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AB INITIO SCF MO CALCULATION OF IONISATION ENERGIES AND CHARGE DISTRIBUTIONS OF TCNQ AND ITS MONO- AND DIVALENT ANIONS

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Ab initio SCF MO calculations using a contracted double zeta basis set of 168 gaussian type functions were performed on TCNQ^+ , TCNQ , TCNQ^- and TCNQ^{2-} . The ionisation potentials obtained from total energy differences are generally 0.25-0.50 eV higher than the corresponding negative orbital energies from the TCNQ calculation and in satisfactory agreement with experimental results. The energy of the disproportionation reaction $2\text{TCNQ}^- \rightarrow \text{TCNQ} + \text{TCNQ}^{2-}$ is calculated to be 4.62 eV. The charge distributions as measured by the gross atomic populations generally deviate from those obtained in earlier p -electron calculations as a consequence of taking the s -electron distribution into account. The atomic charges are in good agreement with the limited experimental data available.

1. Introduction

Recently one of the present authors reported on the calculation of a number of properties of the TCNQ (tetracyanoquinodimethane) molecule (fig. 1) and its mono- and divalent anions [1] by means of an SCF MO CI treatment of the p -electron system using the approximations proposed by Pariser, Parr and Pople (PPP) [2]. Since the physical properties of TCNQ in salts, particularly its electrical conductivity [3] continue to be of interest we decided to carry out a more detailed and less approximate theoretical investigation of the electronic wavefunctions. To this end a number of ab initio closed and open shell restricted SCF calculations [4] were performed on the ground states and a variety of excited states of TCNQ^+ , TCNQ , TCNQ^- and TCNQ^{2-} using the same structural parameters as in ref. [1] (see also fig. 1). In this note the results of the calculation for the ground states and for the states of the positive ion will be presented and briefly discussed.

2. Computational details

The calculations were performed with the program system SYMOL developed by one of the authors (van

der Velde). As usual a fixed set of cartesian gaussian basis orbitals is employed to span the function space of the molecular orbitals to be determined. The principal feature of the program is the advantage it takes of any spatial symmetry present in the molecule considered. In particular the integrals needed are computed directly in terms of symmetry adapted basis orbitals so that for symmetric molecules significant savings

Fig. 1. The TCNQ molecule and the internuclear distances [9] used in the calculations.

in computer time and storage can be obtained both in the integral computation section and in the SCF iteration section of the program.

The basis set employed consisted of 63/3 sets (6s, 3p for C and N, 3s for H) of primitive gaussians from which 42/2 sets of contracted functions were constructed. The contraction coefficients and exponents, which were optimized with respect to the total energies of the atoms in their respective ground states, are displayed in table 1. The total basis size amounted to 252 primitive functions and 168 contracted functions. The distribution of the latter over the eight symmetry species of the pointgroup D_{2h} is given in table 2 together with the number of occupied MO's for each species in the ground state electronic configuration.

3. Results

Total energies were obtained from independent SCF calculations on the ground states of TCNQ, TCNQ^- and TCNQ^{2-} and on the states of TCNQ^+ that result when one electron is removed from the highest occupied MO of each symmetry species in

Table 2
Distribution of basis orbitals and occupied molecular orbitals over symmetry species

Type	<i>i</i>	M_i	N_i	Type	<i>i</i>	M_i	N_i
s	a_g	38	13	p	a_u	6	1
s	b_{1g}	30	9	p	b_{1u}	10	3
p	b_{2g}	10	2,3 ^{a)}	s	b_{2u}	30	10
p	b_{3g}	6	2	s	b_{3u}	38	12

^{a)} In the anions.

TCNQ. In table 3 these energies are listed using the energy of TCNQ as the reference state together with the ionisation energies in the same energy region that would follow from the orbital energies obtained in the TCNQ calculation. Included in table 3 are some of the results of ultraviolet excited photoelectron spectroscopy (UPS) measurements on solid TCNQ [10].

The electronic charge distributions corresponding to the molecular orbitals calculated for TCNQ, TCNQ^- and TCNQ^{2-} are summarized in table 4 in terms of

Table 3
Electron affinities and ionisation potentials of TCNQ

Ion	$f^a)$	ΔE (eV) ^{b)}	UPS ^{c)}	$-E^{d)}$
TCNQ^{2-}	$3b_{2g}$	-1.04		
TCNQ^-	$3b_{2g}$	-2.83		
TCNQ^+	$3b_{1u}$	8.38	[8.4]	8.94
	$2b_{3g}$	10.45	10.2	11.69
	$2b_{2g}$	11.69		12.14
	$10b_{2u}$	13.33	11.5-13.5	13.66
	$9b_{1g}$	13.33		13.65
	$1a_u$	13.73		14.01
	$1b_{3g}$		13.9-14.5	14.02
	$12b_{3u}$	13.81		14.07
	$13a_g$	13.93		14.19
	$2b_{1u}$			14.81
	$8b_{1g}$		15.9-16.4	15.26

^{a)} Orbital involved in electron addition or removal.

^{b)} $\Delta E = E(\text{ion}) - E(\text{TCNQ})$.

^{c)} Scaled to let first observed transition coincide with calculated first ionisation energy. Energy ranges indicate broad unresolved bands.

^{d)} Negative orbital energies of TCNQ. The total energy of the TCNQ molecule is -673.054506 au.

Table 1
Exponents and contraction coefficients defining the basis set

Atom	Function	Exponent	Coefficient
carbon	s	490.404	0.03330498
		73.7839	0.23233429
		16.4654	0.81681938
		4.36231	1.
		0.565720	1.
		0.178954	1.
	p	4.19582	0.21144665
		0.856630	0.87965386
		0.200293	1.
nitrogen	s	674.747	0.03324821
		101.781	0.23170689
		22.8280	0.81700124
		6.09211	1.
		0.834888	1.
		0.257130	1.
	p	6.11783	0.21630662
		1.26012	0.87578788
		0.291484	1.
hydrogen	s	4.46834	0.15699764
		0.678538	0.90407691
		0.151055	1.

Table 4
Gross atomic and overlap populations in TCNQ(0), TCNQ⁻(-1) and TCNQ²⁻(-2)

	$N_s^{a)}$			$N_p^{a)}$			$Q^{a)}$			$Q_p^{a)}$		
	0	-1	-2	0	-1	-2	0	-1	-2	0	-1	-2
C ₁	5.13	5.12	5.09	0.97	1.01	1.07	-0.10	-0.13	-0.16	0.01	-0.04	-0.09
C ₂	5.33	5.27	5.21	0.88	0.92	0.98	-0.21	-0.20	-0.18	0.05	0.05	0.02
C ₃	4.68	4.60	4.54	1.13	1.36	1.54	0.19	0.05	-0.07	-0.03	-0.28	-0.42
C ₄	4.94	4.98	5.01	0.97	0.93	0.89	0.09	0.09	0.09	0.20	0.26	0.27
N	6.21	6.21	6.21	1.05	1.17	1.28	-0.26	-0.38	-0.49	-0.22	-0.36	-0.48
H	0.71	0.76	0.81				0.29	0.24	0.19			
C ₁ -C ₂	0.41	0.48	0.55	0.10	0.18	0.26						
C ₂ -C ₃	0.58	0.60	0.61	0.38	0.19	0.01						
C ₃ -C ₄	0.61	0.59	0.58	0.01	0.04	0.09						
C ₄ -N	1.24	1.30	1.35	0.51	0.50	0.48						
C ₁ -H	0.74	0.75	0.75									

^{a)} $N_s(A)$, $N_p(A)$: s and p gross populations on atom A. $N_s(A-B)$, $N_p(A-B)$: s and p overlap population in bond A-B. $Q(A)$ gross charge on atom A. $Q_p(A)$ p -charge on atom A according to ref. [1].

gross atomic and overlap populations and gross charges on the atoms [6]. The condensed, albeit crude, picture of the charge distributions provided by these quantities is well suited to indicate how the excess charge distributes itself in the anions. For comparison purposes the gross charges found in the p -electron calculations of ref. [1] are included. Finally, table 5 shows the spin densities calculated for TCNQ⁻, i.e., the gross atomic populations corresponding to the open shell $3b_{2g}$ orbital. Again the results reported in ref. [1] are included in the table.

4. Discussion

The present results confirm the relatively high stability of the anions found earlier [1] although the energy required for the hypothetical disproportionation process in the gas phase $2\text{TCNQ}^- \rightarrow \text{TCNQ} + \text{TCNQ}^{2-}$ is calculated to be 4.62 eV instead of 3.50 eV. The atomic charges differ substantially from those found previously, which is caused by the shifts in the s -electron distributions that are now taken into account. This has an appreciable influence on the effective charge on the cyanide groups, where the charge on carbon comes out much less positive whereas the nitrogen charge is about the same as in the p -electron

Table 5
Spin densities in TCNQ⁻

Center	This work	PPP [1]
C ₁	0.059	0.066
C ₂	0.109	0.116
C ₃	0.191	0.174
C ₄	0.002	0.012
N	0.039	0.027

calculation in spite of the smaller p -contribution to it. The changes with respect to TCNQ that occur in the charge distributions of the anions are also generally different in the two calculations. The net change in nitrogen charge on going from TCNQ to TCNQ⁻ is not very considerable, however. The presently computed value of 0.12 e for this change as well as the p -electron result of 0.14 e compare well with the value of 0.13 e derived from NQR measurements [5]. The nearly linear dependence of the atomic charges on the ionic charges is worth noting. According to table 5 the calculated spin densities do not show appreciable differences. They are all necessarily positive as a consequence of the restricted orbital formalism employed. Hydrogen and nitrogen coupling constants can be calculated from the relations $A^H = Q_{CH}^H r_C$, $Q_{CH}^H = 23.7\text{G}$ [7] and $A^N = Q_{CN}^N r_C + Q_{NC}^N r_N$, $Q_{CN}^N = -6.3\text{G}$, $Q_{NC}^N = 23.1\text{G}$ [8].

The present results yield $A^N = 0.89\text{G}$ (experimental 1.02G [7]) and $A^H = 1.40\text{G}$ (experimental 1.44G [7]). The calculated ionisation energies finally seem to agree reasonably well with the observed UPS spectrum. With one exception the reorganisation energies, as measured by the difference between the directly computed ionisation energies and those obtained from the orbital energies of TCNQ, are small and lie between $0.25\text{--}0.50\text{ eV}$. The exception occurs for the ${}^2B_{3g}$ state which may be connected with the fact that the $2b_{3g}$ orbital involved primarily consists of p -orbitals on the ring.

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