February, 1973] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 423—426 (1973) 423

The Electronic States of Tetracyanoethylene and Its Anion Radical as Studied by Their Infrared Spectra

Yôichi Iida

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo

(Received August 3, 1972)

The infrared spectra of tetracyanoethylene (TCNE) and its anion radical in the rock-salt region were examined in order to observe any appreciable frequency differences between their corresponding bands. The vibrational assignments were made, and the basic Urey-Bradley force field was determined for the TCNE anion radical. By comparing them with those of the neutral TCNE, we discussed the difference in the electronic states between the neutral TCNE and its anion radical. The half-occupied molecular orbital of the TCNE anion radical was found to belong to the B_{2g} irreducible representation.

The infrared spectrum of an ion radical is known to be appreciably different from that of its neutral molecule.[1-11] The spectrum difference may be attributed to the difference in their intramolecular force fields. In a previous paper,[8] we examined the infrared spectra (650—4000 cm^{-1}) of *p*-chloranil and its anion radical. In order to explain the appreciable frequency differences between their corresponding bands, the fundamental frequencies were assigned, and the simple Urey-Bradley force fields were determined for both the neutral and anion radical molecules. It was found that the difference in the infrared spectra between these two molecules could be understood on the basis of the difference in their electronic structures caused by an extra electron on the *p*-chloranil anion radical.

The tetracyanoethylene (TCNE) molecule is known to be a strong electron acceptor, and its anion radical is stable.[12] The infrared and Raman spectra of the neutral TCNE were measured by Takenaka and Hayashi.[13] In order to make vibrational assignments and determine the force constants for this molecule, they carried out normal coordinate treatments for the in-plane vibrations by using the basic Urey-Bradley force field. On the other hand, Stanley *et al.* examined the infrared spectra of the sodium and potassium salts of the TCNE anion radical by using thin polycrystalline films.[5] Although they reported that the spectrum of the TCNE anion radical differs appreciably from that of the neutral TCNE, they did not assign the fundamental frequencies quantitatively or determine the force constants for the TCNE anion radical. Therefore, in the present paper, the fundamental frequencies were assigned and the basic Urey-Bradley force field was determined for the TCNE anion radical. The purpose of the present paper is to compare these data with those of the neutral TCNE and to investigate the difference in the electronic states between the neutral TCNE and its anion radical.

Calculations

First, let us consider the experimental and theoretical results on the neutral TCNE reported by Takenaka and Hayashi.[13] The observed fundamental frequencies in the infrared and Raman spectra of the neutral TCNE are given in Table 1. In order to assign the vibrational spectra, they used the ***GF*** matrix method developed by Wilson.[14] It was assumed that the vibrational spectra could be treated under the molecular point group V_h. A representative of each type of internal coordinate is shown in Fig. 1. The equilibrium bond lengths adopted are those determined from X-ray analysis by Bekoe and Trueblood:[15] $R_0=1.317$ Å, $r_0=1.449$ Å, and $l_0=1.15$ Å. For the

Table 1. The observed and calculated frequencies (cm^{-1}) for in-plane fundamental vibrations of the neutral TCNE and its anion radical

Species		The neutral TCNE		Its anion radical	
		Obsd[a]	Calcd[a]	Obsd[b],[c]	Calcd
A_g	ν_1	2250	2250		2193
	ν_2	1573	1573	(1371)	1365
	ν_3	679	647		650
	ν_4	536	525		523
	ν_5	—	122		121
B_{1g}	ν_6	2237	2232		2181
	ν_7	1284	1304		1331
	ν_8	508	503		505
	ν_9	251	251		251
B_{2u}	ν_{10}	2230	2239	2183	2191
	ν_{11}	1155	1152	1187	1181
	ν_{12}	429	433	—	434
	ν_{13}	—	111	—	111
B_{3u}	ν_{14}	2262	2257	2208	2202
	ν_{15}	959	980	970	996
	ν_{16}	579	591	—	593
	ν_{17}	—	157	—	156

a) Ref. 13. b) Ref. 5. c) Ref. 12.

---

[1] Y. Matsunaga, *Can. J. Chem.*, **38**, 1172 (1960).

[2] Y. Matsunaga, *Helv. Phys. Acta*, **36**, 800 (1963).

[3] Y. Matsunaga, *J. Chem. Phys.*, **41**, 1609 (1963).

[4] M. Kinoshita and H. Akamatu, *Nature*, **207**, 291 (1965).

[5] J. Stanley, D. Smith, B. Latimer, and J. P. Devlin, *J. Phys. Chem.*, **70**, 2011 (1966).

[6] Y. Matsunaga, *Nippon Kagaku Zasshi*, **89**, 905 (1968).

[7] Y. Iida, *J. Phys. Soc. Jap.*, **27**, 1371 (1969).

[8] Y. Iida, This Bulletin, **43**, 345 (1970).

[9] Y. Iida, *ibid.*, **44**, 1271 (1971).

[10] J. C. Moore, D. Smith, Y. Youhne, and J. P. Devlin, *J. Phys. Chem.*, **75**, 325 (1971).

[11] I. N. Juchnovski and I. G. Binev, *Chem. Phys. Lett.*, **12**, 40 (1971).

[12] O. W. Webster, W. Mahler, and R. E. Benson, *J. Amer. Chem. Soc.*, **84**, 3678 (1962).

[13] T. Takenaka and S. Hayashi, This Bulletin, **37**, 1216 (1964).

[14] E. B. Wilson, Jr., *J. Chem. Phys.*, **7**, 1047 (1939); **9**, 76 (1941).

[15] D. A. Bekoe and K. N. Trueblood, *Z. Kristallogr.*, **113**, 1 (1960).

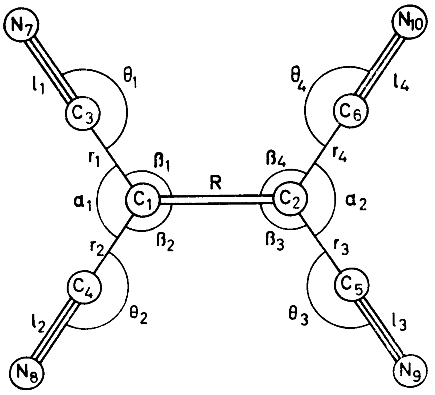

Fig. 1. The internal coordinates for the neutral TCNE or its anion radical.

bond angles, $\alpha_0=\beta_0=120°$ and $\theta_0=180°$ were assumed for the sake of simplicity. The normal vibrations of TCNE were reduced to the symmetry species:

$$\Gamma = 5A_g(R)+4B_{1g}(R)+4B_{2u}(IR)+4B_{3u}(IR) + 2A_u\ (\text{inactive})+2B_{1u}(IR)+2B_{2g}(R)+B_{3g}(R), \qquad (1)$$

where the first four are the in-plane vibrations and the rest are the out-of-plane vibrations. (R) and (IR) indicate the Raman and infrared active modes respectively. In order to calculate the fundamental frequencies, the basic Urey-Bradley force field was used as the potential function for TCNE. For the in-plane vibrations, three bond-stretching (K(C=C), K(C-C), and K(C≡N)), three angle-bending (H(C-C-C), H(C-C=C), H(C-C≡N)), and four non-bonded repulsion force constants (F(C-C-C), F(C-C=C), F(C-C≡N), and C) were necessary. The constant, C, represents the repulsion between two carbon atoms in the *cis*-position.[16-18] Repetitions of the calculation with several sets of force constants were then carried out by the trial-and-error method by the use of the Jacobian matrix. For the in-plane vibrations, Takenaka and Hayashi obtained the final set of force constants shown in Table 2.[13] The fundamental frequencies calculated with these constants are compared in Table 1 with the observed values. The agreement is satisfactory except in the case of the 679 cm^{-1} frequency (ν_3) of the A_g species.

Table 2. The force constants estimated for the neutral TCNE and its anion radical (md/Å)[a)]

Force constant	The neutral TCNE[b)]	Its anion radical
K(C=C)	6.31	4.00
K(C-C)	4.80	5.23
K(C≡N)	16.84	15.70
H(C-C-C)	0.05	
H(C-C=C)	0.16	
H(C-C≡N)	0.13	
F(C-C-C)	1.11	
F(C-C=C)	1.04	
F(C-C≡N)	0.08	
C	0.11	

a) $F' = -0.1F$, $C' = -0.1C$. b) Ref. 13.

Next, let us consider the vibrational spectrum of the TCNE anion radical. The fundamental frequencies in the infrared spectrum of the potassium salt of the TCNE anion radical measured by Stanley *et al.* are also given in Table 1.[5,12] Since the counter cation of the salt is a simple alkali metal cation, the observed spectrum of the salt in the rock-salt region must be due solely to that of the TCNE anion radical itself. Its spectroscopic features are found to be appreciably dissimilar to those of the neutral TCNE. The most interesting new features in the TCNE anion radical spectrum are: (1) the very intense band at 1371 cm^{-1}, (2) the appreciable red-shifts of the doublet 2208 and 2183 cm^{-1} bands in the cyanide-stretching region compared to the 2262 and 2230 cm^{-1} bands in the neutral TCNE, and (3) the marked absence of absorption in the 600—1300 cm^{-1} region, where the strongest TCNE fundamental absorptions occur.[5] The C-C modes, which absorb strongly at 1155 and 959 cm^{-1} in the neutral TCNE, can be designated as the source of the very weak bands at 1187 and 970 cm^{-1} in the TCNE anion radical.

In order to explain these appreciable frequency differences, let us analyze the vibrational spectrum of the TCNE anion radical. Since the molecular and crystal structures of the potassium salt of the TCNE anion radical have not yet been ascertained, it was assumed that the molecular structure of the anion radical was almost identical with that of the neutral TCNE. This assumption means that the ***G*** matrix calculated for the neutral TCNE was also used for the anion radical (see below). Since only the intramolecular vibrations are expected to appear in the rock-salt region, the vibrational spectra of the crystalline compound can be approximately treated under the molecular point group V_h. In general, the effects of crystal fields on vibrational frequencies are small. Therefore, to a first approximation, its contribution to the spectrum of the TCNE anion radical was ignored in our treatment. Hence, twenty-four normal modes of vibrations for the TCNE anion radical were also reduced to the same symmetry species as in Eq. (1) of the neutral TCNE. (We calculated only the in-plane vibrations, because no out-of-plane vibration is expected to appear in the region now under consideration.) We have designated the very weak bands at 1187 and 970 cm^{-1} as the C-C modes in the TCNE anion radical. Since no other infrared-active fundamental modes occur between 600 and 2000 cm^{-1}, there is no apparent source for the intense 1371 cm^{-1} band in the anion radical. The assignment of this band is important in estimating the force constants of the TCNE anion radical. If a strong charge-transfer interaction takes place between the neighbouring TCNE anion radical species,[19] the

---

16) J. R. Scherer and J. Overend, *J. Chem. Phys.*, **33**, 1681 (1960).

17) D. E. Mann, T. Shimanouchi, J. H. Meal, and L. Fano, *ibid.*, **27**, 43 (1957).

18) D. E. Mann, L. Fano, J. H. Meal, and T. Shimanouchi, *ibid.*, **27**, 51 (1957).

19) The charge-transfer interaction between neighbouring ion radical molecules has been found with a number of crystalline ion radical salts. See, for example, Y. Iida and Y. Matsunaga, This Bulletin, **41**, 2615 (1968); Y. Iida, *ibid.*, **42**, 71, 637 (1969); Y. Iida, *ibid.*, **43**, 2772 (1970); Y. Iida, *ibid.*, **44**, 663, 1777 (1971); Y. Iida, *ibid.*, **45**, 105, 624 (1972).

Ferguson-Matsen theory of activation then applies and certain intense bands in the infrared spectrum can be assigned to totally symmetric modes.[20-22] By the use of this approach with the TCNE anion radical, the strong band at 1371 cm^{-1} can be assigned to the totally symmetric C=C stretching A_g mode,[5,10] which was observed at 1573 cm^{-1} in the Raman spectrum of the neutral TCNE.[13] The 202 cm^{-1} red shift seems to be consistent with the following discussion of the electronic states of TCNE and its anion radical (see below).

In order to calculate the fundamental frequencies, Wilson's ***GF*** matrix method was also applied to the TCNE anion radical; a representative of each type of internal coordinate for in-plane fundamental vibrations is given in Fig. 1. The basic Urey-Bradley force field was employed as the potential function. The notations for the three bond-stretching, three angle-bending, and four non-bonded repulsion force constants used are those for the neutral TCNE. At this time, it is assumed that the stretching force constants of the TCNE anion radical are different from those of the neutral TCNE, while the other force constants remain almost constant. Rigorously speaking, this treatment is not correct, but it is justified as long as the observed fundamental frequencies are mostly due to the bond stretching modes. Then, the trial force constant for the TCNE anion radical were taken by modifying the stretching force constants for the neutral TCNE determined by Takenaka and Hayashi.[13] Refinements of the force constants for the TCNE anion radical were then carried out by the trial-and-error method, making use of the Jacobian matrix. The final set of force constants thus obtained for the TCNE anion radical is given in Table 2, while in Table 1 the frequencies calculated with these constants are compared with the observed values. The calculated values of the fundamental vibrations were found to agree well with the observed values.

Discussion

Since a total of 10 force constants of the anion radical were evaluated from an experimental assignment of 5 frequencies, we suspect that these values of the force constants are not the best ones for the TCNE anion radical. However, the stretching force constants are still meaningful, because the observed fundamental frequencies are almost all due to the stretching modes. Therefore, below we will discuss only the difference in the stretching force constants between the neutral TCNE and its anion radical. As is shown in Table 2, $K(\mathrm{C{=}C})=6.31$ md/Å, $K(\mathrm{C{-}C})=4.80$, and $K(\mathrm{C{\equiv}N})=16.84$ for the neutral TCNE, while $K(\mathrm{C{=}C})=4.00$, $K(\mathrm{C{-}C})=5.23$, and $K(\mathrm{C{\equiv}N})=15.70$ for its anion radical. We can see that the extra electron on the TCNE anion radical causes the decrease in the $K(\mathrm{C{=}C})$ and $K(\mathrm{C{\equiv}N})$ values and the increase in the $K(\mathrm{C{-}C})$ value.

It is well known that the stretching force constant, $K(12)$, of a bond (12) in a conjugated system is greatly affected by its bond order, $p(12)$. According to Coulson and Longuet-Higgins,[23] $K(12)$ can be expressed by:

$$K(12) = \{(1-p(12))K_s+p(12)K_d\} + \left\{\frac{K_sK_d(s-d)}{K_s(1-p(12))+K_dp(12)}\right\}^2 \frac{\pi(1212)}{2}, \qquad (2)$$

where K_s and K_d are the force constants associated with pure single and double bonds respectively, where π-(1212) is the self-polarizability of the bond (12), and where s and d are the bond lengths of pure single and double bonds respectively.

In a homopolar carbon-carbon bond, the second term involving the self-polarizability may be small.[24] In this case, the stretching force constant, $K(12)$, is predominantly determined by the bond order, $p(12)$. Therefore, the extra electron on the TCNE anion radical causes a decrease in the C=C bond order, $p(\mathrm{C{=}C})$, and an increase in the C–C bond order, $p(\mathrm{C{-}C})$, compared to those of the neutral TCNE. From the values of $K(\mathrm{C{=}C})$ and $K(\mathrm{C{-}C})$ in the infrared spectra, the decrease in $p(\mathrm{C{=}C})$ was estimated to be 0.36, while the increase in $p(\mathrm{C{-}C})$ was estimated to be 0.08, by using the empirical relationship between $K(12)$ and $p(12)$.[8]

On the other hand, in order to confirm these results, we further calculated the $p(\mathrm{C{=}C})$ and $p(\mathrm{C{-}C})$ values of the neutral TCNE and its anion radical by the use of the Hückel molecular orbital theory.[25] It was assumed that the extra electron on the TCNE anion radical enters in the lowest-vacant molecular orbital of the neutral TCNE. This orbital has the irreducible representation of B_{2g}, where the coefficients of the C_1, C_3, and N_7 atomic orbitals are given by 0.5305,

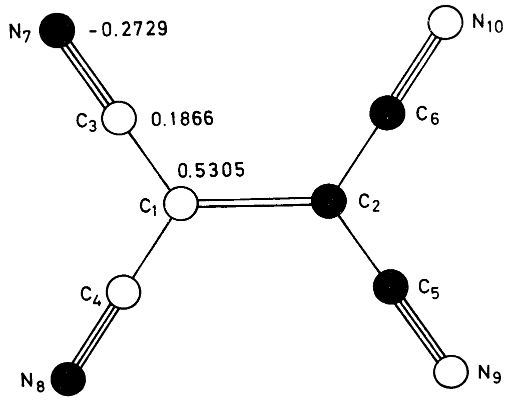

Fig. 2. Schematic representation of the half-occupied molecular orbital of the TCNE anion radical calculated from the Hückel molecular orbital method. The open and closed circles indicate that the coefficients of the atomic orbitals are positive and negative, respectively.

---

[20] E. E. Ferguson and F. A. Matsen, *J. Chem. Phys.*, **29**, 105 (1958).

[21] E. E. Ferguson and F. A. Matsen, *J. Amer. Chem. Soc.*, **82**, 3268 (1960).

[22] E. E. Ferguson, *J. Chim. Phys.*, **61**, 257 (1964).

[23] C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc. Ser. A*, **193**, 456 (1948).

[24] A. Streitwieser, Jr., "Molecular Orbital Theory", John Wiley & Sons, New York and London (1961).

[25] In calculating the Hückel molecular orbitals for the neutral TCNE, the Coulomb integrals of the C and N atoms are taken as α and $\alpha+\beta$, respectively, while the resonance integrals of the C=C, C–C and C≡N bonds, as β, 0.9β and 2.0β, respectively.

0.1866, and −0.2729 respectively (see Fig. 2). Therefore, the extra electron causes a decrease in p(C=C) by 0.28, and an increase in p(C–C) by 0.10, compared to the values of the neutral TCNE. These molecular orbital results are found to agree well with those evaluated from the infrared spectra.

In the heteropolar C≡N bond, although the expression of K(C≡N) *versus* p(C≡N) of the neutral TCNE or its anion radical is not so simple, the extra electron on the TCNE anion radical causes a decrease in K(C≡N); this decrease will definitely lead to a decrease of p(C≡N). In accordance with this view, the Hückel molecular orbital theory shows a decrease in p(C≡N) by 0.05 when an extra electron enters into the lowest-vacant orbital of the neutral TCNE.

Concluding Remarks

The present investigation clearly shows that the difference in the vibrational spectra between the neutral TCNE and its anion radical can be understood on the basis of the difference in their electronic structures. By using these differences, the half-occupied molecular orbital of the TCNE anion radical was found to belong to the B_{2g} irreducible representation. On the other hand, the crystal-field effect may make some contribution to the frequency shifts in these vibrational spectra. In fact, Moore *et al.* observed that certain vibrational frequencies of the TCNE anion radical salts are influenced by the species of the counter cations.[10] However, in a first approximation, this contribution can be neglected in comparison with that of the intramolecular force field.

Rigorously speaking, the $\boldsymbol{G}$ matrix for the anion radical is not identical with that for the neutral TCNE, since the molecular structure of the anion radical is slightly different from that of the neutral TCNE. The difference in their $\boldsymbol{G}$ matrices may make some contribution to the frequency difference. However, this contribution is negligibly small for the bands due to the bond-stretching modes.

The set of force constants obtained for the TCNE anion radical cannot be regarded as a unique solution, since the observation of the fundamental frequencies is limited to the infrared spectra. In this sense, it is also quite desirable to measure the Raman spectrum of the TCNE anion radical. We consider, however, that the set of force constants presented here is reliable enough for studying the difference in the stretching force constants between the neutral TCNE and its anion radical.

In conclusion, the application of the infrared spectra of a neutral molecule and its ion radical can provide valuable knowledge on their electronic structures as well as on their molecular structures. It is interesting to see that their frequency differences give some information concerning the nature of the half-occupied orbital in the ion radical molecular orbitals.