Electronic Spectra and Structures of Organic π-Systems. III. Electronic Spectra of Nitrocyclopentadienide Anion and Formylcyclopentadienide Anion[1]

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The electronic spectra of sodium nitrocyclopentadienide and sodium formylcyclopentadienide have been measured in several solvents. The electronic states of these compounds have been calculated by variable integrals methods I and II (modified Pariser-Parr-Polpe method). The longest wave-length strong absorption band of nitrocyclopentadienide (304 mμ) or formylcyclopentadienide (280 mμ) in isooctane has been assigned to the superimposed band of two intramolecular chage-transfer transitions from the five-membered ring to the nitro or formyl group. Agreement between the calculated and observed transition energies in isooctane is satisfactory.

Among nonbenzenoid aromatic systems the $(CH)_{4n+1}$ ring system having $(4n+2)\pi$ electrons is expected to have interesting electronic characteristics. Cyclopentadienide anion ($n=1$) is the most typical one of this system. However, no detailed investigations have been carried out on the electronic spectra and structures of substituted cyclopentadienide anions. This paper deals with the electronic states of nitro- and formylcyclopentadienide anions.

Experimental

Materials. Sodium nitrocyclopentadienide was prepared by Thiele's[2] method. Sodium formylcyclopentadienide was prepared by the method of Hafner and his co-workers.[3] Since the latter compound is quite unstable in atmosphere, treatment was carried out in a nitrogen dry box.

Measurements. Ultraviolet-visible spectra were measured by a Hitachi Model EPS-3T spectrophotometer in isooctane, ether, methanol, water, and acetonitrile.

Results. The ultraviolet-visible spectra of sodium nitrocyclopentadienide and sodium formylcyclopentadienide are shown in Fig. 1. The peak wavelengths are summarized in Table 1.

The ultraviolet and visible spectra of sodium nitrocyclopentadienide in water have been reported also by Kerber and Chick.[4]

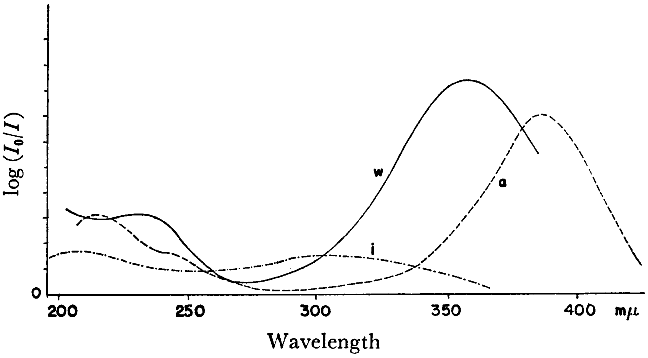

Fig. 1a. Ultra-violet and visible spectra of sodium nitrocyclopentadienide.
Solvents: water (w), acetonitrile (a), and isooctane (i).

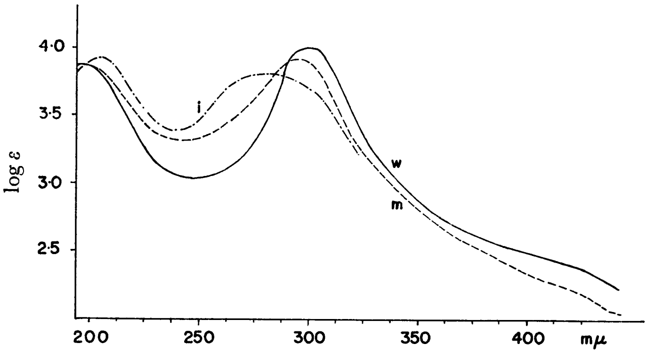

Fig. 1b. Ultra-violet and visible spectra of sodium formylcyclopentadienide.
Solvents: water (w), methanol (m), and isooctane (i).

Theoretical

Methods. The variable integrals methods, VI/1, VI/2/only NNβ, and VI/2/allβ are used.[5] Only the nearest-neighbour β's are taken into consideration in the VI/2/only NNβ, and VI/1 methods while in the VI/2/allβ method all the β's are.

Numberings of the atomic orbitals are shown in Fig. 2. The structures of these molecules are assumed to be as shown in Fig. 2 with reference to the crystallographic data of nitro- and formyl compounds.[6,7] The five-membered rings are assumed to be regular pentagons, and the C–C bond lengths of the pentagons to be 1.40 Å.

The necessary parameters W_p's, α_p's, and $\bar{\alpha}_p$'s are summarized in Table 2.

For the sake of simplicity the variable integrals are reevaluated only in the first five and ten iteration steps of SCF procedures of the VI/1 method and the VI/2 method, respectively.

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[5] Z. Yoshida and T. Kobayashi, *Theor. Chim. Acta*, **19**, 377 (1970); *J. Chem. Phys.*, **54**, 4538 (1971).

[6] "Interatomic Distances," Sp. Pub. No. 11, ed. by L. E. Sutton, The Chem. Soc., London, 1958.

[7] "Interatomic Distances," Sp. Pub. No. 18, ed. by L. E. Sutton, The Chem. Soc., London, 1965.

TABLE 1. THE PEAK WAVELENGTHS OF SODIUM NITROCYCLOPENTADIENIDE AND SODIUM FORMYLCYCLOPENTADIENIDE IN SEVERAL SOLVENTS IN mμ $\lambda_{\max}$[a)] and $\varepsilon_{\max}$[b)]

Solvents	Sodium nitrocyclopentadienide			Sodium formylcyclopentadienide		
Isooctane	201,		304	205,	280	
Ether					283	
Methanol				200 (7120),	291 (8590),	430^{sh} (200)
Water	232 (4300),		361 (11400)	198 (7280),	297 (12300),	425^{sh} (250)
Acetonitrile	213,	244^{sh},	386	208,	311,	436^{w}

a) in mμ b) in l/(mole·cm), in parentheses

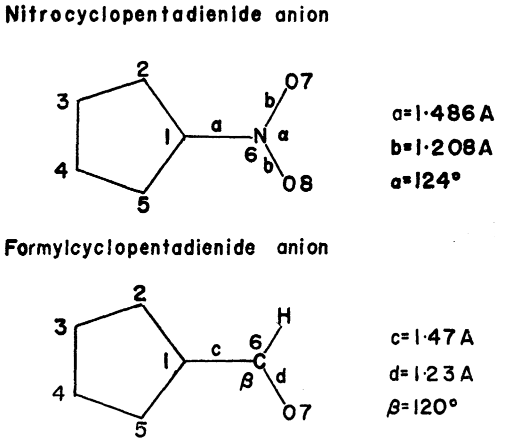


Fig. 2. Assumed structures of molecular species.

TABLE 2. PARAMETERS

	W_p (eV)	α_p	$\bar{\alpha}_p$
C^+	−11.16	3.8379	3.3697
N^{2+}	−28.71	4.2949	3.7631
O^+	−17.28	3.6357	3.0593

All the singly excited configurations are taken into account in the configuration interactions.

Results. The SCF eigenvalues and eigenvectors given by the VI/2/only NNβ method are shown in Table 3. The π-electron densities and bond orders are given in Table 4, and the calculated ${}^1\pi^*-{}^1\pi$ transition energies in Table 5 together with the observed values.

Discussion

The β's given by the VI/1 method are on the whole similar to those given by the VI/2 method. The VI/1, VI/2/only NNβ, and VI/2/allβ methods give similar SCF eigenvalues and eigenvectors in the case of nitrocyclopentadienide anion, but slightly different eigenvectors in the case of formylcyclopentadienide anion.

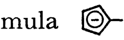
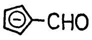
The π-electron densities and bond orders given by these methods resemble each other as shown in Table 4. It is presumed that the contribution of the canonical formula  or  to the ground state of each anion is large. It may be anticipated that in

TABLE 3. SCF EIGENVALUES AND EIGENVECTORS GIVEN BY THE VI/2/ONLY NNβ

Nitrocyclopentadienide anion

φ_i	Sym.	C_1	C_2	C_3	C_6	C_7	E_i (eV)
1	b_1	0.1989	0.0646	0.0190	0.6526	0.5126	−12.7434
2	b_1	0.4561	0.4335	0.4292	−0.0072	−0.1545	−8.1958
3	a_2	0	0.0088	0.0027	0	−0.7070	−8.1189
4	b_1	0.6201	0.1001	−0.5004	0.1300	−0.1972	−4.5572
5	a_2	0	0.6020	0.3709	0	0.0090	−4.3972
6	b_1	−0.0008	−0.3090	0.1777	0.6642	−0.3903	4.7152
7	a_2	0	0.3709	−0.6020	0	0.0023	7.8773
8	b_1	0.6066	−0.4499	0.1829	−0.3406	0.1491	8.0330

Formylcyclopentadienide anion

φ_i	C_1	C_2	C_3	C_4	C_5	C_6	C_7	E_i (eV)
1	0.3287	0.2016	0.1324	0.1276	0.1831	0.5212	0.7158	−8.5987
2	0.3241	0.4017	0.4503	0.4387	0.3754	−0.1300	−0.4248	−7.1881
3	0.4602	0.4992	−0.1399	−0.6222	−0.2585	0.1117	−0.2303	−3.6260
4	0.4085	−0.3665	−0.5862	0.0048	0.5506	0.1118	−0.1990	−3.6093
5	0.0474	−0.3364	0.2083	0.1480	−0.3403	0.7205	−0.4295	5.7716
6	0.0628	−0.4047	0.6017	−0.5833	0.3537	−0.0612	0.0319	8.4809
7	−0.6341	0.3708	−0.1051	−0.2048	0.4634	0.4045	−0.1705	9.3373

TABLE 4. π-ELECTRON DENSITIES AND BOND ORDERS

Electron densities				Bond orders			
Atom	VI/1	VI/2/ only NNβ	VI/2/ all β	Bond	VI/1	VI/2/ only NNβ	VI/2/ all β
Nitrocyclopentadienide anion							
1	1.2700	1.2642	1.2585	1—2	0.5166	0.5452	0.5395
2	1.1093	1·1291	1.1269	1—6	0.4692	0.4142	0.4272
3	1.1396	1.1450	1.1418	2—3	0.7403	0.7210	0.7269
6	0.9044	0.8856	0.8984	3—4	0.5766	0.5948	0.5874
7	1.6639	1.6510	1.6529	6—7	0.6012	0.6200	0.6148
Formylcyclopentadienide anion							
1	1.1805	1.1834	1.1756	1—2	0.5328	0.5530	0.5469
2	1.1596	1.1711	1.1699	1—5	0.5624	0.5755	0.5709
3	1.1638	1.1670	1.1637	1—6	0.4937	0.4524	0.4679
4	1.1966	1.1918	1.1907	2—3	0.7224	0.7052	0.7112
5	1.0641	1.0888	1.0831	3—4	0.5786	0.5974	0.5900
6	0.6198	0.6271	0.6385	4—5	0.7169	0.7031	0.7084
7	1.6156	1.5709	1.5785	6—7	0.7211	0.7607	0.7511

TABLE 5. CALCULATED $^1\pi^*$-$^1\pi$ ELECTRONIC TRANSITIONS IN eV

VI/1					VI/2/only NNβ					VI/2/all β					Obsd.[b)]
Sym.	E	f	CI Composition[a)]		Sym.	E	f	CI Composition[a)]		Sym.	E	f	CI Composition[a)]		E
Nitrocyclopentadienide anion															
$^1A_1$	4.267	0.440	4—6	0.935	$^1A_1$	4.028	0.426	4—6	0.947	$^1A_1$	3.992	0.425	4—6	0.947	4.06
$^1B_2$	4.386	0.066	5—6	0.972	$^1B_2$	4.110	0.036	5—6	0.989	$^1B_2$	3.999	0.040	5—6	0.988	
$^1A_1$	6.075	0.439	2—6	−0.353	$^1B_2$	5.848	0.200	3—6	0.897	$^1A_1$	5.801	0.176	5—7	0.705	
			5—7	0.743				5—8	0.352				4—8	−0.656	
			4—8	−0.528											
$^1B_2$	6.279	0.067	3—6	0.729	$^1A_1$	6.064	0.116	5—7	0.695	$^1B_2$	5.865	0.080	3—6	0.627	6.14
			4—7	0.530				4—8	−0.656				4—7	0.336	
			3—8	0.301									5—8	0.666	
$^1B_2$	6.325	0.170	3—6	−0.360	$^1B_2$	6.331	0.013	4—7	0.719	$^1B_2$	6.107	0.061	3—6	0.649	
			4—7	0.654				5—8	0.640				4—7	−0.664	
			5—8	0.606									5—8	−0.322	
Formylcyclopentadienide anion															
	4.159	0.423	3—5	0.387		4.331	0.364	3—5	0.380		4.245	0.258	3—5	0.437	
			4—5	0.866				4—5	0.880				4—5	0.855	
	4.258	0.080	3—5	0.898		4.455	0.129	3—5	0.882		4.308	0.210	3—5	0.832	4.43
			4—5	−0.379				4—5	−0.410				4—5	−0.468	
	5.945	0.342	2—5	0.386		6.230	0.365	2—5	−0.305		5.988	0.463	3—6	−0.479	
			3—6	0.658				3—6	0.645				4—6	0.662	
			4—6	−0.456				4—6	−0.488				3—7	0.395	
			4—7	0.380				3—7	−0.326						
								4—7	−0.330						
	6.082	0.146	3—6	0.422		6.351	0.091	3—6	0.540		6.044	0.102	3—6	0.708	6.05
			4—6	0.757				4—6	0.653				4—6	0.460	
			3—7	−0.373				3—7	0.374				4—7	−0.412	
								4—7	−0.318						
	6.983	0.088				7.385	0.092				7.144	0.299			

a) The transition denoted i-j refers to a one-electron excitation from orbital i to virtual orbital j. The second column gives the CI coefficient of the configuration i-j.

b) In isooctane.

the ground states the five-membered rings are not regular pentagons but slightly bond alternated pentagons in which the C_2–C_3 and C_4–C_5 bonds are slightly shorter than the C_1–C_2, C_1–C_5, and C_3–C_4 bonds.

As is seen in Table 1, the first band (~300 mμ in isooctane) of nitrocyclopentadienide shows a remarkable red shift by the change of solvent from isooctane to acetonitrile, *viz.*, the energy of this band decreases with the increase in the dielectric constant of the solvent. Thus the band is presumed to be due to the transitions to the excited states with dipolemoments larger than those of the ground state. On the other hand the cyclopentadienide ring is an electron donating group and the nitro group a strong electron accepting group. Thus the first band is also expected to be composed of intramolecular charge-transfer transitions associated with electron transfer from the five-membered ring to the nitro group. As is seen in Table 5 the VI methods explain that this band is composed of two transitions ($^1A_1$, $^1B_2$) associated with electron transfer from the five-membered ring to the nitro group.

From our calculation, the 201 mμ band of nitrocyclopentadienide anion observed in isooctane is expected to be composed of at least two transitions. The fact that this band reveals a shoulder when the solvent is changed from isooctane to acetonitrile may support this interpretation.

The agreement between the calculated and observed transition energies in isooctane is satisfactory in the case of nitrocyclopentadienide (Table 5).

In the case of formylcyclopentadienide the 280 mμ band observed in isooctane is also shifted to 311 mμ by the change of solvent from isooctane to acetonitrile, *viz.*, this band shows a large red shift when the dielectric constant of the solvent increases. Thus the band is expected to be composed of transitions to the excited states with dipole moments larger than those of the ground state. On the other hand, our calculations also explain that this band can be composed of two intramolecular charge-transfer bands caused by electron migration from the five-membered ring to the formyl group (Table 5).

The band around 200 mμ of formylcyclopentadienide shows only a slight solvent shift by the change of solvent from a polar to a nonpolar solvent. This band is predicted to be composed of two transitions localized in the five-membered ring. The prediction is in line with the experimental data.

The longest wavelength weak band around 430 mμ of formylcyclopentadienide can be assigned to a π^*-n transition because it shows a blue shift when the solvent is changed from an aprotic to a protic solvent.

As is seen in Table 5 the argeement between the calculated and observed transition energies in isooctane is satisfactory also in case of formylcyclopentadienide. On the whole the effect of sodium cation on electronic spectra of nitro- and formylcyclopentadienide can be neglected in the calculations.

In conclusion the variable integrals methods[5] give a satisfactory explanation of the electronic spectra of both compounds chosen in this study.

The calculations have been carried out on a HITAC 5020 E computer at the Computer Centre of the University of Tokyo.