Electronic Structure and Spectra of Some Disubstituted Benzenes

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A modified Pariser-Parr-Pople method has been applied in the study of the ground state properties and electronic transitions of all the isomers of the chloronitrobenzenes and dinitrobenzenes.

The study of the electronic structure and spectra of the disubstituted benzenes offers some interesting theoretical problems arising from the interpretation of the differences in the physico-chemical properties of the o-, m-, and p-isomers.

Tanaka and Nagakura [1] explained the main differences concerning the electronic structure and spectra of disubstituted benzenes, the two substituents having different nature, on the basis of the simple molecular orbital theory including charge-transfer states.[2,3] On the basis of their study they concluded that the o- and m-isomers possess similar physico-chemical properties, whereas the p-isomer is different.

The purpose of the present investigation is to study the properties of the chloronitrobenzenes and the dinitrobenzenes (all isomers) by using a modified Pariser-Parr-Pople (PPP) method,[4,5] suggested by Roos and Skancke.[6] All molecules are assumed to be planar.

CALCULATION METHOD AND PARAMETERS

As stated above, the method used in the present investigation is a modified PPP method developed for pure hydrocarbons, and extended later on to many other groups of compounds.[7-15] The method is briefly outlined below.

The one-electron parameter W_μ is made dependent on the surroundings to atom μ through the relation

$$W_\mu = W_\mu{}^\circ + \sum_\nu \Delta W_\mu(\nu) \tag{1}$$

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where the symbols have the same meaning as in the original paper.[6] $\Delta W_\mu(\nu)$ of (1) varies with the nature of the neighbouring atom ν and also with the bond distance $R_{\mu\nu}$ through an assumed linear relation

$$\Delta W_\mu(\nu) = \Delta W_\mu^\circ(\nu) + \delta_{\mu\nu}^W (R_{\mu\nu} - R_{\mu\nu}^\circ) \tag{2}$$

The core resonance integral and the two-electron two-center Coulomb repulsion integral between nearest neighbours are expressed by a linear distance dependent relation

$$\beta_{\mu\nu} = \beta_{\mu\nu}^\circ + \delta_{\mu\nu}^\beta (R_{\mu\nu} - R_{\mu\nu}^\circ) \tag{3}$$

$$\gamma_{\mu\nu} = \gamma_{\mu\nu}^\circ + \delta_{\mu\nu}^\gamma (R_{\mu\nu} - R_{\mu\nu}^\circ) \tag{4}$$

The numerical values of the parameters were obtained from the papers mentioned above.[6,9,12]

The two-electron two-center repulsion integrals for non-nearest neighbours have been determined by the uniformly charged sphere approximation,[4] and the one-center Coulomb integrals have been obtained from spectral data.[16]

Since not all experimental geometries are available, we have chosen the geometrical parameters in the same way for all three isomers. The experimental geometry of nitrobenzene [17] and the C − Cl distance for chlorobenzene [18,19] were considered as geometrical characteristics of the chloronitrobenzenes.

For the dinitrobenzenes, a benzene structure of the ring has been assumed together with the nitro group geometry from nitrobenzene.[17]

RESULTS AND DISCUSSION

The molecular ground states were described by a single determinant wave function, whereas configurational mixing, including all singly excited configurations, was invoked in the description of the excited states.

Bond lengths, vertical ionization potentials, net charges, dipole moments and electronic spectra are presented in Tables 1−5, together with available experimental information.

1. *Ground state properties*. To estimate the bond distances, the semi-empirical relations proposed in previous papers have been applied.[6,8,12]

$$R_{\mu\nu}(C,C) = 1.517 - 0.18 p_{\mu\nu} \tag{5}$$

$$R_{\mu\nu}(C,N) = 1.458 - 0.18 p_{\mu\nu} \tag{6}$$

$$R_{\mu\nu}(N,O) = 1.325 - 0.18 p_{\mu\nu} \tag{7}$$

In these eqns., $p_{\mu\nu}$ is the mobile bond order between atoms μ and ν. In Table 1, the calculated bond distances are presented together with available experimental results. Unfortunately, the only available experimental data are those for *m*-chloronitrobenzene [20] and *m*- and *p*-dinitrobenzenes.[21] In these cases, however, we got a satisfactory agreement between calculated and experimental bond distances, except for a few cases. As mentioned elsewhere,[12] it is most likely to relate this discrepancies to perturbations of the σ-skeleton not accounted for in our calculations.

Table 1. Calculated, assumed, and observed bond distances (all values in Å).

Molecule	Bond	Assumed	Bond distance Calculated	Observed
I	4 – 3	1.208	1.209	
	5 – 4	1.208	1.208	
	6 – 2	1.367	1.403	
	6 – 4	1.486	1.418	
	7 – 6	1.367	1.401	
	8 – 7	1.426	1.399	
	9 – 8	1.363	1.397	
	10 – 2	1.426	1.402	
	10 – 9	1.363	1.396	
II	2 – 1	1.718		1.79[a]
	3 – 2	1.426	1.400	1.39
	5 – 4	1.208	1.208	1.25
	6 – 5	1.208	1.209	1.22
	7 – 3	1.367	1.401	1.41
	7 – 5	1.486	1.416	1.48
	8 – 7	1.367	1.401	1.43
	9 – 8	1.426	1.399	1.38
	10 – 2	1.363	1.398	1.38
	10 – 9	1.363	1.396	1.40
III	2 – 1	1.718		
	3 – 2	1.363	1.400	
	4 – 3	1.426	1.397	
	7 – 5	1.208	1.210	
	7 – 6	1.208	1.210	
	8 – 4	1.367	1.410	
	8 – 7	1.486	1.421	
	9 – 8	1.367	1.410	
	10 – 2	1.363	1.400	
	10 – 9	1.426	1.397	
IV	2 – 1	1.397	1.406	
	3 – 2	1.397	1.401	
	4 – 3	1.397	1.399	
	5 – 4	1.397	1.398	
	6 – 1	1.397	1.401	
	6 – 5	1.397	1.397	
	8 – 1	1.486	1.414	
	8 – 7	1.208	1.212	
	9 – 8	1.208	1.202	
	11 – 2	1.486	1.414	
	11 – 10	1.208	1.202	
	12 – 11	1.208	1.212	
V	2 – 1	1.397	1.403	1.38[b]
	3 – 2	1.397	1.403	1.34
	4 – 3	1.397	1.404	1.41
	5 – 4	1.397	1.397	1.42
	6 – 1	1.397	1.404	1.34
	6 – 5	1.397	1.397	1.39
	8 – 1	1.486	1.419	1.49
	8 – 7	1.208	1.208	1.23
	9 – 8	1.208	1.207	1.22
	11 – 3	1.486	1.419	1.51
	11 – 10	1.208	1.207	1.20
	12 – 11	1.208	1.208	1.18

Table 1. Continued.

VI	2 − 1	1.397	1.403	1.36[b]
	3 − 2	1.397	1.396	1.36
	4 − 3	1.397	1.403	1.36
	5 − 4	1.397	1.403	1.36
	6 − 1	1.397	1.403	1.36
	6 − 5	1.397	1.396	1.36
	8 − 1	1.426	1.415	1.49
	8 − 7	1.208	1.209	1.20
	9 − 8	1.208	1.209	1.19
	11 − 4	1.486	1.415	1.49
	11 − 10	1.208	1.209	1.20
	12 − 11	1.208	1.209	1.19

[a] Ref. 20. [b] Ref. 21.

Table 2. Calculated and observed ionization potentials (eV units).

Molecule	Ionization potentials	
	Calculated	Observed
I	10.02, 10.32, 12.00	
II	10.05, 10.28, 11.96	
III	9.48, 9.97, 11.65	9.99, 10.46[a]
IV	10.30, 10.94, 12.91	
V	10.41, 11.02, 13.45	
VI	10.15, 11.33, 13.43	

[a] Ref. 22.

The ionization potentials estimated by Koopmans' theorem are presented in Table 2, together with available experimental information. Again we are suffering from scarce experimental information. Nevertheless, from the qualitative point of view our results seem to be reasonable, at least in the chloronitrobenzene cases, where the expected similarity between the *ortho* and *meta* compounds are reproduced. The measured ionization potential of
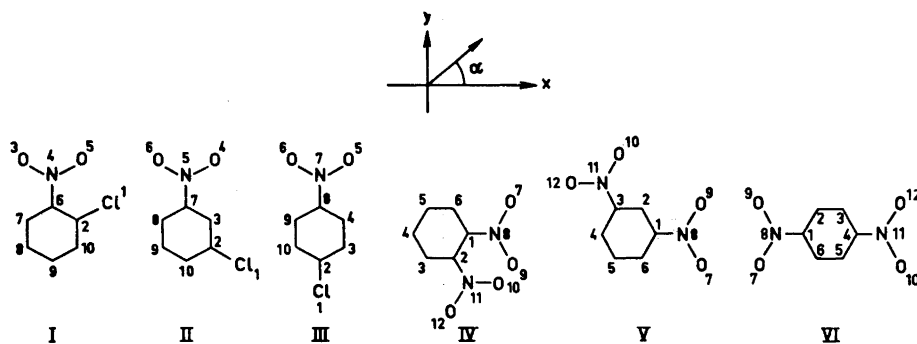

Fig. 1. Labelling of molecules and notation of atoms.

p-chloronitrobenzene does not fit very well to the calculated values. The reported values are, however, vertical ionization potentials, and taking into consideration that the applied parameters are fitted mainly to adiabatic ones, the disagreement is not unreasonable. We have no adiabatic values for p-chloronitrobenzene, but in the case of chlorobenzene, the reported [9] difference between adiabatic and vertical values is 0.36 eV. Making a comparative adjustment on the observed IP of p-chloronitrobenzene, we get a fairly good agreement between calculated and observed values.

Table 3. Calculated π-electron charges.

Atom	Molecule					
	I	II	III	IV	V	VI
1	1.9745	1.9724	1.9812	0.8971	0.7572	0.7974
2	1.1708	1.0189	1.2108	0.8971	1.2270	1.0719
3	1.6704	1.0627	0.8477	1.0733	0.7572	1.0719
4	0.7117	1.6683	1.2389	0.9724	1.1203	0.7974
5	1.6686	0.7183	1.6817	0.9723	0.9273	1.0719
6	0.8059	1.6684	1.6817	1.0734	1.1203	1.0719
7	1.0960	0.8339	0.6885	1.6711	1.6673	1.6667
8	0.9277	1.0836	0.5828	0.7754	0.7156	0.7254
9	1.0600	0.9384	1.2398	1.6107	1.6624	1.6667
10	0.9143	1.0349	0.8477	1.6107	1.6624	1.6667
11				0.7754	0.7156	0.7254
12				1.6711	1.6673	1.6667

The π-electron charges are presented in Table 3, and the calculated π-component of the dipole moments are collected in Table 4, where also experimental values are included for comparison. A direct comparison of the two sets of values is in principle inconsistent, as the contribution from the σ-electrons is neglected in our calculation.

2. *Electronic spectra.* The electronic spectra were calculated by configurational mixing, including all singly excited configurations. The oscillator

Table 4. Calculated π and observed dipole moments (Debye units).

Molecule	Dipole moment	
	π-Component calc.	Observed
I	3.92	3.65[a] 4.41[b] 4.33[c] 4.90[d]
II	3.92	3.05[a] 3.44[e] 3.40[c]
III	3.26	2.4[d] 2.47[a] 2.59[f] 2.62[e] 2.57[c]
IV	6.19	6.9[d] 5.98[c]
V	3.75	4.0[d] 3.83[f] 3.78[c]
IV	0.00	0.00[d] 0.58[c]

[a] Ref. 23. [b] Ref. 24. [c] Ref. 25. [d] Ref. 26. [e] Ref. 27. [f] Ref. 28.

Table 5. Calculated and observed transition energies and prevailing configurations. Energies in eV.

Mole-cule	Calculated		Observed		Prevailing configurations
	ΔE	f	ΔE	f	
I	4.47	0.005	4.19[a]	$\log \varepsilon = 3.041$	$0.7709\Psi_{67} - 0.4834\Psi_{58}$
	4.92	0.164	5.06	$\log \varepsilon = 3.602$	$0.4361\Psi_{67} + 0.8086\Psi_{51}$
	5.59	0.188	5.54	$\log \varepsilon = 3.954$	$0.4231\Psi_{67} + 0.6091\Psi_{58} - 0.4582\Psi_{57} - 0.3126\Psi_{69}$
	6.12	0.468			$0.8441\Psi_{68} - 0.3594\Psi_{58}$
	6.51	0.137			$0.3405\Psi_{69} + 0.8585\Psi_{37}$
	6.85	0.134			$0.9450\Psi_{47}$
	7.33	1.184			$0.8029\Psi_{69} + 0.4583\Psi_{58} - 0.3370\Psi_{37}$
II	4.50	0.005	4.00[a]	$\log \varepsilon = 2.903$	$0.7161\Psi_{67} + 0.5517\Psi_{58}$
	5.05	0.247	4.87	$\log \varepsilon = 3.892$	$0.9162\Psi_{57}$
	5.65	0.161	5.67	$\log \varepsilon = 4.146$	$0.6034\Psi_{67} + 0.6450\Psi_{58}$
	6.15	0.473			$0.9012\Psi_{68}$
	6.51	0.130			$0.8551\Psi_{37} - 0.3916\Psi_{69}$
	7.15	0.910			$0.7196\Psi_{69} + 0.4029\Psi_{58} + 0.3327\Psi_{47} + 0.3014\Psi_{37}$
	7.30	0.669			$0.8510\Psi_{59} - 0.3020\Psi_{68}$
III	4.45	0.232	4.26[a]	$\log \varepsilon = 3.477$	$0.9468\Psi_{67}$
	4.45	0.0003	4.53	$\log \varepsilon = 4.041$	$0.5664\Psi_{68} + 0.7860\Psi_{57}$
	5.44	0.188	5.64[b]	$\log \varepsilon = 3.954$	$0.7168\Psi_{68} + 0.6080\Psi_{57}$
	6.31	0.282			$0.8843\Psi_{58} + 0.3996\Psi_{69}$
	6.65	0.250			$0.9281\Psi_{37}$
	7.08	0.716			$0.8350\Psi_{69} - 0.4246\Psi_{58}$
	7.40	0.838			$0.3954\Psi_{68} + 0.8668\Psi_{59}$
IV	4.36	0.045 ⎫	4.41	$\log \varepsilon = 3.14$	$0.7272\Psi_{79} - 0.5404\Psi_{68} - 0.3081\Psi_{710}$
	4.50	0.082 ⎭			$0.9345\Psi_{78}$
	5.40	0.548	5.15	$\log \varepsilon = 3.90$	$0.6004\Psi_{79} + 0.6964\Psi_{68}$
	5.68	0.187	5.83	$\log \varepsilon = 4.19$	$0.7414\Psi_{69} - 0.5205\Psi_{48} + 0.3296\Psi_{59}$
	6.04	0.570		0.4[d]	$0.6188\Psi_{69} - 0.4043\Psi_{59} + 0.4886\Psi_{48}$
	6.25	0.045			$0.8042\Psi_{710} - 0.3290\Psi_{611} + 0.4299\Psi_{68}$
	6.70	0.002			$0.7399\Psi_{711} + 0.5673\Psi_{610}$
V	4.34	0.046 ⎫	4.17	$\log \varepsilon = 2.88$	$0.7202\Psi_{79} - 0.5572\Psi_{68} + 0.3450\Psi_{710}$
	4.91	0.168 ⎭			$0.9509\Psi_{78}$
	5.19	0.489 ⎫	5.44	$\log \varepsilon = 4.33$	$0.6431\Psi_{79} + 0.6531\Psi_{68} - 0.3041\Psi_{710}$
	5.52	0.054 ⎭		0.5[d]	$0.9479\Psi_{69}$
	6.12	0.114			$0.4528\Psi_{68} + 0.7804\Psi_{710}$
	6.52	0.232			$0.6077\Psi_{48} - 0.5880\Psi_{59} - 0.3797\Psi_{610}$
	6.53	0.299			$0.6184\Psi_{58} - 0.6086\Psi_{49}$
VI	4.40	0.038	4.20[c,d]	$\log \varepsilon = 3.28$	$0.7790\Psi_{710} - 0.5529\Psi_{68}$
	4.46	0.525	4.84	$\log \varepsilon = 4.18$	$0.9753\Psi_{78}$
	5.12	0.00		0.4[d]	$0.9723\Psi_{79}$
	5.79	0.126			$0.7715\Psi_{68} + 0.4985\Psi_{710}$
	6.28	0.00			$0.9597\Psi_{69}$
	6.51	0.576			$0.9232\Psi_{610}$
	6.52	0.00			$0.7103\Psi_{48} - 0.6112\Psi_{59}$

[a] Ref. 30. [b] The assignment is doubtful. [c] Ref. 31. [d] Ref. 32.

strengths have been evaluated by using the formula of Mulliken and Rieke.[29] Calculated and available experimental data [30-32] are collected in Table 5. The agreement between calculated and observed values is fairly good.

The calculated value for the lowest transition of the three isomers of chloronitrobenzene is, however, a little too high, compared with the observed value, but this band corresponds probably to the lowest band of nitrobenzene, which was also hard to reproduce.[12]

In the case of p-chloronitrobenzene, there are some difficulties in comparing the calculated electronic transitions with the observed bands. Two strong bands, of considerable intensity, corresponding to the transition energies of 4.26 eV and 4.53 eV, respectively, are observed in a region, where our calculation has predicted one transition of reasonable intensity, and one transition which is almost forbidden, but both of the same energy. Our calculation is clearly indicating that one should expect only one band in this region, but the lack of detailed information about the observed spectra makes a further discussion difficult. One should, however, bear in mind that the experimental values are obtained in solution.

The interpretation of the measured transition energies for the dinitro-benzenes is more complicated. In Table 5 we have indicated a correspondence between calculated and observed values, taking both the transition energies and the oscillator strengths into consideration.

In order to get a better understanding of the nature of the electronic transitions, an analysis of the prevailing configurations in an excited state has been made.

For the molecules studied here, two kinds of configurations are possible, $viz.$ locally excited and charge-transfer configurations.[32-35]

As is seen from the tables, the experimental spectra of the molecules studied here have been obtained in the near ultraviolet, and accordingly we mainly consider the electronic transitions whose energies are located in this part of the spectra.

Denoting the molecular orbitals ϕ_1, ϕ_2, ϕ_3, ..., ϕ_n, the order being that of increasing energy, the ground state is represented by the following wave function, where m is the number of doubly occupied orbitals:

$$\Psi_0 = |\phi_1\bar{\phi}_1\phi_2\bar{\phi}_2\phi_3\bar{\phi}_3\cdots\phi_m\bar{\phi}_m| \tag{8}$$

A singly excited singlet state, corresponding to an electronic transition from the occupied molecular orbital ϕ_i to the vacant orbital ϕ_j, is described as

$$\Psi_{ij} = 2^{-\frac{1}{2}}\{|\phi_1\bar{\phi}_1\phi_2\bar{\phi}_2\cdots\phi_i\bar{\phi}_j\cdots\phi_m\bar{\phi}_m|$$
$$+ |\phi_1\bar{\phi}_1\phi_2\bar{\phi}_2\cdots\phi_j\bar{\phi}_i\cdots\phi_m\bar{\phi}_m|\} \tag{9}$$

The prevailing configurations, contributing to the different excited states, are given in Table 5. To decide which of the electronic transitions have charge-transfer character, the charges on the substituents, corresponding to different molecular orbitals taking part into the electronic transition, are collected in Table 6.

From the data given in Tables 5 and 6 is seen that the spectra of o- and m-compounds are more or less similar, but rather different from that of p-compounds.

Table 6. Charge densities on the substituents corresponding to different molecular orbitals taking part into electronic transitions.

I

ϕ	$q_3 + q_4 + q_5{}^a$	$q_1{}^b$
ϕ_3	1.9994	0.0000
ϕ_4	0.0002	1.2906
ϕ_5	0.0566	0.0166
ϕ_6	0.0108	0.4734
ϕ_7	1.5684	0.0058
ϕ_8	0.0060	0.0142
ϕ_9	0.3024	0.0004

II

ϕ	$q_3 + q_4 + q_5{}^a$	$q_1{}^b$
ϕ_3	1.9994	0.0000
ϕ_4	0.0148	1.3408
ϕ_5	0.0652	0.0178
ϕ_6	0.0024	0.3778
ϕ_7	1.5574	0.0008
ϕ_8	0.0050	0.0176
ϕ_9	0.3104	0.0056

III

ϕ	$q_3 + q_4 + q_5{}^a$	$q_1{}^b$
ϕ_3	1.9994	0.0000
ϕ_5	0.0004	0.0000
ϕ_6	0.0544	0.2744
ϕ_7	1.6150	0.0024
ϕ_8	0.0000	0.0000
ϕ_9	0.1482	0.0146

IV

ϕ	$q_7 + q_8 + q_9$	$q_{10} + q_{11} + q_{12}$
ϕ_4	0.9996	0.9940
ϕ_5	0.9960	1.0002
ϕ_6	0.0176	0.0176
ϕ_7	0.0650	0.0650
ϕ_8	0.7552	0.7552
ϕ_9	0.5988	0.5988
ϕ_{10}	0.3476	0.3476
ϕ_{11}	0.1788	0.1788

V

ϕ	$q_7 + q_8 + q_9$	$q_{10} + q_{11} + q_{12}$
ϕ_4	1.3158	0.6836
ϕ_5	0.6830	1.3154
ϕ_6	0.0150	0.0150
ϕ_7	0.0456	0.0456
ϕ_8	0.7192	0.7188
ϕ_9	0.7366	0.7370
ϕ_{10}	0.1924	0.1924

VI

ϕ	$q_7 + q_8 + q_9$	$q_{10} + q_{11} + q_{12}$
ϕ_4	0.5000	0.5000
ϕ_5	0.5000	0.5000
ϕ_6	0.0006	0.0006
ϕ_7	0.0722	0.0722
ϕ_8	0.7654	0.7654
ϕ_9	0.8942	0.8942
ϕ_{10}	0.0000	0.0000

[a] Charge on the nitro group. [b] Charge on the chlorine atom.

The lowest electronic transition is predicted to have approximately 50 % charge-transfer character and to be almost forbidden for o- and m-chloronitrobenzene, while in the case of p-chloronitrobenzene it becomes more intense, and the charge-transfer character here is around 90 %. The next electronic transition, which becomes intense in o- and m-chloronitrobenzene, is predicted to be forbidden in p-chloronitrobenzene. The corresponding band is located at the same wave length as that for the lowest transition in this case.

The situation is slightly modified in the case of dinitrobenzene compounds. Here, the lowest transition has almost the same behaviour in all isomers, but the next one has an increased intensity and charge-transfer character in the order $o < m < p$.

In the case of chloronitrobenzenes, charge-transfer bands are to be expected in the vacuum ultraviolet part of the spectra due to charge-transfer in opposite direction compared with that appearing in the nitro group case.

Nevertheless, Kimura and Nagakura [33] did not observe this kind of bands in the vacuum ultraviolet spectra of the chlorobenzene, and accordingly they will hardly appear in the spectra of chloronitrobenzenes.

From the data presented in Tables 5 and 6, as well as from other similar data,[32] we may conclude that in the near ultraviolet spectra of the compounds studied here, the absorption bands are a mixture of the locally excited states and the charge-transfer ones. In fact, this result is to be expected in any molecular orbital theory dealing with the problem of the substitution, the charge-transfer being a measure of the interaction between the π-electron system of the substituent and that of benzene.

An earlier calculation, including only seven configurations, is reproducing the experimental data of the dinitrobenzenes fairly good.[32] Nevertheless, our calculation, including all excited singlet states, seems to lead to a better agreement with observed transition energies.

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