パラ置換安息香酸誘導体と 1,4 ジアザビシクロ[2.2.2]オクタンの共結晶の X 線構造解析

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1,4-Diazabicyclo[2.2.2]octane (DABCO) is a molecule characterized by basicity and low steric hindrance, which acts as an electron donor and hydrogen bond acceptor, forming co-crystals with various molecules. In this study, three types of benzoic acid derivatives, 4-nitrobenzoic acid (pNBA), 4-aminobenzoic acid (pABA), and 4-fluorobenzoic acid (pFBA), were co-crystallized with DABCO by the solvent evaporation method and X-ray structure analyses were performed. The results of the X-ray structural analysis are shown in the table below. The co-crystal (I) shows a disoder in the orientation of the DABCO molecule, and a change in the unit lattice was observed when measured at 250 K, suggesting that a structural phase transition phenomenon is taking place. In the co-crystal (II), water molecules formed a network by hydrogen bonding to fill the gap between pNBA and DABCO. In co-crystal (III), acetone was incorporated into the co-crystal even though acetone was not actively added as a solvent. Co-crystal (IV) is a 1:1 co-crystal, but there are two independent pairs in the unit lattice, and an orientation disoder was observed in one of the DABCOs.

Keywords : co-crystals, X-ray structure analysis, 1,4-Diazabicyclooctane

1,4 ジアザビシクロ[2.2.2]オクタン(以下 DABCO)は塩基性と低い立体障害という特徴をもつ分子であり,この分子は電子供与体や水素結合受容体として働き, 種々の分子と共結晶を形成する.本研究では,4-ニトロ安息香酸(pNBA), 4-アミノ安息香酸(pABA), 4-フルオロ安息香酸(pFBA)の三種類の安息香酸誘導体と DABCO の共結晶を溶媒蒸発法で作成し, X 線構造解析を行った. X 線構造解析の結果を下表に示す. 各共結晶の特徴として, 共結晶(I)は DABCO 分子に配向の disoder が確認され, 250K で測定したところ単位格子の変化が観測され構造相転移現象が起こると示唆される. 共結晶(II)は pNBA と DABCO の隙間を埋めるように水分子が水素結合してネットワークを形成した. 共結晶(III)は積極的にアセトンを溶媒として添加していないにも拘わらずアセトンが共結晶中に取り込まれた. 共結晶(IV)は 1:1 の共結晶であるが単位格子中に二組が独立して存在していて, 片方の DABCO に配向の disoder が確認できた.

Table 1. 安息香酸誘導体とDABCO共結晶の構造解析の結果

	pNBA－DABCO (2:1) (Ⅰ)	pNBA－DABCO－H_2O (2:3:8) (Ⅱ)	pABA－DABCO－acetone (1:1:1) (Ⅲ)	pFBA―DABCO (1:1) (Ⅳ)
結晶化溶媒	ジクロロメタン	酢酸エチル	ヘキサン・アセトン	酢酸エチル
測定温度(K)	295	130	250	295
空間群	*C*2/m	*P*nma	$P2_12_12_1$	$P2_12_12_1$
a /Å	23.2286(17)	13.3917(4)	6.3797(4)	7.879(4)
b /Å	6.8070(5)	44.2896(13)	11.7353(7)	16.097(8)
c /Å	6.6091(5)	6.6361(2)	21.5788(13)	20.246(9)
β/°	96.9092(15)			
V/Å³	1037.42(17)	3934.2(2)	1651.55(17)	2568.0(2)
Z	1	2	4	8
R	0.0756	0.0511	0.0512	0.0501
wR	0.2342	0.1623	0.0939	0.1496