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A Study of Electronic Structure of 1,2,4,5-Tetracyanobenzene Anion Radical by Resonance Raman Effect

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Resonance Raman spectrum of 1,2,4,5-tetracyanobenzene anion radical (TCNB$^-$) was measured and compared with that of the neutral molecule (TCNB). Particularly, a Raman line assigned to C_1C_2 stretching vibration decreased its frequency remarkably when TCNB was converted to TCNB$^-$. This decrease indicated that the lowest unoccupied molecular orbital (LUMO) of TCNB had a node on C_1C_2 bonding, showing that the LUMO belonged to an a_u species. Furthermore vibrational analyses of TCNB and TCNB$^-$ were carried out and the assignment of their Raman lines was confirmed.

1,2,4,5-Tetracyanobenzene (TCNB, see Fig. 1) is a familiar molecule as an electron acceptor and many spectroscopic studies have been carried out in connection with its charge transfer interaction. However, the symmetry of the lowest unoccupied molecular orbital (LUMO) of TCNB has not been certified clearly. A simple theory such as linear combination of molecular orbital (LCMO) method shows only that both of an a_u and a b_{1u} MO can become the LUMO but does not indicate which MO really is the LUMO. ESR studies do not lead to a clear conclusion, either.[1)]

Recently, Takahashi and Maeda reported resonance Raman spectra of some aromatic anion radicals and found the striking resonance enhancement of their skeletal stretching vibrations.[2)] They studied the change of frequency of the respective Raman lines when a neutral molecule was converted to an anion radical and showed that the change was closely related to the distribution of nodes of the LUMO which is occupied by an unpaired electron.

Therefore, in the present study, resonance Raman spectrum of TCNB anion radical (TCNB$^-$) was measured and compared with that of TCNB in order to certify the assignment of the LUMO more clearly. Furthermore TCNB$^-$ has a pseudo degeneracy in the ground electronic state, which is an interesting case among the complicated vibronic potentials. Consequently vibrational analyses were carried out taking a vibronic effect into account.

Experimental

Commercially available TCNB (Frinton Laboratories) was used after sublimation, together with one offered by Dr. M. Tahara, our laboratory. TCNB-d_2 was offered by Prof. T. Takenaka, Kyoto University. Tetracyanoethylene (TCNE), tetracyanoquinodimethane (TCNQ) and hexamethylbenzene (HMB) (Tokyo Kasei) were used after sublimation and recrystallization. Tetrahydrofuran (THF), 1,2-dimethoxyethane (DME), and *N,N*-dimethylformamide (DMF) (Wako, Special Grade) were degassed and dehydrated repeatedly *in vacuo* after distillation and used as solvents for anion radicals. Acetonitrile and dichloromethane (Wako, Spectroscopic Grade) were used without further purification.

TCNB$^-$ was prepared by reduction with alkali metals *in vacuo* as usual.[3)]

Raman spectra were obtained with a JEOL 400D spectrometer equipped with a HTV 649 photomultiplier, using a CR 52G Ar$^+$ laser as a continuous exciting source. All measurements were carried out at room temperature.

Results and Discussion

Resonance Raman Spectra and Their Assignment. TCNB$^-$ showed an intense absorption band at 463 nm, as shown in Fig. 2, which is in good agreement with the result by Ishitani and Nagakura.[3)] Figure 3 shows the resonance Raman spectrum of TCNB$^-$ by 457.9 nm excitation in THF solution, together with the Raman spectrum of TCNB in acetonitrile solution. The observed values of Raman shift and depolariza-

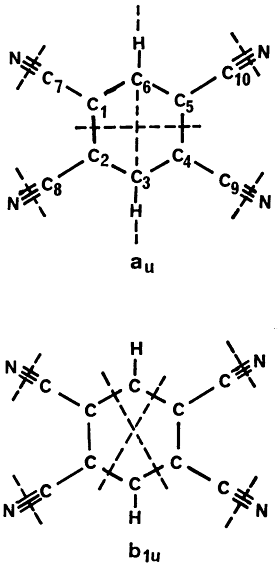

Fig. 1. The a_u MO and the b_{1u} MO of TCNB.

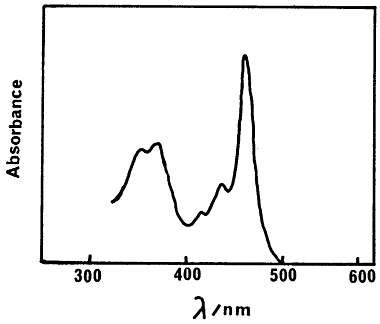

Fig. 2. Absorption spectrum of K$^+$TCNB$^-$ in THF solution.

TABLE 1. OBSERVED RAMAN FREQUENCIES, DEPOLARIZATION RATIOS AND THEIR ASSIGNMENT FOR TCNB$^-$ AND TCNB-d_2^-

	ν (cm^{-1})		ρ_l	Assignment
K$^+$TCNB$^-$	408	m	0.22	a_g ring bend. (402 cm^{-1})
	522	s	0.27	a_g CN bend.
	679	w	0.34	a_g ring bend. (725 cm^{-1})
	792	w	0.25	
	928	s	0.34[a]	
	991	w	+	
	1039	m	0.26[b]	522×2=1044
	1279	m	0.25	a_g C_1C_6 and C_1C_7 str. (1260 cm^{-1})
	1456	s	0.29	a_g C_1C_2 str. (1546 cm^{-1})
	1791	w	+	1279+522=1801
	1858	m	0.22	928×2=1856 1456+408=1864
	1976	m	0.26	1456+522=1978
	2198	m	0.19	a_g CN str. (2237 cm^{-1})
	2283	w	0.31	1456+928=2384
K$^+$TCNB-d_2^-	409	w	0.35	a_g ring bend. (403 cm^{-1})
	520	s	0.38	a_g CN bend.
	917	s	0.32[a]	
	980	w	0.33	
	1043	m	0.31[b]	520×2=1040
	1266	m	0.35	a_g C_1C_6 and C_1C_7 str. (1250 cm^{-1})
	1446	s	0.27	a_g C_1C_2 str. (1539 cm^{-1})
	1792	w	0.36	1266+520=1786
	1844	w	0.25	917×2=1834 1446+409=1855
	1967	w	0.37	1446+520=1966
	2198	w	0.33	a_g CN str. (2243 cm^{-1})
	2362	w	0.36	1446+917=2363

a) In DME. b) In DMF. s; Strong, m; medium, w; week. +; Polarized but cannot be presented numerically. ( ); Observed frequencies of corresponding lines of TCNB.

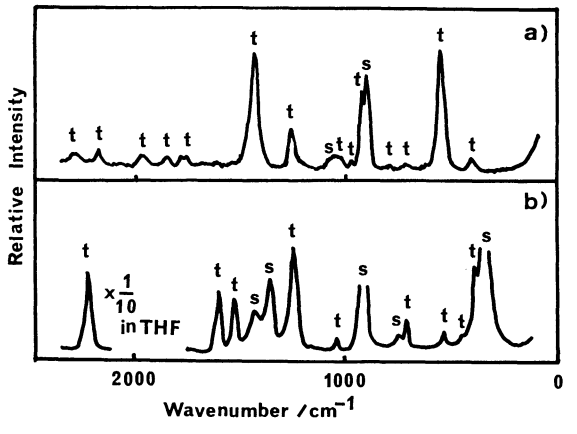

Fig. 3. Raman spectrum of TCNB$^-$ and TCNB. a) Resonance Raman spectrum of K$^+$TCNB$^-$ in THF solution (1.8×10^{-3} mol·dm^{-3}) by 457.9 nm excitation. s) Lines of solvent, t) Lines of TCNB$^-$. b) Raman spectrum of TCNB in acetonitrile solution (2.8 mol·dm^{-3}) by 488.0 nm excitation. s) Lines of solvent, t) Lines of TCNB. A 2237 cm^{-1} line was measured in THF solution.

tion ratio of TCNB$^-$ are shown in Table 1. All of the observed lines are totally symmetric because they were strongly polarized. The spectrum is not affected by varying solvents (THF, DME, and DMF) and cations (Na$^+$ and K$^+$).

The assignment of the observed Raman lines of TCNB$^-$ was carried out by referring to the assignment of Raman lines of TCNB. Table 1 shows the assignment for TCNB$^-$ and TCNB. TCNB has three totally symmetric lines, 1260, 1546, and 2237 cm^{-1} in the region of their skeletal stretching vibrations. Takenaka *et al.* assigned these lines to a mixing mode of C_1C_6 stretching and C_1C_7 stretching, a C_1C_2 stretching and a CN stretching vibration, respectively.[4] The three lines of TCNB$^-$, 1279, 1456, and 2198 cm^{-1}, should correspond to the fundamental vibrations of TCNB, 1260, 1546, and 2237 cm^{-1}, respectively. A 725 cm^{-1} line of TCNB may correspond to one of a few weak lines of TCNB$^-$ observed in 600—700 cm^{-1} region. A 402 cm^{-1} line of TCNB corresponds to a 408 cm^{-1} line of TCNB$^-$.

The present correspondence of the three Raman lines assigned to the skeletal stretching vibrations between TCNB and TCNB$^-$, which is essential in the later discussion, was confirmed by the resonance Raman study of CT complex of TCNB. Kaya *et al*,

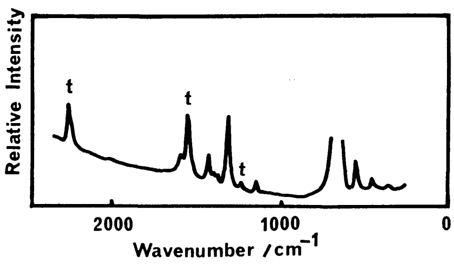

Fig. 4. Resonance Raman spectrum of HMB–TCNB in dichloromethane solution (TCNB; 0.17 mol·dm^{-3}, HMB; 0.58 mol·dm^{-3}) by 457.9 nm excitation. t) Lines of TCNB moiety.

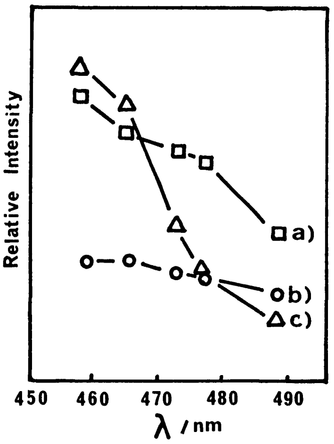

Fig. 5. Excitation profiles of the three Raman lines of HMB–TCNB.
a) 2237 cm^{-1} line, b) 1260 cm^{-1} line, c) 1546 cm^{-1} line.

reported the resonance Raman effect of weak CT complex[5] and obtained an interesting result where the degree of resonance enhancement of Raman lines of an acceptor moiety by the excitation at CT absorption band was closely related to the change in frequency of the acceptor molecule when it was converted to the anion radical. In a weak CT complex, an acceptor moiety in an excited CT state can be regarded as an anion radical. According to the Franck-Condon mechanism of Raman intensity, when a deviation of molecular geometry of an acceptor from neutral molecule to anion radical is large along a vibrational coordinate, the Raman lines of the acceptor moiety which relate to the vibrational coordinate show resonance enhancement by the excitation at CT absorption band.

TCNB forms CT complex with HMB and the complex has an absorption band of CT character at 426 nm. Figure 4 shows the observed resonance Raman spectrum of HMB–TCNB by the excitation with 457.9 nm line. The change of intensity by complex formation was observed for the three skeletal stretching vibrations of TCNB but any frequency changes were not observed. A striking enhancement was observed to take place for 1546 cm^{-1} line and a mild enhancement for 2237 cm^{-1} line, while 1260 cm^{-1} line showed an inappreciable change of intensity, as shown in Fig. 5. On the other hand, when TCNB is converted to TCNB$^-$, the above mentioned three lines of TCNB show the frequency changes, 1546−1456=90, 2237−2198=37, and 1260−1279=−19 cm^{-1}, respectively. These values correspond to the change of force constants, −11.6, −3.3, and +3.0%, respectively. These imply, in turn, the changes of bond order, that is, bond length of the relating CC and CN bondings. Therefore it is reasonably supported that the change of bond length from TCNB to TCNB$^-$ is striking for C_1C_2, mild for CN and C_1C_7 bondings. This inclination is parallel to that of resonance enhancement of the Raman intensity for the CT complex by the excitation at CT absorption band. Consequently, it is confirmed that the present relations of the three Raman lines between TCNB and TCNB$^-$ are reasonable.

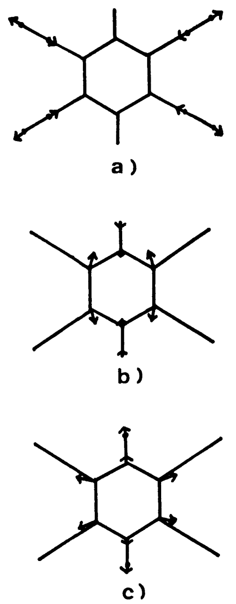

Fig. 6. The Cartesian displacements of normal vibrations of TCNB$^-$.
a) a_g 2215 cm^{-1}, b) a_g 1466 cm^{-1}, c) a_g 1259 cm^{-1}.

Assignment of the LUMO of TCNB. The present analysis of Raman spectra of TCNB$^-$ led to a clearcut assignment of the LUMO of TCNB, as follows. As TCNB has four substituents on 1,2,4, and 5 positions, the two components of e_{2u} MO of benzene (one a_u MO, the other b_{1u} MO) are able to form bonding MO's with orbitals of substituents (see Fig. 1). When TCNB is reduced to TCNB$^-$, an unpaired electron occupies the LUMO of TCNB. If the a_u MO is occupied, C_1C_2 and CN bondings become to have more antibonding character, while C_1C_7 bonding becomes to have more bonding character. Therefore the force constants of the former bondings decrease, but that of the latter bonding increases. Consequently, the Raman lines assigned to C_1C_2 and CN stretching vibrations decrease their frequencies, while the line assigned to C_1C_7 stretching vibration increases its frequency. If the b_{1u} MO is occupied, the Raman lines assigned to C_1C_6 and CN stretching vibrations decrease their frequency, while the lines assigned to C_1C_7 and C_1C_2 stretching vibrations increase their frequency.

The present result shows the large decrease in fre-

TABLE 2. OBSERVED AND CALCULATED FUNDAMENTAL FREQUENCIES OF TCNE

Species	ν_{obsd}[a)]	ν_{calcd}	Assignment
a_g	2235 cm^{-1}	2243 cm^{-1}	CN str.
	1569	1561	C_1C_2 str.
	595	610	C_1C_3 str.
	535	512	$(C_3C_1C_4+CCN)$ bend.
		126	$C_3C_1C_4$ bend.
b_{1g}	2247	2238	CN str.
	1282	1287	C_1C_3 str. + $C_2C_1C_3$ bend.
		498	$(CCN+C_2C_1C_3)$ bend.
	254	271	CCN bend.
b_{2u}	2230	2224	CN str.
	1155	1138	C_1C_3 str.
	429	428	CCN bend.
		102	$C_2C_1C_3$ bend.
b_{3u}	2262	2249	CN str.
	959	975	C_1C_3 str.
	579	576	$C_3C_1C_4$ bend.
		168	CCN bend.

a) For b_{2u} and b_{3u} species, the values reported by Takenaka and Hayashi[7)] were used. For a_g and b_{1g} species, the values observed in the present work were used, based on the assignment by Michaelian *et al.*[8)]

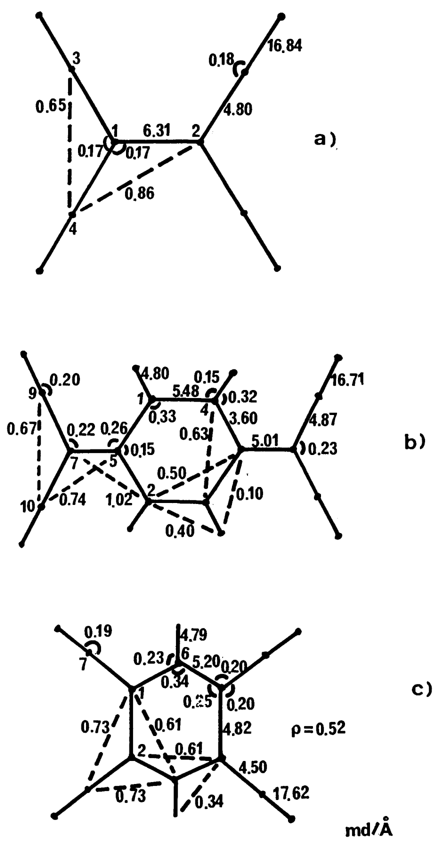

Fig. 7. The force constants of TCNE, TCNQ, and TCNB.
a) TCNE, b) TCNQ, c) TCNB,

TABLE 3. OBSERVED AND CALCULATED FUNDAMENTAL FREQUENCIES OF TCNQ

Species	ν_{obsd}[a)]	ν_{calcd}	Assignment
a_g	3048 cm^{-1}	3050 cm^{-1}	CH str.
	2229	2228	CN str.
	1602	1608	$(C_1C_4+C_5C_7)$ str.
	1454	1451	C_5C_7 str.
	1207	1207	CH bend.
	948	960	$(C_1C_5+C_7C_9)$ str. + $(C_9C_7C_{10}+\text{ring})$ bend.
	711	724	C_1C_5 str. + ring bend.
	602	600	$(C_9C_7C_{10}+CCN)$ bend.
	334	330	$(C_9C_7C_{10}+CCN+\text{ring})$ bend.
	114	130	$C_9C_7C_{10}$ bend.
b_{1g}	3030	3053	CH str.
	2223	2226	CN str.
	1451	1454	CH bend.
	1323	1342	$(C_1C_5+C_7C_9)$ str. + $(C_1C_5C_7+C_5C_7C_9)$ bend.
	1187	1182	
	609	620	ring bend.
	519	529	$(\text{ring}+C_1C_5C_7)$ bend.
		407	CCN bend.
		127	$C_5C_7C_9$ bend.
b_{2u}	3053	3048	CH str.
	2228	2226	CN str.
	1540	1538	C_1C_4 str.
	1354	1344	$(C_7C_9+C_1C_5)$ str. + $(C_1C_5C_7+C_5C_7C_9)$ bend.
		1231	CH bend.
	1125	1108	$(C_7C_9+C_1C_5)$ str.
	498	496	$(CCN+C_5C_7C_9)$ bend.
		321	
		77	CCN bend.
b_{3u}	3065	3055	CH str.
	2228	2227	CN str.
	1545	1540	C_5C_7 str. + CH bend.
	1405	1413	
	998	999	$(C_1C_5+C_7C_9)$ str. + $(C_9C_7C_{10}+\text{ring})$ bend.
	962	952	C_1C_5 str. + ring bend.
	600	605	C_7C_9 str. + $C_9C_7C_{10}$ bend.
	549	542	$(\text{ring}+CCN)$ bend.
	146	160	CCN bend.

a) The values reported by Girando and Pecile.[9)] The observed values in the present study were in good agreement with them.

quency from 1546 cm^{-1} for TCNB to 1456 cm^{-1} for $TCNB^-$, as shown in Table 1. The line at 1456 cm^{-1} for $TCNB^-$ has the character of C_1C_2 stretching vibration according to our calculation, as shown in Fig. 6. The Cartesian displacement of this mode was almost unchanged for TCNB. Therefore, this result asserts that an additional electron does occupy the a_u MO but not the b_{1u} MO. This is also supported by the moderate decrease of CN stretching vibration fre-

TABLE 4. OBSERVED AND CALCULATED FUNDAMENTAL FREQUENCIES OF TCNB AND TCNB-d_2

Species	TCNB		TCNB-d_2		Assignment
	ν_{obsd}[a)]	ν_{calcd}	ν_{obsd}[a)]	ν_{calcd}	
a_g	3087 cm^{-1}	3083 cm^{-1}	2298 cm^{-1}	2274 cm^{-1}	CH(D) str.
	2251	2249	2251	2249	CN str.
	1541	1529	1535	1534	C_1C_2 str.
	1259	1240	1256	1234	$(C_1C_6+C_1C_7)$ str.
	726	749	711	728	ring bend.
		491		491	$(C_2C_1C_7+CCN)$ bend.
	407	421	405	420	ring bend.
	143	119	143	119	CCN bend.
b_{1g}	2247	2250	2247	2250	CN str.
	1605	1596	1590	1576	C_1C_6 str.
	1256	1254	970	978	CH(D) bend.
	1041	1045	1040	1045	C_1C_7 str.
	707	702	655	656	$C_2C_1C_7$ bend.
	350	352	350	352	ring bend.
	224	254	220	250	CCN bend.
b_{2u}	3087	3084	2292	2276	CH(D) str.
	2249	2251	2249	2250	CN str.
	1388	1409	1379	1402	C_1C_6 str.
		1221		1202	(ring$+C_2C_1C_7$) bend.
	628	608	620	601	(ring+CCN) bend.
	466	472	466	472	$(C_2C_1C_7+CCN)$ bend.
	152	145	151	145	CCN bend.
b_{3u}	2252	2248	2251	2249	CN str.
	1485	1506	1427	1440	CH(D) bend. + C_1C_6 str.
	1278	1282	1272	1281	C_1C_2 str.
	1181	1142	945	929	CH(D) str.
	762	801	710	734	C_1C_7 str.
	498	486	497	486	$(CCN+C_2C_1C_7)$ bend.
	128	127	127	127	CCN bend.

a) The values reported by Takenaka *et al.*[4)] are adopted as ν_{obsd}, except for a doubtful line. The observed values for a_g species in the present study were in good agreement with them.

quency and the slight increase in frequency of the mixing mode of C_1C_6 and C_1C_7 stretching vibrations. These Cartesian displacements are also shown in Fig. 6. Thus it is concluded clearly that the LUMO of TCNB is the a_u MO. This conclusion agrees with the result of PPP-SCF-MO calculation of TCNB by Iwata *et al.*[6)]

Vibrational Analyses of In-plane Vibrations of TCNB and TCNB$^-$. A normal coordinate calculation based on Urey-Bradley force field with Kekulé potential was carried out for TCNB and TCNB$^-$. In this calculation, the library programs, BGLZ and LSMB, of the computer center, the University of Tokyo, were used.

First, normal vibrations of TCNE and TCNQ were investigated in order to get an initial set of force constants for TCNB. The observed frequencies of TCNE and TCNQ are shown in Tables 2 and 3.[7–9)] Their molecular parameters are the same as previously reported.[7,9)] A more reasonable and transferable set of force constants was obtained by a trial and error method for TCNE and TCNQ as shown in Fig. 7. The calculated frequencies show good agreements with the observed values as shown in Tables 2 and 3.

An initial set of force constants of TCNB was derived from those of benzene,[10)] 1,2,4,5-tetrachlorobenzene,[11)] TCNE, and TCNQ. Table 4 shows the observed frequencies of TCNB reported by Takenaka *et al.*[4)] The values of molecular parameters reported by Niimura *et al.* were used.[12)] The distribution pattern of the Kekulé potential function of TCNB has been estimated from bond-bond polarizability, $\pi_{rs,tu}$, using PPP-SCF-MO of TCNB[6,13)] under the approximation that $d\beta/dr$=constant for various bonds, as shown in Fig. 8 (β; resonance integral). Kekulé constant has been taken zero, initially. An adjustment by a trial and error method was carried out for the skeletal stretching force constants and the Kekulé constant. The final set of force constants of TCNB is shown in Fig. 7. Their values were reasonable in view of the bond orders of the corresponding bondings.[6)] The calculated frequencies agree with the observed values as shown in Table 4.

For TCNB$^-$, the skeletal stretching force constants were changed according to the following equation, (bond order)$\propto$[(stretching force constant)$-$(Kekulé constant)$\times$(self bond-bond polarizability)].

TABLE 5. OBSERVED AND CALCULATED FUNDAMENTAL FREQUENCIES OF TCNB$^-$ AND TCNB-d_2^-

Species	TCNB$^-$		TCNB-d_2^-		Assignment
	ν_{obsd}	ν_{calcd}	ν_{obsd}	ν_{calcd}	
a_g	cm^{-1}	3083 cm^{-1}	cm^{-1}	2274 cm^{-1}	CH(D) str.
	2198	2215	2198	2216	CN str.
	1456	1466	1446	1456	C_1C_2 str.
	1279	1259	1266	1254	$(C_1C_6+C_1C_7)$ str.
		732		712	ring bend.
	522	490	520	490	$(C_2C_1C_7+CCN)$ bend.
	408	422	409	422	ring bend.
		119		119	CCN bend.
b_{1g}		2149		2148	CN str.
		1312		1016	CH(D) bend.
		1060		1062	C_1C_7 str.
		810		810	C_1C_6 str.
		644		599	ring bend.
		263		257	(CCN+ring) bend.
		234		234	$(C_2C_1C_7+\text{ring})$ bend.
b_{2u}		3084		2276	CH(D) str.
		2176		2176	CN str.
		1415		1408	C_1C_6 str.
		1226		1206	C_1C_7 str. + ring bend.
		611		603	C_1C_7 str. + (ring+CCN) bend.
		473		473	$(CCN+C_2C_1C_7)$ bend.
		145		145	CCN bend.
b_{3u}		2157		2158	CN str.
		1418		1343	C_1C_6 str. + CH(D) bend.
		1305		1250	$(C_1C_6+C_1C_2+C_1C_7)$ str.
		1048		904	C_1C_6 str. + ring bend.
		798		727	C_1C_7 str.
		482		482	$(C_2C_1C_7+CCN)$ bend.
		127		127	CCN bend.

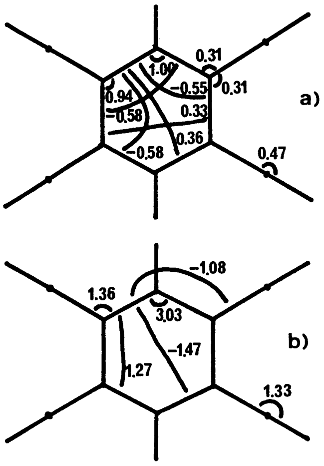

Fig. 8. Distribution patterns of $\pi_{rs,tu}$ of TCNB and TCNB$^-$. a) TCNB, b) TCNB$^-$.
The values are normalized as $\pi_{16,65}$ of TCNB=1.00.

The distribution pattern of Kekulé potential function of TCNB$^-$ is considerably changed from that of TCNB as shown in Fig. 8. As previously mentioned, the vacant b_{1u} MO of TCNB$^-$ must be located close to the a_u MO. Therefore, the denominator $E_{a_u}-E_{b_{1u}}$ in the formula of $\pi_{rs,tu}$ is fairly small, resulting in a large change in the Kekulé potential function. The pattern of the Kekulé potential of TCNB$^-$ (Fig. 8 b)) is similar to the pattern of the symmetry coordinate of C_1C_6 stretching vibration belonging to b_{1g} species, that is to say, there is a strong vibronic interaction between the a_u and the b_{1u} MO through this vibrational mode.

The calculated frequencies of TCNB$^-$ and their assignment based on L_x matrix and potential energy distribution are shown in Table 5. They agree with the observed values. Figure 6 shows the Cartesian displacements of the totally symmetric skeletal stretching vibrations derived from the L_x matrix. A Raman line of TCNB$^-$ at 520 cm^{-1} was assigned to C_1C_7N bending vibration of a_g species on the basis of this calculation. The C_1C_6 stretching vibration belonging to b_{1g} species shows remarkable decrease in frequency from 1605 cm^{-1} for TCNB to 810 cm^{-1} for TCNB$^-$, as shown in Tables 4 and 5. This decrease is due to the vibronic interaction between the a_u and the b_{1u} MO. A Raman line of TCNB$^-$ at 928 cm^{-1} cannot be assigned so far. This totally symmetric line is strong and has a combination line at

$2383 \approx 928 + 1456 \text{ cm}^{-1}$. So it may be assigned to a totally symmetric fundamental, but TCNB has not such a line in 750—1200 cm^{-1} region, nor other 1,2,4,5-tetrasubstituted benzene, for example 1,2,4,5-tetrachlorobenzene.[11] The assignment of this line has not been resolved rigorously and will be a further problem whereas it is guessed that this line may originate from the vibronic interaction.

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References

1) A. Zweig, J. E. Lehnsen, W. G. Hodgson, and W. H. Jura, *J. Am. Chem. Soc.*, **85**, 3937 (1963).

2) C. Takahashi and S. Maeda, *Chem. Phys. Lett.*, **22**, 364 (1973); **24**, 584 (1974); **28**, 22 (1974).

3) A. Ishitani and S. Nagakura, *Theoret. Chim. Acta*, **4**, 236 (1966).

4) J. Umemura and T. Takenaka, *Bull. Inst. Chem. Res., Kyoto Univ.*, **51**, 206 (1973); T. Takenaka, J. Umemura, and S. Tadokoro, The Symposium on Molecular Structure, Kyoto, 1971, Abstr. No. 1A05; J. Umemura, T. Takenaka, and S. Oka, The Symposium on Molecular Structure, Sendai, 1972, Abstr. No. 6C09; T. Takenaka, Private Communication.

5) K. Kaya, A. Nakatsuka, N. Kubota, and M. Ito, *J. Raman Spectrosc.*, **1**, 595 (1973).

6) S. Iwata, J. Tanaka, and S. Nagakura, *J. Am. Chem. Soc.*, **88**, 894 (1966).

7) T. Takenaka and S. Hayashi, *Bull. Chem. Soc. Jpn.*, **37**, 1216 (1964).

8) K. H. Michaelian, K. E. Rieckhoff, and E. M. Voigt, *Spectrosc. Lett.*, **10**, 99 (1977).

9) A. Girando and C. Pecile, *Spectrochim. Acta, Part A*, **29**, 1859 (1973).

10) J. R. Scherer and J. Overend, *Spectrochim. Acta*, **17**, 719 (1961).

11) J. R. Scherer and J. C. Evans, *Spectrochim. Acta*, **19**, 1739 (1963).

12) N. Niimura, Y. Ohashi, and Y. Saito, *Bull. Chem. Soc. Jpn.*, **41**, 1815 (1968).

13) C. A. Coulson and H. C. Longuet-Higgins, *Proc. R. Soc. London, Ser. A*, **191**, 39 (1947).