# *Spectroscopic Studies on Molecular Configurations of Some Aliphatic Dinitriles. II. Infrared Spectra of Glutaronitrile and Bis(glutaronitrilo)copper(I) Nitrate*

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In the preceding paper[1] the author has reported on the analysis of the infrared spectrum of bis(succinonitrilo)copper(I) nitrate, which proved to be quite useful for the understanding of the spectrum of succinonitrile. As a continuation of the spectroscopic studies on the series of aliphatic dinitriles, the infrared spectrum of bis(glutaronitrilo)copper(I) nitrate, $[Cu\{NC-(CH_2)_3-CN\}_2]NO_3$, has been investigated in connection with the molecular configuration of glutaronitrile. This molecule has four possible spectroscopically distinguishable rotational isomers, *TT*, *TG*, *GG* and *GG'*[2], and the complexity of its spectrum in the liquid state, which may be ascribed to the coexistence of these rotational isomers, makes its analysis almost impossible. Recently the author has studied the infrared spectrum of glutaronitrile by the use of low-temperature techniques and found that this molecule forms two different crystalline solid phases, depending on the mode of crystallization[3]. Determination of the molecular configuration of glutaronitrile in each crystalline solid phase has been made possible by comparing the two solid-state spectra with that of bis(glutaronitrilo)copper(I) nitrate, the X-ray analysis of which has revealed that in the crystals of this complex the ligand glutaronitrile molecule takes the *GG* configuration[4]. The detailed analysis of the infrared spectrum of this complex which will be presented in this paper has been undertaken to interpret the whole spectrum of glutaronitrile both in the liquid and in the crystalline solid states. Calculation of the skeletal vibrations for each isomeric form of glutaronitrile also proved useful in determining the configuration of this molecule.

### Experimental

Bis(glutaronitrilo)copper(I) nitrate was prepared in the same way as that described in the previous paper[4].

The infrared spectra in the 4000~400 cm$^{-1}$ region of glutaronitrile and the complex were recorded using a Perkin-Elmer Model 21 and a Perkin-Elmer Model 13 spectrophotometer (with sodium chloride

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[1] I. Matsubara, This Bulletin, 34, 1710 (1961).

[2] For the nomenclature of the rotational isomers see S. Mizushima, "Structure of Molecules and Internal Rotation", Academic Press Inc., New York (1954), Part I, Chapter V.

[3] I. Matsubara, *J. Chem. Phys.*, 35, 373 (1961).

[4] Y. Kinoshita, I. Matsubara and Y. Saito, This Bulletin, 32, 1216 (1959).

and potassium bromide optics, respectively). The spectrum of glutaronitrile in the liquid state is shown in Fig. 1a. As has already been reported3), glutaronitrile can form two different crystalline solid phases. By rapid cooling of the liquid down to $-60$°C a metastable crystalline form is obtained. This has the spectrum shown in Fig. 1b. When the solid is warmed up to $-40$°C an irreversible transition occurs giving a more stable crystalline form which has the spectrum shown in Fig. 1c. The spectrum of bis(glutaronitrilo)copper(I) nitrate was obtained using both Nujol mull and potassium bromide disk methods. The spectrum obtained from a Nujol mull of the complex by using KRS-5 supporting plates is shown in Fig. 2a. The spectrum in Fig. 2b is that obtained from a Nujol mull of the complex by using potassium bromide plates. (This spectrum was recorded after the specimen had been placed in the laboratory for one day.) These two spectra are very different from each other, showing that a reaction occurred between the complex and potassium bromide as in the case of bis(succinonitrilo)copper(I) nitrate1). The use of sodium chloride plates resulted in a spectrum identical with that in Fig. 2a and no time dependent change of the spectrum was observed. Potassium bromide disks of the complex gave different spectra depending on the pressure applied to prepare the disk. In Figs. 3a and 3b are shown the spectra obtained from the disks which were prepare by applying pressures of 8 tons and 10 tons, respectively. The potassium bromide disk having the spectrum shown in Fig. 3a, when repressed under a pressure of 10 tons, undergoes an irreversible change and

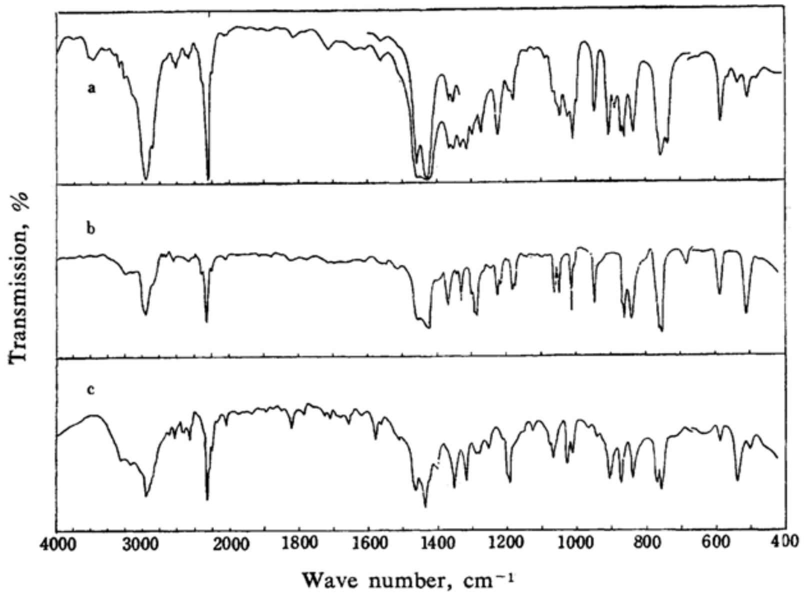

Fig. 1. Infrared spectra of glutaronitrile in various states. (a) liquid; (b) solid (metastable form); (c) solid (stable form).

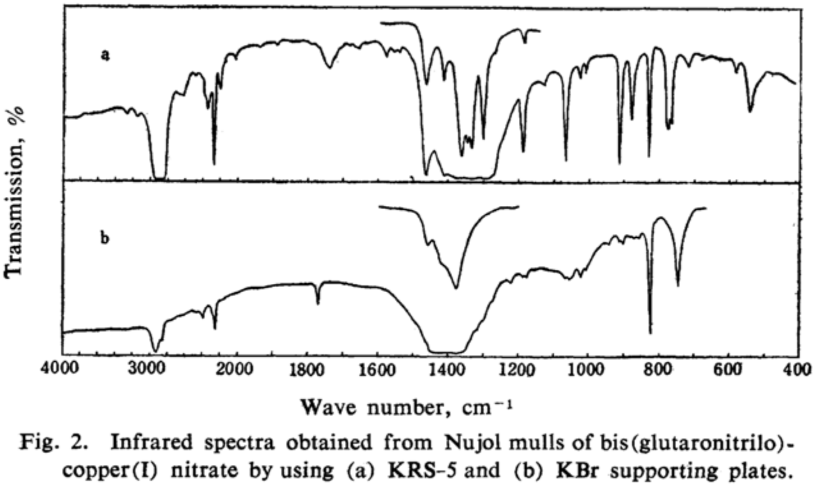

Fig. 2. Infrared spectra obtained from Nujol mulls of bis(glutaronitrilo)-copper(I) nitrate by using (a) KRS-5 and (b) KBr supporting plates.

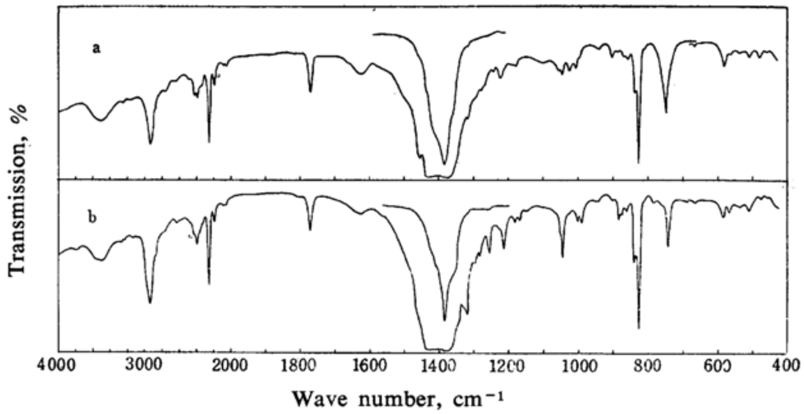

Fig. 3. Infrared spectra obtained from KBr disks of bis(glutaronitrilo)-copper(I) nitrate prepared by applying pressures of (a) 8 tons and (b) 10 tons.

comes to exhibit a spectrum identical with that shown in Fig. 3b. The absorption frequencies of glutaronitrile and bis(glutaronitrilo)copper(I) nitrate are listed in Table I together with the assignment.

## Results and Discussion

The symmetry types and the selection rules for the fundamental vibrations of glutaronitrile in the 1400~400 cm$^{-1}$ region[5,6] are given in Table II. All the fifteen fundamental vibrations in this region are expected to be infrared active for the *TG*, *GG* and *GG'* isomers, while for the *TT* isomer two $CH_2$ twisting and one $CH_2$ rocking modes belonging to class $A_2$ are infrared inactive. As long as the ligand glutaronitrile takes the *GG* configuration in the crystals of bis(glutaronitrilo)copper(I) nitrate[4], its spectrum should be explained as due to the vibrations of the *GG* form of glutaronitrile. The spectrum obtained from a Nujol mull of this complex by using KRS-5 supporting plates (Fig. 2a) seems to be in good agreement with the selection rules for the *GG* isomer of glutaronitrile. On the other hand, the Nujol mull spectrum obtained by the use of potassium bromide plates (Fig. 2b) and the potassium bromide disk spectrum (Fig. 3a) are very different from the spectrum in Fig. 2a and are quite similar to that of the liquid glutaronitrile (Fig. 1a). This means that free glutaronitrile has been produced as a result of interaction between the complex and potassium bromide. This interaction caused the shifts of the nitrate bands of the complex observed at 1748, 1361 and 830 cm$^{-1}$ in Fig. 2a to 1770, 1385 and 826 cm$^{-1}$, respectively, as shown in Figs. 2b and 3. The latter frequencies agree quite well with those of potassium nitrate[7], showing that the mechanism of reaction of the complex and potassium bromide should be ascribed largely to an ion interchange between the two phases as in the case of bis(succinonitrilo)copper(I) nitrate[1].

As reported in the previous paper[3] the spectrum of glutaronitrile in the stable crystalline form (Fig. 1c) is closely correlated with that of bis(glutaronitrilo)copper(I) nitrate shown in Fig. 2a. The one to one correspondences between the individual bands of the two spectra are almost complete except for the regions where absorptions due to nitrate vibrations or skeletal vibrations of the complex take place. From this result it has been concluded that glutaronitrile takes the *GG* configuration in the stable crystalline solid state[3]. The vibrational assignment of these two spectra, though tentative in nature, are made with reference to the work of Brown and Sheppard[8] on trimethylene halides which were also found to take the *GG* configuration in the crystalline solid state. Thus, the bands observed at 1350, 1316 and 1250 cm$^{-1}$ in the spectrum of the stable solid form (Fig. 1c) may be assigned to the $CH_2$ wagging modes and those at 1287/79, 1190 and 1125 cm$^{-1}$ to the $CH_2$ twisting modes. The behaviors of the $CH_2$ wagging modes are somewhat anomalous in the case of the complex (Fig. 2a). There are quite intense bands at 1334 and 1300 cm$^{-1}$ but no band is observable around 1250 cm$^{-1}$. Although this may be ascribed to the effect of the crystalline force field of the complex, no further discussions will be made at this stage. The bands observed at 1271, 1188 and 1130 cm$^{-1}$ in the spectrum

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[5] J. K. Brown, N. Sheppard and D. M. Simpson, *Phil. Trans. Roy. Soc. London*, **A247**, 35 (1954).

[6] E. Funck, *Z. Elektrochem.*, **62**, 901 (1958).

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

[8] J. K. Brown and N. Sheppard, *Proc. Roy. Soc.*, **A231**, 555 (1955).

TABLE I. INFRARED ABSORPTION BANDS OF GLUTARONITRILE AND BIS(GLUTARONITRILO)COPPER(I) NITRATE

| Glutaronitrile | | | Bis(glutaronitrilo) copper(I) nitrate | | Assignment | |
|---|---|---|---|---|---|---|
| Liquid | Solid | | Nujol mull[a] | KBr disk[b] | | |
| | Metastable form | Stable form | | | | |
| | | 3247 vw | 3279 vw | 3257 vw | | |
| 3205 vw | 3195 vw | | | | | |
| | | | 3165 vw | | | |
| 3115 vw sh | | 3125 vw | | 3125 vw | | |
| 2959 s | 2950 ms | 2950 s | | 2933 ms | *TT*, *TG*, *GG* | C–H stretch. |
| | | 2924 s sh | | 2915 m sh | | |
| 2890 m | 2874 w | 2890 w sh | | 2874 w sh | *TT*, *TG*, *GG* | C–H stretch. |
| | | 2688 vw | 2695 vw | | | |
| 2646 vw sh | | | | | | |
| 2618 vw | 2625 w | 2625 w | 2632 w | 2618 vw | | |
| | | 2532 vw | | | | |
| 2506 vw | | 2500 vw | 2488 vw | | | |
| 2463 vw | 2451 w | | | | | |
| 2445 vw sh | | 2445 w | 2421 vw sh | 2427 w sh | | |
| | | | | 2398 mw | | |
| | | | 2353 mw | 2364 w sh | | |
| 2299 vw sh | 2304 w | 2288 vw sh | | | | |
| | | | 2278 s | | *GG* | C≡N stretch. (bound) |
| 2249 vs | 2245 ms | 2247 s | | 2252 ms | *TT*, *TG*, *GG* | C≡N stretch. (free) |
| 2198 vw | 2198 w | 2198 w | 2208 w | 2198 mw | | |
| | | | | 2096 vw | | |
| 2049 vw | | | | | | |
| 2016 vw | 2016 vw | 2020 w | 2037 w | | | |
| | | 1931 vw | 1942 vw | | | |
| 1890 vw | | 1890 vw | 1890 vw | | | |
| 1812 w | 1818 vw | 1818 w | | | | |
| 1786 vw | 1773 vw | 1783 vw | 1776 vw | | | |
| | | 1721 vw | 1724 vw sh | | | |
| 1712 w | | 1706 vw | 1706 w sh | | | |
| | | 1675 vw | 1672 vw | | | |
| 1634 vw | | 1653 w | 1658 vw | | | |
| 1608 vw | 1605 vw | 1613 vw | | | | |
| | 1570 vw | 1575 w | 1580 w | | | |
| 1563 w | 1553 vw | 1560 vw | 1558 vw | 1563 vw | | |
| 1548 vw sh | 1543 vw | 1536 vw sh | 1543 vw | | | |
| 1511 vw sh | 1508 w | 1508 vw | 1506 vw sh | | | |
| 1458 s | 1451 ms | 1460 ms | | | *TT*, *TG*, *GG* | $CH_2$ bend. |
| 1429 vs | 1420 s | 1433 s | 1414 s | | *TT*, *TG*, *GG* | $CH_2$ bend. |
| | 1395 vw | 1399 w | | | | |
| 1366 m | 1364 m | | | | *TG* | $CH_2$ wag. |
| 1355 m | | 1350 ms | 1334 vs | | *GG* | $CH_2$ wag. |
| | 1339 w | | | | | |
| 1333 m | 1328 m | | | 1328 w sh | *TG* | $CH_2$ wag. |
| 1314 m | | 1316 ms | 1300 vs | 1319 mw | *TT*, *GG* | $CH_2$ wag. |
| 1299 m | 1300 w | | | 1297 vw | *TG* | $CH_2$ twist. |
| 1289 vw sh | | 1287 w | 1271 ms sh | 1280 w | *GG* | $CH_2$ twist. |
| | 1289 ms sh | 1279 w | | | | |
| 1272 m | 1282 ms | | | 1272 vw sh | *TG* | $CH_2$ wag. |
| | | 1250 w | | 1256 mw | *TT*, *GG* | $CH_2$ wag. |
| | 1241 vw | | | | | |

Table I. (Continued)

| Glutaronitrile | | | Bis(glutaronitrilo) copper(I) nitrate | | Assignment | |
|---|---|---|---|---|---|---|
| Liquid | Solid | | Nujol mull[a] | KBr disk[b] | | |
| | Metastable form | Stable form | | | | |
| 1224 ms | 1224 m | | | 1224 vw sh | *TG* | $CH_2$ twist. |
| | 1214 mw | | | 1214 mw | *TT* | $CH_2$ twist. |
| | | 1208 vw | | | | |
| 1193 vw | | 1190 ms | 1188 s | | *GG* | $CH_2$ twist. |
| 1181 m | 1181 m | | | 1179 w | *TG* | $CH_2$ twist. |
| 1170 vw sh | 1174 m | | | 1168 w | *TT* | $CH_2$ twist. |
| 1145 vw | 1148 vw | | | 1149 vw | | |
| | 1140 vw | | | | | |
| 1120 vw | | 1125 w | 1130 w | | *GG* | $CH_2$ twist. |
| 1087 vw | | 1075 w | | | | |
| 1066 w sh | 1060 m | 1065 m | 1066 s | 1064 vw sh | *TG*, *GG* | C-C stretch. |
| 1056 w sh | | | | 1050 w sh | *TT* | C-C stretch. |
| 1047 m | 1045 m | | | 1044 m | *TT*, *TG* | C-C stretch. |
| 1022 m | | 1026 m | 1027 mw | 1026 vw sh | *GG* | C-C stretch. |
| 1008 ms | 1009 ms | 1010 m | 1009 w | | *TG*, *GG* | C-C stretch. |
| | 1003 w sh | | | | | |
| 998 w | | | | 1000 w | *TT* | C-C stretch. |
| 991 vw sh | | | | 990 w | | |
| | | 964 w | 971 vw | 953 vw | | |
| 945 m | 943 ms | 943 w | | 943 vw | *TG* | $CH_2$ rock. |
| 904 ms | | 903 ms | 913 s | 902 vw | *GG* | $CH_2$ rock. |
| | | 899 ms sh | | | | |
| 888 w | | | | 885 mw | *TT* | C-C stretch. |
| 870 ms | | 873 ms | 880 ms | 877 w | *GG* | C-C stretch. |
| | | 871 ms | | | | |
| | 864 m sh | 864 w sh | | | | |
| 860 ms | 859 ms | | | 861 w | *TG* | C-C stretch. |
| 835 ms | 839 ms | 837 ms | 830 s | 839 m | *TG*, *GG* | $CH_2$ rock. |
| | 835 ms sh | | | 833 m | | |
| | 800 vw | | 808 vw | 812 vw sh | | |
| 757 s | 757 s | 768 ms | 778 ms | 784 w | *TG*, *GG* | $CH_2$ rock. |
| | 751 s | 754 ms | 767 ms | 758 vw sh | | |
| 737 ms | | | | 742 m | *TT* | $CH_2$ rock. |
| | 681 mw | | | | | |
| | | | | 666 vw | | |
| 648 vw | | | | | | |
| 583 ms | 586 ms | 588 w | 586 w | 584 mw | *TG*, *GG* | C-C-C bend. |
| 565 w | | | | 564 w | *TT* | C-C-C bend. |
| 535 w | | 537 ms | 544 ms | 532 vw | *GG* | C-C-C bend. |
| 507 m | 511 ms | 503 vw | | 508 w | *TG* | C-C-C bend. |
| 481 vw | | | 475 vw | 473 vw | *TT* | C-C-C bend. |
| | | | | 458 vw | | |

a) KRS-5 supporting plates were used to obtain the spectrum.
b) The disk was prepared by applying a pressure of 10 tons.

of the complex are assigned to the $CH_2$ twisting modes. Absorptions corresponding to the C–C stretching modes are found at 1065, 1026, 1010 and 873 cm$^{-1}$ in the spectrum of the stable solid form and at 1066, 1027, 1009 and 880 cm$^{-1}$ in the spectrum of the complex. To the $CH_2$ rocking modes may correspond the bands observed at 903, 837 and 768/54 cm$^{-1}$ in the spectrum of the stable solid form and those observed at 913, 830 and 778/67 cm$^{-1}$ in the spectrum of the complex.

The configuration of glutaronitrile in the metastable crystalline solid state must be the *TG* form as the *TT* form can be excluded from

TABLE II. THE SYMMETRY TYPES AND SELECTION RULES FOR THE FUNDAMENTAL VIBRATIONS OF GLUTARONITRILE IN THE 1400∼400 $cm^{-1}$ REGION

| Types of symmetry coordinates | | $TT(C_{2v})$ | | | | $GG(C_2)$ | | $TG(C_1)$ | $GG'(C_s)$ | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | $A_1$ | $A_2$ | $B_1$ | $B_2$ | A | B | | A′ | A″ |
| $CH_2$ wagging | | 1 | 0 | 2 | 0 | 1 | 2 | 3 | 1 | 2 |
| $CH_2$ twisting | | 0 | 2 | 0 | 1 | 2 | 1 | 3 | 1 | 2 |
| C-C stretching | | 2 | 0 | 2 | 0 | 2 | 2 | 4 | 2 | 2 |
| $CH_2$ roking | | 0 | 1 | 0 | 2 | 1 | 2 | 3 | 2 | 1 |
| C-C-C bending | | 1 | 0 | 1 | 0 | 1 | 1 | 2 | 1 | 1 |
| Selection rules | IR | + | − | + | + | + | + | + | + | + |
| | Raman | + | + | + | + | + | + | + | + | + |

consideration of the selection rules and the existence of the *GG′* form is considered improbable from steric reasons[3]. The vibrational assignment of the spectrum shown in Fig. 1b was made on this basis. Thus, the bands observed at 1364, 1328 and 1289/82 $cm^{-1}$ may be assigned to the $CH_2$ wagging modes, and those at 1300, 1224/14 and 1181/74 $cm^{-1}$ to the $CH_2$ twisting modes of the *TG* form. The bands at 1060, 1045, 1009 and 859 $cm^{-1}$ correspond to the C–C stretching modes and those at 943, 839/35 and 757/51 $cm^{-1}$ must be ascribed to the $CH_2$ rocking modes.

The majority of the bands in the liquid-state spectrum of glutaronitrile (Fig. 1a) can be satisfactorily explained as due to the vibrations of the *TG* and the *GG* isomers, and a few remaining bands must be ascribed to the vibrations of the *TT* form, because one of them at 737 $cm^{-1}$ certainly corresponds to the $CH_2$ rocking vibration of the methylene chain of the planar all-trans configuration[5,9]. These conclusions are further confirmed by the calculation of the skeletal deformation vibrations for each isomeric form of glutaronitrile (see Appendix). The results of the calculation show that each isomer should have two C–C–C bending frequencies in the 650∼450 $cm^{-1}$ region. From the potential energy distributions it is shown that the energetical contributions of both the C–C–C bending and the C–C≡N (in-plane) bending motions are important in these skeletal deformation vibrations as in the case of succinonitrile[1]. The frequencies of 586 and 511 $cm^{-1}$ observed in the spectrum of the metastable solid form (Fig. 1b) agree quite well with the values of 567 and 507 $cm^{-1}$ calculated for the *TG* form. The frequencies of 588 and 537 $cm^{-1}$ observed in the spectrum of the stable solid form (Fig. 1c) and those of 586 and 544 $cm^{-1}$ in the spectrum of the complex (Fig. 2a) are in excellent agreement with the values of 590 and 535 $cm^{-1}$ calculated for the *GG* form. In the spectrum of the liquid glutaronitrile there are weak bands at 565 and 481 $cm^{-1}$ which disappear at low temperatures. These frequencies correspond well with the values of 546 and 441 $cm^{-1}$ calculated for the *TT* form. The values of 616 and 510 $cm^{-1}$ calculated for the *GG′* form seem not to be appropriate to explain the observed frequencies in all cases. The potassium bromide disk spectrum of the complex shown in Fig. 3b is different from the spectrum in Fig. 3a in that the absorptions corresponding to the vibrations of the *TT* form as described above are anomalously intense. It seems that the applied pressure of 10 tons must have favored the selective formation of the *TT* isomer in the reaction of the complex with potassium bromide. The spectrum in Fig. 3b shows a few other anomalously intense bands besides those mentioned above. These bands must also correspond to the vibrations of the *TT* form which could not be identified in the spectrum of the liquid glutaronitrile because of the overlapping of absorptions due to the *TG* or the *GG* form.

Spectral features of the complex in the C≡N stretching frequency region are similar to those of bis(succinonitrilo)copper(I) nitrate[1]. The sharp band observed at 2278 $cm^{-1}$ in the Nujol mull spectrum (Fig. 2a) should correspond to the C≡N stretching mode of the complex. The C≡N vibrational shift of 29 $cm^{-1}$ towards higher frequencies as compared with the free glutaronitrile may be explained from a consideration of the structure of the complex. From X-ray analysis of this complex[4] it has been found that the carbon-nitrogen bond distance is 1.14 Å and that the Cu–N–C–$CH_2$ group is close to linear. This 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, and the C≡N stretching frequency is thereby increased. The effect of coupling 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. As shown in Figs. 2b and 3, reaction with potassium bromide results in the appearance of the band at 2252 $cm^{-1}$ which corresponds to the C≡N stretching frequency of the free glutaronitrile. The band observed at 2353 $cm^{-1}$ in

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9) H. Tschamler, *J. Chem. Phys.*, 22, 1845 (1954).

the Nujol mull spectrum is considered to be characteristic of the tetrahedral configuration of the complex as in the case of bis(succinonitrilo)copper(I) nitrate[1]. The origin of the band observed at 2208 cm$^{-1}$ is hard to explain, because its intensity tends to vary from specimen to specimen and no other homologues of this series of complex show any absorption at the corresponding frequency. For the present, it may be ascribed to a certain combination vibration or to a vibration of some impurities in the complex.

## Summary

The infrared spectra of glutaronitrile and bis(glutaronitrilo)copper(I) nitrate, $[Cu\{NC-(CH_2)_3-CN\}_2]NO_3$, have been studied. The spectrum of the complex has been analyzed on the basis of the result of X-ray analysis which disclosed that the ligand glutaronitrile takes the *GG* configuration in the crystals of this compound. This complex reacts with alkali halides such as potassium bromide, resulting in the isolation of free glutaronitrile. Considering

TABLE III. FORCE CONSTANTS OF GLUTARONITRILE (in millidyne/Å)[a]

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

a) Transferred from succinonitrile. See Appendix in Ref. 1.

TABLE IV. SYMMETRY COORDINATES OF GLUTARONITRILE

| $C_{2v}$ | $C_2$ | $C_s$ | | |
|---|---|---|---|---|
| $A_1$ | A | A′ | $S_1=(\Delta r_1+\Delta r_1')/\sqrt{2}$ | ($CH_2$-$CH_2$ sym. 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) |
| | | | $S_4=\Delta\alpha_0$ | ($CH_2$-$CH_2$-$CH_2$ bending) |
| | | | $S_5=(\Delta\alpha+\Delta\alpha')/\sqrt{2}$ | ($CH_2$-$CH_2$-C sym. bending) |
| | | | $S_6=(\Delta\beta+\Delta\beta')/\sqrt{2}$ | ($CH_2$-C≡N sym. in-plane bending) |
| $A_2$ | | | $S_7=(\Delta\gamma+\Delta\gamma')/\sqrt{2}$ | ($CH_2$-C≡N sym. out-of-plane bending) |
| $B_1$ | B | A″ | $S_8=(\Delta r_1-\Delta r_1')/\sqrt{2}$ | ($CH_2$-$CH_2$ antisym. stretching) |
| | | | $S_9=(\Delta r_2-\Delta r_2')/\sqrt{2}$ | ($CH_2$-C antisym. stretching) |
| | | | $S_{10}=(\Delta r_3-\Delta r_3')/\sqrt{2}$ | (C≡N antisym. stretching) |
| | | | $S_{11}=(\Delta\alpha-\Delta\alpha')/\sqrt{2}$ | ($CH_2$-$CH_2$-C antisym. bending) |
| | | | $S_{12}=(\Delta\beta-\Delta\beta')/\sqrt{2}$ | ($CH_2$-C≡N antisym. in-plane bending) |
| $B_2$ | | | $S_{13}=(\Delta\gamma-\Delta\gamma')/\sqrt{2}$ | ($CH_2$-C≡N antisym. out-of-plane bending) |

TABLE V. CALCULATED AND OBSERVED FREQUENCIES OF GLUTARONITRILE (in cm$^{-1}$)

| | *TT*($C_{2v}$) | | | *GG*($C_2$) | | | *TG*($C_1$) | | | *GG′*($C_s$) | Assignment |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Calcd. | Obs. Liquid[a] | | Calcd. | Obs. Solid[b] | Obs. Complex[c] | Calcd | Obs. Solid[d] | | Calcd. | |
| $A_1$ | 2259 | | A | 2259 | | | 2259 | | A′ | 2259 | C≡N sym. stretching |
| | 993 | | | 980 | | | 984 | | | 980 | C-C sym. stretching |
| | 909 | | | 825 | | | 829 | | | 826 | C-CN sym. stretching |
| | 441 | 481 | | 590 | 588 | 586 | 507 | 511 | | 616 | C-C-C bending |
| | 315 | | | 358 | | | 336 | | | 364 | C-C-C bending |
| | 107 | | | 157 | | | 205 | | | 226 | C-C≡N bending |
| $A_2$ | 398 | | | 384 | | | 368 | | | 399 | C-C≡N bending |
| $B_1$ | 2259 | | B | 2259 | | | 2259 | | A″ | 2259 | C≡N antisym. stretching |
| | 1069 | | | 1062 | | | 1067 | | | 1062 | C-C antisym. stretching |
| | 843 | | | 853 | | | 883 | | | 851 | C-CN antisym. stretching |
| | 546 | 565 | | 535 | 537 | 544 | 567 | 586 | | 510 | C-C-C bending |
| | 230 | | | 241 | | | 174 | | | 169 | C-C≡N bending |
| $B_2$ | 398 | | | 387 | | | 388 | | | 365 | C-C≡N bending |

a) Obtained by subtracting the bands which correspond to the vibrations of the *GG* and the *TG* isomers.
b) Stable crystalline solid state.
c) Obtained from a Nujol mull by using KRS-5 supporting plates.
d) Metastable crystalline solid state.

TABLE VI. POTENTIAL ENERGY DISTRIBUTIONS OF THE *TT* FORM OF GLUTARONITRILE[a)]

| | $A_1$ | | | | | | $A_2$ |
|---|---|---|---|---|---|---|---|
| $\nu_{\text{calcd}}$ | 2259 | 993 | 909 | 441 | 315 | 107 | 398 |
| $S_1$ | 0 | +82 | +11 | + 9 | + 3 | + 1 | — |
| $S_2$ | − 8 | −20 | +60 | + 1 | +13 | 0 | — |
| $S_3$ | +95 | − 1 | + 3 | 0 | + 1 | 0 | — |
| $S_4$ | 0 | − 1 | −20 | − 1 | +60 | −22 | — |
| $S_5$ | 0 | − 7 | −18 | +20 | + 6 | +53 | — |
| $S_6$ | 0 | − 1 | − 1 | +65 | − 7 | −26 | — |
| $S_7$ | — | — | — | — | — | — | +100 |

| | $B_1$ | | | | | $B_2$ |
|---|---|---|---|---|---|---|
| $\nu_{\text{calcd}}$ | 2259 | 1069 | 843 | 546 | 230 | 398 |
| $S_8$ | 0 | +93 | + 7 | 0 | − 2 | — |
| $S_9$ | + 8 | − 9 | +85 | + 1 | 0 | — |
| $S_{10}$ | −95 | 0 | + 5 | 0 | 0 | — |
| $S_{11}$ | 0 | 0 | − 5 | +58 | +41 | — |
| $S_{12}$ | 0 | 0 | 0 | +40 | −59 | — |
| $S_{13}$ | — | — | — | — | — | +100 |

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

TABLE VII. POTENTIAL ENERGY DISTRIBUTIONS OF THE *GG* FORM OF GLUTARONITRILE[a)]

| | A | | | | | | |
|---|---|---|---|---|---|---|---|
| $\nu_{\text{calcd}}$ | 2259 | 980 | 825 | 590 | 358 | 157 | 384 |
| $S_1$ | 0 | +77 | +27 | + 1 | − 1 | 0 | 0 |
| $S_2$ | + 8 | −29 | +61 | + 5 | 0 | 0 | 0 |
| $S_3$ | −95 | − 1 | + 3 | 0 | 0 | 0 | 0 |
| $S_4$ | 0 | − 7 | 0 | −28 | −44 | +14 | +10 |
| $S_5$ | 0 | 0 | −11 | +31 | − 7 | +45 | −11 |
| $S_6$ | 0 | − 1 | − 2 | +20 | −46 | −47 | 0 |
| $S_7$ | 0 | 0 | 0 | + 5 | +20 | +15 | +74 |

| | B | | | | | |
|---|---|---|---|---|---|---|
| $\nu_{\text{calcd}}$ | 2259 | 1062 | 853 | 535 | 241 | 387 |
| $S_8$ | 0 | +96 | + 4 | + 3 | 0 | 0 |
| $S_9$ | + 8 | − 7 | +85 | + 2 | 0 | 0 |
| $S_{10}$ | −95 | 0 | + 5 | 0 | 0 | 0 |
| $S_{11}$ | 0 | − 3 | −12 | +39 | +27 | −23 |
| $S_{12}$ | 0 | − 1 | − 1 | +33 | −79 | − 2 |
| $S_{13}$ | 0 | 0 | 0 | + 7 | +26 | +83 |

a) See the footnote of Table VI.

TABLE VIII. POTENTIAL ENERGY DISTRIBUTIONS OF THE *TG* FORM OF GLUTARONITRILE[a)]

| $\nu_{\text{calcd}}$ | 2259 | 984 | 839 | 507 | 336 | 205 | 368 | 2259 | 1067 | 883 | 567 | 174 | 388 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $S_1$ | 0 | +83 | +13 | + 5 | + 1 | 0 | + 1 | 0 | + 1 | − 1 | − 1 | 0 | + 1 |
| $S_2$ | − 7 | −21 | +57 | + 1 | + 2 | + 1 | + 1 | + 1 | 0 | −13 | 0 | 0 | 0 |
| $S_3$ | +80 | − 1 | + 3 | 0 | 0 | 0 | 0 | −15 | 0 | − 1 | 0 | 0 | 0 |
| $S_4$ | 0 | − 4 | − 1 | − 3 | +55 | + 4 | + 1 | 0 | 0 | +11 | − 8 | −14 | + 2 |
| $S_5$ | 0 | − 2 | −14 | +17 | 0 | +34 | +20 | 0 | − 2 | + 1 | + 6 | + 8 | − 1 |
| $S_6$ | 0 | − 1 | − 1 | +26 | + 3 | −54 | +14 | 0 | 0 | 0 | + 7 | − 8 | 0 |
| $S_7$ | 0 | 0 | 0 | +10 | + 1 | +16 | −73 | 0 | 0 | 0 | + 2 | + 1 | +13 |
| $S_8$ | 0 | + 1 | 0 | 0 | 0 | 0 | 0 | 0 | −93 | − 6 | − 1 | − 1 | 0 |
| $S_9$ | + 1 | 0 | −17 | 0 | + 3 | 0 | 0 | + 7 | + 9 | −59 | − 5 | 0 | + 1 |
| $S_{10}$ | −15 | 0 | − 1 | 0 | 0 | 0 | 0 | −80 | 0 | − 3 | − 1 | 0 | 0 |
| $S_{11}$ | 0 | − 2 | 0 | + 5 | − 1 | − 5 | + 1 | 0 | 0 | +11 | −32 | +32 | +15 |
| $S_{12}$ | 0 | 0 | 0 | +12 | −31 | + 6 | + 1 | 0 | + 1 | + 1 | −19 | −45 | 0 |
| $S_{13}$ | 0 | 0 | 0 | + 3 | +16 | − 2 | −10 | 0 | 0 | 0 | − 4 | +13 | −68 |

a) See the footnote of Table VI.

the frequency shifts of the nitrate vibrations the reaction of the complex with potassium bromide should be ascribed largely to an ion interchange between the two phases. The increase of 29 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. Glutaronitrile can form two different crystalline solid phases, depending on the mode of crystallization. From comparison of the two solid-state spectra with that of the complex and from consideration of the vibrational selection rules it has been concluded that glutaronitrile takes the *GG* configuration in one crystalline solid state and the *TG* in the other, and that it exists as a mixture of three isomers, *GG*, *TG* and *TT* in the liquid state. Calculation of the skeletal deformation frequencies for each isomeric form has given the results which support this conclusion. Vibrational assignment of glutaronitrile in various states has been made satisfactorily on the basis of the above results.

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### Appendix: Calculation of Skeletal Vibrations

The skeletal vibrations of glutaronitrile were calculated as a seven-body problem. Calculations were carried out on all the four isomeric forms, $TT(C_{2v})$, $GG(C_2)$, $GG'(C_s)$ and $TG(C_1)$. A potential function of the Urey-Bradley type[10] was used, and the values of force constants were transferred from succinonitrile[1] as shown in Table III. The symmetry coordinates of glutaronitrile listed in Table IV were constructed from the internal coordinates shown in Fig. 4. Except for the case of the *TT* form, coupling between the C-C≡N in-plane and out-of-plane bending motions occurs. As in the case of succinonitrile[1] a cross term $k$(C-C≡N) corresponding to the interaction of the two C-C≡N bending coordinates was introduced into the potential function (Table III). For the calculation of the kinetic energy matrices the assumed bond lengths of $r(CH_2\text{-}CH_2)=1.54$ 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.

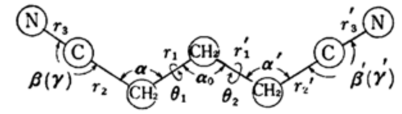

Fig. 4. Internal coordinates of glutaronitrile. $\beta$ (or $\beta'$) and $\gamma$ (or $\gamma'$) denote bending of C≡N bond in and out of the plane of the adjacent C-C-C linkage, respectively. $\theta_1=\theta_2=180°$ for *TT*, $\theta_1=\theta_2=60°$ for *GG*, $\theta_1=-\theta_2=60°$ for *GG*′, and $\theta_1=180°$ and $\theta_2=60°$ for *TG*.

The calculated frequencies are listed in Table V, in which the observed frequencies for the skeletal deformation vibrations are also included, although the observed data are not available for the region below 400 cm$^{-1}$. For each isomeric form there exist two vibrations corresponding to the C-C-C bending modes in the 650∼450 cm$^{-1}$ region. The potential energy distributions listed together with the signs of the corresponding L matrix elements in Tables VI—IX show that these vibrations correspond to the in-phase coupling of the C-C-C bending and the C-C≡N (in-plane) bending motions. The agreement between the observed and the calculated frequencies of these vibrations are satisfactory, showing that the skeletal deformation frequencies of glutaronitrile are quite useful in determining the configurations of rotational isomers of this molecule.

TABLE IX. POTENTIAL ENERGY DISTRIBUTIONS OF THE *GG*′ FORM OF GLUTARONITRILE[a)]

| | A′ | | | | | | |
|---|---|---|---|---|---|---|---|
| $\nu_{calcd}$ | 2259 | 980 | 826 | 616 | 364 | 226 | 399 |
| $S_1$ | 0 | +77 | +27 | + 1 | + 1 | 0 | 0 |
| $S_2$ | + 8 | −29 | +59 | + 6 | 0 | 0 | 0 |
| $S_3$ | −95 | − 1 | + 3 | + 1 | 0 | 0 | 0 |
| $S_4$ | 0 | − 8 | 0 | −22 | +62 | +13 | 0 |
| $S_5$ | 0 | 0 | −13 | +41 | + 4 | +27 | −19 |
| $S_6$ | 0 | − 1 | − 2 | +16 | +34 | −63 | 0 |
| $S_7$ | 0 | 0 | 0 | + 3 | − 2 | +30 | +81 |

| | A″ | | | | | |
|---|---|---|---|---|---|---|
| $\nu_{calcd}$ | 2259 | 1062 | 851 | 510 | 169 | 365 |
| $S_8$ | 0 | +96 | + 4 | + 2 | 0 | 0 |
| $S_9$ | − 8 | − 8 | +85 | + 1 | 0 | 0 |
| $S_{10}$ | +95 | 0 | + 5 | 0 | 0 | 0 |
| $S_{11}$ | 0 | − 3 | −10 | +23 | +49 | −18 |
| $S_{12}$ | 0 | − 1 | − 1 | +41 | −56 | −18 |
| $S_{13}$ | 0 | 0 | 0 | +13 | +11 | +91 |

a) See the footnote of Table VI.

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