Preparation of α-Linked 6-Deoxy-D-*altro*-heptopyranosidic Residues

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α-Linked D-*altro*pyranosidic derivatives were obtained by configurational change at C-3 of α-D-*manno*pyranosides as the key step in preparation of allyl and methyl α-D-glycopyranosides of 6-deoxy-D-*altro*-heptose. The *manno-altro* conversion was effected by sequential reactions of Swern oxidation and stereoselective borohydride reduction. Allyl 4,6-*O*-benzylidene-2-*O*-p-methoxybenzyl-α-D-mannopyranoside was transformed to the corresponding altropyranoside *via* 3-oxo-*arabino*-hexopyranoside. Allyl 7-*O*-benzyl-6-deoxy-3,4-O-isopropylidene-α-D-*altro*-heptopyranoside has been prepared as a glycosyl acceptor to be coupled with β-D-Glc*p*NAc-(1→3)-α-D-Gal*p* glycosyl donor for the synthesis of an O-antigen repeating unit of *Campylobacter jejuni* serotypes O : 23 and O : 36. Stereoselective borohydride reduction also succeeded in yielding methyl 2,4,7-tri-*O*-benzyl-6-deoxy-α-D-*altro*-heptopyranoside from the corresponding 3-oxo-α-D-*arabino*-heptopyranoside. C-6 Homologation was achieved by sequential reactions of cyanide displacement of 6-sulphonates, reduction of the resulting heptopyranosidurononitrile with diisobutylaluminum hydride, hydrolysis of the imine, and further reduction with sodium borohydride.

Introduction

Campylobacter jejuni species are major causes of human enteritis.[1~3] Studies on the LPS structures from *C. jejuni* serotypes O : 23 and O : 36 showed the O-antigen chains contain closely related trisaccharide repeating units of →3)-β-D-Glc*p*NAc-(1→3)-α-D-Gal*p*-(**1**→**2**)-α-D-*alt*-Hep*p*-(**1** in which the heptose residues vary in the presence or absence of deoxygenation at C-6 and methylation at O-3.[4] These heptose variants are regarded as a basis for serotypic discrimination, or a potentially important virulence factor. For the investigation of the role of -α-D-*alt*-Hep*p*- and structural requirements for the antigenic property it is necessary to synthsize neoglycoproteins of different oligosaccharide sizes and reading frames maintaining the repeating sequences. A prerequisite for the synthesis is to develop an efficient synthetic method for α-linked *altro*-heptopyranosidic residue.

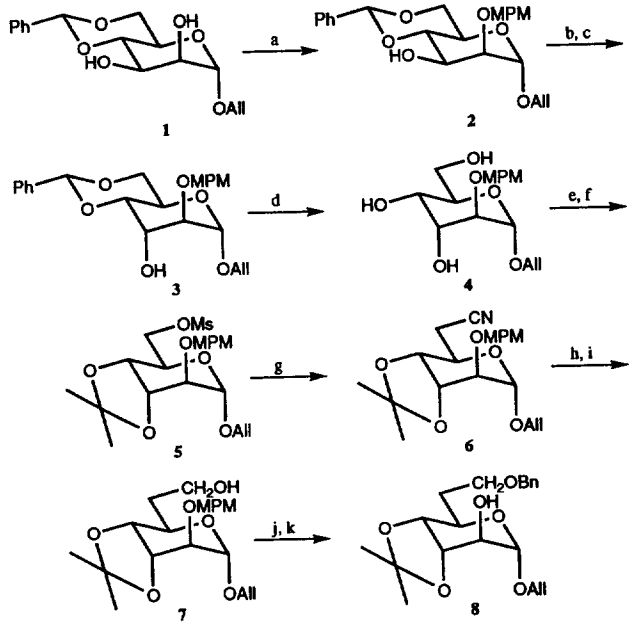
Two routes seemed possible to obtain 6-deoxy-α-D-*alt*-Hep*p*- : (A) starting from α-D-*Glcp*-, 2,3-inversion to gain entry into the D-*altro*pyranose series,[5] followed by C-6 homologation;[6~8] and (B) 3-inversion of α-D-*manp*- to α-D-*altp* and C-6 homologation. Route B seemed more favorable due to easier access to α-D-mannopyranosidic linkage in syntheses of various oligosaccharide epitopes containing the repeating sequence →3)-β-D-Glc*p*NAc-(**1**→**3**)-α-D-Gal*p*-(**1**→**2**)-α-D-*alt*-Hep*p*-(**1**. 3-Epimerization of α-D-*manp*- to α-D-*altp*- was achieved by sequential reactions of Swern oxidation[9,10] and borohydride reduction of the resulting 3-oxo-*arabinop*-. High stereoselectivity for α-D-*altrop*- has been observed in borohydride reduction of 3-oxo-*arabinop*-. Allyl 4,6-*O*-benzylidene-2-*O*-p-methoxybenzyl-α-D-mannopyranoside(**2**) was transformed to allyl 4,6-*O*-benzylidene-2-*O*-p-methoxybenzyl-α-D-altropyranoside(**3**) *via* allyl 4,6-*O*-benzylidene-2-*O*-p-methoxybenzyl-3-oxo-α-D-*arabino*-hexopyranoside.

Stereoselectivity of sodium borohydride reduction of 3-oxo-α-D-*arabinop*- was even higher in the conversion of methyl 2,4,6-tri-*O*-benzyl-3-oxo-α-D-*arabino*-hexopyranoside and methyl 2,4,7-tri-*O*-benzyl-6-deoxy-3-oxo-α-D-*arabino*-heptopyranoside to the corresponding α-D-*altro*-hexopyranoside and 6-deoxy-α-D-*altro*-heptopyranoside derivatives.

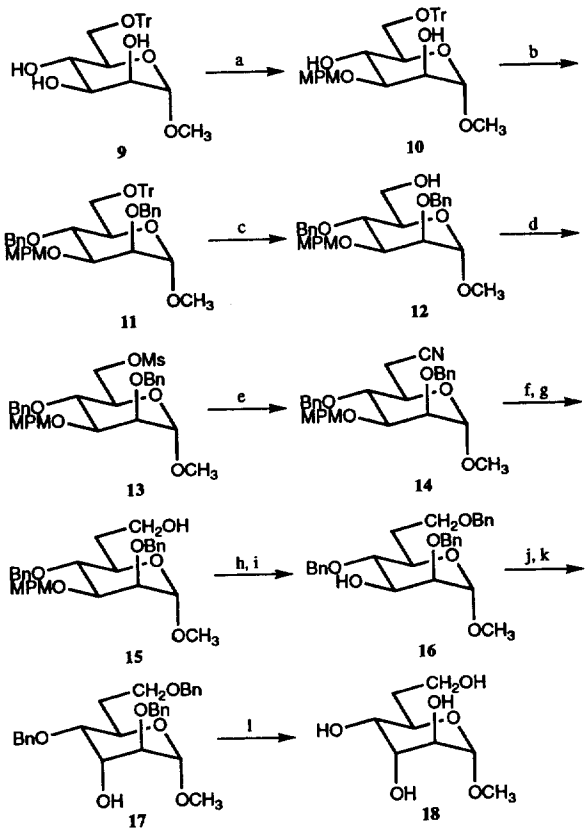
To homologate at C-6, we employed the method of the cyanide displacement of 6-sulphonate esters first used by Baer *et al.*[6] and Mitsunobu *et al.*[7] in the preparation of 6-deoxy-D-*gluco*-Hep*p* and proved efficient by Aspinall *et al.*[8] in the synthesis of methyl 2,3,4-tri-*O*-benzyl-6-deoxy-α-D-*altro*-Hep*p*. This procedure involves the reduction of the cyanide with diisobutylaluminum hydride (DIBAH), hydrolysis of the resulting imine, and further reduction with sodium borohydride. Employing route B together with Swern oxidation and borohydride reduction, we have synthesized allyl 7-*O*-benzyl-6-deoxy-3,4-*O*-isopropylidene-α-D-*altro*-heptopyranoside (**8**) which will be used as a glycosyl acceptor to β-D-Glc*p*NAc-(**1**→**3**)-α-D-Gal*p*- glycosyl donor for our synthesis of β-D-Glc*p*NAc-(**1**→**3**)-α-D-Gal*p*-(**1**→**2**)-α-D-6-deoxy-*alt*-Hep*p*-(**1**-spacer, a trisaccharide epitope of O-antigens of *C. jejuni* serotypes O : 23 and O : 36. Synthesis of **8** and creation of the α-D-*altro*-heptopyranosidic linkage are discussed.

Results and Discussion

Allyl 7-*O*-benzyl-6-deoxy-3,4-*O*-isopropylidene-α-D-*altro*-heptopyranoside(**8**) was synthesized from allyl 4,6-*O*-benzylidene-α-D-mannopyranoside (**1**) as shown in Scheme 1. Regioselective benzylation[11,12] of allyl 4,6-*O*-benzylidene-α-D-mannopyranoside (**1**) in the presence of a phase transfer catalyst, tetra-n-butylammonium iodide produced allyl 4,6-*O*-benzylidene-2-*O*-p-methoxybenzyl-α-D-mannopyranoside (**2**) in 55% yield. Swern oxidation[9,10] of **2** with oxalyl chloride and DMSO at −60 ℃ followed by reduction with sodium borohydride produced a mixture of the C-3-epimerized compound, allyl 4,6-*O*-benzylidene-2-*O*-p-methoxybenzyl-α-D-altropyranoside (**3**) and the starting compound **2** in 78% yield. The ^{13}C NMR spectrum showed the presence of two compounds assignable to **2**, the starting *manno*- and **3**, 3-epimer *altro*- in the approximate ratio of 1 : 4. The configuration of **3** was further confirmed by comparison of the ^{13}C NMR



Scheme 1. a) 15% aq. NaOH, CH_2Cl_2, $(n\text{-}Bu)_4NI$, $CH_3OC_6H_4CH_2Cl$, r.t., 48 hr; b) $(COCl)_2$, DMSO, CH_2Cl_2, −60 ℃, 2 hr/TEA, −60 ℃, 7 min; c) $NaBH_4$, DMF, MeOH, r.t., 5 min; d) 80% aq. HAc, 60 ℃, 2 hr; e) MsCl, pyridine, −15 ℃, 2 hr; f) $(CH_3)_2C(OCH_3)_2$, p-TsOH, THF, r.t., 1 hr; g) KCN, 18-crown-6, DMSO, 60 ℃, 7 hr; h) 1 M DIBAH/Hexane, THF, r.t., 1 hr/MeOH, 2N HCl, r.t., 45 min; i) $NaBH_4$, MeOH, r.t., 5 min; j) NaH, DMF, BnBr, r.t., 3 hr; k) DDQ, CH_2Cl_2, H_2O, r.t., 1 hr.



Scheme 2. a) Bu_2SnO, MeOH, reflux, 2 hr/$CH_3OC_6H_4CH_2Cl$, $(n\text{-}Bu)_4NI$, Toluene, 90 ℃, 19 hr; b) NaH, DMF, BnBr, r.t., 3 hr; c) TFA, Dioxane, MeOH, reflux, 2 hr; d) MsCl, pyridine, r.t., 6 hr; e) KCN, 18-crown-6, DMSO, 60 ℃, 7 hr; f) 1 M DIBAH/Hexane, THF, r.t., 1 hr/MeOH, 2N HCl, r.t., 45 min; g) $NaBH_4$, MeOH, r.t., 5 min; h) NaH, DMF, BnBr, r.t., 3 hr; i) DDQ, CH_2Cl_2, H_2O, r.t., 1 hr; j) $(COCl)_2$, DMSO, CH_2Cl_2, −60 ℃, 2 hr/TEA, −60 ℃, 7 min; k) $NaBH_4$, DMF, MeOH, r.t., 5 min; l) H_2 10% Pd/C, EtOH, r.t., 4 hr.

spectrum of allyl α-D-altropyranoside (**4a**) which was obtained by sequential de-*O*-benzylidenation and de-*O*-p-methoxybenzylation with that of methyl α-D-mannopyranoside. It is noteworthy that unlike 4,6-*O*-benzylidene acetals of *gluco*- or *manno*-derivatives[13,14] no selectivity was observed in the reductive cleavage of the benzylidene acetal group of *altro*-derivatives using $LiAlH_4$-$AlCl_3$, diisobutylaluminum hydride (DIBAH)[15] or $NaBH_3CN$-HCl[16]; treatment of **3** with $LiAlH_4$-$AlCl_3$ gave allyl 4-*O*-benzyl-2-*O*-p-methoxybenzyl-α-D-altropyranoside and allyl 6-*O*-benzyl-2-*O*-p-methoxybenzyl-α-D-altropyranoside in the approximate ratio of **1** : **1**. Thus compound **3** was hydrolyzed to allyl 2-*O*-p-methoxybenzyl-α-D-altropyranoside (**4**) with 80% aqueous acetic acid[17] in 74% yield. Selective mesylation of 6-OH of **4** with methanesulphonyl chloride at −15 ℃, following acetonation with 2,2'-dimethoxypropane in the presence of catalytic amount of p-toluenesulphonic acid[18] gave allyl 3,4-*O*-isopropylidene-6-*O*-mesyl-2-*O*-p-methoxybenzyl-α-D-altropyranoside (**5**) in 64% overall yield. The C-6 homologation of the mesylate **5** by displacement with KCN in the presence of 18-crown-6 (0.1 eq) in DMSO[7] afforded allyl 6-deoxy-3,4-*O*-isopropylidene-2-*O*-p-methoxybenzyl-α-D-*altro*-heptopyranosidurononitrile (**6**) in 50 % yield. Two-step reduction[8] of **6** with DIBAH at −60 ℃, with hydrolysis of the resulting imine with 2N HCl and further treatment with $NaBH_4$ gave the C-6 homologated allyl 6-deoxy-3,4-*O*-isopropylidene-2-*O*-p-methoxybenzyl-α-D-*altro*-heptopyranoside (**7**) in 30% overall yield. Benzylation of 7-OH of **7** with benzyl bromide-NaH and subsequent selective de-*O*-p-methoxybenzylation by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) oxidation[19] afforded the desired glycosyl acceptor, allyl 7-*O*-benzyl-6-deoxy-3,4-*O*-isopropylidene-α-D-*altro*-heptopyranoside (**8**), which is being used for the synthesis of a trisaccharide β-D-Glc*p*NAc-(**1**→**3**)-α-D-Gal*p*-(**1**→**2**)-α-D-6-deoxy-*alt*-Hep*p*-1-spacer.

It was necessary to study the steric effects on Swern oxidation and the subsequent borohydride reduction in order to employ this α-D-*manp*- to α-D-*altp*- conversion in syntheses of other oligosaccharides containing an α-D-6-deoxy-*alt*-Hep*p*- residue. A preliminary study with methyl 2,4,6-tri-*O*-benzyl-α-D-mannopyranoside to examine the effect of 4,6-*O*-benzylidene ring on Swern oxidation-borohydride reduction showed a higher stereoselectivity yielding the 3-epimerized product, methyl 2,4,6-tri-*O*-benzyl-α-D-altropyranoside with a trace amount of the starting manno derivative in overall yields of 69%. The effect of the C-6 homologation on the stereoselectivity also needed to be assessed in order to utilize this conversion method in the syntheses of oligosaccharides containing an α-6-deoxy-D-*alt*-Hep*p* residue, for example, the conversion of an α-D-6-deoxy-*man*-Hep*p*-(**1**→**3**)-β-D-Glc*p*NAc to an α-D-6-deoxy-*alt*-Hep*p*-(**1**→**3**)-β-D-Glc*p*NAc.

Methyl 2,4,7-tri-*O*-benzyl-6-deoxy-α-D-*manno*-heptopyrano-

side(**16**) was synthesized from methyl 6-*O*-trityl-α-D-mannopyranoside(**9**) as shown in Scheme 2. Compound **9** was transformed to its cyclic stannylene derivative by reaction with dibutyltin oxide.[20,21] Treatment of the stannylene complex with p-methoxybenzyl chloride in the presence of tetra-n-butylammonium iodide produced methyl 3-*O*-p-methoxybenzyl-6-*O*-trityl-α-D-mannopyranoside (**10**) regioselectively in 66% yield. The remaining 2-,4-OH groups of **10** were benzylated with benzyl bromide and sodium hydride,[22] giving methyl 2,4-di-*O*-benzyl-3-*O*-p-methoxybenzyl-6-O-trityl-α-D-mannopyranoside (**11**) in 90% yield. Detritylation of **11** with a catalytic amount of trifluoroacetic acid gave methyl 2,4-di-*O*-benzyl-3-*O*-p-methoxybenzyl-α-D-mannopyranoside (**12**) in 95% yield. In an identical manner to the previous synthesis of **7**, allyl 6-deoxy-3,4-*O*-isopropylidene-2-*O*-p-methoxybenzyl-α--D-*altro*-heptopyranoside, compound **12** was homologated to methyl 2,4-di-*O*-benzyl-6-deoxy-3-*O*-p-methoxybenzyl-α-D-*manno*-heptopyranoside (**15**).

Mesylation of **12** to 6-O-sulphonate (**13**) in 91% yield and the subsequent cyanide displacement produced methyl 2,4-di-*O*-benzyl-6-deoxy-3-*O*-p-methoxybenzyl-α-D-*manno*-heptosiduronitrile (**14**) in 83% yield. Two-step reduction of **14** with DIBAH and $NaBH_4$ gave **15** in 61% yield. Benzylation of 7-OH in **15** and the subsequent selective deprotection of p-methoxybenzyl group by DDQ oxidation gave methyl 2,4,7-tri-*O*-benzyl-6-deoxy-α-D-*manno*-heptopyranoside (**16**) in 74% overall yield. Swern oxidation of **16** to the corresponding 3-oxo-*arabino*-heptopyranoside followed by an immediate reduction with sodium borohydride gave *altro* derivative **17** in 74% overall yield. From the preceding results we may conclude that the stereochemical outcome of the α-D-*manp* to α-D-*altp* conversion by Swern oxidation and subsequent borohydride reduction is predominantly governed by the α-glycosidic linkage rather than by the steric environment provided by 4- or 6-OH protecting groups. Debenzylation of methyl 2,4,7-tri-*O*-benzyl-6-deoxy-α-D-*altro*-heptopyranoside (**17**) by hydrogenolysis with palladium 10% on carbon catalyst[23] gave methyl 6-deoxy-α-D-*altro*-heptopyranoside (**18**). ^{1}H-Nmr and ^{13}C-nmr spectral data of **18** were identical to the reported values[8].

In Summary, reduction of 3-oxo-α-D-*arabino*pyranosyl derivatives is highly diastereoselective favoring the corresponding α-D-*altro*pyranosyl derivatives in which 3-OH has 1,3-syn diaxial relationship with the α-glycosidic linkage. The high diastereoselectivity of the transformation is little affected by the nature of the 4- and 6-OH protecting groups. This α-D-*manp* to α-D-*altp* conversion offers a stereoselective synthetic route to the synthesis of oligosaccharides containing a 6-deoxy-α-D-*altro*-heptopyranosyl residue. Our prime purpose, synthesis of allyl 7-*O*-benzyl-6-deoxy-3,4-*O*-isopropylidene-α-D-*altro*-heptopyranoside (**8**) as a glycosyl acceptor to couple with β-D-Glc*p*NAc-(**1→3**)-α-D-Gal*p* glycosyl donor has been achieved.

Experimental

General Methods. Concentrations were performed under reduced pressure at below 40 ℃ (bath). Solvents were dried and distilled before use. NMR spectra were recorded with Varian Gemini-200 or Bruker ARX-300 spectrometers. Chloroform-d solutions were referenced to internal tetramethylsilane. D_2O solutions were referenced to internal methanol-d. IR spectra were recorded as films on KBr pellet with Mattson 3000 FT-IR spectrometer. Preparative column chromatography was performed on silica gel Merck 60 (Art 7734 70-230 mesh and Art 9385 230-400 mesh). TLC was conducted on plates coated with a 0.2 mm layer of silica gel $60F_{254}$ (Merck) : the components were located by charring the plate with 5% sulfuric acid.

Allyl 4,6-*O*-benzylidene-2-*O*-p-methoxybenzyl-α-D-mannopyranoside (2). To the solution of allyl 4,6-*O*-benzylidene-α-D-mannopyranoside (**1**) (2.21 g, 72 mmol) in CH_2Cl_2 (26 mL) aqueous NaOH (29 mL, 15%), p-methoxybenzyl chloride (2.08 mL, 2.1 equiv) and tetra-n-butylammonium iodide (0.26 g, 0.1 equiv) were added. After stirring for 48h at room temperature, the mixture was diluted with CH_2Cl_2, washed with water, dried (Na_2SO_4), and then concentrated under reduced pressure. The residual syrup was chromatographed on silica gel (benzene-EtOAc, 40 : 1) to give **2** (1.69 g, 55%) : ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.50-7.44 (m, 2H, C_6H_5 aromatic H), 7.36-7.31 (m, 3H, C_6H_5 aromatic H), 7.29 and 6.88 (both d, 2H each, J=8.8 Hz each, $CH_3OC_6H_4$ aromatic H), 5.96-5.76 (m, 1H, C<u>H</u>=CH_2), 5.54 (s, 1H, C_6H_5C<u>H</u>), 5.31-5.15 (m, 2H, CH=C<u>H</u>$_2$), 4.85 (d, 1H, $J_{1,2}$=1.46 Hz, H-1), 4.63 (d, 2H, $CH_3OC_6H_4C\underline{H}_2$), 4.24-3.79 (m, 11H), 2.51-2.41 (br.s, 1H, OH); ^{13}C NMR ($CDCl_3$, 200 MHz) δ 159.5 ($CH_3OC_6H_4$, Ar C-1″), 137.3 (C_6H_5, Ar C-1′), 133.4 (<u>C</u>H=CH_2), 129.6 (×3), 129.0, 128.2 (×2), and 126.2 (×2), 117.5 (CH=<u>C</u>H$_2$), 113.9 (×2, $CH_3OC_6H_4$, Ar C-2″ and C-6″), 102.0 (C_6H_5<u>C</u>H), 97.5 (C-1), 79.5 (C-4), 78.1 (C-2), 73.4 ($CH_3OC_6H_4C\underline{H}_2$), 68.7 and 68.6 (C-6 and O<u>C</u>H$_2$CH=CH_2), 68.0 (C-3), 63.5 (C-5), 55.2 (OCH_3).

Allyl 4,6-*O*-benzylidene-2-*O*-p-methoxybenzyl-α-D-altropyranoside (3). To a cooled (−60 ℃) solution of oxalyl chloride (1.8 mL) in CH_2Cl_2 (10 mL) DMSO (3.0 mL) was added dropwise. After stirring for 15 min at −60 ℃, a solution of compound **2** (2.25 g, 5.25 mmol) in CH_2Cl_2 (12 mL) was added dropwise and stirred for additional 2h at −60 ℃. After the dropwise addition of triethylamine (14 mL), the solution was stirred for 7 min at −60 ℃, and water was added. The solution was diluted with CH_2Cl_2, and washed with 0.2N HCl, aqueous $NaHCO_3$, and water in sequence. The organic layer was dried and concentrated. Without further purification the residual syrup was immediately reduced with sodium borohydride (2.02 g) in DMF (13 mL) and MeOH (360 mL). The solution was stirred at room temperature for 5 min and evaporated to dryness. The residue in CH_2Cl_2 was washed successively with water, dried, and concentrated to a syrup, which was chromatographed on silica gel (toluene-EtOAc, 15 : 1) to give a mixture (2.37 g, 78%) of **3** and **2** (ratio 4 : 1) : ^{1}H NMR ($CDCl_3$, 200 MHz) for **3** δ 7.52-7.45 (m, 2H, C_6H_5 aromatic H), 7.36-7.31 (m, 3H, C_6H_5 aromatic H), 7.25 and 6.87 (both d, 2H each, J=8.8 Hz each, $CH_3OC_6H_4$ aromatic H), 5.88-5.79 (m, 1H, C<u>H</u>=CH_2), 5.60 (s, 1H, $C_6H_5C\underline{H}$), 5.30-5.16 (m, 2H, CH=C<u>H</u>$_2$), 4.84 (s, 1H, H-1), 4.53 (s, 2H, $CH_3OC_6H_4C\underline{H}_2$), 4.34-4.13 (m, 4H), 4.04-3.93 (m, 2H), 3.89-3.66 (m, 5H), 3.06-3.02 (d, 1H, OH); ^{13}C NMR ($CDCl_3$, 200 MHz) for **3** δ 159.4 ($CH_3OC_6H_4$, Ar C-1″), 137.3 (C_6H_5, Ar C-1′), 133.1(<u>C</u>H=CH_2), 129.5, 129.4 (×2), 128.9, 128.1 (×2), and 126.1 (×2), 118.0 (CH=<u>C</u>H$_2$), 113.8 (×2, $CH_3OC_6H_4$, Ar C-2″ and C-6″), 102.0 (C_6H_5<u>C</u>H), 97.9 (C-1), 76.6 and 76.4 (C-2 and C-4), 72.1 ($CH_3OC_6H_4C\underline{H}_2$), 69.0, 68.4, and 67.0, 58.3 (C-5), 55.1 (OCH_3).

Allyl 2-*O*-p-methoxybenzyl-α-D-altropyranoside (4). A solution of **3** (2.6 g, 6.08 mmol) in 80% aqueous acetic acid (17 mL) was heated at 60 ℃ for 2h. The cool mixture was concentrated to give a syrup, which was chromatographed on silica gel (toluene-EtOAc, 1 : 1) to give **4** (1.53 g, 74%) : ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.24 and 6.87 (both d, 2H each, J=8.6 Hz each, $CH_3OC_6H_4$ aromatic H), 5.90-5.79 (m, 1H, C$\underline{H}$=CH_2), 5.28-5.18 (m, 2H, CH=C$\underline{H_2}$), 4.85 (s, 1H, H-1), 4.53-4.52 (d, 2H, $CH_3OC_6H_4C\underline{H_2}$), 4.24-4.18 (m, 1H), 4.00-3.66 (m, 10H), 3.47-3.44 (d, 1H, OH), 3.23 (br.s, 1H, OH), 2.93 (br.s, 1H, OH); ^{13}C NMR ($CDCl_3$, 200 MHz) δ 159.3 ($CH_3OC_6H_4$, Ar C-1'), 132.9 (C$\underline{H}$=CH_2), 129.3 (×3, $CH_3OC_6H_4$, Ar C-3', C-4', C-5'), 118.0 (CH=C$\underline{H_2}$), 113.8 (×2, $CH_3OC_6H_4$, Ar C-2' and C-6'), 97.3 (C-1), 75.2 (C-2), 71.8 ($CH_3OC_6H_4C\underline{H_2}$), 68.6, 68.5, and 68.2, 64.9 (C-4), 62.6 (C-6), 55.1 (OCH_3); ^{13}C NMR (D_2O, 200 MHz) for allyl α-D-altropyranodside (**4a**) 134.4 (C$\underline{H}$=CH_2), 119.4 (CH=C$\underline{H_2}$), 99.8 (C-1), 71.0 (×2) and 70.9 (C-2,3,5), 69.8 ($\underline{C}H_2CH=CH_2$), 65.6 (C-4), 61.9 (C-6).

Allyl 3,4-*O*-isopropylidene-6-*O*-methanesulfonyl-2-*O*-p-methoxybenzyl-α-D-altropyranoside (5). Methanesulfonyl chloride (0.3 mL, 1.1 equiv) was added to a solution of compound **4** (1.2 g, 3.53 mmol) in pyridine (10 mL) at −15 ℃. The mixture was stirred at −15 ℃ for 2h. After addition of ice-water to the mixture, the aqueous layer was extracted with several portions of CH_2Cl_2. The combined organic layers were washed with 2N HCl, aqueous $NaHCO_3$, and water successively, dried with Na_2SO_4, and then concentrated. To the solution of residual syrup dissolved in THF (7 mL) p-toluenesulfonic acid (106.7 mg, 0.18 equiv) and 2,2'-dimethoxypropane (0.87 mL, 2 equiv) were added and stirred for 1h. After addition of triethylamine (3.5 mL), the solution was evaporated to a syrup. Chromatography on silica gel (toluene-EtOAc, 15 : 1) gave **5** (1.05 g, 64%) which was crystallized from MeOH : mp 81-83 ℃; IR 1358.77 cm^{-1} and 1177.47 cm^{-1} (SO_2); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.29 and 6.86 (both d, 2H each, J=8.5 Hz each, $CH_3OC_6H_4$ aromatic H), 6.0-5.81 (m, 1H, C$\underline{H}$=CH_2), 5.39-5.15 (m, 2H, CH=C$\underline{H_2}$), 4.78 (d, 1H, $J_{1,2}$=4.4 Hz, H-1), 4.66 (s, 2H, $CH_3OC_6H_4C\underline{H_2}$), 4.51-3.87 (m, 7H), 3.79 (s, 3H, OCH3), 3.69-3.62 (m, 1H), 3.09 (s, 3H, $SO_2C\underline{H_3}$), 1.45-1.30 (2×s, 6H, 2×CH3, isoprop.); ^{13}C-NMR ($CDCl_3$, 200 MHz) δ 160.0 ($CH_3OC_6H_4$, Ar C-1'), 133.9 (C$\underline{H}$=CH_2), 129.9 (×3), 117.6 (CH=C$\underline{H_2}$), 113.9 (×2, $CH_3OC_6H_4$, Ar C-2' and C-6'), 110.8 (C$\underline{(CH_3)_2}$), 99.2 (C-1), 78.1, 76.0, 72.7, 71.5, 69.6, 68.6, 68.4, 55.4 (OCH_3), 37.6 ($SO_2\underline{C}H_3$), 27.6 and 25.4 (C($\underline{C}H_3)_2$).

Allyl 6-deoxy-3,4-*O*-isopropylidene-2-*O*-p-methoxybenzyl-α-D-*altro*-heptopyranosiduronononitrile (6). To a stirred solution of **5** (0.86 g, 1.88 mmol) and 18-crown-6 (0.0497 g, 0.1 equiv) in DMSO (20 mL) at 60 ℃ was added KCN (0.8568 g). After stirring at 60 ℃ for 7h, the solution was concentrated, and the residue was dissolved in CH_2Cl_2, washed with 1N HCl, aqueous $NaHCO_3$, water, dried, and concentrated. The residual syrup was chromatographed on silica gel (toluene-EtOAc, 40 : 1) to give **6** (0.366 g, 50%) : IR ν 2252.72 cm^{-1} (CN); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.26 and 6.65 (both d, 2H each, J=8.5 Hz each, $CH_3OC_6H_4$ aromatic H), 6.0-5.80 (m, 1H, C$\underline{H}$=CH_2), 5.35-5.16 (m, 2H, CH=C$\underline{H_2}$), 4.75 (d, 1H, $J_{1,2}$=4.15 Hz, H-1), 4.63 (s, 2H, $CH_3OC_6H_4C\underline{H_2}$), 4.4-4.17 (m, 2H), 4.08-3.96 (m, 2H), 3.92-3.85 (m, 1H), 3.77 (s, 3H, OCH_3), 3.63 (m, 1H), 2.75 (dd, 1H, $J_{6,5}$=3.08 Hz, $J_{6,6'}$= 16 Hz, H-6), 2.54 (dd, 1H, $J_{6',5}$=7.8 Hz, H-6'), 1.4 and 1.3 (2×s, 6H, 2×CH_3, isoprop.); ^{13}C NMR ($CDCl_3$, 200 MHz) δ 159.9 ($CH_3OC_6H_4$, Ar C-1'), 134.2 (C$\underline{H}$=CH_2), 130.3, 130.1 (×2), 118.1 (CH=C$\underline{H_2}$), 117.3 (CN), 114.3 (×2, $CH_3OC_6H_4$, Ar C-2' and C-6') 111.0 (C$\underline{(CH_3)_2}$), 99.7 (C-1), 78.7, 76.7, 75.1, 73.1, 69.0, 66.8, 55.7 (OCH_3), 27.9 and 25.7 (C($\underline{C}H_3)_2$), 22.6 (C-6).

Allyl 6-deoxy-3,4-*O*-isopropylidene-2-*O*-p-methoxybenzyl-α-D-*altro*-heptopyranoside (7). DIBAH (1 M in hexane, 10 mL) was added to a solution of **6** (1.249 g, 3.2 mmol) in dry THF (30 mL) at −60 ℃. After stirring at room temperature for 1h, methanol (2 mL) was added. After 3 min aqueous 2N HCl (12 mL) was added, stirred for 45 min, and filtered. The aqueous layer in the filtrate was extracted with ether. The combined organic layers were washed with 2N HCl, aqueous $NaHCO_3$, and water, dried, and concentrated. Sodium borohydride (86 mg) was added to the residual syrup in methanol (18 mL). The solution was stirred at room temperature for 5 min and evaporated to dryness. The residue in CH_2Cl_2 was washed successively with water, dried, and concentrated to give a syrup, which was chromatographed on silica gel (toluene-EtOAc, 5 : 1) to give **7** (0.3851 g, 30%) : IR ν 3471.68 cm^{-1} (OH).

Allyl 7-*O*-benzyl-6-deoxy-3,4-*O*-isopropylidene-α-D-*altro*-heptopyranoside (8). Compound **7** (342.4 mg, 0.87 mmol) and sodium hydride (60% in mineral oil, 166.7 mg) were dissolved in DMF (10 mL) at 0 ℃ for 1h. To the solution benzyl bromide (0.21 mL, 2 equiv) was added dropwise at 0 ℃. The solution was stirred at room temperature for 3h, added MeOH and evaporated to dryness. The residue in CH_2Cl_2 was washed with water, dried, and concentrated to give a syrup. To a stirred CH_2Cl_2 (13 mL) solution of the residual syrup containing a small amount of water (0.7 mL, 1/18 of CH_2Cl_2) was added DDQ (295.6 mg, 1.5 equiv) and the reaction mixture was stirred at room temperature for 1h. The reduced DDQ ($DDQH_2$) formed during the oxidation was removed by filtration over a pad of celite. The filtrate was washed with aqueous $NaHCO_3$, water, dried, and concentrated to give a syrup, which was chromatographed on silica gel (toluene-EtOAc, 5 : 1) to give **8** (262.8 mg, 83%) : IR ν 3464.91 cm^{-1} (OH); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.34-7.19 (m, 5H, aromatic H), 5.91-5.85 (m, 1H, C$\underline{H}$=CH_2), 5.31-5.16 (m, 2H, CH=C$\underline{H_2}$), 4.61 (d, 1H, $J_{1,2}$=5.7 Hz, H-1), 4.51 (S, 2H, $C_6H_5C\underline{H_2}$), 4.27-4.18 (m, 1H), 4.11-4.04 (m, 3H), 3.85 (m, 2H), 3.61 (m, 2H), 2.95 (s, 1H, OH), 2.12-2.06 and 1.84-1.76 (both m, 1H each, H-6 and H-6'), 1.48 and 1.34 (2×s, 6H, 2×CH_3, isoprop.); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 138.4 (C_6H_5, Ar C-1'), 134.1 (C$\underline{H}$=CH_2), 128.3 (×2), 127.6 (×2), and 127.5, 117.5 (CH=C$\underline{H_2}$), 110.6 (C$\underline{(CH_3)_2}$), 99.8 (C-1), 77.1, 76.9, 73.3, 73.0, 68.4, 68.3, and 66.4, 34.1 (C-6), 27.4 and 25.1 (C($\underline{C}H_3)_2$).

Methyl 3-*O*-p-methoxybenzyl-6-*O*-trityl-α-D-mannopyranoside (10). A solution of compound **9** (12.5 g, 28.7 mmol) and dibutyltin oxide (7.85 g, 1.1 equiv) in MeOH (172 mL) was heated under reflux for 2h. The solvent was evaporated and the resulting syrup was dissolved in toluene (3× 35 mL) and concentrated. The residue was redissolved in toluene (172 mL) and tetra-n-butylammonium iodide (4.47 g, 0.42 equiv) and p-methoxybenzyl chloride (4.67 mL, 1.2 equiv) were added. After stirring for 19h at 90 ℃, the reaction mixture was concentrated and the residue was dissolved in CH_2Cl_2, washed with aqueous $NaHCO_3$ and water, dried,

and concentrated. The residual syrup was chromatographed on silica gel (toluene-EtOAc, 10 : 1) to give **10** (10.6 g, 66%) : ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.47-7.13 (m, 17H, aromatic H), 6.82 (d, 2H, J=8.5 Hz, $CH_3OC_6H_4$ aromatic H), 4.73 (s, 1H, H-1), 4.54 (s, 2H, $CH_3OC_6H_4C\underline{H}_2$), 3.91-3.61 (m, 7H, H-2,3,4,5,$C\underline{H}_3OC_6H_4$), 3.40-3.35 (m, 5H, OCH_3 and H-6,6′), 2.63 (bs, 2H, OH); ^{13}C NMR ($CDCl_3$, 200 MHz) δ 159.5 ($CH_3OC_6H_4$, Ar C-1″), 143.9 (Tr, Ar C-1′), 130.1-127.1, 114.0 (×2, $CH_3OC_6H_4$, Ar C-2″ and C-6″), 100.4 (C-1), 87.0 ($\underline{C}Ph_3$), 79.3, 71.7, 70.6, 68.3, 67.9, 64.6 (C-6), 55.2 and 54.8 (OCH_3 and $\underline{C}H_3OC_6H_4$).

Methyl 2,4-di-*O*-benzyl-3-*O*-p-methoxybenzyl-6-*O*-trityl-α-D-mannopyranoside (11). Solution of compound **10** (4.57 g, 8.22 mmol) with sodium hydride (60% in mineral oil, 1.18 g) in DMF (64 mL) was stirred at 0 ℃ for 30 min. To the solution benzyl bromide (2.4 mL, 2.5 equiv) was added dropwise at 0 ℃, stirred at room temperature for 3h. Excess of hydride was destroyed by the addition of MeOH and evaporated to dryness. The residue was diluted with CH_2Cl_2, washed with water, dried, and concentrated to give a syrup, which was chromatographed on silica gel (toluene) to give **11** (5.44 g, 90%). **11** was crystallized from EtOH : mp 124-125 ℃; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.68-6.91 (m, 29H, aromatic H), 4.99-3.85 (m, 14H), 3.67-3.36 (m, 5H); ^{13}C NMR ($CDCl_3$, 200 MHz) δ 159.8 ($CH_3OC_6H_4$, Ar C-1″), 144.8 (Tr, Ar C-1′), 139.4 and 139.0 (Bn, Ar C-1), 131.5-127.4, 114.4 (×2 $CH_3OC_6H_4$, Ar C-2″ and C-6″), 99.4 (C-1), 86.9 ($\underline{C}Ph_3$), 80.6, 76.1, 75.6, 75.6, 73.3, 72.6, 72.4, 63.9 (C-6), 55.8 and 55.1 (OCH_3 and $\underline{C}H_3OC_6H_4$).

Methyl 2,4-di-*O*-benzyl-3-*O*-p-methoxybenzyl-α-D-mannopyranoside (12). A solution of compound **11** (2.92 g, 3.96 mmol) in mixture of MeOH (5 mL)-dioxane (2.5 mL) and trifluoroacetic acid (0.25 mL, 0.82 equiv) was heated under reflux for 2h. The reaction mixture was cooled to room temperature, neutralized with potassium carbonate (114 mg) and concentrated. The residue was dissolved in CH_2Cl_2 and the solution was washed with water, dried, and concentrated to give a syrup, which was chromatographed on silica gel (toluene-EtOAc, 5 : 1) to give **12** (1.85 g, 95%) : ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.48-7.29 (m, 12H, aromatic H), 6.93 (d, 2H, J=8.5 Hz, $CH_3OC_6H_4$ aromatic H), 5.06-4.64 (m, 7H), 4.1-3.65 (m, 9H), 3.35 (s, 3H, OCH_3), 2.57 (bs, 1H, OH); ^{13}C NMR ($CDCl_3$, 200 MHz) δ 159.8 ($CH_3OC_6H_4$, Ar C-1″), 139.2 and 138.9 (Bn, Ar C-1′), 131.2-128.2, 114.4 (×2, $CH_3OC_6H_4$, Ar C-2″ and C-6″), 99.9 (C-1), 80.5, 75.6, 75.5, 75.4, 73.5, 72.8, 72.5, 62.8 (C-6), 55.8 and 55.3 (OCH_3 and $\underline{C}H_3OC_6H_4$).

Methyl 2,4-di-*O*-benzyl-6-*O*-methanesulfonyl-3-*O*-p-methoxybenzyl-α-D-mannopyranoside (13). Methanesulfonyl chloride (0.446 mL, 4.3 equiv) was added to a solution of compound **12** (666.7 mg, 1.35 mmol) in pyridine (8 mL) at 0 ℃. The mixture was stirred at room temperature for 6h. Ice-water was added to the mixture, the aqueous layer was extracted with CH_2Cl_2, and the combined organic layers were washed with 2N HCl, aqueous $NaHCO_3$, and water, dried, and concentrated to give a syrup, which was chromatographed on silica gel (toluene-EtOAc, 15 : 1) to give **13** (700.5 mg, 91%) : ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.42-7.26 (m, 12H, aromatic H), 6.88 (d, 2H, J=8.5 Hz, $CH_3OC_6H_4$ aromatic H), 5.02-4.4 (m, 9H), 3.97-3.73 (m, 7H), 3.33 (s, 3H, OCH_3), 3.01 (s, 3H, CH_3SO_2).

Methyl 2,4-di-*O*-benzyl-6-deoxy-3-*O*-p-methoxybenzyl-α-D-*manno*-heptopyranosidurononitrile (14). Reaction of compound **13** (604.3 mg, 1.06 mmol) with KCN, as described for the preparation of **6**, yielded **14** (440.4 mg, 83%) : ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.48-7.25 (m, 12H, aromatic H), 6.89 (d, 2H, J=8.5 Hz, $CH_3OC_6H_4$ aromatic H), 5.05-4.56 (m, 7H), 3.95-3.73 (m, 7H), 3.39 (s, 3H, OCH_3), 2.76 (dd, 1H, $J_{6,5}$=3.08 Hz, J=6,6′=16 Hz, H-6), 2.51 (dd, 1H, $J_{6',5}$=7.8 Hz, H-6′); ^{13}C NMR ($CDCl_3$, 200 MHz) δ 159.8 ($CH_3OC_6H_4$, Ar C-1″), 138.6 and 138.5 (Bn, Ar C-1′), 130.7-128.3, 118.0 (CN), 114.4 (×2, $CH_3OC_6H_4$, Ar C-2″ and C-6″), 99.8 (C-1), 80.2, 77.6, 75.7, 75.1, 73.5, 72.3, 68.4, 55.8 and 55.5 (OCH_3 and $\underline{C}H_3OC_6H_4$), 21.5 (C-6).

Methyl 2,4-di-*O*-benzyl-6-deoxy-3-*O*-p-methoxybenzyl-α-D-*manno*-heptopyranoside (15). Reduction of **14** (338.9 mg, 0.67 mmol) with DIBAH, as described for the preparation of **7**, yielded **15** (209 mg, 61%) : ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.44-7.23 (m, 12H, aromatic H), 6.85 (d, 2H, J=8.5 Hz, $CH_3OC_6H_4$ aromatic H), 4.99-4.56 (m, 7H), 3.9-3.7 (m, 9H), 3.32 (s, 3H, OCH_3), 2.42-1.62 (m, 3H, OH, H-6,6′). ^{13}C NMR ($CDCl_3$, 200 MHz) δ 159.2 ($CH_3OC_6H_4$, Ar C-1″), 138.5 and 138.3 (Bn, Ar C-1′), 130.6-127.7, 113.8 (×2, $CH_3OC_6H_4$, Ar C-2″ and C-6″), 99.2 (C-1), 79.9, 78.2, 75.2, 74.8, 73.0, 71.9, 71.5, 61.2 (C-7), 55.3 and 54.8 (OCH_3 and $\underline{C}H_3OC_6H_4$), 33.9 (C-6).

Methyl 2,4,7-tri-*O*-benzyl-6-deoxy-α-D-*manno*-heptopyranoside (16). Reaction of compound **15** (177.9 mg, 0.35 mmol) with benzyl bromide and subsequent treatment with DDQ, as described for the preparation of **8**, yielded **16** (123.6 mg, 74%) : ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.43-7.25 (m, 15H, aromatic H), 4.96-4.51 (m, 7H), 4.03-3.91 (m, 1H), 3.79-3.64 (m, 4H), 3.46-3.37 (t, 1H), 3.3 (s, 3H, OCH_3), 2.38-1.6 (m, 3H, OH, H-6,6′); ^{13}C NMR ($CDCl_3$, 200 MHz) δ 139.0 and 138.3 (×3, Bn, Ar C-1′), 129.0-128.0, 98.4 (C-1), 81.1, 79.0, 75.3, 73.6, 73.4, 72.3, 68.2, 67.3, 55.1 (OCH_3), 32.4 (C-6).

Methyl 2,4,7-tri-*O*-benzyl-6-deoxy-α-D-*altro*-heptopyranoside (17). Reaction of compound **16** (93.9 mg, 0.2 mmol) with oxalyl chloride/DMSO and subsequent treatment with $NaBH_4$, as described for the preparation of **3**, yielded **17** (69.8 mg, 74%) and **16** (1.6 mg, 1.7%) : ^{1}H NMR ($CDCl_3$, 200 MHz) for **17** δ 7.42-7.24 (m, 15H, aromatic H), 4.67-4.5 (m, 7H), 4.17-4.0 (m, 2H), 3.71-3.5 (m, 4H), 3.32 (s, 3H, OCH_3), 2.38-1.6 (m, 3H, OH, H-6,6′); ^{13}C NMR ($CDCl_3$, 200 MHz) for **17** δ 139.1 and 138.2 (×3, Bn, Ar C-1′), 129.0-127.9, 99.9 (C-1), 76.9, 76.2, 73.4, 72.9, 71.6, 67.1, 66.6, 63.7, 55.7 (OCH_3), 32.2 (C-6).

Methyl 6-deoxy-α-D-*altro*-heptopyranoside (18). Compound **17** (50.9 mg, 0.11 mmol) was hydrogenated in EtOH (1 mL) in the presence of 10% Pd/C for 4h at room temperature. Filtration over a pad of celite and concentration of the filtrate yielded **18** (20.5 mg, 93%) : ^{1}H NMR (D_2O, 200 MHz) δ 4.54 (d, 1H, $J_{1,2}$=3.2 Hz, H-1), 4.0-3.65 (m, 6H), 3.37 (s, 3H, OCH_3), 2.03-1.64 (m, 2H, H-6,6′); ^{13}C NMR (D_2O, 200 MHz) δ 100.8 (C-1), 70.3 (×2, C-2,3), 68.8 and 68.0 (C-4,5), 58.5 (C-7), 55.8 (OCH_3), 32.9 (C-6).

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Application of Cluster Distributions to Energy Transfer in Two-Dimensional Choleic Acid Crystals

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The cluster distributions for different concentrations of 1,4-dibromonaphthalene (DBN) in 4,4'-dibromobenzophenone (DBBP)/1,4-dibromonaphthalene (DBN) choleic acid were determined by a computer simulation in order to model the energy transfer dynamics. The results of the simulation indicate that long range interaction between molecules further apart than nearest does not occur and energy transfer efficiency is restricted by single range interaction. The results also demonstrate that the trapping is diffusion limited. The energy transfer rate is reduced by a factor of 15 in DBBP/DBN choleic acid realtive to that in DBBP/DBN doped into polystyrene due to the larger distance between molecules.

Introduction

It has been shown that the concepts of cluster distributions can describe energy transfer in multi-component systems.[1,2] Cluster distributions for different concentrations of $C_{10}H_8$ and $C_{10}D_8$ in naphthalene choleic acid were determined by a computer simulation to test whether the experimentally observed change in the $C_{10}H_8$ triplet excitation energy transfer efficiency α is due to the cluster distribution of $C_{10}H_8$ molecules.[3] The results of the simulation agree with the experiment indicating that the change in α with increasing $C_{10}H_8$ concentration is caused by the growth of clusters and then limited by the small number of sites visited during the lifetime of the excitation. The energy transfer rate is reduced by a factor of about 10^5 in naphthalene choleic acid relative to that in naphthalene crystals due to the larger distance between the molecules, and the energy transfer topology changes from two to one-dimensional due to the change in molecular orientations and the increasing spacing. In addition, a molecular face-to-edge interaction dominates for nearest neighbors in the naphthalene crystal, and a face-to-face interaction dominates over an edge-to-edge interaction in NCA.

Donor-acceptor energy transfer for 4,4'-dibromobenzophenone(DBBP)/1,4-dibromonaphthalene (DBN) doped into a polymer matrix (polystyrene) has been studied previously.[4] The excitation energy at 386 nm populates the excited singlet state of DBBP (donor) without exciting DBN (acceptor). The lowest singlet absorption band of the donor molecule lies at lower energy than that of the lowest singlet absorption band of the acceptor at 280 nm. The lowest triplet state of DBBP, on the other hand, because of the small singlet-triplet splitting in carbonyl compounds, lies above the lowest