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Polymorphism and the Structure of Bis(dichloromethylene)succinic Acid as Studied by Chlorine NQR

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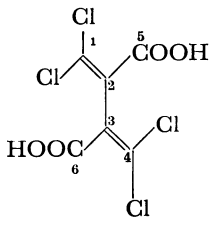
Synopsis. It was found that bis(dichloromethylne) succinic acid (BDCSA) has two crystal forms, the molecule having an *s-trans* conformation in each form. A frequency drop of about 1 MHz found for BDCSA might be explained in terms of a short intramolecular contact between the chlorine and oxygen atoms.

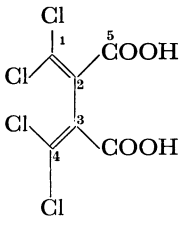
The ^{35}Cl NQR frequencies were measured for bis(dichloromethylene)succinic acid (BDCSA), its anhydride (BDCSAA), trichloroacrylic acid (TCAA), and methyl trichloroacrylate (MTCA) in order to investigate the structure of BDCSA. Details of NQR experiments and methods of preparation of the compound studied were reported.[1,2]

Crystals of BDCSA obtained by recrystallizations from ether gave NQR two lines (designated as α-spect rum), while a specimen crystallized from water afforded four lines (β-spectrum). It is evident that BDCSA has two crystal forms.[3] The resonance frequencies for these two spectra are given in Table 1, together with those for the related compounds. The spectra are also shown as stick diagrams in Fig. 1. Both α-and β-spectra exhibit considerably large frequency splittings of about 1 MHz. In the β-spectrum, the four lines seem to be devided into two frequency groups, a higher (38.430 MHz, average of ν_1 and ν_2) and a lower (37.535 MHz, average of ν_3 and ν_4).

As to the structure of BDCSA, there are two conformational possibilities, *i.e.*, *s-trans* (I) and *s-cis* (II)



(I)



(II)

forms.[4] If BDCSA has an *s-cis* form in both crystalline modifications, the NQR spectrum is expected to be similar to that for BDCSAA being forced to have an *s-cis* form. However, the lower frequency group of the former is situated far below the average (38.238 MHz) of ν_1 and ν_2 of the latter (Fig. 1). This suggests that BDCSA has an *s-trans* form.

From a comparison of the spectrum for TCAA with that of MTCA, their ν_2 and ν_3's can be assigned to geminal vinylic chlorine atoms. The NQR spectra of these two compounds and BDCSAA indicate that the geminal vinylic chlorine atoms in BDCSA would afford their NQR lines in a region, 38.2±0.3 MHz. The higher-frequency lines in BDCSA (ν_a in the α-, and ν_1 and ν_2 in the β-spectrum) appear in this anticipated region, but the lower-frequency lines lie in a frequency region significantly lower by about 1 MHz. Since both α- and β-spectra show a similar pattern, the large frequency drop might be attributed to an intramolecular phenomenon. The abnormal drop causes one to imagine an intramolecular hydrogen-bond formation between one of the chlorine atoms at C-1 position and the carboxyl group (at C-3 position) on the same side.[5] If this is correct, the magnitudes of the temperature coefficient of resonance frequencies for the lower-frequency lines should be smaller than those for the higher-frequency lines.[5] However, no such tendency was observed (Table 2).

Thus, the hydrogen-bond model does not seem to be applicable to the explanation of the large frequency drop. An alternative and most likely interpretation

Table 1. The ^{35}Cl NQR frequencies (f) for bis(dichloromethylene)succinic acid and related compounds at 77 K

Compounds		No. of lines	f/MHz
BDCSA	α-spectrum	ν_a	38.489
		ν_b	37.478
	β-spectrum	ν_1	38.530
		ν_2	38.330
		ν_3	37.772
		ν_4	37.299
BDCSAA		ν_1	38.370
		ν_2	38.106
TCAA		ν_1	39.245
		ν_2	38.549
		ν_3	37.933
MTCA		ν_1	39.648
		ν_2	38.230
		ν_3	38.160

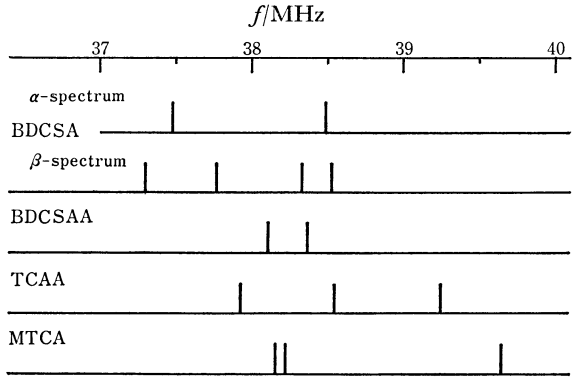


Fig. 1. The ^{35}Cl NQR spectra of bis(dichloromethylene)succinic acid and related compounds at 77 K.

Table 2. Temperature coefficients of resonance frequency (df/dT) in bis(dichloromethylene)-succinic acid

No. of lines	$\frac{df/dT}{kHz/K}$
ν_a	−2.20
ν_b	−3.14
ν_1	−2.45
ν_2	−1.83
ν_3	−2.43
ν_4	−4.05

for the frequency drop would be a short contact between the chlorine atom on position 1 and an oxygen atom in the carboxyl group on 6. A similar frequency drop was reported in the case of chloral hydrate.[6]

References

1) M. Hashimoto, *Bull. Chem. Soc. Jpn.*, **50**, 1746 (1977).
2) A. Fujino, Y. Nagata, and T. Sakan. *Bull. Chem. Soc. Jpn.*, **38**, 295 (1965).
3) Both the elementary analysis (Found: C, 25.74; H, 0.69%. Calcd for $C_6Cl_4H_2O_4$: C, 25.75; H, 0.72%) and the IR data support the absence of water of crystallization for the one crystallized from water. This polymorphism was also confirmed by X-ray diffraction method.
4) No planarity was found in the two double bonds on the basis of the UV spectra of BDCSA (Ref. 2).
5) A. Sasane, T. Matuo, D. Nakamura, and M. Kubo, *Bull. Chem. Soc. Jpn.*, **43**, 1908 (1970).
6) H. Chihara and N. Nakamura, *Bull. Chem. Soc. Jpn.*, **45**, 3530 (1972).