Materials. 2,3-Dicyanobicyclo[2.2.1]hepta-2,5-diene (I(1))[18] and 2,3-dicyanobicyclo[2.2.2]octa-2,5-diene (I(2))[16] were prepared according to the literature methods indicated. 2,3-Dicyano-5,6-dimethylbicyclo-[2.2.1]hepta-2,5-diene (II(1)), 2,3-dicyano-5,6-dimethylbicyclo[2.2.2]-octa-2,5-diene (II(2)),[19] 6,7-dicyano-8,9-dimethylbicyclo[3.2.2]nona-6,8-diene (II(3)), and 6,7-dicyanobicyclo[3.2.2]nona-6,8-diene (I(3)) were newly synthesized as described below. These materials were purified by repeated recrystallization before use.

Details of Syntheses. 2,3-Dicyano-5,6-dimethylbicyclo[2.2.1]hepta-2,5-diene (II(1)). A solution of 1,2-dimethylcyclopent-2-en-1-ol[20] (1.5 g, 13 mmol) in chloroform (10 mL) was added to a solution of an excess amount of freshly prepared dicyanoacetylene[21] in the same solvent (5 mL) at room temperature. After the mixture was heated at 60 °C for 6 h, the solvent was removed under reduced pressure and the residue was chromatographed on silica gel with chloroform. Recrystallization from hexane afforded 1.2 g (52 %) of II(1) as a pale yellow crystalline solid: mp 113 °C; IR (KBr) 2950, 2200, 1580, 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.80 (s, 6 H), 2.26 (s, 2 H), 3.67 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 13.7, 60.3, 70.7, 113.7, 140.7, 141.7; UV (CH_3CN) λ_{max} (ϵ) 256 (5990), 334 nm (212); MS, *m/e* (rel intensity) 170 (M^+, 100), 155 (55), 117 (42), 94 (46), 79 (17), 54 (48). Anal. Calcd for $C_{11}H_{10}N_2$: C, 77.62; H, 5.92; N, 16.46. Found: C, 77.92; H, 5.87; N, 16.40.

2,3-Dicyano-5,6-dimethylbicyclo[2.2.2]octa-2,5-diene (II(2)). 1,2-Dimethylcyclohex-2-en-1-ol was prepared by the reaction of 2-methylcyclohex-2-en-1-one[22] with MeMgBr in ether by a procedure similar to the synthesis of 1,2-dimethylcyclopent-2-en-1-ol.[20] ^1H NMR [($CDCl_3$) δ 1.25 (s, 3 H), 1.67 (s, 3 H), 1.25–2.00 (m, 6 H), 5.40 (s, 1 H)] of the residue oil obtained by usual workup indicated that the material was pure enough, and the alcohol was used for the next step without further purification.

The alcohol (32 g) was heated at 150 °C, and an azeotropic mixture of the volatile products and water was collected. The water was eliminated by adding $MgSO_4$ to afford a 1:2:4 mixture (25 g) composed of 2,3-dimethylcyclohexa-1,3-diene, 1,2-dimethylcyclohexa-1,3-diene, and 3-methylene-2-methylcyclohexene. The mixture of dienes was added with dimethyl acetylenedicarboxylate (20 g, 0.14 mol) and was stirred for 5 h at room temperature. The unreacted diene components were removed under reduced pressure to afford an oily substance, the ^1H NMR spectrum of which indicated that the material was a 1:2 mixture (17.5 g) of 2,3-dicarbomethoxy-5,6-dimethylbicyclo[2.2.2]octa-2,5-diene and 2,3-dicarbomethoxy-1,6-dimethylbicyclo[2.2.2]octa-2,5-diene. The mixture was dissolved in methanol (20 mL) and treated with a solution of 15% KOH in water (100 mL). After stirring for 5 h at room temperature, the solution was acidified carefully with concentrated HCl and a solid precipitate was collected by filtration. The precipitate was dissolved in water (80 mL), and an insoluble material was filtered off. The insoluble material was 1,6-dimethylbicyclo[2.2.2]octa-2,5-diene-2,3-dicarboxylic acid monomethyl ester.[23] The filtrate was concentrated to ca. 40 mL and was acidified to afford a white solid of 5,6-dimethylbicyclo[2.2.2]-octa-2,5-diene-2,3-dicarboxylic acid (2.4 g): ^1H NMR (CD_3CN) δ 1.41 (s, 4 H), 1.73 (s, 6 H), 4.01 (s, 2 H).

To a solution of the diacid (2.4 g, 10.8 mmol) in ether (20 mL) was added a freshly prepared solution of 1.2 equiv of diazomethane[24] in the same solvent. After 10 min several drops of formic acid was added to quench excess diazomethane and the solvent was removed under reduced pressure. The residual was almost pure dimethyl ester (2.65 g, 97%) and was used without further purification: IR (neat) 2950, 1710, 1640 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.42 (m, 4 H), 1.72 (s, 6 H), 3.67 (m, 2 H), 3.75 (s, 6 H).

The diester was converted to the corrsponding diamide by Russell's method[25] in 43% yield: IR (KBr) 3360, 3200, 3000, 1650, 1615, 1590 cm^{-1}; ^1H NMR (CD_3OD) δ 1.50 (m, 4 H), 1.79 (s, 6 H), 3.72 (s, 2 H).

The dinitrile II(2) was obtained from the diamide by a procedure similar to the synthesis of 2,3-dicyanobicyclo[2.2.1]hepta-2,5-diene (I-(1))[18] in 93% yield as a white crystalline solid: mp 119–120 °C; IR (KBr) 3000, 2220, 1600, 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.50 (m, 4 H), 1.75 (s, 6 H), 3.75 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 15.6, 24.5, 47.2, 114.1, 131.7, 132.2; UV (CH_3CN) λ_{max}(ϵ) 240 (8330), 303 nm (172); MS, *m/e* (rel intensity) 184 (M^+, 12), 156 (100), 141 (47). Anal. Calcd for $C_{12}H_{12}N_2$: C, 78.24; H, 6.56; N, 15.20. Found: C, 78.18; H, 6.55; N, 15.28.

6,7-Dicyano-8,9-dimethylbicyclo[3.2.2]nona-6,8-diene (II(3)). 2,3-Dimethylcyclohepta-1,3-diene was prepared by the reaction of biacetyl with pentane-1,5-bis[triphenylphosphonium] dibromide[26] by the method reported by Becker[27] in 6% yield: IR (neat) 2950, 1640 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.78 (s, 6 H), 1.7-2.0 (m, 6 H), 5.82 (m, 2 H); MS, *m/e* (rel intensity) 122 (25, M^+), 107 (30), 78 (100), exact mass, *m/e* 122.1078 (calcd for C_9H_{14}, 122.1079).

The diene (0.5 g, 4.1 mmol) was added to a solution of an excess amount of freshly prepared dicyanoacetylene in chloroform (5 mL). After the mixture was heated at 45 °C for 1.5 h, the solvent was removed under reduced pressure and the residue was chromatographed on silica gel with methylene dichloride. Recrystallization from benzene–hexane afforded 0.57 g (70%) of II(3) as a white crystalline solid: mp 138 °C; IR (KBr) 2900, 2200, 1600, 800 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.54 (m, 6 H), 1.78 (s, 6 H), 3.00 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 17.1, 21.0, 22.0, 45.5, 115.0, 130.6, 131.3; UV (CH_3CN) λ_{max} (ϵ) 248 (7870), 300 nm (178); MS, *m/e* (rel intensity) 198 (M^+, 100), 183 (54), 170 (55), 156 (89), 141 (18). Anal. Calcd for $C_{13}H_{14}N_2$: C, 78.75; H, 7.12; N, 14.13. Found: C, 78.67; H, 7.15; N, 14.10.

6,7-Dicyanobicyclo[3.2.2]nona-6,8-diene (I(3)). 1,3-Cycloheptadiene[28] (1.0 g, 11 mmol) was added to a solution of an excess amount of freshly prepared dicyanoacetylene in methylene dichloride (5 mL). After the mixture was heated at 40 °C for 8 h, the solvent was removed under reduced pressure and the residue was chromatographed on silica gel with benzene. Recrystallization from hexane afforded 0.4 g (21 %) of I(3) as a white crystalline solid: mp 96–97 °C; IR (KBr) 2950, 2220, 1640, 800 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.56 (m, 6 H), 3.32 (m, 2 H), 6.31 (m, 2 H); UV (CH_3CN) λ_{max} (ϵ) 246 nm (8110); MS, *m/e* (rel intensity) 170 (M^+, 82), 155 (16), 142 (100), 129 (81), 115 (18), 104 (10). Anal. Calcd for $C_{11}H_{10}N_2$: C, 77.62; H, 5.92; N, 16.46. Found: C, 77.87; H, 5.73; N, 16.75.

Computational Details. CNDO-type SCF–CI calculations were carried out on a FACOM M380 computer at the Institute of Physical and Chemical Research with the method described formerly.[12] All the singly excited configurations between 10 HOMOs and 10 LUMOs were taken into account in the configuration interaction (CI) calculations. The molecular structural parameters were properly assumed based on the data for 1,4-cyclohexadiene by the electron diffraction method[29] and for 2,3-dicyano-1,5,6-trimethylbicyclo[2.2.1]hepta-2,5-diene by the X-ray diffraction method.[30]

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