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ELECTRONIC SPECTRUM AND STRUCTURE OF 11,11,12,12-TETRACYANO-1,4-NAPHTHAQUINODIMETHANE*

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Abstract—The lower π-electronic states of 11,11,12,12-tetracyano-1,4-naphthaquinodimethane (TCNNQ) were calculated by the usual SCF-CI and the VESCF-CI methods within a Pariser-Parr-Pople scheme. The absorption spectrum of TCNNQ was measured in cyclohexane and methanol. The observed lower excitation energies were 3·14, 4·32, 4·5, 5·6 and 5·96 eV. The lower three excitation energies calculated by both methods are in good agreement with the observed values. It was shown that the effect of doubly excited configurations is far from being negligible. As for charge distribution, the VESCF method was found to give more reasonable results than the usual SCF method. Theoretical bond lengths obtained from bond orders suggest partial breakdown of the quinoid structure, which may be associated with the fact that the electron affinity of TCNNQ is relatively small compared with those of the 2,6-analogue and TCNQ.

INTRODUCTION

11,11,12,12-Tetracyano-1,4-naphthaquinodimethane (hereafter abbreviated as TCNNQ) was synthesized first by Chatterjee[1] in 1967. The compound is a new cyanocarbon acceptor with the electron affinity 1·49 eV[1] which is a little smaller than those for the other cyanocarbons like tetracyanoethylene (TCNE) and 7,7,8,8-tetracyano-*p*-benzoquinodimethane (TCNQ). On the other hand, TCNNQ is known to form sufficiently strong charge-transfer π-complexes with aromatic hydrocarbons.[1] If its anion-radical salts were obtained, they might be expected to show relatively high conductivities like those of TCNQ.[2]

Calculations of the π-electronic structure of the TCNNQ molecule are of interest from the following points of view: (i) reasonably good estimate of the electronic wave function of TCNNQ may provide a basis for the calculation of various properties of its charge-transfer complexes and/or its anion-radical salts; (ii) to what extent the VESCF (Variable Electronegativity Self Consistent Field) method[3] is preferable to the usual SCF method within a PPP (Pariser–Parr–Pople) scheme for the explanation of the electronic spectrum of such a cyanocarbon molecule as TCNNQ.

In the present communication, calculations of the lower excited states of TCNNQ are carried out by the usual SCF and VESCF methods to make possible a comparison between both methods with regard to the electronic absorption spectrum. In both methods, we examine the effect of doubly excited configurations as well as that of singly excited configurations. From the calculated bond orders, the possible structure of TCNNQ is discussed and its relation to the electron affinity of TCNNQ is suggested.

METHOD OF CALCULATION

The TCNNQ molecule is assumed to have a planar structure of the symmetry group C_{2v}, and treated as a 20-center 20-electron problem within the framework of the π-electron theory. The accurate bond lengths in TCNNQ are not known. However, the

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bond lengths between adjacent C atoms in their trigonal valence states can be estimated from a bond order-bond length linear relation obtained by Dewar and Gleicher,[4] where we have calculated the bond orders by the usual SCF method assuming appropriate bond lengths on the basis of the X-ray data for TCNQ.[5] The bond lengths between the trigonally and digonally hybridized carbons and between carbon and nitrogen were assumed to be the same as those in TCNQ. The molecular geometry of TCNNQ finally adopted is shown in Fig. 1.

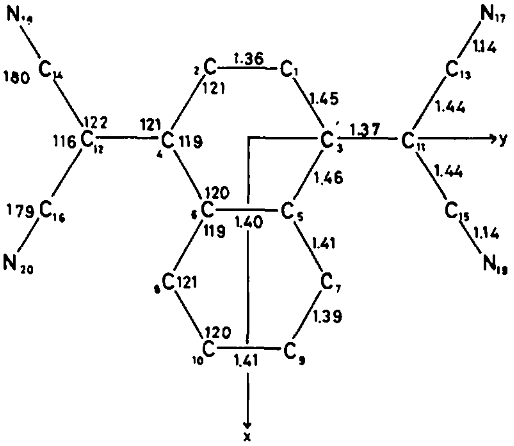

FIG 1. Assumed molecular geometry of TCNNQ; bond lengths in Å and bond angles in degree.

Calculations of the MO functions and their energies in a PPP scheme are carried out by the usual SCF and VESCF methods. In both methods, we start from appropriate Hueckel MO's with the assumption of the zero differential overlap. Core resonance integrals β_{pq} are evaluated from the following formula:[6]

$$\beta_{pq} = -K/2 \cdot S_{pq}(I_p + I_q)$$

where S_{pq} is the overlap integral between 2pπ atomic orbitals (AO) on atoms p and q, and I_p and I_q the valence state ionization potentials of atoms p and q, respectively. The constant K is chosen as 0·85494 for C—C bonds so that the value of β_{pq} for benzene fits the empirical value −2·371 eV[7] when the bond length (r) is taken as 1·396 A and the effective nuclear charge (Z_C) as 3·25, and K = 0·97626 for C—N bonds so that β_{CN} yields the empirical value −2·576 eV in the case of r = 1·36 A, Z_C = 3·25, and Z_N = 3·90.[8] Non nearest neighbour β_{pq}'s are also taken into consideration. Penetration integrals over Slater AO's are estimated purely theoretically with the assumption of a Goeppert-Mayer and Sklar potential.[9] Non nearest neighbour penetration integrals are included but penetration integrals involving the hydrogen atoms are neglected. One center electronic repulsion integrals γ_{pp} are taken as the difference between I_p and the valence state electron affinity A_p.[8] Two center integrals γ_{pq} are calculated theoretically for large distances ($r \geq$ 2·80 A) by the multipole expansion method,[10] while for small distances ($r \leq$ 2·80 A) they are evaluated by the use of a Pariser–Parr type quadratic equation.[8]

TABLE 1. IONIZATION POTENTIALS (I) AND ELECTRON AFFINITIES (A) FOR THE ISOELECTRONIC SERIES B^-, C^0, N^+, O^{++}, AND F^{+++} (eV)

	Z	trtrtrπ		didiππ	
		I	A	I	A
B^-	2·25	1·06,[b] 0·96[c]	....	1·02[b]	....
C^0	3·25	11·16,[a] 11·22,[c] 11·42[d]	0·62,[c] 0·58,[d] 0·69[7]	11·19,[a] 11·24[c]	0·68[c]
N^+	4·25	28·72[b]	11·96[b]	28·72[b]	12·06[b]
O^{++}	5·25	53·26[b]	31·11[b]	53·28[b]	31·19[b]
F^{+++}	6·25	....	57·13[b]	....	57·18[b]

[a] J. M. Hinze and H. H. Jaffe, *J. Am. Chem. Soc.* **84**, 540 (1962).

[b] Estimated from the promotion energies and the electron affinities listed in above reference and the ionization potentials appeared in C. E. Moore: Atomic Energy Levels, Natl. Bureau of Standards, Circular No. 467, Vol. 1 (1949)

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TABLE 2. IONIZATION POTENTIALS (I) AND ELECTRON AFFINITIES (A) FOR THE ISOELECTRONIC SERIES C^-, N^0, O^+, AND F^{++} (eV)

	Z	di²diππ	
		I	A
C^-	2·90	1·57,[c] 1·24[a]	.....
N^0	3·90	14·18,[a] 14·47[c]	1·62,[b] 1·66[a]
O^+	4·90	34·19[b]	15·24[b]
F^{++}	5·90	.....	36·75[b]

[a, b, c, d] See footnotes *a*, *b*, *c* and *d* of Table 1.

In the VESCF method, I_p and A_p are assumed to be parabolically dependent upon Z_p.[6] The following formulas are obtained from the values of these quantities of the isoelectronic atoms listed in Tables 1 and 2 by the method of least squares:

$$\left.\begin{aligned} I &= 3{\cdot}5745\,Z^2 - 9{\cdot}3896\,Z + 4{\cdot}0370 \\ A &= 3{\cdot}6818\,Z^2 - 16{\cdot}1221\,Z + 14{\cdot}1222 \end{aligned}\right\} \text{for } V_{\mathrm{trtrtr}\pi}$$

$$\left.\begin{aligned} I &= 3{\cdot}5987\,Z^2 - 9{\cdot}5589\,Z + 4{\cdot}2932 \\ A &= 3{\cdot}6508\,Z^2 - 15{\cdot}8198\,Z + 13{\cdot}4884 \end{aligned}\right\} \text{for } V_{\mathrm{didi}\pi\pi}$$

$$\left.\begin{aligned} I &= 3{\cdot}4725\,Z^2 - 10{\cdot}6930\,Z + 3{\cdot}2110 \\ A &= 3{\cdot}9525\,Z^2 - 21{\cdot}1800\,Z + 24{\cdot}1235 \end{aligned}\right\} \text{for } V_{\mathrm{di^2di}\pi\pi}$$

All the integrals over AO's including the penetration integrals are modified by new Z_p's at each iteration in the SCF routine.

The present configuration interaction (CI) calculation for the lower singlet excited states is divided into two classes: one including only singly excited configurations (S.CI) and the other doubly excited configurations included as well (D.CI). In both CI calculations the cut-off level was set at 10 eV above the ground configuration, due to the insufficient capacity of the computer used. The oscillator strengths for the lower singlet-singlet transitions were calculated in both cases of S.CI and D.CI.[11]*

For the lower triplet excited states, only the D.CI calculation was carried out with the cut-off level assumed at 9 eV above the ground configuration. The oscillator strengths for the triplet-triplet transitions were not evaluated.

ELECTRONIC SPECTRUM

TCNNQ was synthesized by Chatterjee's method.[1] The absorption spectrum of TCNNQ was measured in various organic solvents in the wavelength region of 200 to 500 mμ by a JASCO ORD/UV-5 spectrometer. The shape of the spectrum depends upon whether the solvent has an OH group or not. In comparison with non-polar solvents, polar solvents yield only small shifts of the absorption band maxima. The spectrum measured in cyclohexane and methanol is illustrated in Fig 2. The spectrum

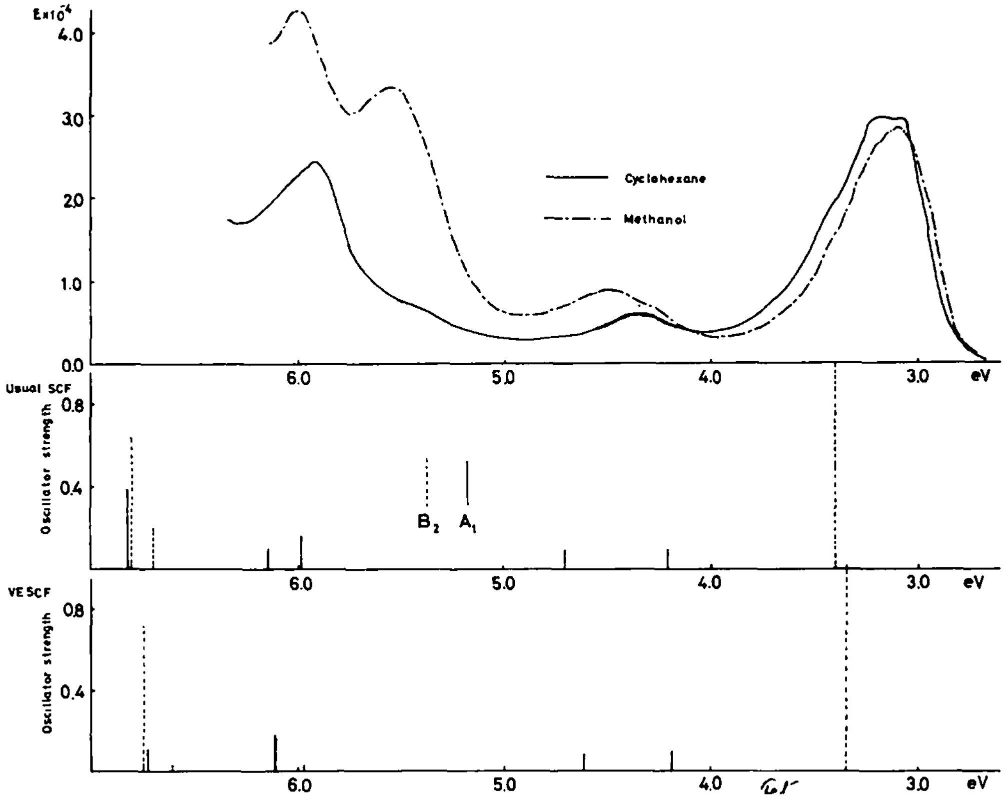

FIG 2. Electronic absorption spectrum and calculated excitation energies and intensities of TCNNQ.

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* We are indebted to Dr. K. Sakamoto for the use of his CI and oscillator strength programmes.

in cyclohexane consists of three main bands, each having a few vibrational structures, which maxima are located at 3·14, 4·32 and 5·96 eV. The peak of the first band was estimated from the envelope of its vibrational structures. In methanol, on the other hand, the second band maximum shifts to 4·48 eV and a new band with its maximum at 5·55 eV appears strongly. This phenomenon is explained reasonably by the fact that the H-bonding between the N atoms in the solute molecule and the OH group of methanol intensifies the absorption bands with their maxima around at 4·5 and 5·6 eV which are not clearly observed in cyclohexane due to the disturbance of the neighbouring stronger bands.

From the above discussion, it may be concluded that the excitation energies for TCNNQ in the visible and ultraviolet region are 3·14, 4·32, 4·5, 5·6 and 5·96 eV.

RESULTS AND DISCUSSION

The calculations of the excitation energies and intensities were performed on a HIPAC 103 digital computer at Tokyo Kyoiku University. These values for the excited states up to about 7 eV are collected in Table 3 together with the corresponding observed values. The table shows that the usual SCF and the VESCF methods yield not very different features for these quantities in both S.CI and D.CI approximations, though the excitation energies calculated by the VESCF are a little lower than those obtained by the usual SCF as a whole.

TABLE 3. CALCULATED ENERGIES (eV) AND INTENSITIES FOR TCNNQ LOWER EXCITED SINGLET STATES*

Method	S.CI		D.CI		Exptl.	
	SCF	VESCF	SCF	VESCF	Cyclohexane	Methanol
1	3·296(1·310)B_2	3·235(1·332)B_2	3·389(0·032)A_1	3·347(1·023)B_2	3·14(0·66)	3·10(0·56)
2	3·756(0·115)A_1	3·882(0·072)A_1	3·401(1·000)B_2	3·402(0·009)A_1		
3	3·940(0·030)B_2	3·999(0·037)B_2	3·915(0·014)B_2	4·004(0·017)B_2		
4	4·432(0·115)A_1	4·273(0·147)A_1	4·212(0·093)A_1	4·187(0·099)A_1	4·32(0·13)	
5	4·831(0·043)B_2	4·744(0·020)B_2	4·646(0·025)B_2	4·537(0·017)B_2		
6	5·157(0·019)A_1	5·121(0·032)A_1	4·709(0·077)A_1	4·617(0·091)A_1		4·48(0·21)
7	5·344(0·106)$B_2{}^a$	5·329(0·118)$B_2{}^a$	5·220(0·033)$B_2{}^a$	5·264(0·047)$B_2{}^a$		5·55(0·59)
8	5·865(0·095)A_1	5·843(0·036)A_1	5·286(0·000)A_1	5·292(0·000)A_1		
9	5·926(0·002)B_2	5·940(0·000)B_2	5·704(0·041)B_2	5·632(0·012)B_2		
10	6·159(0·110)$A_1{}^c$	6·129(0·146)$A_1{}^c$	5·985(0·158)$A_1{}^c$	5·976(0·037)A_1	5·96(0·45)	6·02(0·67)
11	6·515(0·403)$B_2{}^b$	6·446(0·218)$B_2{}^b$	6·147(0·094)A_1	6·113(0·175)$A_1{}^c$		
12	6·557(0·226)A_1	6·485(0·018)A_1	6·154(0·014)B_2	6·167(0·024)B_2		
13	6·684(0·963)B_2	6·622(0·741)B_2	6·654(0·016)A_1	6·613(0·034)$B_2{}^b$		
14	7·078(0·425)A_1	6·778(0·426)B_2	6·704(0·221)$B_2{}^b$	6·619(0·066)A_1		
15	7·081(0·041)B_2	6·855(0·922)A_1	6·808(0·649)B_2	6·726(0·101)A_1		
16	7·148(0·870)A_1	7·043(0·561)A_1	6·832(0·387)A_1	6·751(0·715)B_2		

* Figures in parentheses denote values of the corresponding oscillator strength. The transition dipole moment in A_1 states lies in parallel with the short molecular axis (x-axis in Fig 1) and that in B_2 states parallel with the long molecular axis (y-axis).

However, it is seen from the table that the effect of lower doubly excited configurations is rather remarkable in the calculation of both excitation energies and intensities. For example in the usual SCF calculation, the energy depression of the first A_1

excited state due to D.CI (mainly attributable to the $\psi_{10,10}^{11,11}$ doubly excited configuration whose energy is 5·66 eV relative to the ground configuration) is 0·61 eV which is much larger than that of the first B_2 excited state, 0·13 eV, the ground state energy being lowered by 0·24 eV due to D.CI. Consequently, we have a level sequence inversion of the first B_2 and the first A_1 excited states in the D.CI calculation. A similar situation is seen at several other excited states. Thus the effect of doubly excited configurations are far from being negligible, so that only the results calculated by the D.CI approximation will be discussed below.

The calculated excited states marked as (a), (b) and (c) in Table 3 correspond to the first two $^1B_{2u}^+$ states and the first $^1B_{3u}^+$ state in naphthalene[7] perturbed by the introduction of two dicyanomethylene groups. This fact and a comparison of the calculated and observed oscillator strengths lead to the band assignments listed in Table 3 and shown schematically in Fig 2. The calculated transition energies are in accord with the corresponding observed values within 0·3 eV in both methods.

TABLE 4. CALCULATED ENERGIES (eV) FOR LOWER EXCITED TRIPLET STATES OF TCNNQ

Method	SCF		VESCF	
1	1·674	B_2	1·617	B_2
2	2·876	A_1	2·870	A_1
3	3·237	B_2	3·252	B_2
4	3·768	A_1	3·835	A_1
5	3·921	B_2	3·908	B_2
6	4·391	B_2	4·271	A_1
7	4·395	A_1	4·355	B_2
8	4·740	B_2	4·688	B_2

The lower triplet excitation energies calculated by the D.CI are listed in Table 4. Since we have no experimental data for triplet states with which to compare them, we cannot make any comment on them. However, their dependence on the methods of computation is found to be similar to that for the singlet transitions described in the opening paragraph of this section.

TABLE 5. CHARGE DISTRIBUTION

Method	TCNNQ		TCNQ[12]
	SCF	VESCF	SCF
Atom			
1	0·9734	0·9802	0·9953
3	0·9188	0·9657	0·9850
5	1·0478	1·0240	0·9953
7	0·9571	0·9776	......
9	0·9676	0·9791	......
11	1·0674	1·0171	1·0041
13	0·8268	0·9130	0·9240
15	0·8247	0·9119	0·9240
17	1·2083	1·1165	1·0861
19	1·2081	1·1149	1·0861

Table 5 shows the calculated charge distribution in TCNNQ, together with that in TCNQ obtained by Lowitz.[12] The usual SCF gives each N atom a great excess charge of 0·21, and its adjacent carbon atom a large deficiency, 0·17. On the other hand, the VESCF reduces the excess charge on the nitrogen atom to 0·12 and the deficiency on the carbon atom to 0·09. The above inspection suggests that the latter method yields more reasonable charge distribution than the former.

The charge distribution in TCNQ obtained by Lowitz[12] does not show a large scale migration. This is probably because he used values of core coulomb integrals α_p and β_{pq} different from ours and neglected penetration integrals in his SCF routine.

Table 6. Bond orders and bond lengths (A)

Method	TCNNQ			TCNQ		
	SCF	VESCF		SCF		
Bond	Bond order		Calculated bond length[a]	Bond order[12]	Calculated bond length[a]	Observed bond length[5]
1–2	0·8930	0·8937	1·357	0·8887	1·356	1·346
1–3	0·3328	0·3324	1·455	0·3466	1·453	1·448
3–5	0·3095	0·3080	1·460	0·3466	1·453	1·448
5–6	0·6177	0·6252	1·404	0·8887	1·356	1·346
5–7	0·6194	0·6155	1·406	......	.....	.....
7–9	0·6910	0·6963	1·391	......	.....	.....
9–10	0·6323	0·6286	1·403	......	.....	.....
3–11	0·8224	0·8258	1·369	0·8118	1·371	1·374
11–13	0·2718	0·2707	.....	0·2685	.....	1·441
11–15	0·2756	0·2744	.....	0·2685	.....	1·441
13–17	0·9422	0·9554	.....	0·9554	.....	1·140
15–19	0·9406	0·9541	.....	0·9554	.....	1·140

[a] Calculated from the bond order-bond length relation expressed by the following formula:

$$r_{pq} = 1{\cdot}514 - 0{\cdot}176P_{pq}$$

where r_{pq} is the bond length between adjacent atoms p and q, and P_{pq} the bond order of the bond p—q (Ref 4).

In Table 6 are given the bond orders estimated by both methods together with those in TCNQ.[12] The C—N bond orders are computed a little larger by the VESCF than by the usual SCF, while the other bond orders obtained by both methods are not very different. It is seen from the table that the bond orders in TCNNQ are almost the same as those in TCNQ, except for the 3–5 and 5–6 bonds. In particular, the 5–6 bond order in TCNNQ is predicted to be considerably lower, and this is because we have used a somewhat larger bond length (1·401 Å) for the 5–6 bond at the initial stage of the SCF routine. This point will be discussed later.

We have included in Table 6 theoretical bond lengths calculated by a bond order–bond length relation.[4] Since both SCF and VESCF methods yield not very different bond orders, they predict the same value for each bond length with the accuracy of 10^{-3} Å. The theoretical bond lengths for the 5–6, 5–7, 7–9 and 9–10 bonds are sufficiently close to those in benzene, although a slight bond alternation is predicted.

In the preliminary SCF calculation of estimating a starting molecular geometry, we took the same value 1·37 Å for both 1–2 and 5–6 bond lengths and obtained quite different bond orders corresponding to bond lengths 1·359 and 1·401 Å, respectively. This leads to a conclusion that the attachment of an extra benzene ring to TCNQ weakens the 5–6 bond so that the quinoid structure in TCNQ, caused by two dicyanomethylene groups, is no longer preserved in TCNNQ. This partial breakdown of the quinoid structure in TCNNQ may be associated with the fact that the electron affinity of TCNNQ (1·49 eV) is smaller than that of TCNQ (1·7 eV).[13] Moreover, this suggestion may be supported by another fact that the linearly conjugated 2,6-analogue (11,11,12,12-tetracyano-2,6-naphthaquinodimethane), for which a quinoid structure is undoubtedly predominant, has a higher electron affinity (1·65 eV)[1] than that of TCNNQ.

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