Spectroscopic Studies on Molecular Configurations of Some Aliphatic Dinitriles. I. Infrared Spectra of Succinonitrile and Bis(succinonitrilo)copper(I) Nitrate

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Although the infrared spectra of many substances with polymethylene chains of the type $X-(CH_2)_n-X$ have been studied in relation to their molecular configurations(1), no detailed spectroscopic studies seem to have been made on the series of aliphatic dinitriles except for the case of succinonitrile(2,3). An interpretation of the spectra of such compounds is always a difficult problem because of the complexity caused by the existence of a number of rotational isomers. By the use of low-temperature techniques, however, the spectra of single rotational isomers in the crystalline solid state may be obtained. It is true that the spectra in the solid state may be explained in part by comparing them with those of like molecules, but it would be of great value if the direct determination of their molecular configurations in the crystalline solid state could be made by other physical methods such as by X-ray crystal structure analysis. Incidentally aliphatic dinitriles form stable copper(I) complexes of the type $[Cu\{NC-(CH_2)_n-CN\}_2]NO_3$ $(n=2, 3\cdots)$(4). The crystal structures of the first few members of this homologous series were studied recently by X-ray method and the configuration of the ligand dinitrile molecule in the crystals of each complex was determined(5-7). The infrared spectra of these complexes, which may be analyzed on the basis of these results, would supply much useful data for the complete understanding of the spectra of dinitrile molecules. Naturally a rigorous analysis of the spectrum of a complex compound would be a complicated problem. Therefore, it should

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1) N. Sheppard, "Advances in Spectroscopy", Ed. by H. W. Thompson, Vol. 1, Interscience Publishers Inc., New York (1959), p. 288; see the references cited there.

2) W. E. Fitzgerald and G. J. Janz, *J. Molec. Spectroscopy*, **1**, 49 (1957).

3) I. Nakagawa and K. Tokumaru, Private communication.

4) H. H. Morgan, *J. Chem. Soc.*, **123**, 2901 (1923); H. Rath, H. Rehm, H. Rummler and E. Specht, *Melliand Textilber.*, **38**, 431, 538 (1957).

5) Y. Kinoshita, I. Matsubara and Y. Saito, This Bulletin, **32**, 741 (1959).

6) Y. Kinoshita, I. Matsubara and Y. Saito, ibid., **32**, 1216 (1959).

7) Y, Kinoshita, I. Matsubara, T. Higuchi and Y. Saito, ibid., **32**, 1221 (1959).

first be assumed that the interaction forces between the ligand molecules are so small that the main features of the spectrum may be explained from the consideration of an isolated ligand molecule[8].

This paper will report on the study of the infrared spectrum of bis(succinonitrilo)copper(I) nitrate, $[Cu(NC-CH_2-CH_2-CN)_2]NO_3$, in connection with the configuration of the ligand succinonitrile. The result of X-ray analysis[5] shows that in the crystals of this complex the ligand succinonitrile molecule is coordinated tetrahedrally with its nitrogen atoms of both ends to two different copper atoms and takes the gauche configuration. Therefore, the infrared data of this complex may be of interest in relation to the results of the spectroscopic studies on succinonitrile by Fitzgerald and Janz[2], and Nakagawa and Tokumaru[3], who concluded that this molecule exists as a mixture of two rotational isomers, trans and gauche, the latter being the more stable configuration at low temperatures. The spectral changes due to decomposition of the complex as a result of interaction with alkali halides have been of help in assigning the vibrational frequencies of succinonitrile. The assignments of the skeletal deformation vibrations were successfully carried out on the basis of the result of a normal coordinate treatment.

Experimental

The method of preparation and the properties of bis(succinonitrilo)copper(I) nitrate are as described in the previous paper[5].

The infrared spectra of the complex and of succinonitrile in the 4000~400 cm^{-1} region were obtained using a Perkin-Elmer Model 21 and a Perkin-Elmer Model 13 spectrophotometer (with sodium chloride and potassium bromide optics, respectively). Spectra in the cesium bromide region were also obtained using a Perkin-Elmer Model 21 spectrophotometer*. The spectrum of succinonitrile was recorded at room temperature and at −50°C. A low-temperature transmission cell of the type described by Nukada[9] was used to obtain the spectra at low temperatures. The results shown in Figs. 1a and 1b are essentially the same as those obtained by Fitzgerald and Janz[2]. The spectrum of the complex was obtained using both Nujol mull and potassium bromide disk techniques. Nujol mulls of the complex gave different spectra depending on the type of alkali halide cell windows used as supporting plates. The spectrum obtained by using KRS-5 plates and that obtained by using sodium chloride plates were at first identical with each other, but the latter soon began to change gradually with time. This suggests that some interaction exists between the complex and sodium chloride plates. When potassium bromide plates were used the reaction occurred so rapidly that the spectrum changed while it was being recorded. These changes are clearly seen in Fig. 2. The spectrum in Fig. 2a is that obtained by using KRS-5 plates. The spectra in Figs. 2b and 2c are those obtained respectively by the use of sodium chloride and potassium bromide plates. (These were recorded after the specimens had been placed in the laboratory for one day.) These two spectra are in some respects different from each other, showing that the reaction products are not the same in the two cases. The spectrum obtained from a potassium bromide disk of the complex is shown in Fig. 3, which agrees quite well with that obtained from a Nujol mull by the use of potassium bromide plates (Fig. 2c). This means that the same type of reaction occurred between the complex and potassium bromide in the two cases. The absorption frequencies of succinonitrile and bis(succinonitrilo)copper(I) nitrate are listed in Table I together with the assignment.

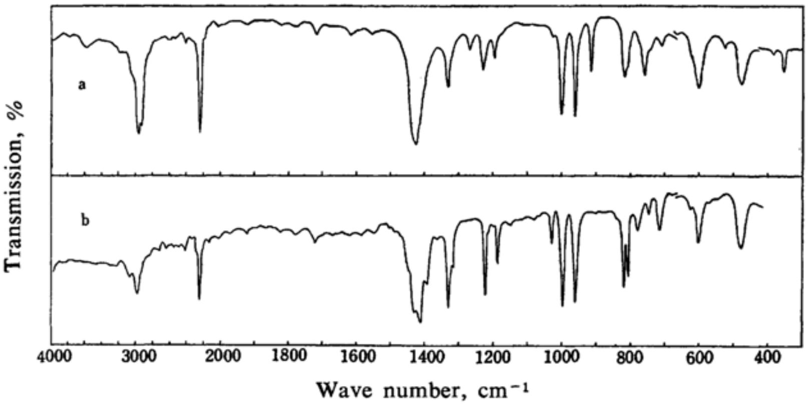

Fig. 1. Infrared spectra of succinonitrile. (a) at room temperature; (b) at −50°C.

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[8] See for example: F. A. Cotton, "Modern Coordination Chemistry", Ed. by J. Lewis and R. G. Wilkins, Interscience Publishers Inc., New York (1960), Chapter 5.

* By the courtesy of Government Chemical Industrial Research Institute of Tokyo.

[9] K. Nukada, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **80**, 218 (1959).

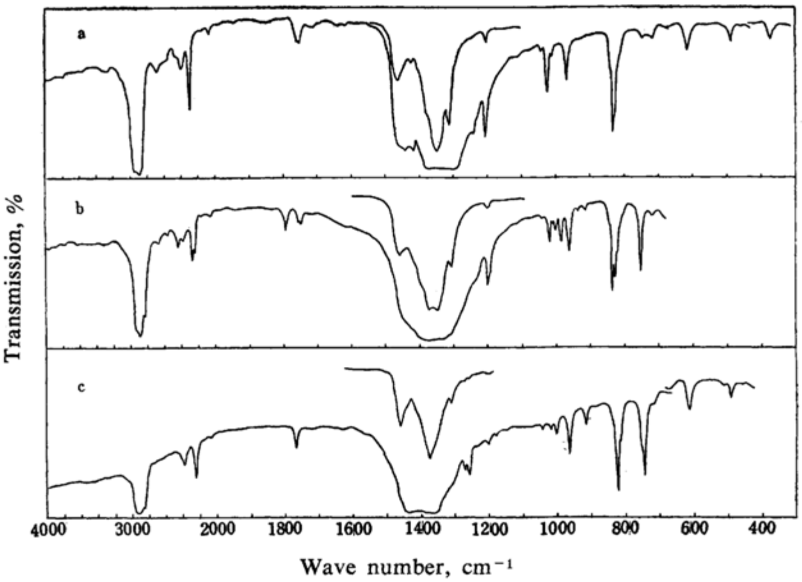

Fig. 2. Infrared spectra obtained from Nujol mulls of bis(succinonitrilo)copper(I) nitrate by using (a) KRS-5, (b) sodium chloride and (c) potassium bromide supporting plates.

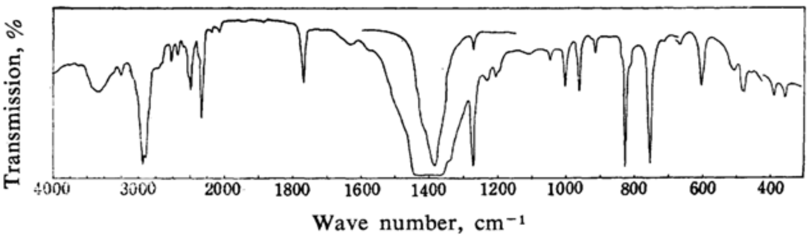

Fig. 3. Infrared spectrum obtained from a potassium bromide disk of bis(succinonitrilo)-copper(I) nitrate.

In Table II are included the absorption frequencies due to the nitrate ion in the complex.

Results and Discussion

The spectral simplification that occurred when succinonitrile was cooled down to $-50°C$ is clearly seen in Fig. 1. In the 1400~400 cm^{-1} region there are four absorption bands that disappear at low temperatures. Fitzgerald et al.[2] and Nakagawa et al.[3] assigned these bands, which are at frequencies of 1271, 917, 761 and 527 cm^{-1}, to the vibrations of the trans form (symmetry C_{2h}) and assigned all the remaining bands to the vibrations of the gauche form (symmetry C_2). As long as the ligand succinonitrile takes the gauche form in the crystals of bis(succinonitrilo)copper(I) nitrate[5], the spectrum of this complex should be closely correlated with that of succinonitrile at low the temperatures. In complete agreement with expectation, the Nujol mull spectrum of the complex (Fig. 2a) corresponds well with the low-temperature spectrum of succinonitrile (Fig. 1b) except for the regions where absorptions due to nitrate vibrations or skeletal vibrations of the complex take place. The fact that no absorptions occur at the four frequencies which were ascribed by the previous authors[2,3] to the vibrations of the trans form gives additional support to their conclusion. On the other hand, the spectra in Figs. 2b, 2c and 3 have absorptions corresponding to the trans vibrations and show spectral features similar to that of succinonitrile at room temperature (Fig. 1a). This means that splitting of copper-nitrogen coordinate bonds occurred and succinonitrile was isolated as a result of the interaction between the complex and alkali halides. The intense bands observed at 1348 and 830 cm^{-1} in Fig. 2a must be ascribed to infrared active fundamentals of the nitrate ion in the complex. The weak doublet with peaks at 1757 and 1751 cm^{-1} must be a certain combination band of the nitrate ion, because some

TABLE I. INFRARED ABSORPTION BANDS OF SUCCINONITRILE AND BIS(SUCCINONITRILO)-COPPER(I) NITRATE

Succinonitrile		Bis(succinonitrilo)copper(I) nitrate		Assignment	
Solid (Room temp.)	Solid (−50°C)	Nujol mull[a]	KBr disk	Gauche(C_2)	Trans(C_{2h})
		3300 vw	3322 vw sh		
	3226 vw				
3205 w			3205 w		
3058 mw sh	3067 mw				
2985 vs	2994 m		2950 s	C–H stretch.	C–H stretch.
2950 s sh	2959 w sh		2924 s	C–H stretch.	C–H stretch.
2849 vw sh	2849 vw				
			2786 w		
	2732 w	2725 vw sh	2740 vw sh		
		2681 mw			
2646 vw sh	2639 w				
2597 vw	2611 vw		2611 w		
2558 vw	2545 vw	2564 w sh	2551 w		
	2494 vw				
			2475 vw		
	2445 vw	2451 w sh			
2427 w	2421 w		2415 mw sh		
		2398 mw	2398 m		
	2283 w sh	2283 ms	2283 w sh	C≡N stretch. (bound)	
2257 vs	2257 s		2257 ms	C≡N stretch. (free)	C≡N stretch.
2203 vw sh	2203 vw				
2151 vw	2141 w		2155 vw		
2045 vw	2041 vw	2066 w	2066 vw		
		1942 vw	1942 vw		
1923 vw	1923 w				
			1883 vw		
1825 vw	1825 w				
1786 vw	1786 w				
1721 w	1721 mw	1709 vw			
1621 w		1639 vw			
		1613 vw			
	1590 w		1570 vw sh		
1558 w	1550 w	1538 vw sh			
	1445 mw sh				
1425 vs	1431 vs sh			B $\mathrm{CH_2}$ bend.	$\mathrm{B_u}$ $\mathrm{CH_2}$ bend.
1416 s sh	1414 vs	1418 ms	1410 m sh	A $\mathrm{CH_2}$ bend.	
	1395 m sh				
	1361 w				
1337 ms	1332 s	1310 vs	1339 s sh	B $\mathrm{CH_2}$ wag.	
1323 w sh	1319 m sh		1307 m sh		
1271 mw			1272 s		$\mathrm{B_u}$ $\mathrm{CH_2}$ wag.
1231 ms	1225 s	1242 m sh	1232 w	A $\mathrm{CH_2}$ wag.	
1198 m	1189 m	1202 ms	1206 w	A $\mathrm{CH_2}$ twist.	($\mathrm{A_u}$ $\mathrm{CH_2}$ twist.)
			1199 w sh		
1179 vw sh					
	1152 w				
		1105 vw	1111 vw		
	1081 w	1074 vw			
1027 w	1032 m	1021 m	1021 vw	A C–C stretch.	
1001 s	999 vs	1010 w	1003 m	B C–CN stretch.	

TABLE I. (Continued)

Succinonitrile		Bis(succinonitrilo)copper(I) nitrate		Assignment	
Solid (Room temp.)	Solid (-50°C)	Nujol mull$^{a)}$	KBr disk	Gauche(C_2)	Trans(C_{2h})
962 s	963 vs	966 m	963 m	A CH_2 rock.	
	954 mw sh				
			929 vw		
917 ms			917 w		B_u C–CN stretch.
839 vw sh	842 w sh	837 mw sh	838 w sh		
818 ms	820 s	826 ms sh		B CH_2 rock.	
813 ms sh	810 ms	813 mw sh	812 w sh	A C–CN stretch.	
776 vw sh	780 m			$603+170^{b)}$	
761 ms			754 s		A_u CH_2 rock.
746 mw sh	750 mw	746 w		$385+356$	
714 mw	718 m	719 w	714 vw	$480+235^{c)}$; 2×356	
668 vw			667 vw		$528+145^{d)}$
623 w sh	628 w				
603 ms	603 ms	615 m	602 m	B C–C–C bend.	
578 vw sh	576 vw				
			524 vw sh		
527 w			509 w		B_u C–C–C bend.
480 ms	483 ms	490 mw	480 mw	A C–C–C bend.	
		458 vw			
385 w			389 w	A C–C≡N bend.	A_u C–C≡N bend.
		(369 mw)			
356 m		360 w sh	356 w	B C–C≡N bend.	

a) KRS-5 supporting plates were used to obtain the spectrum.
b) Raman frequency for the A C–C≡N bending mode of the gauche form.
c) Raman frequency for the B C–C≡N bending mode of the gauche form.
d) Calculated frequency for the B_u C–C≡N bending mode of the trans form.

TABLE II. INFRARED ABSORPTION BANDS DUE TO NITRATE IONS IN BIS(SUCCINONITRILO)-COPPER(I) NITRATE

Nujol mull			KBr disk	$NaNO_3$$^{b)}$	$KNO_3$$^{b)}$
KRS-5$^{a)}$	NaCl$^{a)}$	KBr$^{a)}$			
	1795 mw			1790 vw	
		1770 m	1770 m		1767 vw
1757/51 mw	1757/51 mw				
		1377 vs	1381 vs		1380 vs
	1375/51 vs			1358 vs	
1348 vs					
1043 w	1043 vw	1047 w	1048 w	—	—
	836 ms			836 m	
830 s	830 ms				
		824 s	826 s		824 m

a) Denotes the type of alkali halide cell windows used to support the mull.
b) See Ref. 10 in text.

inorganic nitrates show weak absorptions in this region[10]. As a result of reaction with sodium chloride these nitrate bands have decreased in their intensities and new absorptions appeared at 1795, 1375/51 and 836 cm^{-1} as shown in Fig. 2b. The reaction with potassium bromide caused the appearance of new bands at 1770, 1377 (or 1381) and 824 (or 826) cm^{-1} as shown in Figs. 2c and 3. These new bands observed in the two cases correspond quite well with those of sodium nitrate and potassium nitrate, respectively (see Table II). Considering these results the reaction of the complex with alkali halides should be ascribed largely

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[10] F. A. Miller and C. H. Wilkins, *Anal. Chem.*, 24, 1253 (1952).

to an ion interchange between the two phases. A weak band observed at 1043 cm^{-1} in the spectrum of the complex may correspond to an infrared inactive frequency of the nitrate ion which may have become active due to the effect of the crystalline field of the complex.

The remaining bands of the complex are assigned to the vibrations of the gauche form of succinonitrile with reference to the results of the previous authors[2,3]. Thus the bands observed at 1310 and 1242 cm^{-1} should be assigned to the B and A CH_2 wagging modes, respectively. The bands at 1202 cm^{-1} should correspond to the A CH_2 twisting mode. On the other hand, the B CH_2 twisting mode remains unidentified. According to the result of the normal coordinate treatment by Nakagawa et al.[3] the B CH_2 twisting mode should have a frequency lower than that of the A counterpart, but no appropriate band is found either in the spectrum of the complex or in that of succinonitrile. The weak band at 1027 cm^{-1} and the strong band at 1001 cm^{-1} in the spectrum of succinonitrile are assigned to the A C–C stretching and the B C–CN stretching modes, respectively. This is in agreement with the expectation that a symmetrical skeletal stretching mode is generally weaker than an asymmetrical one in the infrared spectrum. The Raman counterparts of these bands are found at frequencies of 1027 and 1006 cm^{-1} (see Table VIII in Appendix). The fact that the former is much stronger than the latter supports the above assignment because a totally symmetric vibration is expected to be strong in the Raman spectrum. At low temperatures the 1027 cm^{-1} band increases in intensity relative to the 1001 cm^{-1} one (Fig. 1b), showing that the A C–C stretching mode is susceptible to the effect of crystalline field. In the spectrum of the complex a relatively strong band is observed at 1021 cm^{-1}. This band may be assigned to the A C–C stretching mode. To the B C–CN stretching mode may correspond the weak band at 1010 cm^{-1}. The fact that the intensity relation of these two bands is reverse to what is observed in the case of succinonitrile seems not to be in harmony with this assignment, but we may tentatively ascribe it to the effect of the crystalline field of the complex. The strong band at 966 cm^{-1}, which corresponds to the 962 cm^{-1} band in succinonitrile, is assigned to the A CH_2 rocking mode. The 818 cm^{-1} band of succinonitrile with a shoulder at 813 cm^{-1} splits into two components at low temperatures as shown in Fig. 1. One of the components at 820 cm^{-1} is ascribed to the B CH_2 rocking mode and the other at 810 cm^{-1} to the A C–CN stretching mode. In the spectrum of the complex no well-defined band maxima corresponding to these vibrations are observed, due to overlapping by the strong nitrate band at 830 cm^{-1}. However, the shoulder bands at 826 and 813 cm^{-1} are assigned with confidence to the B CH_2 rocking and the A C–CN stretching modes, respectively. The CH_2 rocking frequencies of 1, 2-disubstituted ethanes are known to change conspicuously depending on the azimuthal angle of internal rotation, and therefore can be used to determine the molecular configurations of rotational isomers[11]. The azimuthal angle of internal rotation of succinonitrile in the crystals of the complex has been determined by X-ray analysis to be 53° taking the cis position as the origin[5]. The gauche angle of free succinonitrile must be close to this value, for the two CH_2 rocking frequencies of this molecule agree quite well with the corresponding values of the complex. This conclusion is also in good agreement with what is expected from the calculated frequencies of these vibrations[3].

Assignment of the skeletal deformation vibrations are made with reference to the result of a normal coordinate treatment (see Appendix). The 615 and 490 cm^{-1} bands of the complex correspond each to the 603 and 480 cm^{-1} bands of succinonitrile which are assigned to the B and A C–C–C bending modes, respectively. The weak band at 527 cm^{-1} of succinonitrile which disappears at low temperatures and has no counterpart in the spectrum of the complex (Fig. 2a) corresponds to the B_u C–C–C bending mode of the trans form. The bands at 385 and 356 cm^{-1} of succinonitrile are assigned to the A and B C–C≡N (out-of-plane) bending modes of the gauche form, respectively. The 385 cm^{-1} band may also have some contribution from the A_u C–C≡N out-of-plane bending mode of the trans form. As shown in Fig. 2a the spectrum of the complex has an absorption band at 369 cm^{-1} which probably corresponds to the Cu–N stretching mode, and the shoulder band at 360 cm^{-1} may be correlated with the B C–C≡N bending mode. The absorption corresponding to the A C–C≡N bending mode is not observed, probably due to the overlapping by the 369 cm^{-1} band. The B_u C–C≡N in-plane bending mode of the trans form has a calculated frequency of 145 cm^{-1}, while the A and B C–C≡N (in-plane) bending modes of the gauche form have calculated frequencies of 178 and 247 cm^{-1}, respectively (see Table VIII in Appendix). The values for the gauche form are in good agreement with the observed Raman frequencies, while the infrared data in the region below 300 cm^{-1} are

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[11] I. Nakagawa, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), 76, 813 (1955).

not available for this investigation. The fact that the C–C–C bending modes of nitriles such as acrylonitrile[12], malononitrile[13] and propionitrile[14] always appear in a region as high as 600~450 cm^{-1} and that the C–C≡N (in-plane) bending modes lie in a region as low as 250~150 cm^{-1} suggests that there must be considerable mixing of the two bending coordinates in these skeletal deformation vibrations and no single coordinate may be associated with the individual frequencies. Calculation of the potential energy distributions for the skeletal deformation vibrations has shown that the energies associated with the C–C–C bending and the C–C≡N (in-plane) bending motions are of the same order in these two types of vibration (see Appendix). In the spectrum of succinonitrile there are three absorptions in the 800~700 cm^{-1} region other than that corresponding to the CH_2 rocking mode of the trans form. These bands with peaks at 780, 750 and 718 cm^{-1} are observed to increase remarkably in their intensities at low temperatures (Fig. 1b). As Fujiyama and Shimanouchi[15] suggested, these may be attributed to overtones or combinations of some skeletal deformation vibrations of the gauche form. The proposed assignments for these vibrations are included in Table I.

The sharp band observed at 2283 cm^{-1} in the Nujol mull spectrum (Fig. 2a) may correspond to the C≡N stretching vibration of the complex. The C≡N vibrational shift of 26 cm^{-1} towards higher frequencies as compared with the free succinonitrile may be understood by considering the structure of the complex. X-Ray analysis of this complex[5] has revealed that the carbon-nitrogen bond distance is 1.14 Å and that the Cu–N–C–CH_2 group is close to linear, from which it is expected that the carbon-nitrogen bond is essentially of a triple-bond character, the contributions of polar resonance structures such as $-C^+{=}N^-$ being decreased, and the C≡N stretching frequency is thereby increased. Califano et al.[16] have shown that in the cases of nitriloxides, R–C≡N→O, the C≡N stretching frequencies are about 70 cm^{-1} higher than those of the corresponding nitriles and have explained this as due to the coupling with the N→O stretching vibration. In the case of this complex the effect of the interaction between the C≡N stretching and the Cu–N stretching vibrations, though small, may also contribute to the increase in the C≡N stretching frequency.

Summary

The infrared spectrum of bis(succinonitrilo)-copper(I) nitrate, $[Cu(NC{-}CH_2{-}CH_2{-}CN)_2]NO_3$, has been studied in relation to the molecular configuration of the ligand succinonitrile, which is known from X-ray analysis to be the gauche form. The spectral features of this complex are quite similar to those of free succinonitrile at −50°C in agreement with the conclusion of the previous workers that the gauche isomer of succinonitrile is stable at low temperatures. Thus all the main absorption bands of the complex were satisfactorily explained as due to the vibrations of the gauche isomer. Decomposition of the complex occurs as a result of interaction with alkali halides such as sodium chloride and potassium bromide, which causes the appearance of absorption bands corresponding to the vibrations of the trans isomer. Considering the frequency shifts of the nitrate vibrations the reaction of the complex with alkali halides should be ascribed largely to an ion interchange between the two phases. The increase of 26 cm^{-1} in the C≡N stretching frequency by complex formation may be understood from the linear structure of the Cu–N–C–CH_2 group which suggests that the carbon-nitrogen bond is essentially of a triple-bond character, the contributions of polar resonance structures such as $-C^+{=}N^-$ being decreased. Assignment of the skeletal deformation frequencies has been made with the help of a normal coordinate treatment which also made possible discussions concerning the nature of these vibrations.

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Appendix: Calculation of Skeletal Vibrations

The skeletal vibrations of succinonitrile were calculated as a six-body problem. The in-plane skeletal vibrations of propionitrile (symmetry C_s) were also calculated as a four-body problem in order to obtain more information on the nature of the skeletal deformation vibrations of aliphatic nitriles. A potential function of the Urey-Bradley

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[12] F. Halverson, R. F. Stamm and J. J. Whalen, *J. Chem. Phys.*, **16**, 808 (1948).

[13] F. Halverson and R. J. Francel, ibid., **17**, 694 (1949).

[14] N. E. Duncan and G. J. Janz, ibid., **23**, 434 (1955).

[15] T. Fujiyama and T. Shimanouchi, Paper presented at the 14th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1961.

[16] S. Califano, R. Moccia, R. Scarpati and G. Speroni, *J. Chem. Phys.*, **26**, 1777 (1957).

TABLE III. FORCE CONSTANTS OF PROPIONITRILE AND SUCCINONITRILE (in millidyne/Å)

$K(CH_3\text{-}CH_2)=4.00$[a]
$K(CH_2\text{-}CH_2)=3.70$[a]
$K(CH_2\text{-}C)=3.50$[a]
$K(C\equiv N)=18.10$[b]
$H(CH_3\text{-}CH_2\text{-}C)=0.25$[a]
$H(CH_2\text{-}CH_2\text{-}C)=0.25$[a]
$H(CH_2\text{-}C\equiv N)=0.14_1$[b]
$F(CH_3\text{-}CH_2\text{-}C)=0.45$[a]
$F(CH_2\text{-}CH_2\text{-}C)=0.45$[a]
$F(CH_2\text{-}C\equiv N)=0.50$[b]
$k(C\text{-}C\equiv N)=0.12\,Å^2$[c]

a) Transferred from various hydrocarbons and their derivatives and adjusted to obtain better agreement with the observed values. See for example S. Mizushima, T. Shimanouchi, I. Nakagawa and A. Miyake, *J. Chem. Phys.*, **21**, 215 (1953); M. Hayashi, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*, **78**, 222 (1957).

b) Transferred from acetonitrile with some modifications. See I. Nakagawa, "Infrared Absorption Spectrum" (in Japanese), Vol. 7, Nankodo Co., Ltd., Tokyo (1959) p. 1.

c) Interaction term between the C-C≡N in-plane and out-of-plane bending coordinates introduced to obtain better agreement with the observed values.

TABLE IV. SYMMETRY COORDINATES OF PROPIONITRILE

$S_1=(\Delta r_1+\Delta r_2)/\sqrt{2}$	(CH_3-CH_2-C sym. stretching)
$S_2=(\Delta r_1-\Delta r_2)/\sqrt{2}$	(CH_3-CH_2-C antisym. stretching)
$S_3=\Delta r_3$	(C≡N stretching)
$S_4=\Delta\alpha$	(CH_3-CH_2-C bending)
$S_5=\Delta\beta$	(CH_2-C≡N bending)

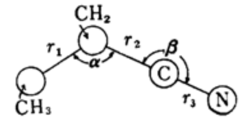

Fig. 4. Internal coordinates of propionitrile.

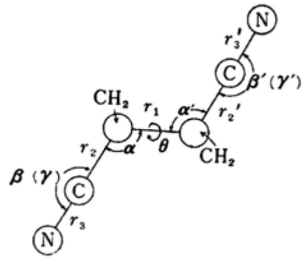

Fig. 5. Internal coordinates of succinonitrile. β (or β') and γ (or γ') denote bending of C≡N bond in and out of the plane of the adjacent C-C-C linkage, respectively. $\theta=180°$ for trans and $\theta=60°$ for gauche.

type[17] was used, and the values of force constants were transferred from other related molecules as shown in Table III. The symmetry coordinates of propionitrile and succinonitrile listed in Tables IV and V were constructed from the internal coordinates shown in Figs. 4 and 5, respectively. In the trans form of succinonitrile (symmetry C_{2h}) there is no coupling between the C-C≡N in-plane bending and out-of-plane bending motions, because they belong to different classes (see Table V). In the gauche form (symmetry C_2), however, these two motions belong to the same classes and accordingly a coupling occurs between them. In the Urey-Bradley type of potential function no cross term corresponding to the interaction between the two C-C≡N bending coordinates is considered, while such an interaction term, k(C-C≡N), was introduced in this calculation to obtain better agreement with the observed frequencies. The value of k(C-C≡N) used in this case is also included in Table III. For the calculation of the kinetic energy matrices the assumed bond lengths of $r(CH_3\text{-}CH_2)=1.54$ Å, $r(CH_2\text{-}CH_2)=1.54$ Å, $r(CH_2\text{-}C)=1.50$ Å and $r(C\equiv N)=1.15$ Å and the bond angle of 109°28′ were used. The result obtained for the in-plane vibrations (A′) of propionitrile agrees well with the observed values[14] as shown in Table VI. In Table VII are listed the diagonal terms of the potential energy distribution[18], which show that the energies associated with the coordinates S_4(C-C-C bending) and S_5(C-C≡N bending) are of the same order in the two skeletal deformation vibrations. The signs of

TABLE V. SYMMETRY COORDINATES OF SUCCINONITRILE

C_2	C_{2h}		
A	A_g	$S_1=\Delta r_1$	(CH_2-CH_2 stretching)
		$S_2=(\Delta r_2+\Delta r_2')/\sqrt{2}$	(CH_2-C sym. stretching)
		$S_3=(\Delta r_3+\Delta r_3')/\sqrt{2}$	(C≡N sym. stretching)
		$S_4=(\Delta\alpha+\Delta\alpha')/\sqrt{2}$	(CH_2-CH_2-C sym. bending)
		$S_5=(\Delta\beta+\Delta\beta')/\sqrt{2}$	(CH_2-C≡N sym. in-plane bending)
	A_u	$S_6=(\Delta\gamma+\Delta\gamma')/\sqrt{2}$	(CH_2-C≡N sym. out-of-plane bending)
B	B_u	$S_7=(\Delta r_2-\Delta r_2')/\sqrt{2}$	(CH_2-C antisym. stretching)
		$S_8=(\Delta r_3-\Delta r_3')/\sqrt{2}$	(C≡N antisym. stretching)
		$S_9=(\Delta\alpha-\Delta\alpha')/\sqrt{2}$	(CH_2-CH_2-C antisym. bending)
		$S_{10}=(\Delta\beta-\Delta\beta')/\sqrt{2}$	(CH_2-C≡N antisym. in-plane bending)
	B_g	$S_{11}=(\Delta\gamma-\Delta\gamma')/\sqrt{2}$	(CH_2-C≡N antisym. out-of-plane bending)

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[17] T. Shimanouchi, ibid., 17, 245, 734, 848 (1949).

[18] Y. Morino and K. Kuchitsu, ibid., 20, 1809 (1952).

TABLE VI. CALCULATED AND OBSERVED FREQUENCIES OF PROPIONITRILE (in cm^{-1})

Calcd.	Obs.[a)]		Assignment
	Infrared	Raman	
2259	2252	2251	C≡N stretching
1016	1075	1078	C-C-C antisym. stretching
840	836	838	C-C-C sym. stretching
514	545	548	C-C-C bending
241	—	226	C-C≡N bending

a) See Ref. 14 in text.

TABLE VII. POTENTIAL ENERGY DISTRIBUTIONS OF PROPIONITRILE$^{a)}$

ν_{calcd}	2259	1016	840	514	241
S_1	−4	+17	+79	+4	0
S_2	+4	+82	−14	0	0
S_3	+95	−1	+4	+1	0
S_4	0	−1	−12	+49	+42
S_5	0	−1	−1	+41	−57

a) The signs of the corresponding L matrix elements are also included.

TABLE VIII. CALCULATED AND OBSERVED FREQUENCIES OF SUCCINONITRILE (in cm^{-1})

Gauche(C_2)				Trans (C_{2h})				Assignment
Class	Calcd.	Obs.		Class	Calcd.	Obs.		
		Infrared	Raman$^{a)}$			Infrared	Raman$^{a)}$	
A	2259	2257	2260	A_g	2258		2260	C≡N sym. stretching
	1036	1027	1027		1036		1027	C-C stretching
	812	813	812		883		812	C-CN sym. stretching
	472	480	483		460		514	C-C-C bending
	178	—	170		242		235	C-C≡N bending
	390	385	386	A_u	398	385		C-C≡N bending
B	2259	2257	2260	B_u	2260	2257		C≡N antisym. stretching
	882	1001	1006		874	917		C-CN antisym. stretching
	601	603	604		500	527		C-C-C bending
	247	—	235		145	—		C-C≡N bending
	369	356	359	B_g	398		386	C-C≡N bending

a) Recorded from an aqueous solution with a Cary Model 81 spectrophotometer.

TABLE IX. POTENTIAL ENERGY DISTRIBUTIONS OF THE TRANS FORM OF SUCCINONITRILE$^{a)}$

	A_g					A_u
ν_{calcd}	2258	1036	883	460	242	398
S_1	0	+84	+16	+5	0	—
S_2	+8	−24	+55	+12	+5	—
S_3	−95	−1	+3	+1	+1	—
S_4	0	0	−39	+27	+39	—
S_5	0	−1	−3	+44	−52	—
S_6	—	—	—	—	—	+100

	B_u				B_g
ν_{calcd}	2260	874	500	145	398
S_7	−8	+91	−1	−2	—
S_8	+95	+6	0	0	—
S_9	0	0	+41	+61	—
S_{10}	0	0	+60	−40	—
S_{11}	—	—	—	—	+100

a) See the footnote of Table VII.

TABLE X. POTENTIAL ENERGY DISTRIBUTIONS OF THE GAUCHE FORM OF SUCCINONITRILE$^{a)}$

	A					
ν_{calcd}	2259	1036	812	472	178	390
S_1	0	+87	+14	+3	0	0
S_2	+8	−20	+74	0	0	0
S_3	−95	−1	+4	0	0	0
S_4	0	−3	−8	+16	+47	−32
S_5	0	−2	−2	+42	−58	−13
S_6	0	0	0	+16	+23	+76

	B				
ν_{calcd}	2259	882	601	247	369
S_7	+8	+88	+4	+1	+1
S_8	−95	+5	+1	0	0
S_9	0	−14	+48	+25	+15
S_{10}	0	0	+28	−84	+3
S_{11}	0	0	+6	+17	−93

a) See the footnote of Table VII.

the L matrix elements have revealed that the vibrations assigned to the C-C-C bending and the C-C≡N bending modes correspond respectively to the in-phase and the out-of-phase coupling of the above two coordinates. The calculated and the observed frequencies of succinonitrile are compared in Table VIII, and the diagonal terms of the potential energy distribution for the trans and the gauche forms are listed in Tables IX and X, respectively. In the case of the trans form, where no coupling between the in-plane (A_g and B_u) and out-of-plane (A_u and B_g) vibrations occurs, situation is the same as in propionitrile and energetically the contributions of both the coordinates S_4(C-C-C bending) and S_5(C–C≡N bending) or those of S_9(C–C–C bending) and S_{10}(C–C≡N bending) are important in producing two each of the skeletal deformation vibrations belonging to class A_g or B_u. It is shown from the signs of the L matrices that the vibrations assigned to the C–C–C bending modes (600∼450 cm^{-1}) correspond to the in-phase coupling and those assigned to the C–C≡N bending modes (250∼150 cm^{-1}) to the out-of-phase coupling of the two types of bending coordinate. The potential energy distributions show that the A_g vibration which corresponds to the symmetric C–CN stretching mode has a large contribution from the C–C–C bending motion. This is in agreement with the result obtained in the case of 1,2-dichloroethane[19]. In the case of the gauche form coupling occurs between S_4, S_5 and S_6 or S_9, S_{10} and S_{11} to produce three each of the skeletal deformation frequencies belonging to class A or B. However, it may be noted that the contribution of S_6 or S_{11} (C–C≡N out-of-plane bending) is predominant in the vibrations assigned to the C–C≡N bending modes (400∼350 cm^{-1}). As in the case of the trans form the energetical contributions of both S_4 and S_5 or of both S_9 and S_{10} are important in two each of the remaining skeletal deformation vibrations belonging to class A or B. The signs of the L matrix elements show that the vibrations assigned to the C–C–C bending modes (600∼450 cm^{-1}) correspond to the in-phase coupling and those assigned to the C–C≡N bending modes (250∼150 cm^{-1}) to the out-of-phase coupling of the two types of bending coordinate.

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[19] I. Nakagawa and S. Mizushima, ibid., **21**, 2195 (1953).