The Vibrational Spectra of Tetracyanothiophene

Jiro NAKANISHI and Tohru TAKENAKA

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611

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The polarized infrared and far-infrared spectra of the tetracyanothiophene (TCNT) crystals were recorded by means of the normal and oblique incidence of radiation upon the (001) and (20$\bar{1}$) sample planes. The Raman spectra of the powdered sample and of a saturated solution in acetonitrile or 1,2-dichloroethane were also obtained. The observed bands were experimentally classified into the symmetry species of the free molecule (the point group C_{2v}) under the assumption of an oriented gas model. Assignments of the observed bands to individual fundamental vibrations were carried out with the aid of the spectral data of the analogous molecules and the normal coordinate analysis of the in-plane vibrations, which was made with a modified Urey-Bradley force field.

Although a number of vibrational studies have been carried out on such fully conjugated tetracyano compounds as tetracyanoethylene (TCNE),[1-7] 7,7,8,8-tetracyanoquinodimethane (TCNQ),[8-11] and 1,2,4,5-tetracyanobenzene (TCNB),[12,13] little attention has been paid to the heterocyclic tetracyano compounds. The present paper will deal with the vibrational spectra of tetracyanothiophene (TCNT), which was first synthesized and physicochemically studied by Simmons and his co-workers.[14]

The infrared and far-infrared spectra of the oriented crystals were measured with a polarized radiation incident, not only normally, but also obliquely upon the (001) and (20$\bar{1}$) sample planes. From the results obtained, the observed bands were classified into three infrared-active species—a_1, b_1 and b_2—of the free molecule (the point group C_{2v}) under the assumption of an oriented gas model. In order to distinguish the lattice vibrations from the molecular vibrations, the far-infrared spectrum of the molten sample was also obtained. The Raman spectra were recorded of the powdered sample and of solutions in acetonitrile and in 1,2-dichloroethane. The observed values of the depolarization ratios in the solutions confirmed the previous findings regarding the classification of the corresponding infrared bands into totally symmetric (a_1) and non-totally symmetric species.

The assignments of the observed bands to individual fundamental vibrations were made with the aid of the spectral data of the analogous molecules and the normal coordinate analysis. The analysis of the in-plane vibrations was carried out using a modified Urey-Bradley force field. The agreements between the observed and calculated frequencies were satisfactory.

Experimental

A sample of TCNT was prepared by the method of Simmons and his co-workers;[14] tetracyano-1,4-dithiin was heated up to 215 °C in 1,2,4-trichlorobenzene, and the products were recrystallized three times from benzene and then sublimed. The colorless crystalline needles of TCNT thus obtained melted at 201—202 °C, while the literature value is 198—199 °C. The ultraviolet spectrum,[14] the results of the elemental analysis, and the X-ray diffraction pattern[15] of this sample were identical with those previously reported. The infrared spectrum of the powdered sample was also the same as that previously reported,[14] except for the 700-cm^{-1} band, which is much weaker in our spectrum. Since this band is considered to be due to a trace of impurities, it may be concluded that our sample is of a higher purity than that of Simmons and his co-workers.[14]

The thin, oriented crystals used for infrared measurements were prepared by the slow, careful cooling of molten samples sandwiched between two potassium bromide plates with a small temperature gradient. The oriented crystals for far-infrared measurements were obtained in the same way between two quartz plates. The crystal structure of TCNT has been reported by Rychnovsky and Britton[15] to be a monoclinic system, $a=13.42$, $b=6.56$, $c=7.07$ Å and $\beta=137°$, with a space group of P_a-C_s^2 with two molecules in a unit cell. The present X-ray diffraction studies showed that the crystal planes developed were either the (001) or (20$\bar{1}$) plane, depending upon the degree of temperature gradient during the crystal preparations.

The infrared spectra between 4000 and 250 cm^{-1} were recorded on a Perkin-Elmer model 521 grating spectrophotometer. For far-infrared measurements between 400 and 30 cm^{-1}, a Hitachi model FIS-3 vacuum grating spectrophotometer was used. The spectrum of the melt in this region was obtained for a sample sandwiched between two silicon plates. In this measurement the double-chopping method was used to eliminate the emission from the heated sample. The polarization measurements in the infrared and far-infrared regions were made with the aid of wire grid polarizers of the silver bromide substrate and of the polyethylene substrate respectively. The Raman spectra of powdered sample and of saturated solutions in acetonitrile and 1,2-dichloroethane at 60 °C were recorded on a Japan Electron Optics Laboratory model JRS-Sl spectrophotometer equipped with an Ar^+ laser as a light source for excitation. A Glan-Thomson prism and polaroid were used for measurements of the depolarization ratios in the solutions.

Selection Rules and Observed Spectra

The TCNT molecule has been reported to have the C_{2v} molecular symmetry.[15] The selection rules for the free molecule and for the molecules in the crystal are given in the correlation diagram of Table 1. The vibrations belonging to the a_1 and b_2 species are of the in-plane mode, while those belonging to the a_2 and b_1 species are of the out-of-plane mode. Table 1 shows that each vibration of the free molecule splits in the crystal into two modes, which are both Raman- and infrared-active, and that there are nine lattice vibrations-three translational and six rotational.

The infrared spectra of the TCNT crystals obtained with the polarized radiation incident normally upon the

TABLE 1. CORRELATION DIAGRAM AND SELECTION RULES[a] OF TCNT

Molecular group C_{2v}	Site group C_1	Factor group C_s^2
12 a_1 (R,p and IR, M_z[b]) 5 a_2 (R, dp) 5 b_1 (R, dp and IR, M_x[b]) 11 b_2 (R, dp and IR, M_y[b])	66 A	33A′ (R and IR, M_{ac}) (t+3r)[c] 33A″ (R and IR, M_b) (2t+3r)[c]

a) R, Raman-active; IR, infrared-active; p, polarized; dp, depolarized. b) For the molecular fixed axes x, y, and z, see Fig. 5. c) t, translational; r, rotational.

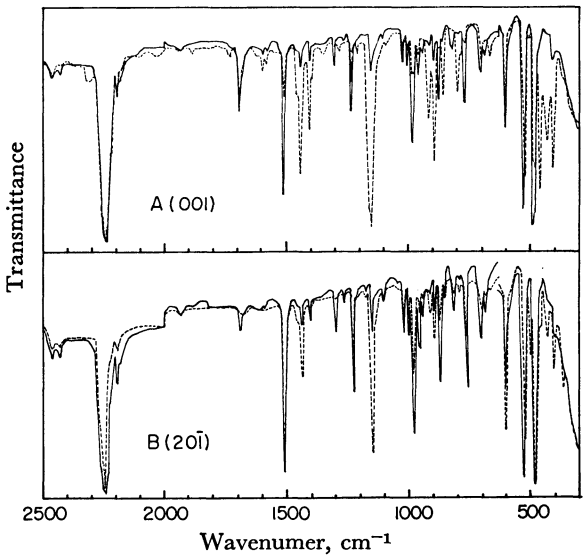

Fig. 1. Polarized infrared spectra of TCNT crystals obtained on normal incidence of radition upon the (001) plane [A] and the (20$\bar{1}$) plane [B].
——: Electric vector parallel to the b axis.
------: Electric vector perpendicular to the b axis.

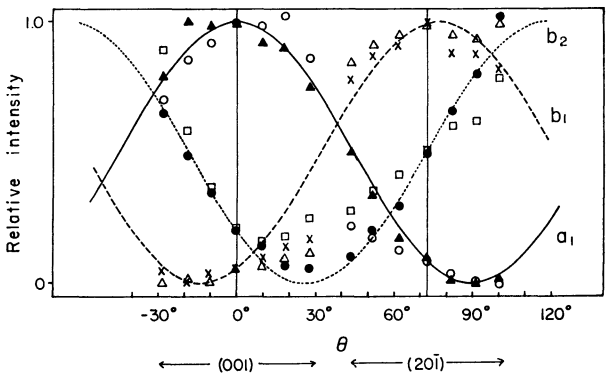

Fig. 2. Relative intensities of the infrared bands as a function of the angle θ between the a axis and the electric vector of the polarized radiation.
□: 1512, ○: 1443, ▲: 1406, ●: 1233, △: 604, ×: 504 cm^{-1} band.

(001) and (20$\bar{1}$) planes are given in Figs. 1A and 1B respectively. The solid lines refer to the orientation of the electric vector parallel to the b axis, while the broken lines refer to the electric vector perpendicular to it. The fact that the factor-group splitting is scarcely observed in Fig. 1 suggests that the effects of the crystal field on the molecular vibrations are small. The agreement between the two solid lines in Figs. 1A and 1B is fairly good, as expected, except for the relative intensity of the band at 1695 cm^{-1}, which may be due to impurities.

Although it is generally known that the observed bands can be classified into three infrared-active species—a_1, b_1, and b_2—by examining the dichroism in Figs. 1A and 1B, there often appear some ambiguities which are due to imperfections in the crystals as well as to experimental errors. To avoid these ambiguities, additional experimental data were introduced by the use of the tilting method, in which the sample plane was rotated in turn by certain angles about the b axis, and the polarized radiation with the electric vector parallel to the ac plane was incident upon the sample plane. The change in the relative intensities of the infrared bands of the a_1, b_1, and b_2 species with the change in the tilting angle was calculated from the crystal data[15] under the assumption of an oriented gas model. The results are given by the solid (a_1), broken (b_1), and dotted (b_2) lines in Fig. 2 as a function of the angle, θ, between the a axis and the electric vector of the polarized radiation. The angles are measured in terms of the rotation which transfers the a axis to the c axis through the obtuse angle.

Experimental data were obtained from the samples of both the (001) and (20$\bar{1}$) planes. The normal incidence of the polarized radiation upon the (001) and (20$\bar{1}$) planes gives the data at $\theta=0°$ and $\theta=72.3°$ in Fig. 2 respectively. The peak intensities of the bands obtained at various angles of θ for the (001) sample were normalized in such a way that the observed intensities at $\theta=0°$ fit into the corresponding calculated values. The same normalization of the observed intensities was carried out on the basis of the values calculated at $\theta=72.3°$ for the (20$\bar{1}$) sample. By the use of both the (001) and (20$\bar{1}$) planes, experimental data could be obtained over a wide range of θ, from $-30°$ to 100°. Although there are some departures of the experimental values from the calculated curves, a glance at the overall θ-dependence of the experimental values leads to unambiguous classifications of the most observed bands into the three infrared-active species. The results of this examination are summarized in Table 2.

Figures 3A and 3B represent the far-infrared spectra of the TCNT crystals recorded on the normal incidence of radiation upon the (001) and (20$\bar{1}$) planes respectively. The solid lines refer to the orientation of the electric vector parallel to the b axis, while the broken lines refer to the electric vector perpendicular to it. The agreements between the two solid lines in Figs. 3A and 3B are good. Figure 3C is the spectrum of TCNT in the molten state. The bands at 90, 83, 76, 74, 54, and 36 cm^{-1} in Fig. 3A or 3B disappear in Fig. 3C, suggesting that they are due to lattice vibrations. We observe

TABLE 2. INFRARED AND RAMAN SPECTRA OF TCNT

Infrared			Raman			Assignment[b]
Crystal	Melt	Species	Powder	Solution	Depolarization	
2258 s[a]		b_2				ν_{13}
2247 s		a_1	2247 sh			ν_1
2239 vs		b_2	2242 vs	2247 s	dp	ν_{14}
2224 s		a_1	2232 vs	2237 vs	p	ν_2
2196 sh		a_1				$\nu_{16}+\nu_{17}=2216$
1695 w						
1512 s		b_2	1510 w	1515 vw	dp	ν_{15}
1443 m		a_1	1444 vs	1444 vs	p	ν_3
1406 w		a_1	1408 vs	1406 vs	p	ν_4
1303 w		b_2				$\nu_7+\nu_{18}=1299$
1233 m		b_2	1232 m	1232 m	dp	ν_{16}
1152 vs		a_1	1153 w	1154 w	p	ν_5
983 s		b_2				ν_{17}
977 sh		a_1				$\nu_{24}+\nu_{26}=979$
916 m		a_1	913 w			$\nu_3-\nu_7=919$
896 m		a_1	900 w	897 sh	p	ν_6
874 m		b_2				$\nu_7+\nu_{21}=867$
859 w		a_1				$\nu_7+\nu_{10}=857$
820 w		b_2				$\nu_{16}-\nu_9=822$
796 m		a_1				$\nu_8+\nu_{10}=796$
770 m		b_2	777 vw			ν_{18}
703, 698 w		b_2	700 vw			$\nu_8+\nu_{22}=687$
604 s		b_1	606 m	606 m	dp	ν_{24}
530 s		b_2				ν_{19}
524 sh			525 s	524 s	p	ν_7
504 w		b_1	504 m	503 m	dp	$\nu_8+\nu_{28}=511$
487 vs		b_1	484 m	485 w	dp	ν_{25}
481 s		a_1		478 m	p	$\nu_6-\nu_9=487$
464 s		a_1	464 sh	467 sh	p	ν_8
436 m		a_1	432 w	430 w	p	$2\nu_{22}=446$
428 sh		b_2		428 w	dp	ν_{20}
410 s		a_1	411 w	411 w	p	ν_9
374 w		b_1	373 vw			ν_{26}
342 vw						ν_{21}
332 vw						ν_{10}
226, 223 m	218 m	b_2	222 w	220 w	dp	ν_{22}
188, 181 vs	168 vs	b_1	184 w			ν_{27}
146 m		a_1	144 sh			$\nu_8-\nu_{10}=132$
128 s		b_1				$\nu_{24}-\nu_8=141$
125 s	120 vs	b_2	126 vs			ν_{23}
118 s		a_1	118 sh			ν_{11}
113 vs	96 s	a_1				ν_{12}
90 vw		A″				
83 m		A′				
76 w		A′	76 sh			
74 m		A″				
58 w	57 w	a_1	59 vs			$\nu_7-\nu_8=61$
54 sh		A″				
46 vw		b_1	48 sh			ν_{28}
36 vw		A′				

a) The relative intensities of this column refer to those of the powder bands, because those of the crystal bands depend largely upon the direction of the electric vector of polarized radiation. b) See Tables 3 and 4.

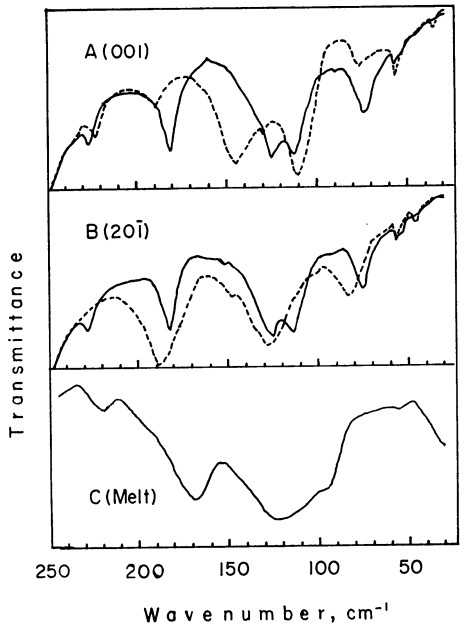

Fig. 3. Polarized far-infrared spectra of TCNT crystals obtained on normal incidence of radition upon the (001) plane [A] and (20$\bar{1}$) plane [B].
——: Electric vector parallel to the b axis.
------: Electric vector perpendicular to the b axis.
[C] Far-infrared spectrum of TCNT in the molten state.

some frequency shifts of the bands with the phase change from crystal to melt. As is apparent from Table 1, the lattice bands at 90, 74, and 54 cm^{-1}, found only in the solid lines of Figs. 3A and 3B, are to be assigned to the A″ vibrations of the factor group, while the bands at 83, 76, and 36 cm^{-1}, found only in the broken lines, are to be assigned to the A′ vibrations. The classification of the far-infrared bands due to molecular vibrations into the respective species was also made by means of the tilting method mentioned above. These results are given in Table 2. In this low-frequency region the factor-group splittings are observed at 226 and 223 cm^{-1} and at 188 and 181 cm^{-1}.

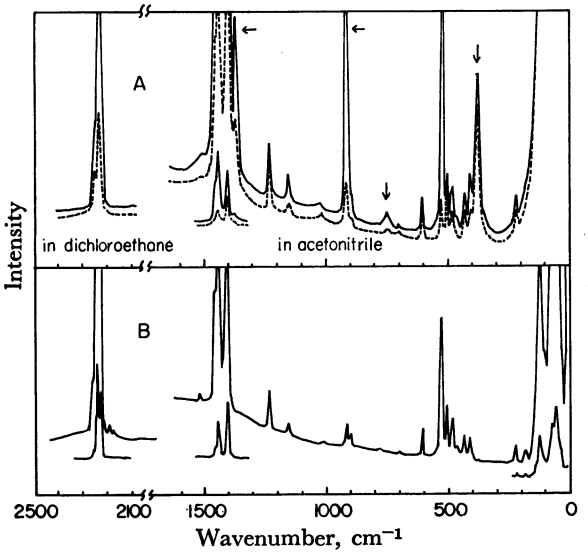

Fig. 4. [A] Raman spectra of TCNT in acetonitrile and in 1,2-dichloroethane. Bands marked with the arrow are due to solvents.
——: $I_{//}$, ------: $I_{\perp}$.
[B] Raman spectrum of TCNT powder.

Figure 4A represents the Raman spectra of the acetonitrile and the 1,2-dichloroethane solutions of TCNT. The bands marked with arrows are solvent bands. The solid and broken lines give the spectra of Raman scatterings with the electric vector parallel and perpendicular to that of the exciting light respectively. The observed values of the depolarization ratios confirmed the previous results regarding the classification of the corresponding infrared bands into the totally symmetric (a_1) and non-totally symmetric species (b_1 and b_2), as is seen in Table 2. The Raman spectrum of the powdered sample is also given in Fig. 4B and Table 2.

Assignments

In order to make the assignments of the observed bands to the individual fundamental vibrations, the following examinations were carried out besides the discussions in the previous section: (a) a comparison of the spectral data with those of the partly analogous molecules, such as TCNE,[1-7] TCNQ,[8-11] TCNB,[12,13] thiophene[16] and the bis(maleonitrile dithiolato) Ni(II) anion,[17] and (b) the normal coordinate analysis of the in-plane vibrations mentioned in the next chapter. In the following discussions, the mean values of the infrared frequencies of the crystal and Raman frequencies of the powder are used as the observed frequencies when both were found.

The assignments of the a_1 bands at 2247, 2228, 1444, 1407, 1153, and 525 cm^{-1} and of the b_2 bands at 2258, 2241, 1511, 1233, 983, 530, 223, and 126 cm^{-1} were straightforward.

The a_1 fundamental band ν_6, mainly due to the C–C stretching vibration, can be expected around 900 cm^{-1} by the normal coordinate analysis. Both the infrared bands at 916 and 896 cm^{-1}, which have been determined by the tilting method to belong to the a_1 species, are assignable to this vibration. Of the corresponding Raman bands in the solution, the low-frequency one at 897 cm^{-1} (900 cm^{-1} for the powder) was found to be polarized, although the high-frequency band (913 cm^{-1} for the powder) could not be observed because of the band overlap with the strong solvent band. Furthermore, in the process of the normal coordinate analysis, where the refinement of the force constants was carried out to get a better agreement between the calculated and the observed values for the above-mentioned fourteen bands which were assigned without ambiguities, it was found that the calculated frequency of the ν_6 vibration showed a tendency to decrease to *ca.* 900 cm^{-1}. Therefore, the 898 cm^{-1} band (on the average) was assigned to this vibration, and the 915-cm^{-1} band, to the combination tone [$\nu_3(a_1)-\nu_7(a_1)=919$ cm^{-1} (a_1)].

Thr b_2 fundamental band ν_{18} is thought to be present between 900 and 750 cm^{-1}. In this region, three infrared bands at 874, 820, and 770 cm^{-1} were found to belong to the b_2 species. Since, however, only one Raman band was observed at 777 cm^{-1}, corresponding to the infrared

band at 770 cm^{-1}, this band (774 cm^{-1} on the average) was assigned to the ν_{18} vibration, and the 874- and 820-cm^{-1} bands, to the combination tones [$\nu_7(a_1)+\nu_{21}(b_2)=$ 867 cm^{-1} (b_2) and $\nu_{16}(b_2)-\nu_9(a_1)=822$ cm^{-1} (b_2) respectively].

In the region from 500 to 400 cm^{-1}, two a_1 fundamental bands, ν_8 and ν_9 are to be expected. Apparently, four infrared bands of the a_1 species and four corresponding polarized Raman bands were found in this region. Since there is no further experimental evidence on the basis of which to choose two of them as the fundamentals, the assignments were carried out by reference to the tendency of the calculated frequency variation found in the refining process of the normal coordinate analysis, as has been mentioned above. Thus, the 464- and 411-cm^{-1} bands (on the average) were assigned to the ν_8 and ν_9 vibrations respectively. The 483-cm^{-1} band (on the average) was attributed to the combination tone [$\nu_6(a_1)-\nu_9(a_1)=487$ cm^{-1} (a_1)], and the 434-cm^{-1} band (on the average), to the overtone [$2\nu_{22}(b_2)=446$ cm^{-1} (a_1)].

The b_2 fundamental band ν_{20}, mainly due to the C–C≡N deformation vibration, can be expected in the same frequency region. Since only one infrared band of the b_2 species and the corresponding depolarized Raman band were observed in this region, this band (430 cm^{-1} on the average) was ascribed to the ν_{20} fundamental vibration.

The a_1 fundamental band ν_{10}, mainly due to the C=C–S bending vibration, and the b_2 fundamental band ν_{21}, mainly due to the C=C–C (ring) bending vibration, are to be expected between 400 and 300 cm^{-1}. Only two infrared bands, at 342 and 332 cm^{-1}, were observed in this region, except for the 374-cm^{-1}, which belongs to the b_1 species. Therefore, these bands were assigned to the ν_{21} and ν_{10} vibrations respectively, although they are very weak.

In the region from 150 to 100 cm^{-1}, three infrared bands of the a_1 species were observed at 146, 118, and 113 cm^{-1}. Correspondingly, two Raman bands were seen at 144 and 118 cm^{-1}; the latter seemed to include two components. By referring to the normal coordinate analysis, the 118- and 113-cm^{-1} bands were assigned to the ν_{11} and ν_{12} vibrations respectively. The 145-cm^{-1} band (on the average) was attributed to the combination tone $[\nu_8(a_1)-\nu_{10}(a_1)=132$ cm^{-1} (a_1)].

A weak infrared band of the a_1 species was observed at 58 cm^{-1} for the crystal and at 57 cm^{-1} for the melt, suggesting that it is due to the molecular vibration. Correspondingly, a very strong Raman band was observed at 59 cm^{-1} for the powdered sample. Since, however, no fundamental vibration belonging to the a_1 species was expected in this low-frequency region, it was assigned to the difference band $[\nu_7(a_1)-\nu_8(a_1)=61$ cm^{-1} (a_1)]. The strong intensity of the Raman band may be interpreted in terms of the overlap with the lattive vibration band.

In the region lower than 700 cm^{-1}, seven infrared bands of the b_1 species were observed at 604, 504, 487, 374, 185, 128, and 46 cm^{-1}, while five b_1 out-of-plane fundamentals (ν_{24}—ν_{28}) were expected. Almost all of these infrared bands had corresponding Raman bands. The assignments of these bands were carried out tentatively by comparison with the spectral data of the analogous molecules. The 605- and 374-cm^{-1} bands (on the average) were assigned without ambiguity to the ν_{24} (C–S torsion) and ν_{26} (C–C≡N deformation) vibrations respectively.

Either one of the infrared bands at 504 and 487 cm^{-1} can be expected to be the fundamental C–C≡N deformation band ν_{25}. The corresponding depolarized Raman bands were observed at 503 and 485 cm^{-1} for the solution (504 and 484 cm^{-1} for the powder). Since the infrared band at 487 cm^{-1} was very much stronger than that at 504 cm^{-1}, while the two Raman bands had nearly the same intensities, the 486-cm^{-1} band (on the average) was assigned to the ν_{25} vibration, and the 504 cm^{-1} band, to the combination tone $[\nu_8(a_1)+\nu_{28}(b_1)=$ 511 cm^{-1} (b_1)].

Although one fundamental vibration, ν_{27}, is thought to appear in the region from 200 to 100 cm^{-1}, two infrared bands of the b_1 species were observed at 185 cm^{-1} (the means value of the factor group splitting) and 128 cm^{-1}. The former band was found to remain in the melt (168 cm^{-1}), while its corresponding Raman band was observed at 184 cm^{-1}. For the latter band, however, the presence of an infrared band in the molten state and of a Raman band was not certain. Thus, the 185-cm^{-1} band was assigned to the ν_{27} vibration, and the 128-cm^{-1} band, to the combination tone $[\nu_{24}(b_1)-\nu_8(a_1)=141$ cm^{-1} (b_1)].

The lowest out-of-plane fundamental vibration, ν_{28}, seems to appear below 100 cm^{-1}. The weak infrared band was observed at 46 cm^{-1} for the crystal in both the solid and broken lines of Figs. 3A and 3B. Although the band could not be observed for the melt, the above fact may suggest that this is due to molecular vibration, because the lattice vibration should appear in either the solid or broken line. Furthermore, the use of the tilting method seemed to show that the crystal band at 46 cm^{-1} belonged to the b_1 species. Thus, this band (47 cm^{-1} on the average) was assigned to the ν_{28} vibration. The corresponding Raman band was found at 48 cm^{-1}. No Raman bands assignable to the five a_2 out-of-plane fundamentals were observed.

The observed infrared and Raman bands which have not been discussed yet were assigned to the overtone and combination tone according to the experimental results regarding the classification of the bands. The results of the discussion in this chapter are summarized in the last column of Table 2. The frequencies of the in-plane and

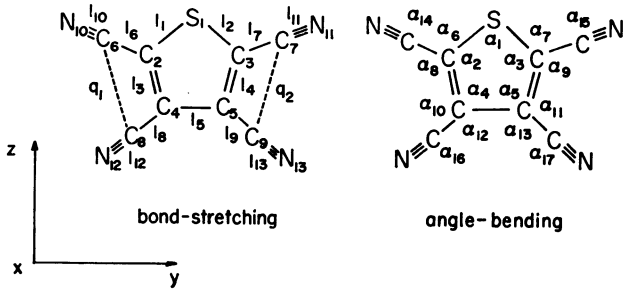

Fig. 5. In-plane internal coordinates of TCNT.

TABLE 3. IN-PLANE FUNDAMENTAL VIBRATIONS OF TCNT

Symmetry species		Obsd[a] freq. (cm^{-1})	Calcd freq. (Initial)	Calcd freq. (Final)	Dev.[b] (%)	P.E.D. (%)[c,d]
a_1	ν_1	2247	2318	2245	−0.1	C≡N (II) stretch. (73)
	ν_2	2228	2314	2242	0.6	C≡N (I) stretch. (74)
	ν_3	1444	1513	1445	0.1	C=C stretch. (71)
	ν_4	1407	1411	1409	0.1	C–C (ring) stretch. (44)
	ν_5	1153	1214	1150	−0.3	C–S stretch. (44)
	ν_6	898	919	894	−0.4	C–C (I) stretch. (27)
	ν_7	525	531	525	0.0	C–C (II) stretch. (31), C–S stretch. (26)
	ν_8	464	505	461	−0.6	C–C≡N(I) deform. (27), $\overset{C}{S}\!\!>$C–CN deform. (26)
	ν_9	411	470	411	0.0	C–C≡N(II) deform. (34)
	ν_{10}	332	315	332	0.0	C=C–S bend. (39)
	ν_{11}	118	135	124	5.1	C–C≡N(I) deform. (53), $\overset{C}{S}\!\!>$C–CN deform. (37)
	ν_{12}	113	123	107	−5.3	$\overset{C}{C}\!\!>$C–CN deform. (47), C–C≡N(II) deform. (46)
b_2	ν_{13}	2258	2319	2245	−0.6	C≡N(II) stretch. (76)
	ν_{14}	2241	2313	2242	0.0	C≡N(I) stretch. (76)
	ν_{15}	1511	1551	1509	−0.1	C=C stretch. (63)
	ν_{16}	1233	1247	1231	−0.2	C–C(I) stretch. (29), C–S stretch. (27)
	ν_{17}	983	1059	986	0.3	C–C(II) stretch. (41), C–S stretch. (29)
	ν_{18}	774	897	773	−0.1	$\overset{C}{C}\!\!>$C–CN deform. (37), C–C(I) stretch. (31)
	ν_{19}	530	541	529	−0.2	$\overset{C}{S}\!\!>$C–CN deform. (35), C–S stretch. (34)
	ν_{20}	430	491	449	4.4	C–C≡N(II) deform. (28)
	ν_{21}	342	387	342	0.0	C=C–C (ring) bend. (39)
	ν_{22}	223	251	221	0.9	C–C≡N(I) deform. (40), C–C≡N(II) deform. (37)
	ν_{23}	126	126	118	−6.3	C–C≡N(I) deform. (30), C–C≡N(II) deform. (29)

a) The mean values of the frequencies are cited whenever both the infrared band of the crystal and Raman band of the powder are observed or when factor group splitting occurs. b) Dev.$=100[\nu(\text{Calcd})-\nu(\text{Obsd})]/\nu(\text{Obsd})$. c) Only contributions greater than 25 per cent are included. d) The mark (I) refers to the C_2–$C_6{\equiv}N_{10}$ and C_3–$C_7{\equiv}N_{11}$ groups, and (II), to the C_4–$C_8{\equiv}N_{12}$ and C_5–$C_9{\equiv}N_{13}$ groups (see Fig. 5).

out-of-plane fundamentals are listed in Tables 3 and 4 respectively.

Normal Coordinate Analysis of In-plane Vibrations

Wilson's ***GF*** matrix method[18] was used for the normal coordinate analysis. The numerical calculations were carried out with the aid of a FACOM 230-75 digital computer of Kyoto University Data Processing Center. The internal coordinates of TCNT are given in Fig. 5. The equilibrium bond lengths and bond angles adopted are the mean values of those determined by Rychnovsky and Britton:[15] $l_1^\circ=l_2^\circ=1.71$ Å, $l_3^\circ=l_4^\circ=1.37$ Å, $l_5^\circ=1.40$ Å, $l_6^\circ=l_7^\circ=l_8^\circ=l_9^\circ=1.41$ Å, $l_{10}^\circ=l_{11}^\circ=l_{12}^\circ=l_{13}^\circ=1.17$ Å, $\alpha_1^\circ=89.1°$ $\alpha_2^\circ=\alpha_3^\circ=114.0°$, $\alpha_4^\circ=\alpha_5^\circ=111.3°$, $\alpha_6^\circ=\alpha_7^\circ=121.4°$, $\alpha_8^\circ=\alpha_9^\circ=124.6°$, $\alpha_{10}^\circ=\alpha_{11}^\circ=125.4°$ and $\alpha_{12}^\circ=\alpha_{13}^\circ=123.3°$. Furthermore, $\alpha_{14}^\circ=\alpha_{15}^\circ=\alpha_{16}^\circ=\alpha_{17}^\circ=180°$ are assumed for the sake of simplicity.

TABLE 4. OUT-OF-PLANE FUNDAMENTAL VIBRATIONS OF TCNT

Symmetry species	Observed frequency[a] (cm^{-1})		Assignment [b]
b_1	ν_{24}	605	C–S torsion
	ν_{25}	486	C–C≡N (I and II) deformation
	ν_{26}	374	
	ν_{27}	185	$\overset{C}{S}\!\!>$C–CN and $\overset{C}{C}\!\!>$C–CN deformation
	ν_{28}	47	

a) See footnote a of Table 3. b) See footnote d of Table 3.

As the potential function for the in-plane vibrations, the modified Urey-Bradley force field (mod. UBFF) given by:

$$2V(\text{mod. UBFF}) = 2V(\text{UBFF}) + 2\alpha(\Delta l_3\Delta l_5+\Delta l_4\Delta l_5) + C\sum_i^2(\Delta q_i)^2 + 2C'\sum_i^2(\Delta q_i)q_i$$

was used. Here, q_i is the equilibrium non-bonded distance between C_6 and C_8 atoms and between C_7 and C_9 atoms. V(UBFF) consists of terms with five bond-stretching, seven angle-bending, and six non-bonded repulsion force constants; those constants are listed in the first column of Table 5. The force constant α is the coefficient of the cross terms between C=C and C–C (ring) stretching coordinates; it is introduced to take account of the presumed resonance interaction in the thiophene ring. The constant C is the coefficient of the *cis* non-bonded repulsion terms between two carbon

TABLE 5. FORCE CONSTANTS[a] (mdyn/Å) OF TCNT

	Force const (Initial)	Force const (Final)	Dispersion
K (C–S)	4.75	4.15	—[b]
K (C–C)	4.58	4.55	0.24
K (C≡N)	18.51	17.41	0.16
K(C=C)	5.05	5.60	0.14
K (C–C, ring)	4.94	4.27	0.28
H (C–S–C)	0.16	0.28	0.41
H (C=C–S)	0.06	0.05	0.25
H (C=C–C, ring)	0.15	0.32	0.21
H (C–C–S)	0.21	0.29	0.10
H (C–C=C)	0.29	0.43	0.13
H (C–C–C)	0.57	0.14	0.08
H (C–C≡N)	0.19	0.15	0.00
F (C–S–C)	0.21	0.11	0.11
F (C=C–S)	0.25	0.98	0.31
F (C=C–C, ring)	0.57	−0.13	0.17
F (C–C–S)	0.22	0.15	0.10
F (C–C=C)	0.71	0.14	0.12
F (C–C–C)	0.48	0.23	0.06
α		0.41	—[b]
C		0.10	—[b]

a) The $F' = -0.10\,F$ and $C' = -0.1\,C$ relations were assumed. b) Fixed.

atoms. The $C' = -0.1C$ relation was assumed, as usual.

For the first calculation, the values of the force constants were transferred from the bis(maleonitrile dithiolato)Ni(II) anion,[17] diethyl ether,[19] TCNQ,[9] and TCNB.[12] These values are shown in the second column of Table 5, while the frequencies calculated with these values are given in the third column of Table 3. The agreements between the calculated and observed frequencies are not very good. For the purpose of obtaining a good agreement, after some refinements of the force constants by the trial-and-error method using the Jacobian matrix, repetitions of the calculations with several sets of force constants were carried out by the least-squares method. The converged set of the force constants and their dispersion values are given in Table 5. The frequencies calculated with this set of force constants are compared with the observed values in Table 3. The agreement is satisfactory. The last column of Table 3 represents the potential energy distribution.

It is apparent from Table 5 that the C–S and C–C (ring) single bonds acquire a partial double-bond character, while the C=C and C≡N bonds, on the other hand, lose their double- and triple-bond characters respectively. These facts, and the necessity of the cross terms with the α coefficient, suggest that the resonance takes place throughout the molecule of TCNT, as is to be expected from the configuration of the molecule.

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