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Separation of Isomeric Alcohols by Selective Complexation with N,N,N',N'-Tetracyclohexylfumaramide and N,N,N',N'-Tetraisopropylfumaramide, and Structures of Two Resulting Crystalline Adducts

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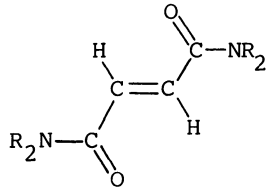
The title host compounds have been utilized in the efficient separation of isomeric alcohols by selective complexation. X-Ray analysis has shown that their 1:2 crystalline adducts with cresols comprise centrosymmetric guest-host-guest aggregates consolidated by O-H...O hydrogen bonding.

Recently we reported that N,N,N',N'-tetracyclohexylfumaramide (1a) exhibits excellent inclusion properties towards alcohols.[1] Further work has shown that 1a has high selectivity for isomers of these alcohols, forming a crystalline adduct with one isomer more easily than the other. We now report some examples of efficient separation of isomeric alcohols by means of selective inclusion with 1a and its isopropyl analogue (1b).



1 a : R = cyclohexyl
b : R = isopropyl

$HOCH_2CH=CHCH_2OH$

2 a : cis isomer
b : trans isomer

For example, when a solution of 1a and a 25.5:74.5 mixture of cis- (2a) and trans-2-butene-1,4-diol (2b) in acetone was kept at room temperature for 10 h, a 2:1 complex of 1a and 2b was obtained as colorless crystals, which upon heating in vacuo gave pure[2] 2b in 72.5% yield. Since 2a (bp 132 °C/16 mmHg) and 2b (131 °C/13 mmHg) have almost the same boiling point, it is otherwise impossible to separate them by fractional distillation.

The separation of m- (3a, bp 202.2 °C) and p-cresol (3b, 201.9 °C) is an important but very difficult problem in the chemical industry. However, the task can easily be achieved by complexation with 1, since 1a and 1b form complexes more easily with 3a and 3b, respectively. For instance, when a solution of 1a and a 2:3 mixture of 3a and 3b in acetone was kept at room temperature for 10 h, a 1:2 complex of 1a and 3a (4a, mp 124-127 °C) was obtained as colorless crystals which upon heating in vacuo gave 99% pure 3a in 75% yield. When 1b was added to the filtrate and the solution maintained at room temperature for another 10 h, a 1:2 complex of 1b and 3b (4b, mp 84-86 °C) deposited as colorless crystals which upon heating in vacuo gave 99% pure 4b in 73% yield.

In order to provide a rationale for the high selectivity of 1 for alcohols, the crystal structures of complexes 4a and 4b have been determined by X-ray diffraction.

Crystal data of $(C_6H_{11})_2NCOCH=CHCON(C_6H_{11})_2 \cdot 2m\text{-}CH_3C_6H_4OH$ (4a): FW = 658.96, monoclinic, space group $P2_1/n$, a = 6.885(1), b = 17.402(7), c = 16.637(7) Å, β =

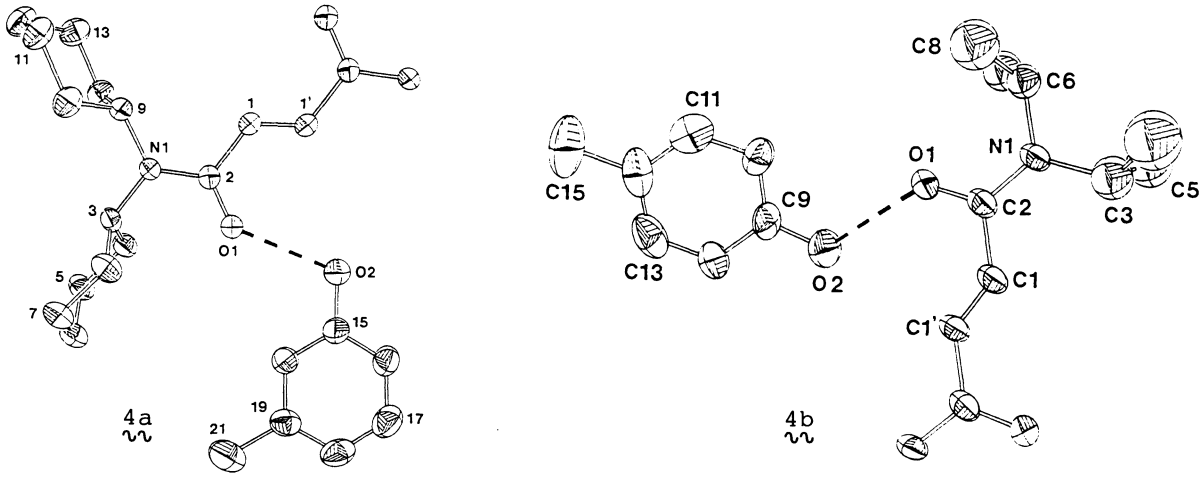


Fig. 1. Host-guest interaction and atom labelling, with the O-H...O hydrogen bond represented by a broken solid line. Thermal ellipsoids are drawn at the 35% probability level. Selected bond distances (σ ≈ 0.004 Å) and angles (σ ≈ 0.3°) for 4a: C1-C1', 1.239; C1-C2, 1.495; O1-C2, 1.239; N1-C2, 1.339; N1-C3, 1.488; N1-C9, 1.480; C1'-C1-C2, 125.3; C1-C2-O1, 118.7; C1-C2-N1, 118.9; O1-C2-N1, 122.4; C2-N1-C3, 119.6; C2-N1-C9, 123.4; C3-N1-C9, 117.0; O1...O2, 2.693; O1...O2-C15, 109.4; C1-C2-O1...O2, -12.0; C2-O1...O2-C15, 169.6. Selected bond distances (σ ≈ 0.01 Å) and angles (σ ≈ 0.9°) for 4b: C1-C1', 1.21; C1-C2, 1.47; O1-C2, 1.23; N1-C2, 1.33; N1-C3, 1.49; N1-C6, 1.49; C1'-C1-C2, 131.2; C1-C2-O1, 118.3; C1-C2-N1, 119.7; O1-C2-N1, 122.0; C2-N1-C3, 124.1; C2-N1-C6, 120.2; C3-N1-C6, 115.4; O1...O2, 2.70; O1...O2-C9, 111.0; C1-C2-O1...O2, -18.9; C2-O1...O2-C9, 145.6.

96.08(2)°, $\underline{V}$ = 1982(1) Å^3, $\underline{Z}$ = 2, $\underline{D}_c$ = 1.104 g cm^{-3}, Mo $\underline{K}\alpha$ radiation (graphite-monochromatized, λ = 0.71069 Å), μ = 0.65 cm^{-1}, $\underline{F}$(000) = 727.90.

Crystal data of $(\underline{i}\text{-}C_3H_7)_2NCOCH{=}CHCON(\underline{i}\text{-}C_3H_7)_2.2\underline{p}\text{-}CH_3C_6H_4OH$ (4b): FW = 498.70, monoclinic, space group $P2_1/\underline{c}$, $\underline{a}$ = 13.247(4), $\underline{b}$ = 8.255(3), $\underline{c}$ = 14.137(4) Å, β = 94.01(2)°, $\underline{V}$ = 1542.2(6) Å^3, $\underline{Z}$ = 2, $\underline{D}_c$ = 1.074 g cm^{-3}, μ(Mo $\underline{K}\alpha$) = 0.66 cm^{-1}, $\underline{F}$(000) = 543.92.

Crystals of 4b gave weak diffraction peaks with broad profiles. Both adducts gradually decomposed upon exposure to air, and each selected crystal was therefore sealed inside a 0.5 mm Lindemann glass capillary. Intensities [$2\theta_{max}$ = 45°; 4a, crystal size 0.40 x 0.38 x 0.26 mm^3, 2200 unique data, 1735 observed with $|\underline{F}_o| > 3\sigma(|\underline{F}_o|)$; 4b, 0.40 x 0.36 x 0.24 mm^3, 1568 unique reflections, 1093 observed] were collected at 20 °C on a Nicolet R3m diffractometer as previously described.[3] Structure solution was effected by direct phase determination guided by negative quartets.[4] All non-hydrogen atoms except those of the two independent isopropyl groups of 4b were varied anisotropically. The methyl groups were treated as rigid groups, the hydroxy and ethylenic H atoms were located from difference maps, and the remaining H atoms generated geometrically (C-H = 0.96 Å). All H atoms were included in structure factor evaluations with fixed isotropic temperature factors. Final $\underline{R}$ factors for 4a (220 variables, $\underline{g}$ = 0.0012 in $\underline{w} = [\sigma^2(|\underline{F}_o|) + \underline{g}|\underline{F}_o|^2]^{-1}$) and 4b (148 variables, $\underline{g}$ = 0.0018) are 0.058 and 0.121, respectively.[5]

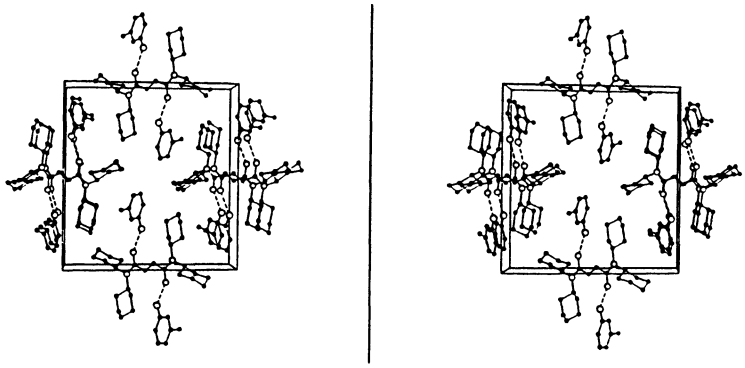


Fig. 2. Stereodrawing of the molecular packing in 4a. The origin of the unit cell lies at the upper left corner, with $\underline{a}$ pointing towards the reader, $\underline{b}$ downwards, and $\underline{c}$ from left to right.

Both complexes are composed of discrete 1:2 host-guest aggregates consolidated by O-H...O hydrogen bonds, the mid-point of the ethylenic double bond being located at a crystallographic inversion centre (Fig. 1). The bonding configuration about each N atom is trigonal planar. The measured dimensions of the host molecule in 4a (Fig. 1) are in good agreement with corresponding values

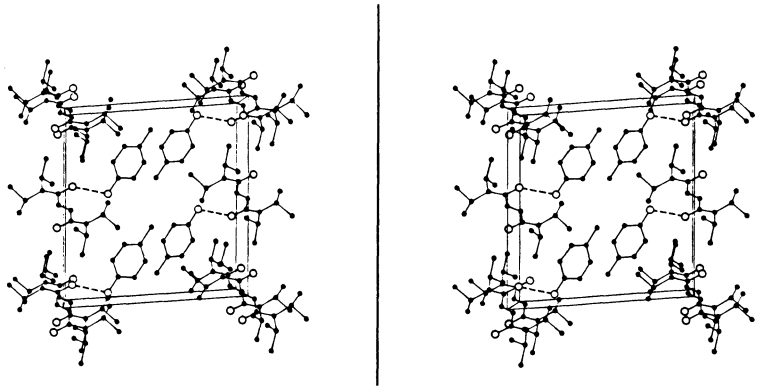


Fig. 3. Stereodrawing of the molecular packing in 4b. The origin of the unit cell lies at the upper left corner, with a pointing from left to right, b towards the reader, and c downwards.

in the previously reported 1a.EtOH adduct,[1] which comprises a packing of centrosymmetric trimeric EtOH...1a...EtOH aggregates and discrete 1a molecules. As measured by the C-O...O-C torsion angle about the hydrogen bond (169.6° for 4a and 145.6° for 4b), the aromatic ring of the cresol guest molecule in 4a lies much closer to the plane of the central skeleton of the fumaramide host system. The modes of molecular packing in 4a and 4b are illustrated in Figs. 2 and 3, respectively.

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