Semi-empirical Calculations on the π-Electron System in Cyclopentadienyl-, Furyl- and Thienyl-sym-trinitrobenzenes

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The π-electron structures of 2-(2,4,6-trinitrophenyl)-thiophene, 2-(2,4,6-trinitrophenyl)furan, 1-(2,4,6-trinitrophenyl)cyclopentadiene, 2-(2,4,6-trinitrophenyl)cyclopentadiene, 2,4,6-trinitrophenylcyclopentadienyl anion, and 2,4,6-trinitrobenzyl anion have been calculated with a modified SCFMO-PPP method. The interaction between the aromatic rings in the biaryls and the structures of the anions are discussed. Calculated and observed values for the electronic transitions are compared, and it is found that the lowest transitions are of an intramolecular charge transfer type.

The fact that 1,3,5-trinitrobenzene (TNB) is a good electron acceptor is easily demonstrated by the numerous known examples of molecular complexes between TNB and electron rich donor molecules.[1] TNB also reacts with several nucleophiles to form σ-complexes, usually called Meisenheimer complexes,[2] and is almost unique in forming stable π- as well as σ-complexes that can be isolated and investigated.

We have recently prepared anionic σ-complexes from thiophene,[3] furan[3] or cyclopentadiene[4] and 1,3,5-trinitrobenzene. The σ-complexes were easily oxidised, under acidic conditions, by p-benzoquinone to 2-(2,4,6-trinitrophenyl)thiophene (*1*) 2-(2,4,6-trinitrophenyl)furan (*2*) and a mixture of 1- and 2-(2,4,6-trinitrophenyl)cyclopentadienes (*3*) and (*4*) (reaction 1). The trinitrophenylcyclopentadienes gave the blue 2,4,6-trinitrophenylcyclopentadienyl anion (*5*), on treatment with base.[5] In order to understand the ground state as well as excited state behaviour of these molecules we have performed semi-empirical quantum chemical calculations on them. The 2,4,6-trinitrobenzyl anion (*6*) is also included in the calculations. The structure formulas for these compounds are given in Fig. 1, where the 1,3,5-trinitrocyclohexadienide anion (*7*) and 1,3,5-trinitrobenzene (*8*) from Ref. 6 are also included for comparison. The numbering system shown for the biaryl *1* is used for convenience.

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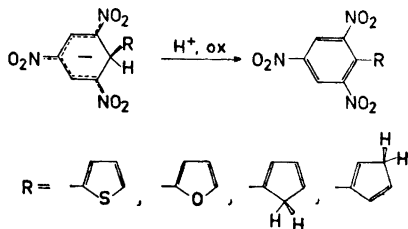
Reaction 1. The oxidation of σ-complexes to substituted sym-trinitrobenzene derivatives.
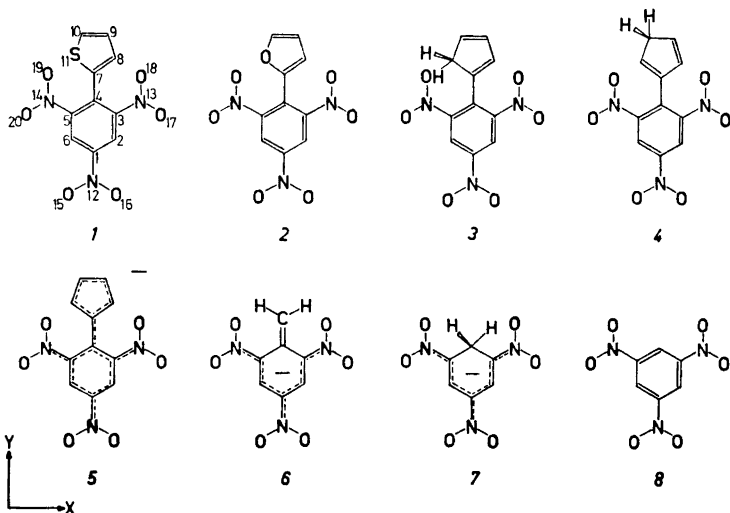

Fig. 1. Structural formulas, numbering of atoms and choice of coordinate axis for the compounds on which calculations were made.

Method of calculation. The calculations were made using the SCFMO-PPP-scheme with a parametrisation method proposed by Fischer-Hjalmars [7] and Roos and Skancke.[8] The parameters used have been worked out in a series of papers.[9] The method is discussed in Refs. 6 and 9.

The calculations were analogous to those described in Ref. 6 with a few exceptions. The bond lengths were calculated from the bond length – bond order relations:[9]

$$R_{\mu\nu}(C,C) = 1.517 - 0.18 \; p_{\mu\nu}$$
$$R_{\mu\nu}(C,N) = 1.458 - 0.18 \; p_{\mu\nu}$$
$$R_{\mu\nu}(N,O) = 1.325 - 0.18 \; p_{\mu\nu}$$
$$R_{\mu\nu}(C,O) = 1.43 - 0.18 \; p_{\mu\nu}$$
$$R_{\mu\nu}(C,S) = 1.773 - 0.18 \; p_{\mu\nu}$$

where $R_{\mu\nu}$ is the bond length between atoms μ and ν and $p_{\mu\nu}$ is the corresponding bond order.

In the calculation of electronic transitions all singly excited states were mixed in a configuration interaction.

RESULTS

The calculated atomic π-electron densities for the compounds are listed in Table 1 and the π-bond orders in Table 2. The results concerning the electronic transitions are given in Tables 3 and 4.

Table 1. Calculated atomic π-electron charges for compounds *1 − 8.*

Atom		Compound							
	1	*2*	*3*	*4*	*5*	*6*	*7*	*8*
C 1	+0.19	+0.19	+0.19	+0.19	+0.12	+0.12	+0.01	+0.25
2	−0.15	−0.14	−0.14	−0.15	−0.14	−0.16	−0.17	−0.22
3	+0.17	+0.17	+0.17	+0.17	+0.11	+0.15	+0.08	
4	−0.10	−0.11	−0.11	−0.10	−0.04	−0.11		
5	+0.16	+0.15	+0.16	+0.16				
6	−0.15	−0.15	−0.15	−0.15				
7	−0.19	−0.13	−0.06	−0.06	−0.10	−0.21		
8	+0.10	±0	+0.04	−0.05	−0.09			
9	+0.04	−0.03	−0.03	+0.03	−0.09			
10	−0.11	−0.03	+0.04	+0.08	−0.09			
11	+0.21[a]	+0.26[b]	+0.08	+0.05	−0.09			
N 12	+1.26	+1.23	+1.23	+1.23	+1.20	+1.21	+1.15	+1.27
13	+1.22	+1.22	+1.22	+1.22	+1.19	+1.20	+1.17	
14	+1.23	+1.22	+1.22	+1.22				
O 15	−0.64	−0.64	−0.64	−0.64	−0.69	−0.72	−0.72	−0.65
16	−0.64	−0.64	−0.64	−0.64				
17	−0.64	−0.64	−0.64	−0.64	−0.70	−0.75	−0.71	
18	−0.65	−0.64	−0.65	−0.64	−0.67	−0.73	−0.74	
19	−0.67	−0.67	−0.65	−0.65				
20	−0.63	−0.63	−0.64	−0.64				

[a] S atom. [b] O atom.

DISCUSSION

The discussion of the reliability of calculations of this type made in Ref. 6 is relevant also to the present work, but here a new serious difficulty arises. In the calculations all compounds have been assumed planar. However, inspection of molecular models reveals that the steric interaction between the *ortho-*nitro groups and the hydrogens in the five-membered rings in compounds *1 − 5* is not negligible. This should cause a twist out of plane of the nitro groups and the five-membered rings and a bending of the carbon-nitrogen bonds. Since the method of calculation can be applied only to planar systems we have reduced the steric interactions to a reasonable value by bending away the *ortho-*nitro groups 10°. This procedure is somewhat arbitrary, however. As a consequence of the assumed planarity, the calculated absorption wavelengths and intensities should be too long and too high, respectively.

Neutral compounds. The calculated ground state properties of the TNB derivatives of thiophene (*1*), furan (*2*), and cyclopentadiene (*3* and *4*) are similar. A small π-electron charge transfer to the trinitrophenyl group (0.06,

Table 2. Calculated π-electron bond orders for compounds *1 – 8*.

Bond		*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*
C–C	1–2	0.63	.63	.63	.63	.59	.58	.52	.62
	1–6	0.63	.63	.63	.64				
	2–3	0.64	.64	.64	.64	.67	.67	.75	
	5–6	0.64	.64	.64	.63				
	3–4	0.60	.60	.60	.60	.48	.41		
	4–5	0.60	.60	.60	.61				
	4–7	0.33	.34	.35	.31	.60	.77		
	7–8	0.78	.75	.83	.38	.45			
	8–9	0.50	.53	.44	.91	.79			
	9–10	0.84	.81	.89	.23[c]	.50			
	10–11	0.37[a]	.43[b]	.24[c]	.25[c]				
	7–11	0.33[a]	.38[b]	.21[c]	.85				
C–N	1–12	0.24	.24	.24	.24	.37	.39	.46	.21
	3–13	0.26	.26	.26	.26	.35	.41	.43	
	5–14	0.27	.27	.26	.26				
N–O	12–15	0.66	.66	.66	.66	.60	.58	.56	.66
	12–16	0.66	.66	.66	.66				
	13–17	0.66	.65	.65	.65	.59	.55	.57	
	13–18	0.65	.65	.65	.65	.62	.56	.55	
	14–19	0.63	.63	.64	.64				
	14–20	0.66	.67	.66	.67				

[a] C–S bond. [b] C–O bond. [c] C–CH$_2$ bond.

Table 3. Calculated and observed electronic transitions for the compounds *1 – 6*.

Compound	Calculated values				Observed values		Ref.
	Frequency nm	Oscillator strength, f	Orbital symmetry and polarisation [a]		Frequency nm	Extinction coeff. $l\,mol^{-1}\,cm^{-1}$	
1	364	0.09			337	4500	3
	352	0.29					
2	387	0.13			353	8000	3
	379	0.24					
3	394	0.18			343[b]		
	380	0.23					
4	383	0.08				6000	5
	345	0.13					
5	660	0.18	S→A, x		542	23000	5
	520	0.05	A→S, x				
	500	0.60	S→S, y				
	483	0.04	A→A, y				
	451	0.24	S→S, y				
6	600	0.43	S→A, x		510	12000	13
	457	0.47	S→S, y				
	404	0.13	S→S, y		370	7000	

[a] For choice of axes see Fig. 1. [b] A mixture of *3* (70 %) and *4* (30 %).

Table 4. Calculated π-electron charges in the ground and excited states for the various groups in compounds $1-6$.

Compound	Group	π-Electron charge Ground state	Excited states				

			352 nm	364 nm			
1	thienyl ring	$+0.06$	$+0.50$	$+0.50$			
	4-nitro($N_{12}O_{15-16}$)	-0.05	-0.09	-0.06			
	2-nitro($N_{13}O_{17-18}$)	-0.07	-0.16	-0.45			
	6-nitro($N_{14}O_{19-20}$)	-0.07	-0.41	-0.17			
			379 nm	387 nm			
2	furyl ring	$+0.07$	$+0.65$	$+0.63$			
	4-nitro	-0.05	-0.08	-0.05			
	2-nitro	-0.07	-0.49	-0.12			
	6-nitro	-0.08	-0.12	-0.53			
			380 nm	394 nm			
3	cyclopentadienyl ring	$+0.07$	$+0.63$	$+0.66$			
	4-nitro	-0.05	-0.08	-0.06			
	2-nitro	-0.07	-0.06	-0.58			
	6-nitro	-0.07	-0.54	-0.06			
			345 nm	383 nm			
4	cyclopentadienyl ring	$+0.05$	$+0.70$	$+0.68$			
	4-nitro	-0.05	-0.08	-0.06			
	2-nitro	-0.06	-0.53	-0.06			
	6-nitro	-0.07	-0.08	-0.63			
			457 nm	600 nm			
6	methylene group (C_7)	-0.21	$+0.07$	$+0.14$			
	4-nitro	-0.23	-0.67	-0.16			
	2-nitro	-0.28	-0.32	-0.49			
			451 nm	483 nm	500 nm	520 nm	660 nm
5	cyclopentadienyl ring	-0.47	$+0.07$	$+0.42$	-0.13	$+0.26$	$+0.10$
	4-nitro	-0.19	-0.55	-0.18	-0.31	-0.25	-0.15
	2-nitro	-0.18	-0.33	-0.52	-0.27	-0.36	-0.41

0.07, 0.07, and 0.05, respectively; see Table 1) is obtained, which parallels the bond order for the single bond between the rings (0.33, 0.34, 0.35, and 0.31, respectively, Table 2).

The calculated electronic transitions shown in Table 3 have some interesting features. Each of the compounds $1-4$ has two calculated allowed transitions at long wavelength 12, 8, 14, and 38 nm apart, respectively. Experimentally the transitions are observed only as one broad band for each compound close to or in the visible region. Calculated and observed values are in fair agreement as can be judged from the limited experimental information (Table 3).

The two transitions with low energy in compounds $1-4$ essentially involve charge-transfer from the five-membered ring to the *ortho*-nitro groups. The *para*-nitro group is little affected (Table 4).

The wavelengths of absorption for a series of charge-transfer complexes with a given acceptor have been correlated with the ionisation potential of the

donor.[10] In compounds *1 – 3* the donor and acceptor are directly bonded to each other. The similarity in the position of the charge-transfer bands in these compounds (337, 353, 343 nm) and the similarity of the ionisation potentials of thiophene, furan, and cyclopentadiene (8.9, 8.9, 8.6 eV [11]) indicate that intramolecular charge-transfer bands can also be correlated with the ionisation potential of the donor.

The charge-transfer complex between thiophene and 1,3,5-trinitrobenzene has been reported by Kraak and Wynberg.[12] It is rather weak ($K_c = 0.51$ l mol^{-1} in cyclohexane) and absorbs at 291 nm ($\varepsilon = 3900$ l mol^{-1} cm^{-1}) which should be compared with the absorption of the thiophene derivative *1* at 337 nm ($\varepsilon = 4500$).

Anions. On treatment with base the 2,4,6-trinitrocyclopentadienes give a deep blue solution due to the formation of 2,4,6-trinitrocyclopentadienyl anion (*5*). Another possible reaction would be the addition of the base to the trinitrophenyl part giving a Meisenheimer-type product.

The corresponding reactions between a base or a nucleophile and 2,4,6-trinitrotoluene involving proton abstraction to give the 2,4,6-trinitrobenzyl anion (*6*), or addition to give a Meisenheimer complex, should also give strongly coloured products.

In the anion *5*, two good electron stabilising systems are directly bonded to each other sharing a negative charge. The anion can be regarded either as a substituted cyclopentadienyl anion or as a fulvenoid Meisenheimer complex. Comparison of the atomic π-electron densities and bond orders for the anions *5* and *7* and *sym*-trinitrobenzene (*8*) in Tables 1 and 2 indicates that in the 2,4,6-trinitrophenylcyclopentadienyl anion (*5*) the two aromatic systems are equally good in stabilising the negative charge in the ground state. The total π-electron charges in the trinitrophenyl part and the cyclopentadienyl part are -0.53 and -0.47, respectively.

In the 2,4,6-trinitrobenzyl anion (*6*) less π-electron charge (-0.21) remains on the methylene carbon (C_7). The exocyclic carbon-carbon bonds ($C_4 - C_7$) have much double bond character. In the anion *6*, as in the anions *5* and *7*, the calculated charges for the three nitro groups are almost identical.

In contrast to experiments, more than one electronic transition above 400 nm is calculated for the anions *5* and *6*. Due to the low resolution of electronic spectra in solution it is probable that the observed absorption band corresponds to more than one allowed transition. Although the anion *5* only has one broad absorption in the visible region,[5] the corresponding indene derivative, 2,4,6-trinitrophenylindenyl anion, has two bands in the same region of the spectrum.[5] Thus it is assumed that all five calculated electronic transitions for *5* contribute to the observed strong absorption centered at 542 nm. In the same way it is assumed that the two calculated transitions of the anion *6* at 600 and 457 nm are observed as one strong band at 510 nm.[13]

REFERENCES

1. Foster, R. *Molecular Complexes*, Academic, London 1969.
2. Strauss, M. J. *Chem. Rev.* **70** (1970) 667.
3. Nilsson, M., Ullenius, C. and Wennerström, O. *Tetrahedron Letters* **1971** 2713.
4. Wahren, R. and Wennerström, O. *Acta Chem. Scand.* **24** (1970) 3064.
5. Moberg, C. and Wennerström, O. *Acta Chem. Scand.* **25** (1971) 2871.
6. Wennerström, H. and Wennerström, O. *Acta Chem. Scand.* **26** (1972) 2883.
7. Fischer-Hjalmars, I. *J. Chem. Phys.* **42** (1965) 1962.
8. Roos, B. and Skancke, P. N. *Acta Chem. Scand.* **21** (1967) 233.
9. Gropen, O. and Skancke, P. N. *Acta Chem. Scand.* **23** (1969) 2685, and references therein.
10. See for example Ref. 1, p. 42.
11. Derrick, P. J., Åsbrink, L., Edqvist, O. and Lindholm, E. *Spectrochim. Acta* **A 27** (1971) 2525.
12. Kraak, A. and Wynberg, H. *Tetrahedron* **24** (1968) 3881.
13. Caldin, E. F. and Long, G. *Proc. Roy. Soc.* **A 228** (1955) 263.