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Ab initio Calculations for the Electronic Structure of Carbazole and Trinitrofluorenone

I. P. Batra, P. S. Bagus, E. Clementi, and H. Seki
IBM Research Laboratory, San Jose, California 95193

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The results of the SCF–LCAO–MO calculations for the electronic structure of carbazole and trinitrofluorenone are reported. Comparison is made with previous computations and with experimental data. A qualitative calculation tends to explain satisfactorily the first electro-absorption peak in amorphous films of polyvinylcarbazole and trinitrofluorenone on the basis of a complete charge transfer model. The singlet-triplet splitting predicted for carbazole also compares favorably with the experimental results.

Key words: Carbazole – Trinitrofluorenone

1. Introduction

The SCF–LCAO–MO approximation has been used in the study of the electronic structure of carbazole ($C_{12}NH_9$; hereafter denoted as CZ) and of 2:4:7 trinitro-9-fluorenone ($C_{13}N_3O_7H_5$; hereafter denoted as TNF). A previously described computer program [1], called IBMOL-5, has been used for the computations here reported. The basis set which describes the one-electron functions is a gaussian set of contracted type [2]. The CZ and TNF molecules have been studied in the SCF–Xα–SW approximation recently [3] and the CZ molecule has been investigated before using semiempirical techniques [4, 5]. The main approximations of the present work are neglect of electron correlation and truncation of the basis set to a minimal basis set: the atoms are described with 2 gaussians for the 1*s* orbitals, 2 gaussians for the 2*s* orbitals, and 2 gaussians for the $2p_x$, $2p_y$ and $2p_z$ orbitals. Comparison with previous computations [3–5] and with experimental data are reported. It is noted that the CZ and TNF compounds are of interest because of the important role they play in the IBM photocopier [6].

Table 1 lists the molecular geometry used in computing CZ and is compiled from X-ray data [7]. This molecule belongs to the C_{2v} symmetry group and we have chosen the principal axis of symmetry as the y axis. The other axis in the molecular plane is the x axis, and the axis perpendicular to the molecular plane is the z axis. A schematic structure of the carbazole molecule is shown in Fig. 1 along with bond lengths (in Å) and bond angles (in degrees).

Table 2 displays the molecular geometry used in computing TNF. This molecule belongs to the C_s symmetry group and is placed in the $x-y$ plane. X-ray data on TNF was not available at the time these calculations were ini-

Table 1. Molecular geometry for the carbazole molecule[a]

Center	x	y
C(21)	-4.685950	-3.210440
C(22)	-6.464800	-1.296160
C(23)	-5.748530	1.229020
C(24)	-3.210620	1.890100
C(25)	3.210620	1.890100
C(26)	5.748530	1.229020
C(27)	6.464800	-1.296160
C(28)	4.685950	-3.210440
C(29)	-2.155100	-2.522830
C(30)	-1.378970	0.0
C(31)	1.378970	0.0
C(32)	2.155100	-2.522830
H(21)	-5.226620	-4.807780
H(22)	-8.264660	-1.698480
H(23)	-7.180840	2.641460
H(24)	-2.759140	3.507090
H(25)	2.759140	3.507090
H(26)	7.180840	2.641460
H(27)	8.264660	-1.698480
H(28)	5.226620	-4.807780
H(29)	0.0	-5.893910
N(01)	0.0	-4.081590

[a] Distances are given in atomic units; the value of the *Z* coordinate is zero.

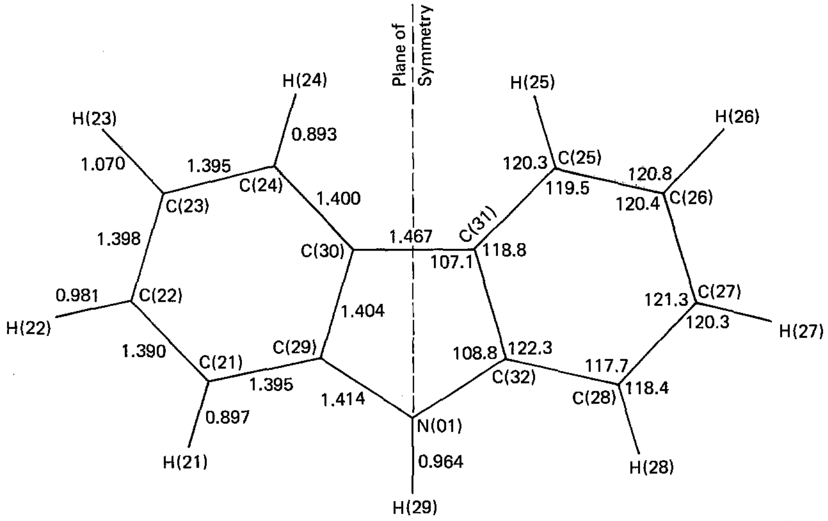

Fig. 1. The structure of the carbazole molecule. Numbers assigned to the atoms are indicated in parentheses. Bond lengths in Å are shown on the left and bond angles on the right side of the drawing. The *Y*-axis is chosen along the axis of rotational symmetry, the *X*-axis in the plane of the molecule and the *Z*-axis out of the plane of the molecule

Table 2. Molecular geometry for the 2,4,7-trinitro-9 fluorenone molecule[a]

Center	x	y
C(01)	-4.733600	-3.052000
C(02)	-6.495700	-1.122300
C(03)	-5.705500	1.368600
C(04)	-3.153300	1.929700
C(05)	3.153300	1.929700
C(06)	5.705500	1.368600
C(07)	6.495700	-1.122300
C(08)	4.733600	-3.052000
C(09)	-2.181300	-2.490900
C(10)	-1.391200	0.0
C(11)	1.391200	0.0
C(12)	2.181300	-2.490900
C(13)	0.0	-4.029700
H(01)	-5.347500	-4.987400
H(03)	-7.074600	2.867900
H(05)	2.539400	3.865100
H(06)	7.074600	2.867900
H(08)	5.347500	-4.987400
N(02)	-9.066300	-1.687500
N(04)	-2.357400	4.438500
N(07)	9.066300	-1.687500
O(13)	0.0	-6.417300
O(21)	-9.754100	-3.855800
O(22)	-10.600200	-0.007600
O(41)	-3.891300	6.118400
O(42)	-0.135700	4.927000
O(71)	9.754100	-3.855800
O(72)	10.600200	-0.007600

[a] Distances are given in atomic units; the value of the Z-coordinate is zero.

tiated, but are available now [8]. We have not recomputed our results because the calculated energy level is insensitive to small errors in atomic positions. A schematic structure of the TNF molecule is shown in Fig. 2.

In Table 3 we report the orbital exponents for the Gaussian functions and their symmetry type (s, p_x, p_y, p_z) for C, H, N, O. We used 148 Gaussians for CZ and 240 for TNF. The orbital exponents were optimized for the separated atoms. In Table 4 the 148 Gaussians for carbazole are contracted to 74 using the expansion coefficients obtained from the computations of the separated atoms. In Table 5 the contracted Gaussians are collected into symmetry-adapted functions which transform as the irreducible representations of the C_{2v} symmetry group. In Table 6 the 240 Gaussians for TNF are contracted to 120 using the expansion coefficients obtained from the computations of the separated atoms.

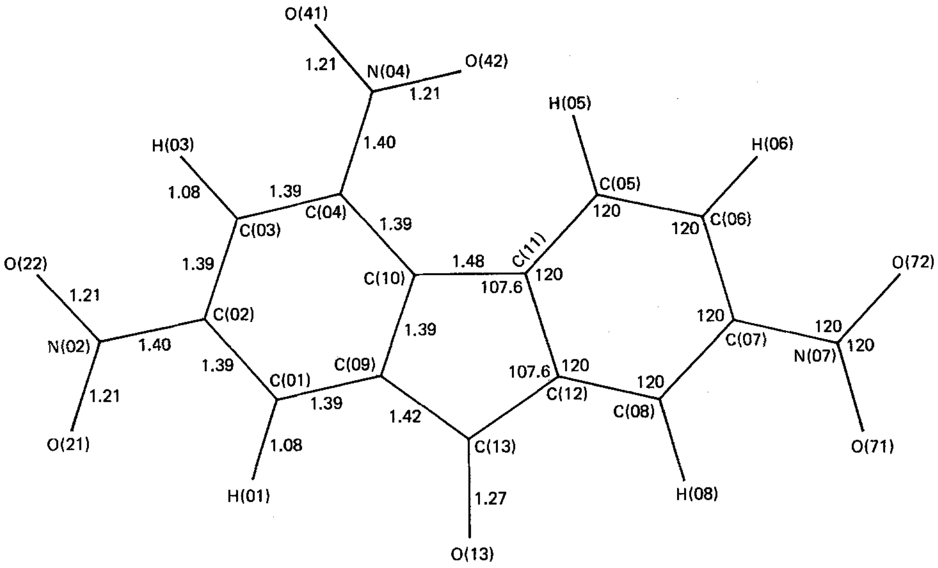

Fig. 2. The trinitrofluorenone (TNF) molecule. Numbers assigned to the atoms are indicated in parentheses. Bond lengths in Å and bond angles chosen for the calculation are also shown. The molecule was placed in the X–Y plane

Table 3. Orbital exponents for various elements in carbazole and TNF in the uncontracted gaussian set

Element	Type	Orbital Exponents
C	s	49.625
C	s	7.177
C	s	0.522
C	s	0.173
C	x,y,z	1.560
C	x,y,z	0.280
H	s	1.333
H	s	0.201
N	s	68.597
N	s	9.983
N	s	0.750
N	s	0.240
N	x,y,z	2.338
N	x,y,z	0.415
O	s	88.127
O	s	12.851
O	s	0.753
O	s	0.269
O	x,y,z	3.175
O	x,y,z	0.547

Table 4. Contracted gaussian set for carbazole

	Contracted Gaussian	Type	Center
A_1, B_2 (σ)	$\gamma_1 = 0.244156\alpha_1 + 0.799063\alpha_2$	s;1s	C(21)
	$\gamma_2 = 0.398814\alpha_3 + 0.677527\alpha_4$	s;2s	C(21)
	$\gamma_3 = 0.339894\alpha_5 + 0.803535\alpha_6$	x;$2p_x$	C(21)
	$\gamma_4 = 0.339894\alpha_7 + 0.803535\alpha_8$[a]	y;$2p_y$	C(21)
	$\gamma_{49} = 0.274350\alpha_{97} + 0.821276\alpha_{98}$[b]	s;1s	H(21)
	$\gamma_{58} = 0.242693\alpha_{115} + 0.794066\alpha_{116}$	s;1s	N(01)
	$\gamma_{59} = 0.411884\alpha_{117} + 0.669260\alpha_{118}$	s;2s	N(01)
	$\gamma_{60} = 0.344259\alpha_{119} + 0.801400\alpha_{120}$	x;$2p_x$	N(01)
	$\gamma_{61} = 0.344259\alpha_{121} + 0.801400\alpha_{122}$	y;$2p_y$	N(01)
A_2, B_1 (π)	$\gamma_{62} = 0.339894\alpha_{123} + 0.803535\alpha_{124}$[c]	z;$2p_z$	C(21)
	$\gamma_{74} = 0.344259\alpha_{147} + 0.801400\alpha_{148}$	z;$2p_z$	N(01)

[a] $\gamma_5, \gamma_6, \gamma_7, \gamma_8$ [centered on $C(22)$], $\gamma_9, \gamma_{10}, \gamma_{11}, \gamma_{12}$, [centered on $C(23)$] …, $\gamma_{45}, \gamma_{46}, \gamma_{47}, \gamma_{48}$ [centered on $C(32)$] are not reported since there is a one-to-one correspondence between these and $\gamma_1, \gamma_2, \gamma_3, \gamma_4$.

[b] $\gamma_{50}, \gamma_{51}, \gamma_{52}, \gamma_{53}, \gamma_{54}, \gamma_{55}, \gamma_{56}, \gamma_{57}$ [centered on $H(22)$, $H(23)$, $H(24)$, $H(25)$, $H(26)$, $H(27)$, $H(28)$, $H(29)$, respectively] are not reported since there is a one-to-one correspondence between these and γ_{49}.

[c] $\gamma_{63}, \gamma_{64}, \ldots, \gamma_{73}$ [centered on $C(22)$, $C(23)$, …, $C(32)$, respectively] are not reported since there is a one-to-one correspondence between those and γ_{62}.

No further symmetry-adapted combinations can be formed because these functions already transform according to the irreducible representations of the C_s symmetry group.

2. Results and Discussion

It is convenient to discuss the results for carbazole (CZ) and trinitrofluorenone (TNF) in separate subsections.

A. The Carbazole Molecule

The calculated total energy and the orbital energies are given in Table 7. The orbital energies are also shown in Fig. 3 labeled according to the various irreducible representations of the C_{2v} symmetry group. In the ground state there are 20 molecular orbitals occupied in A_1 representation, 17 in B_2 representation, 4 in B_1 representation, and 3 in A_2 representation. There are 74 σ electrons and 14 π electrons. The π electron configuration in ground state is: $1b_1^2\, 1a_2^2\, 2b_1^2\, 3b_1^2\, 2a_2^2\, 3a_2^2\, 4b_1^2$. The $1a_1 - 7a_1$, $1b_2 - 6b_2$ are core orbitals which represent the $1s$ electrons for the nitrogen and for the carbon atoms. The remaining σ molecular orbitals are generally delocalized.

The calculation predicts 4 occupied π orbitals in B_1 representation and 3 in A_2 representation. This is because the $2p_z$ orbital of the nitrogen atom is per-

Table 5. Symmetry-adapted functions for carbazole (unnormalized)

A_1 (σ)	B_2 (σ)	B_1 (π)	A_2 (π)
$\chi_1 = \Upsilon_1 + \Upsilon_{29}$	$\chi_{33} = \Upsilon_1 - \Upsilon_{29}$	$\chi_{62} = \Upsilon_{62} + \Upsilon_{69}$	$\chi_{69} = \Upsilon_{62} - \Upsilon_{69}$
$\chi_2 = \Upsilon_2 + \Upsilon_{30}$	$\chi_{34} = \Upsilon_2 - \Upsilon_{30}$	$\chi_{63} = \Upsilon_{63} + \Upsilon_{68}$	$\chi_{70} = \Upsilon_{63} - \Upsilon_{68}$
$\chi_3 = \Upsilon_3 - \Upsilon_{31}$	$\chi_{35} = \Upsilon_3 + \Upsilon_{31}$	$\chi_{64} = \Upsilon_{64} + \Upsilon_{67}$	$\chi_{71} = \Upsilon_{64} - \Upsilon_{67}$
$\chi_4 = \Upsilon_4 + \Upsilon_{32}$	$\chi_{36} = \Upsilon_4 - \Upsilon_{32}$	$\chi_{65} = \Upsilon_{65} + \Upsilon_{66}$	$\chi_{72} = \Upsilon_{65} - \Upsilon_{66}$
$\chi_5 = \Upsilon_5 + \Upsilon_{25}$	$\chi_{37} = \Upsilon_5 - \Upsilon_{25}$	$\chi_{66} = \Upsilon_{70} + \Upsilon_{73}$	$\chi_{73} = \Upsilon_{70} - \Upsilon_{73}$
$\chi_6 = \Upsilon_6 + \Upsilon_{26}$	$\chi_{38} = \Upsilon_6 - \Upsilon_{26}$	$\chi_{67} = \Upsilon_{71} + \Upsilon_{72}$	$\chi_{74} = \Upsilon_{71} - \Upsilon_{72}$
$\chi_7 = \Upsilon_7 - \Upsilon_{27}$	$\chi_{39} = \Upsilon_7 + \Upsilon_{27}$	$\chi_{68} = \Upsilon_{74}$	
$\chi_8 = \Upsilon_8 + \Upsilon_{28}$	$\chi_{40} = \Upsilon_8 - \Upsilon_{28}$		
$\chi_9 = \Upsilon_9 + \Upsilon_{21}$	$\chi_{41} = \Upsilon_9 - \Upsilon_{21}$		
$\chi_{10} = \Upsilon_{10} + \Upsilon_{22}$	$\chi_{42} = \Upsilon_{10} - \Upsilon_{22}$		
$\chi_{11} = \Upsilon_{11} - \Upsilon_{23}$	$\chi_{43} = \Upsilon_{11} + \Upsilon_{23}$		
$\chi_{12} = \Upsilon_{12} + \Upsilon_{24}$	$\chi_{44} = \Upsilon_{12} - \Upsilon_{24}$		
$\chi_{13} = \Upsilon_{13} + \Upsilon_{17}$	$\chi_{45} = \Upsilon_{13} - \Upsilon_{17}$		
$\chi_{14} = \Upsilon_{14} + \Upsilon_{18}$	$\chi_{46} = \Upsilon_{14} - \Upsilon_{18}$		
$\chi_{15} = \Upsilon_{15} - \Upsilon_{19}$	$\chi_{47} = \Upsilon_{15} + \Upsilon_{19}$		
$\chi_{16} = \Upsilon_{16} + \Upsilon_{20}$	$\chi_{48} = \Upsilon_{16} - \Upsilon_{20}$		
$\chi_{17} = \Upsilon_{33} + \Upsilon_{45}$	$\chi_{49} = \Upsilon_{33} - \Upsilon_{45}$		
$\chi_{18} = \Upsilon_{34} + \Upsilon_{46}$	$\chi_{50} = \Upsilon_{34} - \Upsilon_{46}$		
$\chi_{19} = \Upsilon_{35} - \Upsilon_{47}$	$\chi_{51} = \Upsilon_{35} + \Upsilon_{47}$		
$\chi_{20} = \Upsilon_{36} + \Upsilon_{48}$	$\chi_{52} = \Upsilon_{36} - \Upsilon_{48}$		
$\chi_{21} = \Upsilon_{37} + \Upsilon_{41}$	$\chi_{53} = \Upsilon_{37} - \Upsilon_{41}$		
$\chi_{22} = \Upsilon_{38} + \Upsilon_{42}$	$\chi_{54} = \Upsilon_{38} - \Upsilon_{42}$		
$\chi_{23} = \Upsilon_{39} - \Upsilon_{43}$	$\chi_{55} = \Upsilon_{39} + \Upsilon_{43}$		
$\chi_{24} = \Upsilon_{40} + \Upsilon_{44}$	$\chi_{56} = \Upsilon_{40} - \Upsilon_{44}$		
$\chi_{25} = \Upsilon_{49} + \Upsilon_{56}$	$\chi_{57} = \Upsilon_{49} - \Upsilon_{56}$		
$\chi_{26} = \Upsilon_{50} + \Upsilon_{55}$	$\chi_{58} = \Upsilon_{50} - \Upsilon_{55}$		
$\chi_{27} = \Upsilon_{51} + \Upsilon_{54}$	$\chi_{59} = \Upsilon_{51} - \Upsilon_{54}$		
$\chi_{28} = \Upsilon_{52} + \Upsilon_{53}$	$\chi_{60} = \Upsilon_{52} - \Upsilon_{53}$		
$\chi_{29} = \Upsilon_{57}$	$\chi_{61} = \Upsilon_{60}$		
$\chi_{30} = \Upsilon_{58}$			
$\chi_{31} = \Upsilon_{59}$			
$\chi_{32} = \Upsilon_{61}$			

mitted in B_1 representation but not in A_2. The general electronic structure predicted here is similar to the one found in the SCF–Xα method [3]. The main difference is that the levels are compressed closely in the latter approach [3].

The gross population of charges on the individual atoms is reported in Table 8. The electronic configuration for the separated atoms is

$$\text{C: } 1s^2\, 2s^2\, 2p_\sigma^1\, 2p_\pi^1 ,$$

$$\text{N: } 1s^2\, 2s^2\, 2p_\sigma^2\, 2p_\pi^1 ,$$

$$\text{H: } 1s^1 ,$$

Table 6. Contracted gaussian set for TNF

	Contracted Gaussian	Type	Center
A' (σ)	$\gamma_1 = 0.244156\ \alpha_1 + 0.799063\ \alpha_2$	s;1s	C(01)
	$\gamma_2 = 0.398814\ \alpha_3 + 0.677527\ \alpha_4$	s;2s	C(01)
	$\gamma_3 = 0.339894\ \alpha_5 + 0.803535\ \alpha_6$	x;$2p_x$	C(01)
	$\gamma_4 = 0.339894\ \alpha_7 + 0.803535\ \alpha_8$ [a]	y;$2p_y$	C(01)
	$\gamma_{53} = 0.274350\ \alpha_{105} + 0.821276\ \alpha_{106}$ [b]	s;1s	H(01)
	$\gamma_{58} = 0.242693\ \alpha_{115} + 0.794066\ \alpha_{116}$	s;1s	N(02)
	$\gamma_{59} = 0.411884\ \alpha_{117} + 0.669260\ \alpha_{118}$	s;2s	N(02)
	$\gamma_{60} = 0.344259\ \alpha_{119} + 0.801400\ \alpha_{120}$	x;$2p_x$	N(02)
	$\gamma_{61} = 0.344259\ \alpha_{121} + 0.801400\ \alpha_{122}$ [c]	y;$2p_y$	N(02)
	$\gamma_{70} = 0.249186\ \alpha_{139} + 0.806631\ \alpha_{140}$	s;1s	O(13)
	$\gamma_{71} = 0.643571\ \alpha_{141} + 0.429845\ \alpha_{142}$	s;2s	O(13)
	$\gamma_{72} = 0.351888\ \alpha_{143} + 0.799187\ \alpha_{144}$	x;$2p_x$	O(13)
	$\gamma_{73} = 0.351888\ \alpha_{145} + 0.799187\ \alpha_{146}$ [d]	y;$2p_y$	O(13)
A" (π)	$\gamma_{98} = 0.339894\ \alpha_{195} + 0.803535\ \alpha_{196}$ [e]	z;$2p_z$	C(01)
	$\gamma_{111} = 0.344259\ \alpha_{221} + 0.801400\ \alpha_{222}$ [f]	z;$2p_z$	N(02)
	$\gamma_{114} = 0.351888\ \alpha_{227} + 0.799187\ \alpha_{228}$ [g]	z;$2p_z$	O(13)

[a] $\gamma_5, \gamma_6, \gamma_7, \gamma_8$ [centered on *C*(02)], $\gamma_9, \gamma_{10}, \gamma_{11}, \gamma_{12}$ [centered on *C*(03)], ..., $\gamma_{49}, \gamma_{50}, \gamma_{51}, \gamma_{52}$ [centered on *C*(13)] are not reported since there is a one-to-one correspondence between these and $\gamma_1, \gamma_2, \gamma_3, \gamma_4$.

[b] $\gamma_{54}, \gamma_{55}, \gamma_{56}, \gamma_{57}$ [centered on *H*(03), *H*(05), *H*(06), *H*(08), respectively] are not reported since there is a one-to-one correspondence between these and γ_{53}.

[c] $\gamma_{62}, \gamma_{63}, \gamma_{64}, \gamma_{65}$ [centered on *N*(04)], $\gamma_{66}, \gamma_{67}, \gamma_{68}, \gamma_{69}$ [centered on *N*(07)] are not reported since there is a one-to-one correspondence between these and $\gamma_{58}, \gamma_{59}, \gamma_{60}, \gamma_{61}$.

[d] $\gamma_{74}, \gamma_{75}, \gamma_{76}, \gamma_{77}$ [centered on *O*(21)], ..., $\gamma_{94}, \gamma_{95}, \gamma_{96}, \gamma_{97}$ [centered on *O*(72)] are not reported since there is a one-to-one correspondence between these and $\gamma_{70}, \gamma_{71}, \gamma_{72}, \gamma_{73}$.

[e] $\gamma_{99}, \gamma_{100}, \ldots, \gamma_{110}$ [centered on *C*(02), *C*(03), ..., *C*(13), respectively] are not reported since there is a one-to-one correspondence between these and γ_{98}.

[f] $\gamma_{112}, \gamma_{113}$ [centered on *N*(04), *N*(07), respectively] are not reported since there is a one-to-one correspondence between these and γ_{111}.

[g] $\gamma_{115}, \gamma_{116}, \ldots, \gamma_{120}$ [centered on *O*(21), *O*(22), ..., *O*(72), respectively] are not reported since there is a one-to-one correspondence between these and γ_{114}.

and for the atoms in carbazole is

$$\mathrm{N}:\ 1s^{1.96}\, 2s^{1.43}\, 2p_{\sigma_x}^{1.12}\, 2p_{\sigma_y}^{1.23}\, 2p_{\pi}^{1.69}\,,$$

$$\mathrm{C}:\ 1s^{1.96}\, 2s^{1.04}\, 2p_{\sigma_x}^{1.05}\, 2p_{\sigma_y}^{1.06}\, 2p_{\pi}^{1.03}\,,$$

$$\mathrm{H}:\ 1s^{0.77}\,.$$

It is also worth noting that the nitrogen atom has an excess negative charge.

Table 7. Total energy[a] and orbital energies (in atomic units)

A_1 (σ)	B_2 (σ)	B_1 (π)	A_2 (π)
ε_1 = -15.154346	ε_1 = -11.053484	ε_1 = -0.649873	ε_1 = -0.562055
ε_2 = -11.050204	ε_2 = -11.030911	ε_2 = -0.519070	ε_2 = -0.412985
ε_3 = -11.028821	ε_3 = -11.025506	ε_3 = -0.451183	ε_3 = -0.355872
ε_4 = -11.023996	ε_4 = -11.004840	ε_4 = -0.343790	
ε_5 = -11.004423	ε_5 = -11.004019		
ε_6 = -10.988484	ε_6 = -10.984267		
ε_7 = -10.982244	ε_7 = - 1.207052		
ε_8 = - 1.334883	ε_8 = - 1.084820		
ε_9 = - 1.190820	ε_9 = - 1.047194		
ε_{10} = - 1.117079	ε_{10} = - 0.883004		
ε_{11} = - 1.049841	ε_{11} = - 0.856079		
ε_{12} = - 0.942818	ε_{12} = - 0.762571		
ε_{13} = - 0.869417	ε_{13} = - 0.695757		
ε_{14} = - 0.796583	ε_{14} = - 0.655647		
ε_{15} = - 0.744428	ε_{15} = - 0.648252		
ε_{16} = - 0.702234	ε_{16} = - 0.573969		
ε_{17} = - 0.665578	ε_{17} = - 0.542882		
ε_{18} = - 0.639813			
ε_{19} = - 0.567950			
ε_{20} = - 0.537785			

[a] Total energy = −498.1267646 a.u.

The lowest ionization potential for carbazole obtained by taking the difference of the total energies for the molecule and the positive ion was found to be 8.6 eV. If one used Koopmans' theorem instead which ignores relaxation effects the value was 9.4 eV. Our calculated value of 8.6 eV is in good agreement with an experimental value [7] of 7.6 eV. An SCF–Xα calculation [3] predicts about 17 eV; this unrealistic result is due to the muffin-tin approximation in their calculation. The dipole moment in Debyes, $\boldsymbol{\mu} = (0.0, -1.66, 0.0)$ with $|\boldsymbol{\mu}| = 1.66$.

An approximate understanding of the optical spectrum of carbazole can be obtained by carrying out spin-polarized calculations for the excited states. Four principal peaks in the photoabsorption spectrum of carbazole in ethanol have been observed [10] and Emolaev [11] has identified the lowest triplet in fluorescence spectrum. Our calculated values along with these experimental results and earlier [3–5] theoretical results are presented in Table 9. For the Hartree-

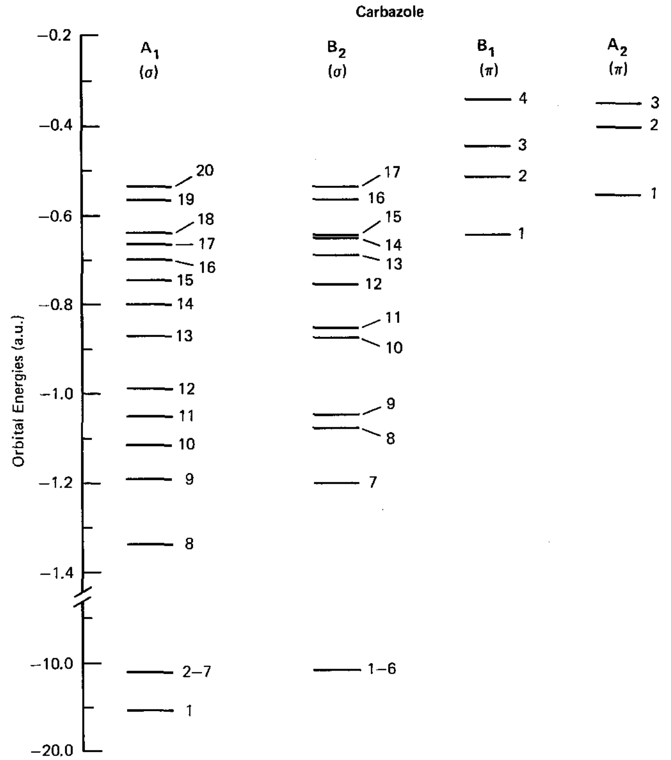

Fig. 3. The calculated ground state energy eigenvalues of carbazole labeled according to the various irreducible representations of the C_{2v} symmetry group. σ orbitals belong to the A_1 and B_2 representations, and π orbitals belong to the A_2 and B_1 representations

Table 8. Carbazole – gross population analysis

Center	1s	2s	$2p_x$	$2p_y$	$2p_z$	Total
C(21)	1.96	1.07	1.03	1.17	1.10	6.33
C(22)	1.96	1.09	1.15	1.04	0.98	6.22
C(23)	1.96	1.08	1.06	1.06	1.03	6.19
C(24)	1.96	1.08	1.06	1.18	1.01	6.29
C(25)	1.96	1.08	1.06	1.18	1.01	6.29
C(26)	1.96	1.08	1.06	1.06	1.03	6.19
C(27)	1.96	1.08	1.15	1.04	0.98	6.21
C(28)	1.96	1.07	1.03	1.17	1.10	6.33
C(29)	1.96	1.00	0.95	0.95	0.97	5.83
C(30)	1.96	1.00	1.01	1.00	1.06	6.03
C(31)	1.96	1.00	1.01	1.00	1.06	6.03
C(32)	1.96	1.00	0.95	0.95	0.97	5.83
H(21)	0.76	-	-	-	-	0.76
H(22)	0.77	-	-	-	-	0.77
H(23)	0.79	-	-	-	-	0.79
H(24)	0.76	-	-	-	-	0.76
H(25)	0.76	-	-	-	-	0.76
H(26)	0.79	-	-	-	-	0.79
H(27)	0.77	-	-	-	-	0.77
H(28)	0.76	-	-	-	-	0.76
H(29)	0.64	-	-	-	-	0.64
N(01)	1.96	1.42	1.12	1.23	1.69	7.43
Total	32.28	14.05	13.64	14.03	14.00	88.00

Table 9a. Energies of excited states of carbazole (in electron volts)

Transition	Hartree Fock Calculations		Experiment	Calculations by Mataga et al[c]		Calculation by Pinkham et al[d]
	Using Koopman's Theorem	With Orbital Relaxation		Approximation A	Approximation B	
$(4b_1 \rightarrow 5b_1)\ {}^1A_1$	7.04	5.22	3.69[a]	5.23	4.84	3.45
$(3a_2 \rightarrow 5b_1)\ {}^1B_2$	7.14	6.65	4.22[a]	5.68	5.76	3.76
$(3a_2 \rightarrow 4a_2)\ {}^1A_1$	8.62	6.71	4.82[a]	6.53	6.16	-
$(4b_1 \rightarrow 4a_2)\ {}^1B_2$	7.93	6.88	5.30[a]	6.65	6.47	-
$(3a_2 \rightarrow 5b_1)\ {}^3B_2$	5.24	4.81	3.04[b]	-	-	-
$(4b_1 \rightarrow 5b_1)\ {}^3A_1$	5.43	4.84	-	-	-	-
$(4b_1 \rightarrow 4a_2)\ {}^3B_2$	6.39	6.01	-	-	-	-
$(3a_2 \rightarrow 4a_2)\ {}^3A_1$	6.73	6.41	-	-	-	-

[a] See Ref. [10]. [b] See Ref. [11]. [c] See Ref. [4]. [d] See Ref. [5].

Table 9b. Weighted singlet-triplet average excitation energies for carbazole (in electron volts)

Transition	Hartree-Fock Calculation	SCF-Xα-SW Calculation[a]
$4b_1 \rightarrow 5b_1$	4.94	2.72
$3a_2 \rightarrow 5b_1$	5.27	3.13
$4b_1 \rightarrow 4a_2$	6.23	3.15
$3a_2 \rightarrow 4a_2$	6.49	3.68

[a] See Ref. [3].

Fock calculations being reported here we have presented the Koopmans' theorem values and also the results of a fully self-consistent field calculation. As expected, the relaxation effects lower the excitation energy. The interesting point is that the ordering of the transitions ${}^1A_1$ ($3a_2 \rightarrow 4a_2$) and ${}^1B_2$ ($4b_1 \rightarrow 4a_2$) is interchanged upon including relaxation effects. Our calculations predict four peaks in the photoabsorption spectrum lying in the range 5.22 eV – 6.88 eV. These results are in good agreement with Mataga *et al.* [4] but as a rule give higher values than the experimentally observed ones. An important reason for this discrepancy is the use of a minimal basis set. Predicted singlet-triplet splitting of 0.41 eV compares favorably with the experimental value [11] of 0.65 eV.

A comparison of our results with the SCF–Xα-scattered wave calculations is carried out in Table 6. Since the latter method gives a weighted average of singlet-triplet excitation energy, we have calculated the same for the Hartree-Fock calculations including orbital relaxation. Both calculations predict the same ordering but the values differ by about a factor of two.

B. *The Trinitrofluorenone Molecule*

It is important to investigate this molecule because it is a well known photosensitizer [6]. A mixture of TNF with poly-*n*-vinylcarbazole (PVK) shows [12] an absorption band extended over the whole visible region, whereas the individual components absorb only in the ultra-violet region. This is believed [9, 12] to be due to the formation of a charge transfer complex with the carbazole group of PVK as donor molecule and TNF as acceptor. Since we have described the electronic structure of CZ above, it should be possible for us to make some remarks about the complex after discussing the TNF molecule.

The calculated total energy and the orbital energies for TNF are listed in Table 10. The orbital energies are also shown in Fig. 4 labeled according to the two irreducible representations of the C_s symmetry group. In the ground state there are 67 molecular orbitals occupied in A' representation and 13 in A'' representation. There are 134 σ electrons and 26 π electrons. The $1a' - 23a'$ are core orbitals which represent the 1*s* electrons for the oxygen, nitrogen and carbon atoms. The lone pair state on the oxygen atom attached to the carbon atom in the five membered ring is the orbital $62a'$ and is *not* the highest occupied orbital in a'' symmetry contrary to the prediction in the SCF–Xα method. The highest occupied orbital $67a'$ and $13a''$ are both concentrated on O(71) and O(72) (see Fig. 2). Since the highest occupied π orbtial lies above the σ orbital, the first optical excitation is predicted to be a $\pi \rightarrow \pi^*$. The lowest transition in the SCF–Xα method is predicted to be an $n \rightarrow \pi^*$ transition. Unfortunately there is no experimental data available at the present time which would resolve this issue.

The gross population of charges on the individual atoms in TNF is given in Table 11. All the oxygen atoms on the nitro groups have symmetric charge distribution excepting O(41) and O(42). The atom O(42) is slightly more negative than O(41) because of its close proximity to H(05) which is slightly negative. This polarized situation is also responsible for the dipole moment which is

Table 10. Total energy[a] and orbital energies for TNF (in atomic units)

A' (σ)		A'' (π)
$\varepsilon_{1} = -20.012597$	$\varepsilon_{2} = -19.930325$	$\varepsilon_{1} = -0.806644$
$\varepsilon_{3} = -19.909401$	$\varepsilon_{4} = -19.893832$	$\varepsilon_{2} = -0.786039$
$\varepsilon_{5} = -19.891225$	$\varepsilon_{6} = -19.870589$	$\varepsilon_{3} = -0.763650$
$\varepsilon_{7} = -19.868069$	$\varepsilon_{8} = -15.465658$	$\varepsilon_{4} = -0.699408$
$\varepsilon_{9} = -15.441670$	$\varepsilon_{10} = -15.417493$	$\varepsilon_{5} = -0.620369$
$\varepsilon_{11} = -11.128928$	$\varepsilon_{12} = -11.125345$	$\varepsilon_{6} = -0.582131$
$\varepsilon_{13} = -11.116940$	$\varepsilon_{14} = -11.096640$	$\varepsilon_{7} = -0.513435$
$\varepsilon_{15} = -11.091712$	$\varepsilon_{16} = -11.086552$	$\varepsilon_{8} = -0.477789$
$\varepsilon_{17} = -11.076758$	$\varepsilon_{18} = -11.071784$	$\varepsilon_{9} = -0.438909$
$\varepsilon_{19} = -11.041104$	$\varepsilon_{20} = -11.028477$	$\varepsilon_{10} = -0.431477$
$\varepsilon_{21} = -11.018345$	$\varepsilon_{22} = -10.987155$	$\varepsilon_{11} = -0.418235$
$\varepsilon_{23} = -10.977747$	$\varepsilon_{24} = -1.686934$	$\varepsilon_{12} = -0.393327$
$\varepsilon_{25} = -1.665605$	$\varepsilon_{26} = -1.643196$	$\varepsilon_{13} = -0.373039$
$\varepsilon_{27} = -1.481837$	$\varepsilon_{28} = -1.449369$	
$\varepsilon_{29} = -1.424364$	$\varepsilon_{30} = -1.401988$	
$\varepsilon_{31} = -1.348884$	$\varepsilon_{32} = -1.286646$	
$\varepsilon_{33} = -1.236891$	$\varepsilon_{34} = -1.208604$	
$\varepsilon_{35} = -1.151832$	$\varepsilon_{36} = -1.114162$	
$\varepsilon_{37} = -1.066403$	$\varepsilon_{38} = -1.052381$	
$\varepsilon_{39} = -1.022434$	$\varepsilon_{40} = -1.000753$	
$\varepsilon_{41} = -0.915346$	$\varepsilon_{42} = -0.900429$	
$\varepsilon_{43} = -0.872477$	$\varepsilon_{44} = -0.843269$	
$\varepsilon_{45} = -0.836152$	$\varepsilon_{46} = -0.808292$	
$\varepsilon_{47} = -0.796227$	$\varepsilon_{48} = -0.791088$	
$\varepsilon_{49} = -0.770856$	$\varepsilon_{50} = -0.758019$	
$\varepsilon_{51} = -0.748472$	$\varepsilon_{52} = -0.720747$	
$\varepsilon_{53} = -0.696118$	$\varepsilon_{54} = -0.686941$	
$\varepsilon_{55} = -0.680190$	$\varepsilon_{56} = -0.665399$	
$\varepsilon_{57} = -0.647866$	$\varepsilon_{58} = -0.633875$	
$\varepsilon_{59} = -0.623994$	$\varepsilon_{60} = -0.564887$	
$\varepsilon_{61} = -0.505719$	$\varepsilon_{62} = -0.495376$	
$\varepsilon_{63} = -0.476646$	$\varepsilon_{64} = -0.458033$	
$\varepsilon_{65} = -0.448578$	$\varepsilon_{66} = -0.446890$	
$\varepsilon_{67} = -0.427426$		

[a] Total energy − 1147.196830 a.u.

directed from the origin towards the nitro group consisting of O(41), N(04) and O(42). The dipole moment in Debyes, $\mu = (-1.89, 0.55, 0.0)$ with $|\mu| = 1.97$. It makes angle of 164° with the x-axis.

As the interesting property of TNF is its ability to accept an excess electron we computed electronic affinities by taking the total energy differences between the TNF molecule and the negative ion. For an excess electron going into a σ orbital, the value was 3.96 eV and for π orbital it was 2.35 eV. Flurry [13] gives a value of 4.32 eV for the lowest electron affinity.

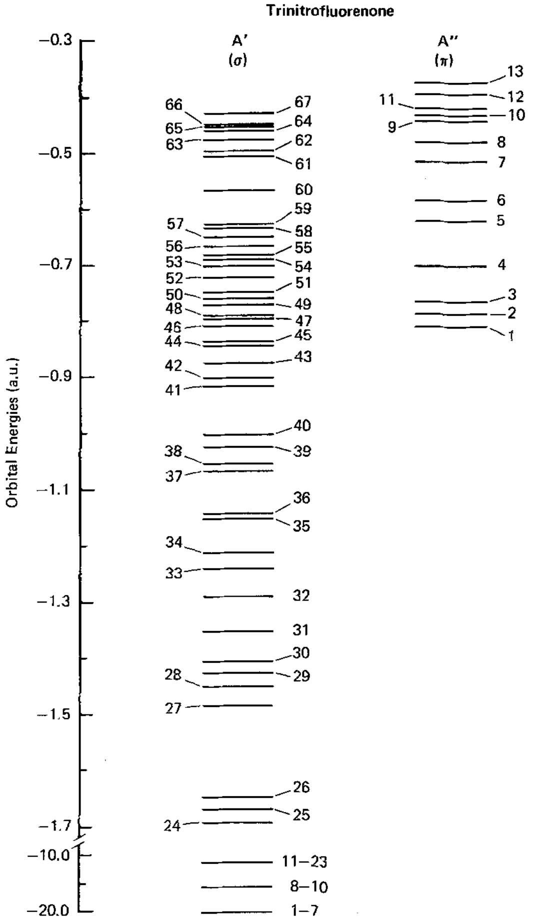

Fig. 4. The calculated ground state energy eigenvalues of trinitrofluorenone labeled according to the two irreducible representations of the C_s symmetry group. σ orbitals belong to the A' representation, and π states belong to the A'' representation

Since CZ and TNF are rather large systems it is not too practical to do a complete self-consistent field calculation for predicting the absorption spectrum of the charge transfer complex. An approximate value for the first absorption peak can however be predicted from simple electrostatic considerations [13] and assuming a complete charge transfer upon illumination. This was done by calculating the maximum coulombic attraction between CZ^+ and TNF^- which we denote by E_m. The detailed charge distribution on each ion was obtained from the gross population which resulted from a complete SCF calculation for each ion. E_m was found to be 2.7 eV when the two molecules are very closely on top of each other with a separation of about 1.5 Å. The absorption peak occurs at

$$\hbar\omega \simeq I.P. - E.A. - E_m ,$$

Table 11. TNF – gross population analysis

Center	1s	2s	$2p_x$	$2p_y$	$2p_z$	Total
C(01)	1.96	1.05	0.98	1.13	0.97	6.09
C(02)	1.96	1.00	0.84	1.04	1.07	5.91
C(03)	1.96	1.09	1.09	1.09	0.95	6.18
C(04)	1.96	0.97	1.07	0.84	1.08	5.92
C(05)	1.96	1.08	1.07	1.25	0.89	6.25
C(06)	1.96	1.09	1.13	1.06	0.97	6.21
C(07)	1.96	1.00	0.84	1.06	1.05	5.91
C(08)	1.96	1.01	1.12	1.11	0.96	6.16
C(09)	1.96	0.95	1.29	1.03	0.96	6.19
C(10)	1.96	1.06	0.98	0.98	0.97	5.95
C(11)	1.96	1.07	0.92	0.95	1.07	5.97
C(12)	1.96	1.02	1.13	1.00	1.02	6.13
C(13)	1.96	0.93	1.04	0.79	1.01	5.73
H(01)	0.74	–	–	–	–	0.74
H(03)	0.71	–	–	–	–	0.71
H(05)	0.70	–	–	–	–	0.70
H(06)	0.75	–	–	–	–	0.75
H(08)	0.76	–	–	–	–	0.76
N(02)	1.97	1.31	1.16	1.07	1.26	6.77
N(04)	1.97	1.31	1.06	1.17	1.25	6.76
N(07)	1.97	1.31	1.17	1.07	1.26	6.78
O(13)	1.99	1.89	1.89	1.35	1.00	8.12
O(21)	1.99	1.87	1.83	1.15	1.37	8.21
O(22)	1.99	1.87	1.52	1.46	1.37	8.21
O(41)	1.99	1.87	1.54	1.45	1.34	8.19
O(42)	1.99	1.83	1.10	1.88	1.43	8.23
O(71)	1.99	1.87	1.84	1.16	1.37	8.23
O(72)	1.99	1.87	1.52	1.46	1.38	8.22
Total	48.98	30.32	28.15	26.55	26.00	160.00

where *I.P.* is the ionization potential ($= 8.6$ eV), *E.A.* the electron affinity ($= 3.96$ eV), and $E_m \simeq 2.7$ eV. This then predicts a photoabsorption peak in the neighborhood of 1.9 eV. Weiser [12] has observed two peaks in the electroabsorption spectrum of amorphous films of polyvinylcarbazole and trinitrofluorenone, one at 2.2 eV and the other at 2.8 eV. This agreement can only be taken as an evidence in support of a complete charge transfer model for the electroabsorption spectrum. A semi-empirical SCF–MO method within the π-electron approximation for computing the electronic structures of charge-transfer complexes has been proposed in the literature [14] but it is also known [13] that a simple electrostatic model like the one we discussed above gives a reasonable estimate.

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Dr. E. Clementi
IBM Research Laboratory
San Jose, California 95193, USA