

Isolation of monomeric *s-trans*-acrylic acid as a hydroxy host inclusion crystal showing anomalous C=O stretching absorptions

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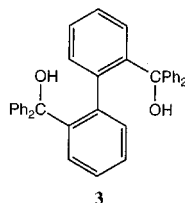
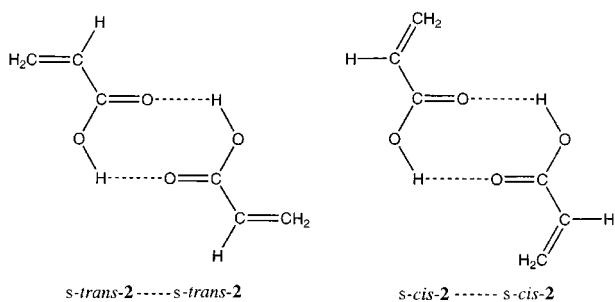
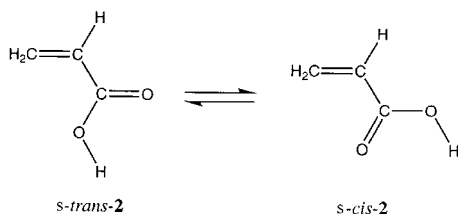
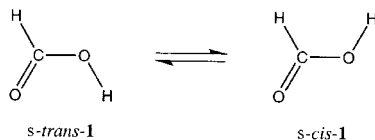
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Received (in Cambridge, UK) 27th July 1998, Accepted 13th October 1998

The structure of monomeric *s-trans*-acrylic acid, trapped in an inclusion complex with an hydroxy host, was elucidated by X-ray analysis.

Studies of the molecular conformations and rotational isomerism of organic compounds are of fundamental importance in chemical research. There has been especial interest in the conformations and rotamers of simple organic acids which can be studied readily using spectroscopic methods. For example, studies in the gas phase of the simplest organic acid, formic acid



1, show that the *s-trans*-1 rotamer is the predominant form. This has been characterized by microwave studies,^{1–3} electron diffraction,^{4–6} and IR spectroscopy.^{7,8} Structural studies of *s-trans*-1 in low temperature matrices have also been accomplished.^{9–11} The other rotamer, *s-cis*-1, has also been detected by microwave^{12,13} and IR spectroscopy.¹⁴ On the other hand in both the liquid and vapor phases of acrylic acid 2, the cyclic dimer *s-trans*-2...*s-trans*-2 is a major component existing in equilibrium with monomeric 2.¹⁵ Microwave spectroscopic

studies have established that in the vapor phase at low pressures, comparable amounts of *s-cis*-2 and *s-trans*-2 coexist with the dimer.^{16,17} In the solid state, however, it was demonstrated that 2 exists as two different cyclic dimers, *s-trans*-2...*s-trans*-2 and *s-cis*-2...*s-cis*-2 by IR spectroscopy.¹⁸ Finally, *s-trans*-2 and *s-cis*-2 have been identified by IR spectroscopy in a matrix.¹⁹

Nevertheless, no rotational isomer of 1 or 2 has never been isolated in the pure state. The challenge to isolate a rotational isomer of 2 might be met by using inclusion crystallization with a hydroxy host compound, since this method has been shown to be useful in trapping an unstable rotamer.²⁰ For example, a nearly eclipsed rotamer of 1,2-dichloroethane (dihedral angle Cl–C–C–Cl = 36°) has been isolated as a host–guest inclusion compound.²¹ Finally, we succeeded in isolating *s-trans*-2 as an inclusion crystal (4) with 2,2'-bis(hydroxydiphenylmethyl)-1,1'-biphenyl 3 and studied its conformation by X-ray analysis.

When a solution of 3 (1 g) in 2 (10 g) was kept at room temperature for 1 h, the 2:1 inclusion compound 4 was obtained as colorless needles [0.84 g, 80% yield, mp 130–150 °C (decomp.); Calc. for C₇₉H₆₄O₆: C, 85.53; H, 5.81. Found: C, 85.37; H, 5.82%]. The 2:1 molar ratio was determined by elemental analysis and thermogravimetric measurement. X-ray analysis of 4 showed that six molecules of 3 make a cubic cage in which three molecules of 2 are accommodated by formation of a circle (Fig. 1).[†] The three acrylic acid molecules comprising the circle were found to be disordered over two sites of equal occupancy. In both sites of disorder, three hydrogen bonds between the OH hydrogen of 2 and the OH oxygen of 3 play an important role in constructing the inclusion lattice of 4. Since the OH hydrogen of 3 does not participate in any hydrogen bond formation, the νOH of 3 in 4 appeared at higher

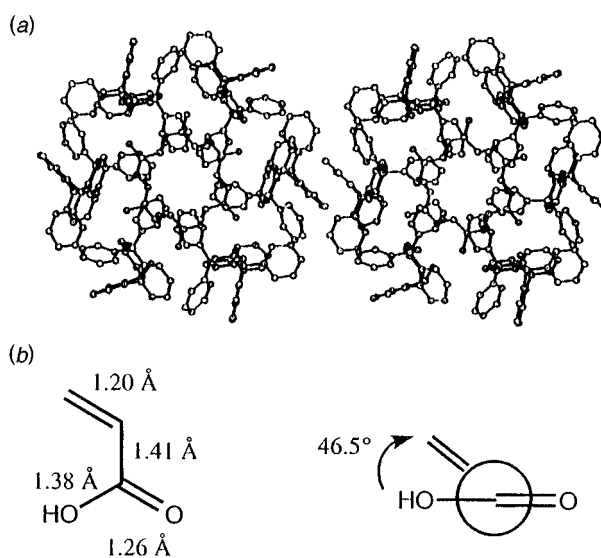


Fig. 1 X-Ray analytical data for 4: (a) stereoview of 4 and (b) bond lengths and dihedral angle for *s-trans*-2 in 4.

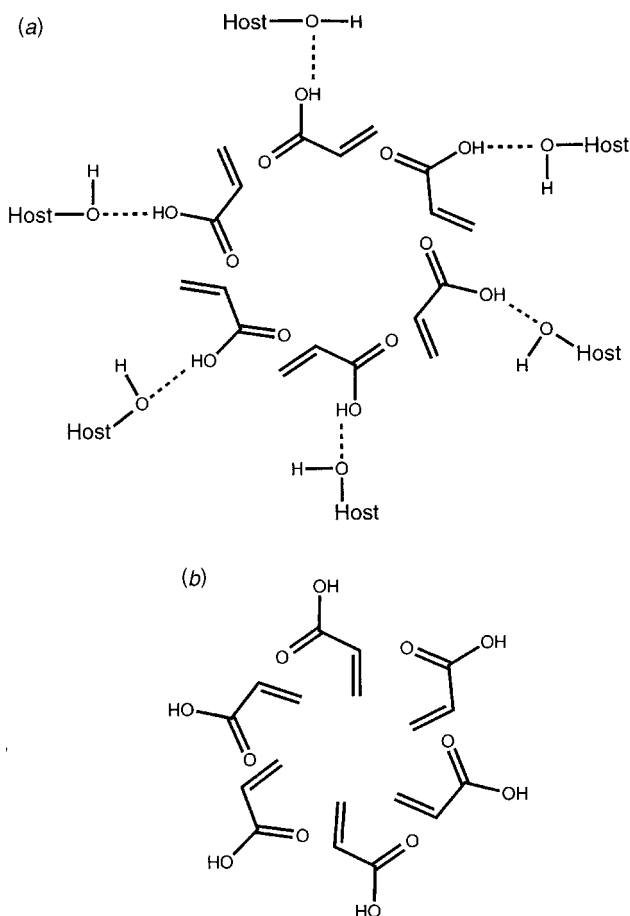


Fig. 2 Schematic drawing: (a) a circle of three *s-trans*-2 molecules in **4** and (b) a circle of three *s-cis*-2 molecules, both involving disorder.

frequency (3290 cm^{-1}) than in pure **3** itself (3230 cm^{-1}). The hydrogen bonds are schematically shown in Fig. 2. It is very clear that **2** exists here as a monomeric form rather than a dimeric one, despite **2** existing as a dimer in the crystalline state at $-115\text{ }^{\circ}\text{C}$.[†] The formation of the 2:1 inclusion complex in the presence of disorder is analogous to that of **3** combining with acetone molecules in a 2:1 ratio.²² In the latter case, however, **3** functions as a hydrogen donor and hydrogen bonds between the OH of **3** and C=O of acetone molecule are formed.²²

This is the first example of the isolation of the monomeric *s-trans* form of **2**, although the dihedral angle between the OH and $\text{H}_2\text{C}=\text{CH}$ groups is a little large (46.5°), as shown in Fig. 1. The C=O and C–OH bonds are also clearly distinguishable (Fig. 1). In the small cavity formed by six host molecules of **3**, the dimer of **2** might be too large to be accommodated. The cavity in **4** might also be too small to accommodate **2** in its *s-cis* form. When three *s-cis*-2 molecules are accommodated to make a similar circle to that of the *s-trans* form, the three vinyl groups are directed inward causing serious steric repulsion, as shown in Fig. 2. Methacrylic acid did not form an inclusion complex with **3** because even if it is included in its *s-trans* form, steric crowding of the methyl groups is significant. These could be the underlying reasons why the monomeric *s-trans*-2 molecule is isolated.

It is impossible to elucidate the mechanism of the molecular movement of **2** into the cavity, since X-ray analysis can determine only an average situation of molecules, and not their dynamic behavior. However, some speculation on this subject would be worthwhile. For example, the two circles, each consisting of three *s-trans*-2 molecules (Fig. 1), are interconvertible by either a shift down or up accompanied by a 60° rotation in the plane of the circle. Since an X-ray analysis of **4** at $-100\text{ }^{\circ}\text{C}$ gave almost the same result as that obtained at room temperature, such molecular movement would occur quite easily. DSC trace of **4** showed two endotherm peaks at 126 and

$255\text{ }^{\circ}\text{C}$, which correspond to release of the guest and the melting point of the host, respectively. Solid-state ^{13}C CP MAS NMR spectroscopy of **4** showed a broad C=O signal for **2** at $\delta 169$.²³ On the other hand, the ^{13}C NMR spectrum of **4** in CDCl_3 showed a sharp C=O signal at $\delta 170$.

It was also found that **2** shows anomalous νOH absorptions in the IR spectrum of **4**. The C=O stretching absorptions are split into three weak bands at 1726 , 1699 and 1687 cm^{-1} . Each of these peaks is comparable in strength to those of the $\nu\text{CH}=\text{CH}_2$ absorptions of **2** at 1632 cm^{-1} and of the benzene ring of **3** at 1597 cm^{-1} . This is an unusual phenomenon since acetone in its inclusion complex with **3** showed a normal strong $\nu\text{C}=\text{O}$ absorption at 1710 cm^{-1} . In order to know whether this anomalous $\nu\text{C}=\text{O}$ absorption appears only in this case or not, some other inclusion compounds with **3** were prepared and their IR spectra studied.

The host **3** formed inclusion compounds with propanoic acid and ethyl acetate in 2:1 ratios. In these inclusion compounds, propanoic acid (1740 , 1735 , 1818 , 1707 , 1700 and 1685 cm^{-1}) and ethyl acetate (1704 and 1686 cm^{-1}) showed similar anomalous $\nu\text{C}=\text{O}$ absorptions as indicated. In both cases, the $\nu\text{C}=\text{O}$ absorptions are split into very weak bands, and the splitting is especially complicated in the case of propanoic acid. Nevertheless, 1:1 inclusion compounds of ethyl acrylate and ethyl propanoate with **3** showed normal strong $\nu\text{C}=\text{O}$ bands at 1698 and 1712 cm^{-1} , respectively. These anomalies might not depend on the host:guest molar ratio, since the 2:1 inclusion compound of **3** with acetone also shows normal $\nu\text{C}=\text{O}$ absorption.²⁴ As far as we are aware, such anomalous behavior has not been previously observed. Although the reason for this anomalous behavior is not clear, it is an interesting subject in solid state chemistry²⁰ and inclusion chemistry, and should be clarified in the future.

Notes and references

[†] Crystal data for **4**: $\text{C}_{79}\text{H}_{64}\text{O}_6$, colorless hexagonal crystals space group $R3$, $a = 35.27(3)$, $b = 35.27(3)$, $c = 12.454(9)\text{ \AA}$, $V = 13416(2)\text{ \AA}^3$, $Z = 18$. Data collection at $T = 156\text{ K}$ on a Picker (Crystal Logic) with Mo-K α radiation, 2θ range = $2.4\text{--}55.0^{\circ}$, $R = 0.069$, and $R_w = 0.082$. CCDC 182/1007.

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Communication 8/05845H