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THE UV SPECTRA AND THEIR CALCULATION OF TCNQ AND ITS MONO- AND DI-VALENT ANION

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The electronic absorption and emission spectra of TCNQ and its mono- and divalent anions were measured. An SCMO CI calculation in the PPP approximation was performed with one set of parameters for the three species yielding good agreement with experiment. The energy of the disproportionation reaction $2\text{TCNQ}^- \rightarrow \text{TCNQ}^0 + \text{TCNQ}^{2-}$ was estimated at 3.5 eV.

1. Introduction

The TCNQ (tetracyanoquinodimethane) molecule and its radical ion have been of considerable interest in recent years. The properties of TCNQ in salts, especially the investigations on partial paramagnetism and electrical conductivity have received much attention [1].

We here present a further theoretical and experimental study of TCNQ, in particular of its binegative ion, which we succeeded in preparing. Theoretically, TCNQ and TCNQ^{1-} have been studied before by Lowitz [2], but it seemed desirable to compare the calculations for TCNQ, TCNQ^{1-} and TCNQ^{2-} , as was done before for TMPD, TMPD^+ and TMPD^{2+} [3]. In these calculations the effects of the core can be minimized, since it remains essentially the same for the three species. Thus a fairly reliable set of parameters can be obtained which can be of use in other calculations such as those of conduction bands in stacks of TCNQ^{1-} ions [4]. After a short description of the experimental results and a short summary of the theory, we present a comparison of the two.

2. Experimental results

TCNQ was prepared as described by Acker and Hertler [5]. Before use, it was sublimed in vacuo.

For the polarographic measurements a Cambridge polarograph with dropping mercury electrode was used. Solvents were dimethoxy ethane, acetonitrile as an 80/20 mixture of those two with tetra-*n*-butylammonium-perchlorate as a supporting electrolyte. Gelatine was added to obtain good polarograms. All data were taken in a nitrogen atmosphere.

The ESR equipment were a Varian V4503 and an E3 spectrometer with appropriate electrolysis cells. Optical absorption spectra were taken with a Cary-14, emission spectra with an Aminco-Bowman spectrofluorimeter.

A polarographic study of a 10^{-4} molar solution of TCNQ yielded a polarogram with two waves with half-wave potentials at $-0.15 (\pm 0.02)$ and $-0.32 (\pm 0.02)$ V (SCE). The first wave corresponds to the reduction of TCNQ to TCNQ^{1-} , the second to either TCNQ to TCNQ^{2-} or to TCNQ^{1-} to TCNQ^{2-} . The slopes of the waves were too undefined to determine whether a one or two electron reduction took place, although the former seems much more reasonable.

Reductions in an electrolysis cell with Pt electrodes were undertaken. The cell could be used for both UV-VIS and ESR measurements. The electronic spectra obtained after what appeared to be complete electrolysis at 0 V, -0.2 V and -0.5 V are given in fig. 1. It is clear that further reduction of TCNQ^{1-} to TCNQ^{2-} takes place with a new spectrum appearing, while the well known spectrum of TCNQ^{1-} disappears.

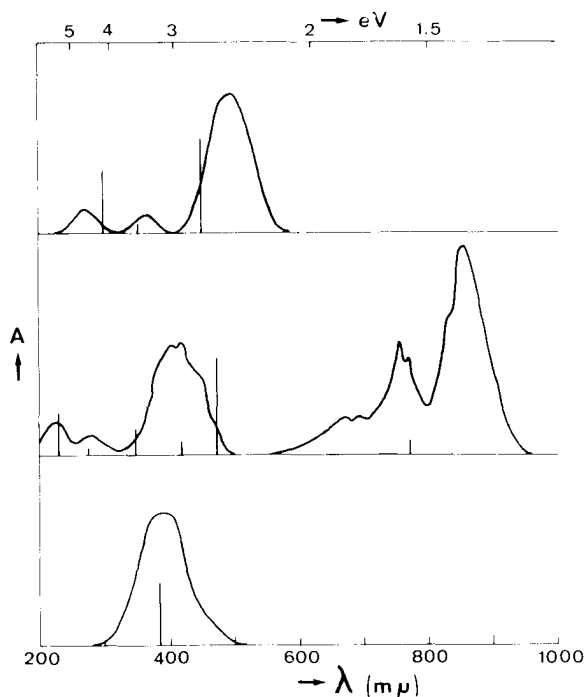


Fig. 1. The UV-VIS absorption spectra of the TCNQ molecule (lower), the TCNQ¹⁻ anion (middle) and the TCNQ²⁻ anion (upper). The theoretical values of the absorptions are indicated by the heavy bars.

ESR measurements confirmed these results. At -0.2 V the strong ESR spectrum of TCNQ¹⁻ appeared and slowly disappeared again at -0.5 V (the coupling constants $a_H = 1.43$ G and $a_N = 1.01$ G were in agreement with those reported earlier [6]). Reversal of the applied voltage made the ESR and UV-VIS spectrum of TCNQ¹⁻ reappear and finally the absorption spectrum of TCNQ was obtained again. Addition of an equimolar amount of TCNQ to the diamagnetic solution electrolysed at -0.5 V yielded the strong ESR spectrum of TCNQ¹⁻. To rule out the possibility of the formation of proton adducts we added a quantity of a base to adjust the pH of the solution to a very high level, which did not affect the spectrum [7]. Therefore we proved beyond doubt that the TCNQ²⁻ is formed in the electrolysis.

In trying to get emission spectra we could not detect any phosphorescence probably because of the very efficient internal quenching of the first excited

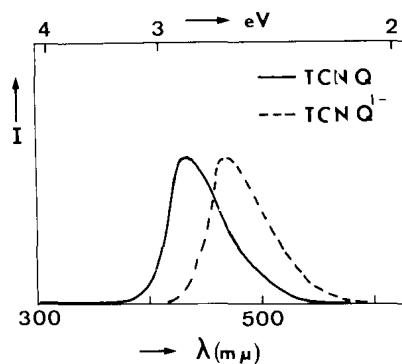


Fig. 2. Fluorescence spectra of the TCNQ molecule and the TCNQ¹⁻ anion.

triplet, originating from the four CN groups. Rather weak fluorescence spectra were obtained from 10^{-4} to 10^{-3} molar solutions of TCNQ and TCNQ¹⁻ (as counter ion of Li⁺ in LiTCNQ) in 2-methyl-tetrahydrofuran at 77°K. They are displayed in fig. 2.

3. SCMO CI calculations

The SCF formalism used has been thoroughly described before [3], SP hybridization was assumed for the nitrogen atoms. Table 1 gives the values for the nuclear charges, for the integrals $\langle pp|G|pp\rangle$, which were approximated by $I_p^p - A_p^p$ as well as the configurations of the nitrogen and carbon atoms in the molecule.

The repulsion integrals $\langle pq|G|pq\rangle$ were evaluated by Parr's uniform charged sphere method [8] with Slater type MO's. The carbon-carbon resonance integrals $H_{pq} = \langle p|h^i|q\rangle$ were approximated by $H_{pq} = H_{pq}^0 \exp(-\mathbf{a}R_{pq})\mathbf{d}_{pq}$, where H_{pq}^0 and \mathbf{a} are empirical parameters, which can be calibrated on other conjugated systems like ethene and benzene. R_{pq} is the distance between the centers. The bondlengths used here were those obtained for TCNQ¹⁻ [9]. They were assumed to be the same for all the ions, which seems to be a reasonable approximation for this kind of calculations.

The nitrogen-carbon resonance integral was also taken as a parameter, the "best" value turned out to be -3.12 eV, consistent with the experimental fact that the CN bond is short. The integrals $H_{pp} = \langle p|h^i|p\rangle$ were approximated by $-I_p^p$. The proton

Table 1

Atom	State	$\langle pp G pp\rangle$	I_p^P	A_p^P	H_{pp}	Nuclear charge
N(1)	di ² di pp	12.52	14.18	1.66	-14.18	7.0
C(5)	didi pp	11.09	11.19	0.10	-11.19	6.0
C(9, 11, 13)	trtrtr p	11.13	11.16	0.03	-11.16	6.0

Table 2

Excitation energies, and oscillator strengths (f), for three sets of parameters of TCNQ⁰

	Set			exp.
	1	2	3	
H_{CN} (eV)	-3.12	-3.12	-3.12	-
\mathbf{a} (\AA^{-1})	-5.007	-5.107	-5.207	-
H_{pq}^0 (eV)	-2517.5	-2517.5	-2517.5	-
(eV)	3.30	3.22	3.12	3.10
B_{3u} $f(x)$	1.814	1.585	1.387	S

Table 4

Excitation energies and oscillator strengths (f), for three sets of parameters of TCNQ²⁻

	Set			exp.
	1	2	3	
H_{CN} (eV)	-3.12	-3.12	-3.12	-
\mathbf{a} (\AA^{-1})	-5.007	-5.107	-5.207	-
H_{pq}^0 (eV)	-2517.5	-2517.5	-2517.5	-
(eV)	3.13	2.85	2.56	2.56
B_{3u} $f(x)$	1.257	1.107	0.973	S
(eV)	3.84	3.43	3.36	3.30
B_{2u} $f(y)$	0.137	0.042	0.464	W
(eV)	4.15	3.92	3.70	3.69
B_{2u} $f(y)$	0.660	0.675	0.109	W

coupling constants were obtained from: $a_H^i = Q\mathbf{r}_i^P$ [10], with $Q = 23.5$ G, a_H^i the proton coupling constant and \mathbf{r}_i^P the spin density on the neighbouring carbon atom. For the nitron coupling constant we used the relation:

$$a_N = Q_1^N \mathbf{r}_N + Q_2^N \sum_i \mathbf{r}_i,$$

with $Q_1^N = 18.5$ G and $Q_2^N = 9.6$ G [11]. \mathbf{r}_N is the

Table 3

Spin densities (\mathbf{r}_i^s), excitation energies, and oscillator strengths (f), for three sets of parameters of TCNQ¹⁻

	Set			exp.
	1	2	3	
H_{CN} (eV)	-3.12	-3.12	-3.12	-
\mathbf{a} (\AA^{-1})	-5.007	-5.107	-5.207	-
H_{pq}^0 (eV)	-2517.5	-2517.5	-2517.5	-
\mathbf{r}_{13}^s	0.062	0.066	0.070	0.066
\mathbf{r}_1^s	0.034	0.027	0.021	0.049
(eV)	1.76	1.59	1.41	1.46
B_{1u} $f(x)$	0.041	0.022	0.014	S
(eV)	2.83	2.57	2.32	2.95
B_{1u} $f(x)$	0.866	0.681	0.530	M
(eV)	3.35	2.93	2.57	2.95
A_u $f(y)$	0.060	0.057	0.052	M
(eV)	3.61	3.62	3.62	?
A_u $f(y)$	0.175	0.156	0.134	?
(eV)	4.96	4.46	3.89	4.40
B_{1u} $f(x)$	0.005	0.002	0.011	W
(eV)	5.95	5.48	5.15	5.33
B_{1u} $f(x)$	0.169	0.227	0.288	W

spin density on the nitrogen atom and \mathbf{r}_i are the spin densities on the neighbouring atoms.

An open-shell Fortran IV* and a closed-shell Algol 60** computer program was used which performed the SCF and configuration interaction operations. The best fit was decided on the basis of the UV-VIS spectrum and the spin densities of the TCNQ¹⁻ ion. With the same parameters calculations were then made for TCNQ and TCNQ²⁻. Usually self-consistency was reached after 10-15 iterations. The results are

* This program was run on the IBM 360/50 computer of the Rekeninstituut, Leiden University.

** This program was run on the Telefunken TR4 computer of the Rekencentrum, Groningen University.

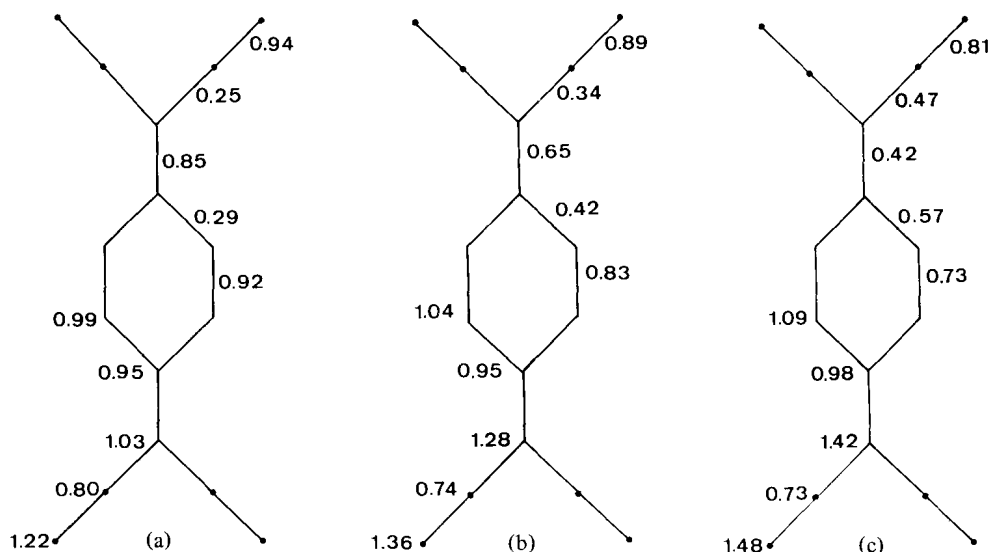
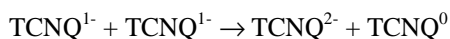


Fig. 3. Charge densities and bond orders in (a) the TCNQ molecule, (b) the TCNQ⁻ anion, (c) the TCNQ²⁻ anion.

compared with experiment in tables 2, 3 and 4. The bond orders are given in fig. 3; they show that TCNQ upon ionization proceeds from a chinoid to a benzoid structure, in agreement with crystallographic data for TCNQ, TCNQ^{1/2-} and TCNQ¹⁻ [9].

The total energies of TCNQ, TCNQ¹⁻ and TCNQ²⁻ show that the energy differences between the species are fairly small, indicative of the comparatively high stability of the TCNQ¹⁻ and TCNQ²⁻ ions in solution, where solvation stabilizes the system. The disproportionation reaction:



requires the fairly low energy of 3.50 eV, fact which may be useful in band calculations of TCNQ¹⁻ stacks, where the ionized states are mixed in with equal weight as the non-ionized states.

In general, good agreement with experiment for one set (set 2 of table 2) of parameters is reached, the intensities of the UV-VIS spectrum from TCNQ¹⁻ are uncertain as is usually the case after configuration interaction in open-shell cases. Except for the theoretically obtained transition at 3.62 eV in TCNQ¹⁻, which does not show up in the experiment all other transitions can be identified experimentally, while the fit to the spin densities is reasonable.

It appears that the wavefunctions obtained in this manner can be confidently used for further work.

References

- [1] W.J. Siemens, P.E. Bierstedt and R.G. Kepler, *J. Chem. Phys.* 39 (1963) 3523.
- [2] D.A. Lowitz, *J. Chem. Phys.* 46 (1967) 4698.
- [3] H.J. Monkhorst and J. Kommandeur, *J. Chem. Phys.* 47 (1967) 391.
- [4] J.G. Vegter and J. Kommandeur, *Phys. Rev.*, submitted for publication.
- [5] D.S. Acker and W.S. Hertler, *J. Am. Chem. Soc.* 84 (1962) 3370.
- [6] P.H.H. Fischer and C.A. McDowell, *J. Am. Chem. Soc.* 85 (1963) 2694.
- [7] R. Buvet, P. Dupuis, J. Néel and J. Péricion, *Bull. Soc. Chim. France* 11 (1969) 3991.
- [8] R. Pariser and R.G. Parr, *J. Chem. Phys.* 21 (1953) 466, 767.
- [9] A. Hoekstra, T. Spoelder and A. Vos, *Acta Cryst. B28* (1962) 14.
- [10] H.M. McConnell and D.B. Chesnut, *J. Chem. Phys.* 28 (1958) 107.
- [11] R.L. Ward, *J. Am. Chem. Soc.* 84 (1962) 332.