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Cyclohexane Inclusion Compound with 2,2-Dibutyl-N,N'-di(1-naphthyl)malonamide

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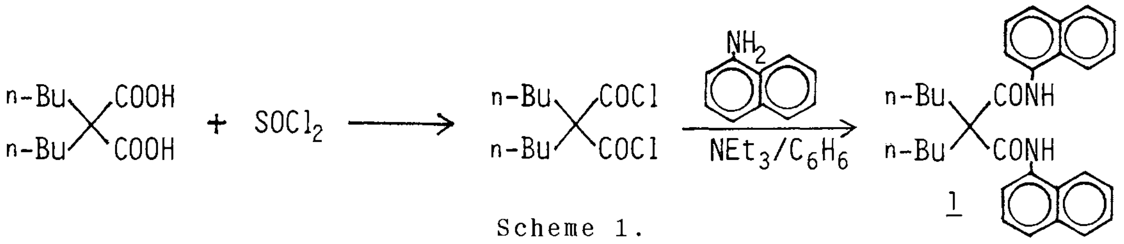
A novel clathrate-type inclusion compound has been formed from recrystallization of 2,2-dibutyl-N,N'-di(1-naphthyl)malonamide with restricted organic molecules, which was characterized by the thermal analyses(DSC and TGA) and the X-ray structural analysis.

Much attention has been paid to the clathrate-type inclusion compounds in view of selective separation and molecular recognition of neutral organic compounds, by utilizing weak intermolecular interactions, i.e., host-guest complexation. So far, many clathrate-type host compounds such as urea, thiourea, naturally-occurring steroids, alkaloids, and Hofmann- and Werner-type inorganic compounds have been well known.1) Furthermore, a number of synthetic clathrate-type organic host compounds for neutral guest molecules have been studied with respect to their ability of guest inclusion, selectivity, and structural features.2) Recently, design of host molecules which can exhibit high selectivity to a special guest has increasingly become important because of their expected-wide applications.3) We report here on a novel organic host molecule and a new class of its inclusion compounds with cyclic alkanes. We investigated also the crystal structure of the inclusion compound with cyclohexane by the X-ray analysis.

The title malonamide(1) was obtained in good yield by the reaction of dibutylmalonic acid with thionyl chloride followed by the treatment with 1-aminonaphthalene in the presence of triethylamine in benzene (Scheme 1).4) When 1 was recrystallized from cyclohexane, fine needle crystals were grown. Even after the crystals were dried at 50 °C for several hours under vacuum (below 1.0 Torr), it was difficult to completely remove cyclohexane from the crystals. Then, it was confirmed from the proton NMR spectrum the recrystallized product, which was filtered off followed by air-drying, was composed of 1 mol of malonamide 1 and 0.5 mol of cyclohexane.5) In the IR spectrum the intensity of the absorption band at 2910 cm^{-1} based on methylene group of cyclohexane increased. After the product was dried at 100 °C overnight under vacuum, cyclohexane completely removed from it.



Scheme 1.

The DSC and TGA of the recrystallized products were measured at the ascending rate of 10 °C/min in air. The results are shown in Fig. 1. In the DSC two endothermic peaks are observed(Peak A : 123 °C; Peak B : 169 °C). The former is attributed to the release of cyclohexane, and the latter the melting point of 1.$^{6)}$ In the TGA the weight loss(7.9%), of which the amount nearly corresponds to the loss of 0.5 mol of cyclohexane toward 1 mol of malonamide 1. This result is completely consistent with that observed in the NMR spectrum. Since the release temperature of the guest molecule from the clathrate is higher than the boiling point of the guest molecule, malonamide 1 seems to include cyclohexane with considerable stability.

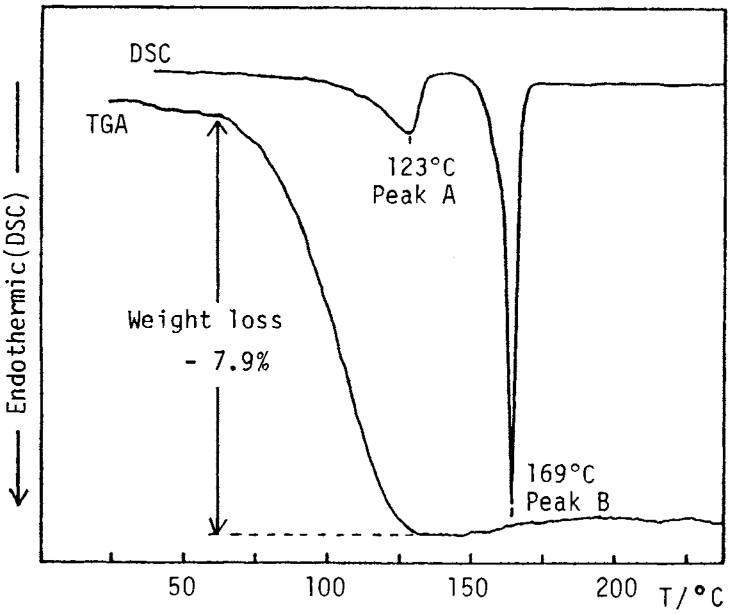


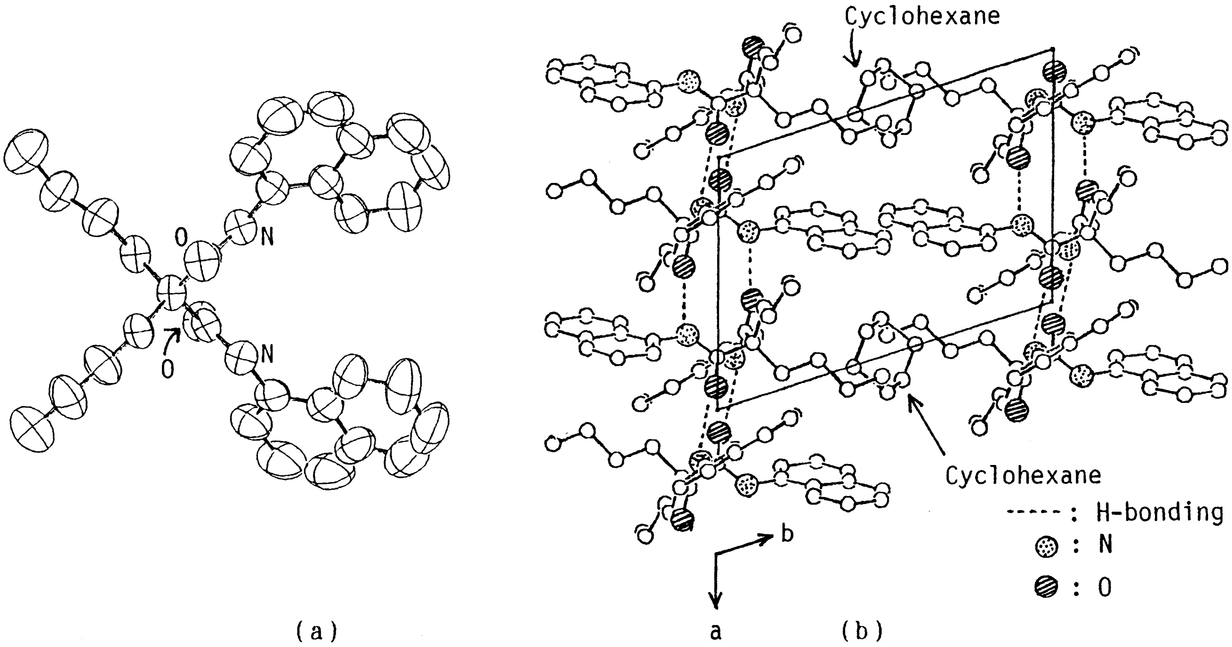
Fig. 1. DSC and TGA curves of 1-cyclohexane(2 : 1) complex.

In order to determine the crystal structure composed of malonamide 1 with cyclohexane by X-ray analysis, the single crystals were grown by slow evaporation from cyclohexane solution. They were colorless needle-like crystals elongated b-axis. A single crystal of 0.06 x 0.8 x 0.045 mm in size was used. All the X-ray data were obtained on a Enraf-Nonius CAD4 four-circle diffractometer by using graphite-monochromated Cu $K\bar{\alpha}$(1.54184

Å) radiation. The 3344 independent reflections with 2θ values up to 130°($|F_o| \geqq 3\sigma(|F_o|)$) were used for analysis. No correction was made for absorption. Crystal data: ($C_{31}H_{34}O_2N_2$ + 0.5(C_6H_{12}) triclinic; space group $P\bar{1}$; a = 9.515(2), b = 13.099(4), c = 13.454(4)Å, α = 101.17(3), β = 104.03(2), γ = 104.49° (3), D_c = 1.115 g/cm^3, μ = 5.42 cm^{-1}, Z = 2. The structure was solved the MULTAN 78 program.[7] Most of the H atoms of malonamide <u>1</u> were found in a difference Fourier map and the remainder were located in calculated positions. The structural parameters were refined by the full-matrix least-squares method, using the UNICS III system.[8] Anisotropic thermal parameters were assumed for the non-hydrogen atoms and isotropic parameters for the hydrogen atoms. The R-value was reduced to 0.078(R_ω = 0.067, $\omega = (18.28(\sin\theta/\lambda)^2 - 16.95(\sin\theta/\lambda) + 4.04)^{-1}$).

The molecular structure of the inclusion complex is shown in Fig. 2. Apparently, a cyclohexane molecule is located in the space which is formed between two chain structures, which is made up by the intermolecular hydrogen bonding among amide groups. One of the features of this inclusion manner is that a guest molecule is confined, not only by two naphthalene rings from both top and bottom along the chain struture, but also by two n-butyl groups from the perpendicular direction to it(see in Fig. 2-a). High release-temperature of cyclohexane from the crystals observed from the DSC and TGA might be attributed to the rigid structure of such inclusion complex.

According to the X-ray analysis of the inclusion complex, guest



(a) (b)

Fig. 2. (a): Perspective view of 1 and (b): Packing diagram(from c-Axis) of the 2 : 1 complex of 1 and cyclohexane.

molecules included may be favorable to be of relatively simple structure and/or of relatively small size, and the inclusion ability of malonamide derivatives is predicted to significantly be affected by the substituents on it. Based on these prediction, when 1 was recrystallized from benzene, cyclohexene, toluene, o-, m-, and p-xylenes, methylcyclohexane, 1,4-dimethylcyclohexane, cyclohexanone, cyclohexanol, cyclopentane, methylcyclopentane, cycloheptane, and cyclooctane instead of cyclohexane, 1 forms comparatively stable 2 : 1 inclusion complexes with benzene(DSC peak 111 °C), cyclohexene(DSC peak 127 °C), and cyclopentane(DSC peak 131 °C), respectively,9) but not with the other compounds. Recrystallization of 1 was unsuccessful with acetone, acetonitrile, dioxane, chloroform, methanol, ethanol, tetrahydrofuran, dimethylformamide, and dimethylsulfoxide because 1 was very soluble in these solvents. As predicted, only cyclic, unsubstituted, and relatively small molecules are apparently included. It should be noticed that unsubstituted five- and six-membered ones can be included but not cyclic molecules more than seven membered one.

In conclusion, malonamide derivative 1 has some remarkable features in its inclusion ability such as guest selectivity and inclusion manner.

References

1) "Inclusion Compounds," ed by J.L. Atwood, J.E.D. Davies, and D.D. MacNicol, Academic Press, London(1984), Vols. 1 - 3.

2) "Topics in Current Chemistry, Vol. 140," ed by E. Weber, Springer-Verlag, Berlin Heidelberg(1987).

3) For example, F. Toda, in: "Topics in Current Chemistry, Vol 140," ed by E. Weber, Springer-Verlag, Berlin Heidelberg(1987), pp. 43 - 69.

4) 1: Yield 83%, Mp 162 - 164 °C, Precise Mass, Found 466.258, Calcd for $C_{31}H_{34}O_2N_2$ 466.262.

5) ^{1}HNMR spectrum of 1 (300 MHz, $CDCl_3$, TMS): δ = 0.93 (6H, t, CH_3), 1.41(4H, m, $C\underline{H}_2CH_3$), 1.47(4H, m, $C\underline{H}_2CH_2CH_3$), 2.23(4H, m. $C\underline{H}_2CH_2CH_2CH_3$), 7.51(6H, m, aromatic), 7.74(2H, d, aromatic), 7.88(2H, m, aromatic), 7.95(2H, m, aromatic), 8.01(2H, d, aromatic), and 9.86(2H, s, NH) ppm.

6) In the second time of DSC, the peak based on the melting point was different from that of the first time because of its different crystal structure after the removal of cyclohexane.

7) P. Main, S.E. Hull, L. Lessinger, G. Germain, J.P. Declercq, and M.M. Woolfson, MULTAN78, Univ. of York, England and Univ. de Louvain, Belgium(1978).

8) T. Sakurai and K. Kobayashi, Rikagaku Kenkyusho Houkoku, 55, 69(1978).

9) They have another endothermic peak at around 170 °C due to the melting point of free 1.

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