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Electronic Structures of the Meisenheimer and Janovsky Complexes

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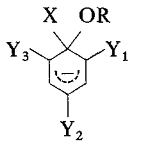
In order to study the electronic spectra and stabilities of the Meisenheimer and Janovsky complexes, the π-electron structures of the 1,3,5-trinitro-, 1,3-dinitro-, 1,5-dinitro-, 2,4-dinitro-, and 3-nitropentadienyl anions were calculated by the method of composite molecules. The Pariser-Parr-Pople type SCF–CI calculation was also performed for the 1,3,5-trinitropentadienyl anion. The lower electronic transitions of these ions are assigned as due to charge-transfer from the pentadienyl group to the nitro group. Calculated transition energies and intensities agree well with the observed values so far as comparison can be done. Relative stabilities of these ions can well be predicted in terms of intramolecular charge-transfer in the ground state, the extent of which is mostly determined by the mode of substitution of nitro groups. The calculated bond order can well explain the bond lengths in the pentadienyl part determined by the X-ray crystal analysis technique.

Zur Untersuchung von Spektrum und Stabilität der Meisenheimer- und Janovsky-Komplexe wurden die π-Systeme der Mono-, Di- und Trinitropentadienylanionen mit der MIM-Methode behandelt. Für das 1,3,5-Trinitropentadienyl-Anion wurde auch eine PPP-CI-Rechnung durchgeführt. Die niedrigeren elektronischen Übergänge entsprechen einem Pentadienyl → Nitro-Ladungsübergang. Die gemessenen Übergangsenergien und Intensitäten passen in die berechneten Spektren. Die relativen Stabilitäten, die vom intramolekularen Ladungsübergang, d. h. von der Nitro-Substitution bestimmt werden, können gut vorausgesagt werden, ebenso die Bindungslängen.

Afin d'étudier les spectres électroniques et les stabilités des complexes de Meisenheimer et Janovsky, les structures d'électrons π ont été calculées par la méthode des molécules composées pour les anions 1,3,5-trinitro-1,3-dinitro, 1,5-dinitro-, 2,4-dinitro- et 3-nitropentadienyle. Un calcul de type Pariser-Parr-Pople SCF CI a aussi été effectué pour l'anion 1,3,5-trinitro-pentadiényle. La transition électronique la plus basse de ces ions est attribuée à un transfert de charge du groupe pentadiényle au groupe nitro. Les énergies de transition calculées ainsi que les intensités sont en bon accord avec l'expérience lorsque la comparaison peut être faite. Les stabilités relatives de ces ions peuvent être prédites en termes de transfert de charge intramoléculaire dans l'état fondamental, dont l'importance est principalement dûe au type de la substitution nitro. Les indices de liaison calculés expliquent bien les longueurs de liaison de la partie pentadiényle déterminées par analyse aux rayons X.

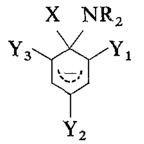
Introduction

In non-aqueous alkaline media (e.g., alcoholic alkaline [1, 7, 12, 20], liquid ammonia [15, 16], and acetone-alkaline [18]) several aromatic polynitro compounds are known to form relatively stable anions, whose formations can be judged by distinct and reversible bathochromic color changes and sometimes by isolation of analyzable salts. The following are the typical examples of these anions (cations being sodium, potassium, ammonium, and the like):



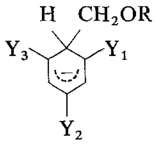
$X = H, OR$, halogen

(I)



$X = H, R, NR_2, OR$, halogen

(II)

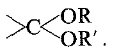


(III)

$Y = NO_2, H$

Some of them are called the Meisenheimer [20] complexes ($I: X = OR$) and others other the Janovsky [18] complexes (III).

Since these complexes are the prototypes of the intermediates of aromatic nucleophilic substitution reactions [3, 6, 22], many studies have been performed for their structures. Attention was especially focussed on the problem whether or not the new bond between the ring carbon and the OR, NR_2 or CH_2OR group can be regarded as an ordinary covalent one as in the case of electrophilic substitution reaction intermediates [21]. Appearance of new strong infrared absorption bands around 8–9 μ in the Meisenheimer complexes seems to suggest a ketal structure [5, 11, 13, 22]



$$>C<^{OR}_{OR'}.$$

Nuclear magnetic resonance studies indicate the existence of some aliphatic hydrogen like $>C<^{H}_{X}$ in a group of compounds ($I: X=H$, $II: X=H$, III) [8, 9, 14, 27]. Very recently two X-ray studies established the existence of equivalent C–O bonds and also bond alternation in the ring of Meisenheimer complexes ($Ia: X=OCH_3$, $R=CH_3$, $Y_1=Y_2=Y_3=NO_2$) [30] and ($Ib: X=OC_2H_5$, $R=C_2H_5$, $Y_1=Y_2=Y_3=NO_2$) [10].

Electronic absorption spectra of these compounds seem to be greatly influenced by the number and positions of nitro groups, but to be rather insensitive to the substituents at the tetrahedral carbon atom [2]. The same is the case for the stability of these complexes. For example, neither *p*-nitroanisole nor 3,5-dinitroanisole [14] gives a stable Meisenheimer type anion. Abe [2] explained with the aid of Hückel molecular orbitals the fact that in the longer wavelength region one and two absorption bands are observed, respectively, for di- and trinitro ions, while the characters of the electronic transitions are unexplained. Caveng *et al.* [8] calculated by the HMO method the charge-density distributions of several Meisenheimer complexes. But our opinion is that nitro compounds are something beyond the limit of the HMO treatment[1].

In the present study, we intend to understand systematically the electronic structures of these ions from the theoretical viewpoint by neglecting a minor

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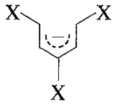
[1] For example, Caveng *et al.* showed that π-electrons in (Ia) are attracted by the three nitro groups to such an extent that the ring becomes *positively* charged. This does not agree with our result as described later.

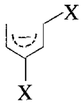
change of absorption bands due to different substituents at the tetrahedral carbon atom[2] and by regarding them as nitro derivatives of the pentadienyl anion.

Methods of Calculation

The π-electron structures of the 1,3,5-trinitropentadienyl anion (IV), the dinitropentadienyl anions (V, VI and VII) and 3-nitropentadienyl anion (VIII) were calculated with the method of composite molecules (CM, or molecules in molecule). The Pariser-Parr-Pople (PPP) type self consistent field (SCF) molecular orbital calculation with configuration interaction (CI) was also made for IV for the purpose of comparison. In actual calculations, only π-electronic singlet states were treated in a differential overlap approximation. Pseudo π-character in the tetrahedral carbon atom and bonds was neglected. The calculations were made by the aid of a Facom 202 electronic computer at the Institute for Solid State Physics.

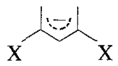


(IV)



(V)

(VI)



(VII)

(VIII)

$X = NO_2$

Since the crystallographical data were not known at the stage of calculation, all the bond angles were set equal to 120°. The ring C–C distances were taken as 1.39 Å, the C–N distances were 1.486 Å as in trinitrobenzene [29], while the N–O distances were 1.21 Å. Numbering of the atoms are shown in Fig. 1.

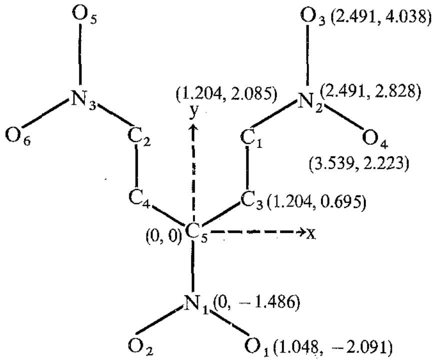


Fig. 1. Atomic coordinates (in Å) and numbering of the 1,3,5-trinitropentadienyl anion

Method of Composite Molecules

Since the π-electron structures of various nitro compounds were studied by the method of composite molecules with success, only a brief account of the method is given here taking IV and V as examples [17, 23, 24, 28]. First of all, the anion under consideration was separated into the pentadienyl anion and nitro groups. We need the π-MO's of each component for the further calculation. The

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[2] For example, Ia; 490 and 428 mμ: IIIa ($R=CH_3$, $Y_1=Y_2=Y_3=NO_2$); 515 and 432 mμ. This problem is studied experimentally by Kimura *et al.* [19].

MO's of the nitro group calculated by Tanaka [28] were taken in the present calculations. The MO's of the pentadienyl anion were calculated according to the so-called VESCF (variation of electronegativity) method [4] with the assumption that the valence state ionization potentials of the carbon atoms are expressed as a quadratic form with respect to the effective charge Z calculated from Slater's rule. The evaluated MO energies and wavefunctions are shown in Table 1.

From the MO's of the components the electron configurations given in Table 2 can be constructed. The LE_{1-3} are locally excited configurations in the pentadienyl anion part, while the LE_{4-6} in the nitro groups. The energies of the former and latter were taken, respectively, from the VESCF calculation and from the measurement of the nitromethane spectrum [24]. Two and three charge-transfer configurations (CT_i's) were constructed for V and IV, respectively, by trans-

Table 1. *Molecular orbitals of the pentadienyl anion*

MO	Symmetry[a]	Orbital Energy (eV)	AO[b] 1, 2	3, 4	5
1	S	−6.6105	0.3047	0.5181	0.5268
2	A	−4.5621	0.4764	0.5225	0.0000
3	S	−1.1077	−0.5618	0.0221	0.6064
4	A	7.0539	−0.5225	0.4764	0.0000
5	S	9.3152	0.3025	−0.4808	0.5956

[a] S: Symmetric with respect to the plane bisecting the molecular plane. A:. Antisymmetric. A: Antisymmetric.

[b] Coefficients of LCAO MO. See Fig. 1 for numbering of atoms.

Table 2. *Electron configurations and energies of the* 1,5-*Dinitro- and* 1,3,5-*Trinitropentadienyl anions*

Ground configuration

$G = |1\ \bar{1}\ 2\ \bar{2}\ 3\ \bar{3}\ a_1\bar{a}_1 b_1\bar{b}_1 a_2\bar{a}_2 b_2\bar{b}_2|$ for V

$|1\ \bar{1}\ 2\ \bar{2}\ 3\ \bar{3}\ a_1\bar{a}_1 b_1\bar{b}_1 a_2\bar{a}_2 b_2\bar{b}_2 a_3\bar{a}_3 b_3\bar{b}_3|$ for IV

Wave function[a]	Symmetry[b]	Energy[c]
Locally excited configurations		
$LE_1 = \psi(3 \to 4)$	A	3.4675
$LE_2 = \psi(3 \to 5)$	S	5.7308
$LE_3 = \psi(2 \to 4)$	S	6.9997
$LE_4 = \psi(b_1 \to c_1)$	A	6.26 (for IV only)
$LE_5 = \psi(b_2 \to c_2)$	[d]	
$LE_6 = \psi(b_3 \to c_3)$	[d]	
Charge-transfer configurations		
$CT_1 = \psi(3 \to c_1)$	S	1.1217
$CT_2 = \psi(3 \to c_2)$	[d]	1.2265 (for IV only)
$CT_3 = \psi(3 \to c_3)$	[d]	

[a] b_i and c_i are, respectively, the highest occupied and vacant π-MO's of the i-th nitro group.

[b] Symmetric character of configurations for the symmetric ion IV. S: Symmetric with respect to the plane bisecting the molecular plane. A: Antisymmetric.

[c] Energy (in eV) above the ground configuration.

[d] For IV these configurations are combined as $LE_{\pm} = (LE_5 \pm LE_6)/\sqrt{2}$ and $CT_{\pm} = (CT_2 \pm CT_3)/\sqrt{2}$ so that LE_+ and CT_+ have S character, while LE_- and CT_- have A character.

ferring an electron from the highest occupied orbital 3 of the pentadienyl anion to one of the antibonding orbitals of the two or three nitro groups. Their energies were calculated by the usual method [17, 23, 24, 28], namely, by subtracting the electron affinity of a nitro group (+0.4 eV) from the calculated ionization potential (1.108 eV) of the pentadienyl anion followed by a small electrostatic correction accompanied by transfer of a charge. For the symmetrical anion (IV) the following transformation was done in order to reduce the order of the matrix (six symmetric and four antisymmetric).

$$LE_{\pm} = (LE_5 \pm LE_6)/\sqrt{2}$$
$$CT_{\pm} = (CT_2 \pm CT_3)/\sqrt{2}\,.$$

The off-diagonal matrix elements between two different LE configurations are expressed as linear combinations of Coulomb repulsion integrals, the greatest one which is the term between LE_2 and LE_3 amounts to 0.58 eV. The off-diagonal matrix elements between the CT configurations, and the ground (G) or LE configurations are proportional to the resonance integral β_{CN} between the nitrogen atom and the adjacent carbon atom. This value was determined to be -2.5 eV by several sets of trial calculations. Similar calculations for the nitrobenzene, nitrobenzene anion radical and 4-nitropyridine anion radical gave -2.4, -3.0, and -3.0 eV, respectively, as the best β_{CN} values [17, 23]. The following off-diagonal terms are zero: between G and any LE configuration, between two CT configurations, and between any CT_i and LE_{3-6}.

Similar calculations were also made for the other three ions VI, VII and VIII.

SCF-CI Method

The PPP type SCF calculation including configuration interaction among singly excited configurations[3] was made for IV, the valence-state ionization potentials (W_{2p}^{π}), one-center Coulomb repulsion integrals ($(pp|pp)_0$) and core resonance integrals (β) given in Table 3 being used. Most of them were taken from Nishimoto *et al.* [26].

Table 3. *Parameters used in the Pariser-Parr-Pople type* SCF–CI *calculation of the trinitropentadienyl anion*

	C	N	O
$-W_{2p}^{\pi}$ (eV)	11.16	26.70	17.70
$(pp\|pp)_0$ (eV)	11.13	17.44	15.23

	C–C	C–N	N–O
$-\beta$ (eV)	2.4	2.0	2.0

Results and Discussion

Tables 4 and 5 show the state wavefunctions and energies of the ions IV and V, respectively. The calculated transition energies and moments are compared with the observed values in Table 6, in which the results of the SCF-CI calculation

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[3] In the actual CI calculation, 28 singly excited configuration were taken. We are indebted to Dr. S. Iwata for this calculation.

Table 4. *State wavefunctions of the trinitropentadienyl anion calculated with the* CM *method*

State	Energy (eV)	Coefficient					
		G	LE_2	LE_3	LE_+	CT_+	CT_1
Symmetric							
0	−2.1207	0.7507	0.1489	−0.0094	0.0031	−0.4913	0.4157
2	1.0961	−0.1078	0.1241	−0.0120	0.0039	0.5601	0.8118
3	2.5903	0.6348	−0.3635	0.0468	−0.0147	0.6173	−0.2853

State	Energy (eV)	Coefficient			
		LE_1	LE_-	LE_4	CT_-
Antisymmetric					
1	0.2012	0.4890	0.0103	0.0144	−0.8721
4	4.4694	0.8662	0.0641	0.0867	0.4879

Table 5. *State wavefunctions of the dinitropentadienyl anion calculated with the* CM *method*

State	Energy (eV)	Coefficient							
		G	LE_1	LE_2	LE_3	LE_4	LE_5	CT_1	CT_2
0	−1.7362	0.7513	0.1080	0.1361	−0.0090	0.0024	0.0033	0.4654	−0.4345
1	0.7965	0.0565	−0.3400	0.0791	−0.0076	−0.0110	−0.0037	0.6191	0.7011
2	2.0474	0.6331	−0.3015	−0.2958	0.0341	−0.0125	−0.0139	−0.5578	0.3288
3	4.0659	0.1350	0.8762	−0.1802	0.0380	0.0702	0.0257	0.0212	0.4173

Table 6. *Calculated and observed transition energies and intensities of* 1,3,5-*trinitro- and* 1,5-*dinitropentadienyl anions*

Transition[a]	Transition energy (eV)			Oscillator strength			Direction[c]	Character[d]
	Calc.		Obs.[b]	Calc.		Obs.[b]		
	CM	SCF–CI		CM	SCF–CI			
1,3,5-Trinitropentadienyl anion								
0→1 (9→10)	2.322	2.379	2.53	0.021	0.284	0.112	90°	CT, ring→NO_2 (+0−)
0→2 (9→11)	3.217	2.797	2.90	0.362	0.389	0.245	0°	CT, ring→NO_2 (+++)
0→3 (9→12)	4.711	4.501	5.0	0.067	0.074	0.2	0°	CT, ring→NO_2 (−+−)
1,3-Dinitropentadienyl anion								
0→1	2.533		2.48	0.346		0.227	155°	CT, ring→NO_2 (in phase)
0→2	3.784		3.65	0.275		0.111	15.5°	CT, ring→NO_2 (out of phase)
0→3	5.802		—	0.177		—	87.5°	LE, ring

[a] For numbering of the states see Tables 4 and 5. In the parentheses for the trinitro compound, major contributions in terms of the SCF MO's are described.

[b] Determined by the present authors for the ions Ia($X=OCH_3$, $R=CH_3$, $Y_1=Y_2=Y_3=NO_2$) and Ic($X=OCH_3$, $R=CH_3$, $Y_1=Y_2=NO_2$, $Y_3=H$) in ethanol.

[c] Angle of the transition moment deviating from the $C_5H_5^-$ molecular axis toward the carbon 5.

[d] Relative signs of the combination of the NO_2 vacant orbitals are shown in the parentheses.

Table 7. *Electronic properties of several nitropentadienyl anions*

	Compound ($X=NO_2$)				
	(IV)	(V)	(VI)	(VII)	(VIII)
Stabilization energy (eV)	2.121	1.736	1.111	0.004	0.832
Net charge					
ring	−0.586	−0.594	−0.669	−0.995	−0.680
1–NO_2	−0.121 (2)	−0.189	−0.165 (2)		
2–NO_2				−0.002 (2)	
3–NO_2	−0.173	−0.217			−0.320
1st band					
Transition energy *E* (eV)	2.322	2.533	1.616	0.609	2.483
Oscillator Strength *f*	0.021	0.346	0.017	0.010	0.499
2nd band					
Transition energy *E* (eV)	3.217	3.784	3.277	0.858	4.288
Oscillator Strength *f*	0.362	0.275	0.005	0.170	0.268

Table 8. SCFMO's *of the* 1,3,5-*trinitropentadienyl anion*

MO	Symmetry[a]	Orbital energy (eV)	Coefficient[b]							
			N_1	O_1,O_2	N_2,N_3	O_3,O_5	O_4,O_6	C_1,C_2	C_3,C_4	C_5
1	*S*	−13.6274	0.6094	0.3347	0.2536	0.1359	0.1358	0.1451	0.1731	0.3166
2	*A*	−13.3567	0.0000	−0.0003	0.5223	0.2993	0.3005	0.2002	0.0848	0.0000
3	*S*	−13.3135	0.3876	0.2274	−0.4528	−0.2599	−0.2619	−0.1585	−0.0206	0.1139
4	*S*	−10.5049	−0.1628	−0.2472	−0.0870	−0.1293	−0.1390	0.2523	0.4486	0.4840
5	*A*	− 8.7684	0.0000	−0.1526	−0.0230	−0.0035	−0.3546	0.4215	0.4157	0.0000
6	*A*	− 8.7353	0.0000	−0.6862	0.0016	−0.0566	0.1233	−0.0765	−0.0694	0.0000
7	*S*	− 8.6659	0.0022	−0.0052	−0.0026	−0.5006	0.4993	0.0017	0.0013	0.0096
8	*A*	− 8.6399	0.0000	0.0760	−0.0114	−0.5339	0.3849	0.1781	0.1706	0.0000
9	*S*	− 6.4321	0.1187	−0.2398	−0.1064	0.2261	0.2202	−0.4534	−0.0059	0.4878
10	*A*	− 1.2118	0.0000	−0.0053	0.3799	−0.3177	−0.3172	0.1183	−0.3742	0.0000
11	*S*	− 1.0252	0.5052	−0.3975	0.2566	−0.2038	−0.2082	0.0402	−0.2472	0.0439
12	*S*	0.4892	0.3703	−0.2282	−0.3642	0.2275	0.2250	0.3027	0.0107	−0.3244
13	*A*	1.7844	0.0000	0.0022	0.2866	−0.1456	−0.1410	−0.4803	0.3822	0.0000
14	*S*	3.4166	0.2134	−0.0869	0.1155	−0.0477	−0.0433	−0.3022	0.4552	−0.5544

[a] *S* and *A* indicate, respectively, symmetric and antisymmetric character of the MO with respect to the symmetry plane perpendicular to the molecular plane.

[b] See Fig. 1 for numbering of atoms.

are also included. In Table 7 calculated values (by the CM method) of several electronic properties of the compounds IV–VIII are compared. SCF iterations were repeated nine times to give the SCF molecular orbitals in Table 8.

Assignment of the Electronic Transitions

The two different methods give almost the same prediction for the nature of the lower three excited states of the ion IV. All of the lowest three and two transitions of IV and V are assigned as due to charge-transfer from the ring to the nitro groups. The number of the charge-transfer bands in the visible and near ultraviolet regions is the same as the number of the nitro groups for all the compounds IV–VIII. According to the PPP type calculation, the lowest three transitions for the ion IV are well represented by electron jumps from the SCFMO 9 to 10, 11 and 12. As is evident from Table 8 the three upper orbitals are mainly composed of the different combinations of the vacant orbitals of the three nitro groups. The lowest transition has the transition moment perpendicular to the symmetrical plane, while the next two transitions are polarized in parallel with it. The results of the CM method are quite the same, leading to the conclusion that these assignments are convincing.

For the ion V only the results of CM method are available. The two longest wavelength absorption bands can be regarded as the charge-transfer band which corresponds to the electron transfer from the ring to the orbital mainly composed of the vacant orbitals of the two nitro groups. The direction of the moment of the lowest transition is along the line connecting the two nitro groups, while the second band is polarized nearly along the symmetry axis of the pentadienyl anion.

The fourth and third transitions of the ions IV and V, respectively, are predicted to have characters of locally excitation in the ring. However, no experimental data are yet available. Usually the intensities of the transition bands calculated with the SCF method are twice or three times as large as the experimental values, whereas the CM method gives a little more reliable values. In view of these limitations the calculated transition moments are thought to have reproduced fairly good relative intensities.

The lowest transition band of VI is reported by Foster *et al.* [14] to be 2.12 eV (intensity undescribed) which is the smallest among the hitherto known ions of this series IV–VI. The calculated value of 1.62 eV is not so good but still gives a qualitative picture when a series of relative values is looked upon. According to our results the lowest transition energy of VIII is predicted to be as large as those of IV and V. This is not in agreement with the prediction by Abe [2] that the excitation energy of VIII is considerably greater than those of IV and V.

The Role of Nitro Groups for the Stabilities of Meisenheimer Complexes

Among the five ions considered, only IV and V are isolated in crystals, while VI is obtained in crude form [14]. Formation of VIII is suggested by a color change and reaction products but never isolated. 3,5-Dinitroanisole seems to give a radical in alkoxide instead of yielding VII [14]. The ground state energy[4] calculated with the CM method is a measure of stabilization of pentadienyl anion by nitro substitution. Roughly speaking, as is evident in Table 7, one nitro substitution at the 1-, 2-, and 3-carbon atom, respectively, lowers the ground state of the pentadienyl anion by about 0.6, 0, and 1.0 eV and these are additive. These values are approximately in parallel with the squares of the coefficients of the highest occupied orbital of the pentadienyl anion. Although there are a number of factors determining the stability of these ions, e.g., solvation energy, steric factors, σ- and pseudo π-electronic contributions, etc., the stabilization energies in Table 7 seem to be important.

Furthermore, the calculated net charge density distributions in these ions are also more or less correlated with their stabilities.

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[4] Since the energy of the ground configuration is taken to be zero, the ground state energy corresponds to the energy stabilization due to the configuration interaction with *CT* configurations.

Charge Densities and Bond Orders of the Ground State

The bond orders of the ion IV were calculated with the aid of the SCFMO's. The results for the C–C bonds are shown in Fig. 2 in comparison with those evaluated by the CM method. In all of these negative ions the C_1–C_3 bond is expected to be shortened, while the C_3–C_5 bond a little longer. This is actually observed in X-ray studies [10, 30]. Table 9 gives the measured bond lengths in the ring compared with the values predicted by the aid of the calculated π-bond orders (P) on the assumption

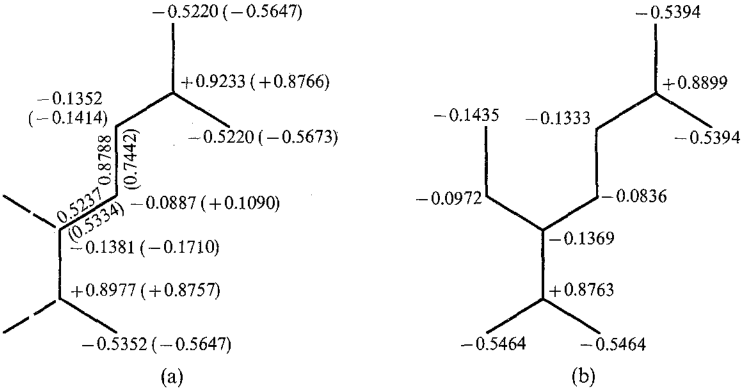

Fig. 2. a Net charge densities and bond orders in the ground state of the 1,3,5-trinitropentadienyl anion. b Net charge densities in the ground state of the 1,3-dinitropentadienyl anion. The values with and without parentheses were calculated by the SCF MO and CM methods, respectively

$$\bar{r} = 1.52 - 0.19P \quad (\text{in Å})\ [25]\,.$$

The net charge density distribution was calculated by the both methods and is given in Fig. 2. In general the CM method gives less amount of charge-transfer than the SCF method. With this in mind, let us compare the net charge densities of the ring in IV calculated by the several methods. The CM, SCF and HMO methods respectively give the values of −0.5859, −0.2358, and +0.881. The last figure was calculated by Caveng *et al.* [8]. Contrary to their prediction, the ring is still believed to carry negative charge. It is interesting to note that in the ion V

Table 9. *Observed and calculated bond distances (in Å) in the trinitropentadienyl anion*

Bond	Observed		Calculated		
	a	b	CM[c]	SCF[c]	HMO[d]
C_1–C_3	1.354 1.353	1.341	1.35	1.38	1.374
C_3–C_5	1.400 1.405	1.425	1.42	1.42	1.420

[a] $K^+[C_6H_2(NO_2)_3(OCH_3)_2]^- \cdot 2H_2O$. Ref. [30].
[b] $M^+[C_6H_2(NO_2)_3(OC_2H_5)_2]^-$ (M = K or Cs). Ref. [10].
[c] Present study.
[d] With inclusion of the ω-technique. Ref. [10].

the magnitude of this negative charge is almost the same as that of IV (−0.594 by CM method), in spite of the difference in the number of electron attracting nitro groups. In conclusion it should be emphasized here again that all the interesting features of the electronic structures of these ions can well be understood as the interaction between the highest occupied orbital of the pentadienyl anion and the vacant orbitals of the nitro groups.

References

1. Abe, T.: Bull. chem. Soc. Japan **31**, 904 (1958); **32**, 339, 778, 997 (1959); **33**, 41 (1960); **34**, 21 (1961).
2. — Bull. chem. Soc. Japan **37**, 508 (1964).
3. Ainscough, J. B., and E. F. Caldin: J. chem. Soc. (London) **1956**, 2528, 2540, 2546.
4. Brown, R. D., and A. Penfield: Trans. Faraday Soc. **53**, 397 (1957); — Brown, R. D., and M. L. Heffernan: Trans. Faraday Soc. **54**, 758 (1958).
5. Byrne, W. E., E. J. Fendler, J. H. Fendler, and C. E. Griffin: J. org. Chem. **32**, 2506 (1967).
6. Bunnett, J. F., and R. E. Zahkerm: Chem. Rev. **49**, 297 (1951).
7. Caldin, E. F., and G. Long: Proc. Roy. Soc. (London) A **228**, 263 (1955).
8. Caveng, P., P. B. Fisher, E. Heilbronner, A. L. Miller, and H. Zollinger: Helv. chim. Acta **50**, 848 (1967).
9. Crampton, M. R., and V. Gold: J. chem. Soc. (London) **1964**, 4293; Chem. Com. **1965**, 549; J. chem. Soc. (London) **1966** B, 893.
10. Destro, R., L. M. Gramaccioli, and M. Simonetta: Nature **215**, 389 (1967).
11. Dyall, L. K.: J. chem. Soc. (London) **1960**, 5160.
12. Foster, R.: Nature **176**, 746 (1955).
13. —, and D. L. Hammick: J. chem. Soc. (London) **1954**, 2685.
14. —, and C. A. Fyfe: Tetrahedron **21**, 3363 (1965); J. chem. Soc. (London) **1966** B, 53.
15. —, and R. K. Macki: Tetrahedron **18**, 161 (1962).
16. Franklin, E. C., and C. A. Krauss: J. Am. chem. Soc. **27**, 181 (1905).
17. Ishitam, A., K. Kuwata, H. Tsubomura, and S. Nagakura: Bull. chem. Soc. Japan **36**, 1357 (1963); Itoh, M., T. Okamoto, and S. Nagakura: Bull. chem. Soc. Japan **36**, 1665 (1963); Itoh, M., and S. Nagakura: Bull. chem. Soc. Japan **38**, 825 (1965). Calculation of negative ion radical of nitro compounds.
18. Kimura, M.: J. pharm. Soc. Japan **73**, 1219 (1953); Kimura, M., M. Kawata, and M. Nakadate: Chemistry and Industry **1965**, 2065.
19. —, N. Obi, and M. Kawazoi: private communication.
20. Meisenheimer, J.: Liebigs Ann. Chem. **323**, 205 (1902).
21. McLean, C., J. H. van der Waals, and E. L. Mackor: Molecular Physics **1**, 247 (1958).
22. Nagakura, S.: Tetrahedron **19**, Suppl. 2, 361 (1963); Nagakura, S., S. Ohsawa, and H. Tsubomura: Symposium on the Electronic States of Molecules, Kyoto, Japan (1958).
23. —, M. Kojima, and Y. Maruyama: J. Molecular spectroscopy **13**, 174 (1964); Kaya, K., K. Kuwata, and S. Nagakura: Bull. chem. Soc. Japan **37**, 1055 (1964); Kojima, M., J. Tanaka, and S. Nagakura: Theoret. chim. Acta (Berl.) **3**, 432 (1965); Kimura, K., and S. Nagakura: Molecular Physics **8**, 117 (1965). See also Ref. [28]. Calculation of neutral nitro compounds.
24. — Molecular Physics **3**, 152 (1960). Calculation of negative ion of nitro compound.
25. Nakajima, T.: Bull. chem. Soc. Japan **38**, 83 (1965).
26. Nishimoto, K., and L. C. Forster: Theoret. chim. Acta (Berl.) **4**, 155 (1966) and private communication.
27. Servis, K. L.: J. Am. chem. Soc. **89**, 1508 (1967).
28. Tanaka, J.: J. chem. Soc. Japan (pure chem. Sec.) **78**, 1643 (1957).
29. Trotter, J.: Acta crystallogr. **12**, 605 (1959).
30. Ueda, H., N. Sakabe, J. Tanaka, and A. Furusaki: Nature **215**, 956 (1967).

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