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<td>Author(s)</td>
<td>Umemura, Junzo; Hayashi, Soichi</td>
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Infrared Spectra and Molecular Configurations of Liquid and Crystalline Acrylic Acids

Junzo UMEMURA and Soichi HAYASHI*
Received September 25, 1974

Polarized infrared spectra of oriented crystals of CH₂=CHCOOH and CH₂=CHCOOD were recorded at various low temperatures. An infrared spectrum of liquid acrylic acid at room temperature was also recorded. Assignments of the observed bands were made with the aid of infrared dichroism and isotopic frequency shift.

It was found that some infrared absorption bands reduced their intensities on crystallization and disappeared on further cooling. This phenomenon was interpreted as due to the cis-trans isomerism of acrylic acid.

INTRODUCTION

Acrylic acid is the simplest unsaturated fatty acid and an important source of highly polymeric products. This material has been known to exist as hydrogen-bonded dimers in the crystalline1,2) and liquid3) phases, and as an equilibrium mixture of monomer and dimer in the gas phase.4) Feairheller and Katon have measured infrared and Raman spectra of liquid acrylic acid, and have given tentative assignments of the observed bands.3) In their assignments, however, no attention has been paid to the presence of the cis-trans isomerism shown in Fig. 1. They have assumed that only the trans isomer is present in liquid acrylic acid. The microwave spectra of monomeric CH₂=CHCOOH and CH₂=CHCOOD have shown that these materials contain a comparable proportion of the cis isomer to that of the trans isomer in the gas phase.5) Infrared studies of other carboxylic acids such as saturated fatty acids have also shown the coexistence of the trans and cis isomers in the crystalline phase.6-8)

Fig. 1. Schematic drawing of the equilibrium due to cis-trans isomerism of acrylic acid dimer.

In the present work, the infrared spectra of liquid and crystalline acrylic acids were recorded at various temperatures. The results obtained were examined from the point of view of the cis-trans isomerism. The polarized infrared spectra of crystalline CH₂=CHCOOH and CH₂=CHCOOD were also recorded in order to make sure of the assignments of the observed bands.

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EXPERIMENTALS

Acrylic acid containing hydroquinone as a stabilizer was obtained from the commercial source and distilled under reduced pressure in a slow stream of nitrogen to prevent polymerization. The sample of CH$_2$=CHCOOD was prepared from CH$_2$=CHCOOH by proton exchange with CH$_3$OD. Oriented crystalline samples were produced from liquid films between KBr or NaCl plates by slow cooling with a slight temperature gradient.

Infrared spectra were recorded on a Perkin-Elmer 521 spectrophotometer. A wire-grid polarizer was used for polarization measurements. The low-temperature cell described before$^9$ was used for obtaining the spectra of crystalline samples.

LIQUID AND CRYSTAL SPECTRA

Figure 2 shows the infrared spectrum of liquid acrylic acid and polarized infrared spectra of an oriented crystalline sample of acrylic acid at $-180^\circ$C*. Some differences in the spectra can be seen between the liquid and crystalline acrylic acids. One of the difference is in frequency between them. For example, the band at 925 cm$^{-1}$ in Fig. 2A shifts to 895 cm$^{-1}$ in Fig. 2B. Its frequency difference, 30 cm$^{-1}$, is the largest one observed. All of the other bands have some frequency differences less than 25 cm$^{-1}$ between the two phases. Such frequency differences can be ascribed to the difference of intermolecular forces between the two phases, as in general cases. It is worthwhile, in this connection, to refer to the factor group splitting. Because, it is a typical phenomenon due to intermolecular forces in the crystal. The change

Fig. 2. Infrared spectra of acrylic acid: (A) liquid at room temperature, (B) oriented crystal at $-180^\circ$C, --- electric vector (e.v.) parallel to the direction of crystal growth, ---; e.v. perpendicular to it. Note the bands due to ice appear at 3240 and 850 cm$^{-1}$.  

* Note that the bands due to ice forming on the outside of the optical plates appear at about 3240 and 850 cm$^{-1}$ without dichroism in Fig. 2B. The situations are the same throughout the crystal spectra in this paper, except for the degree of freezing in each case.
IR Spectra and Molecular Configurations of Acrylic Acid

from the singlet at 1636 cm\(^{-1}\) in Fig. 2A to the doublet at 1634 and 1631 cm\(^{-1}\) in Fig. 2B is an example of the change due to the factor group splitting, as described later.

As another difference between the liquid and crystal spectra, it is cited that the shapes of bands in the crystalline phase are sharper than those in the liquid phase. This is also a common feature in vibrational spectra of chemical compounds. Reorientational motions and collisions of molecules in liquid broaden the band shape but the restriction of these motions in crystal sharpens it.\(^1\) By this sharpening effect in the crystal, the bands at 1808, 1679, 1395, and 1323 cm\(^{-1}\) become clear in Fig. 2B, although they are not distinct in Fig. 2A. These bands in the crystalline phase grow sharper and apparently stronger with lowering temperature, as will be seen later (Fig. 3).

As the last and most important difference, it is cited that some bands observable in Fig. 2A disappear in Fig. 2B. In the region 1100 to 1000 cm\(^{-1}\) of Fig. 2A, a doublet pair is observed at 1068 and 1046 cm\(^{-1}\). While, in the same region of Fig. 2B, only one band is observed at 1078 cm\(^{-1}\). This shows that one component of the doublet in Fig. 2A disappears in Fig. 2B. In the region 600 to 500 cm\(^{-1}\) of Fig. 2A, a doublet is observed at 552 and 525 cm\(^{-1}\), although its components are not well-resolved. In that region of Fig. 2B, only a band is observed at 534 cm\(^{-1}\). The bands at 1279 cm\(^{-1}\) (shoulder) and 628 cm\(^{-1}\) in Fig. 2A also disappear in Fig. 2B. The 1617-cm\(^{-1}\) band in Fig. 2A seems to disappear in Fig. 2B.

In order to examine more closely the spectral changes from Fig. 2A to Fig. 2B, the polarized spectra of the crystal were recorded at three intermediate temperatures. These spectra in the region 1850 to 500 cm\(^{-1}\) are reproduced in Fig. 3, together with the spectrum of the liquid material. In the region 1100 to 1000 cm\(^{-1}\) of Fig. 3B, two bands can be observed, as a doublet, at 1073 and 1048 cm\(^{-1}\), corresponding to the 1068- and 1046-cm\(^{-1}\) bands in Fig. 3A, respectively. The 1048-cm\(^{-1}\) band in Fig. 3B is much weaker than the 1046-cm\(^{-1}\) band in Fig. 3A, while the 1073-cm\(^{-1}\) band in Fig. 3B is stronger than the 1068-cm\(^{-1}\) band in Fig. 3A. The 1048-cm\(^{-1}\) band becomes weaker in Fig. 3C and disappears in Fig. 3D. While, the 1073-cm\(^{-1}\) band slightly increases its intensity with lowering temperature. The two bands in the region 600 to 500 cm\(^{-1}\) also show temperature dependences similar to these bands. The two bands at 552 and 525 cm\(^{-1}\) in Fig. 3A shift their frequencies to 556 and 529 cm\(^{-1}\), respectively, in Fig. 3B, accompanying changes in intensity. The 556-cm\(^{-1}\) band of the crystal decreases in intensity with lowering temperature and become unobservable at \(-120^\circ\text{C}\) (Fig. 3D). While, the 529-cm\(^{-1}\) band slightly increases its intensity with lowering temperature. These facts seem to show that some equilibrium corresponding to the observed spectral changes is present in the crystalline phase.

The above-mentioned spectral changes of acrylic acid with temperature are very similar to those of normal fatty acids with odd carbon number.\(^8\) From the results of a series of infrared studies on crystalline fatty acids,\(^6-8\) we have postulated that such spectral changes with temperature are due to the cis-trans isomerism in the crystal. The postulate has been made on the basis of the facts that: (1) the bands which exhibit temperature dependences are associated with vibrations of the carboxyl group, (2) these bands can be assigned to the cis and trans isomers from the results of normal coordinate analyses of normal fatty acids,\(^11\) and (3) it is difficult to explain the doublet,
Fig. 3. Spectral change of acrylic acid with temperature: (A) liquid at room temperature, (B) crystal at −20°C, (C) at −70°C, (D) at −120°C; — e.v. parallel to the direction of crystal growth, ——; e.v. perpendicular to it.
one of which increases and the other decreases in intensity on cooling, as due to other causes such as factor group splitting or Fermi resonance. The same discussions can be applied to the case of acrylic acid. It is most likely that the spectral change in acrylic acid described above is also due to the cis-trans isomerism.

The X-ray analyses of the crystal of acrylic acid at −135 and −70°C indicate that the molecular configuration is the cis form. Therefore, the more stable isomer which gives rise to the spectra of Fig. 2B is ascribed to the cis isomer, and the less stable isomer which gives rise to the bands such as the 1046- and 552-cm\(^{-1}\) bands in Fig. 2A is ascribed to the trans isomer. In Fig. 2A, the intensities of the 1046- and 552-cm\(^{-1}\) bands ascribed to vibrations of the trans isomer are respectively stronger than those of the 1068- and 525-cm\(^{-1}\) bands ascribed to vibrations of the cis isomer. It is estimated that the proportion of the trans isomer in the liquid is comparable with that of the cis isomer.

As the bands ascribed to vibrations of the trans isomer disappear before the temperature is lowered to that of liquid nitrogen, the crystal at liquid-nitrogen temperature contains the cis isomer only. In the following sections, the discussions will be made only of the spectra recorded near liquid-nitrogen temperatures.

**SELECTION RULES AND CRYSTAL SPECTRA AT LOW TEMPERATURES**

X-Ray analyses of crystalline acrylic acid have been made at −135°C by Higgs and Sass and at −70°C by Chatani et al. The results obtained by both groups are similar to each other. The crystal is orthorhombic and the space group is \(Ibam\). There are two dimers in a Bravais cell. The point group of the dimer is \(C_{2v}\), all of the atoms being coplaner on the ac-plane. The site symmetry of the dimer is also \(C_{2v}\).

The correlation diagram among dimer, site, and crystal symmetries is given in Table I, together with the spectral activities. The infrared active in-plane vibrations (the \(b_u\) modes) of the dimer split in the crystal into the \(B_{2u}\) and \(B_{2g}\) modes, whose transition moments are parallel to the \(a\)- and \(b\)-axes of the crystal, respectively. The infrared active out-of-plane vibrations (the \(a_u\) modes) become infrared active as the \(B_{1u}\)

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<tr>
<th>Dimer symmetry</th>
<th>Site symmetry</th>
<th>Crystal symmetry</th>
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<tbody>
<tr>
<td>(C_{2v})</td>
<td>(C_{2v})</td>
<td>(D_{2h}^{1})</td>
</tr>
<tr>
<td>17(a_g)(R)</td>
<td>17(A_g)</td>
<td>17(A_g)(R)</td>
</tr>
<tr>
<td>(b_g)(R)</td>
<td>7(B_g)</td>
<td>7(B_{2g})(R)</td>
</tr>
<tr>
<td>8(a_u)(IR, (T))</td>
<td>8(A_u)</td>
<td>8(A_u)(inactive)</td>
</tr>
<tr>
<td>16(b_u)(IR, (T_x, T_y))</td>
<td>16(B_u)</td>
<td>16(B_{2u})(IR, (T_u))</td>
</tr>
</tbody>
</table>

* \(R\): Raman-active, IR: infrared-active, \(T_x, T_y\): transition moments along the axes x–c. The molecular-fixed z-axis is perpendicular to the molecular plane.

(589)
modes in the crystal, whose transition moments are parallel to the c-axis of the crystal.

Since the orientation of the crystal between KBr or NaCl plates could not be controlled in our experiments, the polarized spectra differed in each experiment, according to the difference in orientation. Fig. 2B represents the polarized spectra of the crystal with one of the orientations. In that figure, factor group splittings are clearly seen in some of the bands assignable to the in-plane vibrations. The C=C stretching vibration, for example, appears as a doublet at 1634 and 1631 cm\(^{-1}\). The C=O stretching and CO\(_2\) bending vibrations also appear as doublets, at 1719 and 1705 cm\(^{-1}\), and at 660 and 655 cm\(^{-1}\), respectively. The intensity of the C=O stretching vibration is stronger in the broken line than in the full line of Fig. 2B. While, the intensity of the OH stretching vibration observed at about 2900 cm\(^{-1}\) as a very broad band is stronger in the full line. As the C=O bond lies nearly parallel to the a-axis\(^*\) and the OH bond forms a smaller angle with the b-axis than with the a-axis,\(^{1,2}\) it may be estimated that the a-axis forms a small angle with the direction of the crystal growth, and the b-axis forms a large angle with it, as shown in the left side of Fig. 4. Therefore, each component of a doublet can be assigned to the B\(_{2u}\) or B\(_{3u}\) crystal modes by referring to the dichroism in Fig. 2B. In Fig. 2B, the OH out-of-plane bending vibration (the B\(_{1u}\) mode) observed at 895 cm\(^{-1}\) has a stronger intensity in the broken line than in the full line. As the transition moment of the B\(_{1u}\) crystal mode is parallel to the c-axis, the c-axis lies fairly parallel to the direction of the crystal growth. The projections of the three crystal axes onto the plane of the KBr plates in this case were drawn schematically in the left side of Fig. 4.

Figure 5 shows the polarized infrared spectra of the acrylic acid crystal with a different orientation from that in Fig. 2B. The dichroic ratios of all the observed bands are large in this figure. The factor group splittings observed in Fig. 2B can not be seen in Fig. 5. As deduced from the disappearance of the 1705-cm\(^{-1}\) band (B\(_{3u}\)) observed in Fig. 2B, the a-axis may be very close to the propagating direction of the incident beam in this orientation. The c-axis is closely parallel to the direction of the crystal growth, as easily estimated from the dichroism of the OH out-of-plane bending

\* The choice of the a- and b-axes in Ref. 2 is reversed from that in Ref. 1. We follow the choice of Ref. 1.
vibration at 999 cm⁻¹. The projections of the crystal axes on the flat plane of the sample in this case were given in the middle of Fig. 4. Since the c-axis is almost parallel to the direction of the crystal growth and the a- and b-axes are perpendicular to it, bands due to the out-of-plane vibrations can be well distinguished from those due to the in-plane vibrations by referring to the dichroism in Fig. 5. All the bands which have stronger intensities in the broken line than in the full line are assigned to the out-of-plane vibrations.

Figure 6 shows the polarized infrared spectra of the oriented crystalline sample of CH₂=CHCOOD. The spectra are similar to those of Fig. 5 where the out-of-plane vibrations are stronger in the broken line, and the in-plane vibrations are stronger in the full line. However, some of the bands due to the in-plane vibrations appear as doublets, as represented by that at 1632 and 1628 cm⁻¹. All of the doublets can be explained as due to the factor group splitting, from analogy with those in the spectra of CH₂=CHCOOH. Consequently, it is apparent that the spectrum represented by the full line in Fig. 6 contains the B₂₂ and B₃₃ crystal modes of the in-plane vibrations. The estimated orientation for this case is also given in the right side of Fig. 4.
VIBRATIONAL ASSIGNMENTS

The observed frequencies of liquid and crystalline CH₂=CHCOOH and crystalline CH₂=CHCOOD are given in Table II, together with their assignments. The classifications of the bands in the crystal into the $B_{1u}$, $B_{2u}$, and $B_{3u}$ crystal modes are made by referring to the dichroism as mentioned above. Most of the observed

Table II. Observed Infrared Frequencies (cm⁻¹) and Assignments of Acrylic Acids*

<table>
<thead>
<tr>
<th>Frequency (cm⁻¹)</th>
<th>CH₂=CHCOOH</th>
<th>CH₂=CHCOOD</th>
<th>Assignments</th>
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<tr>
<td>3200</td>
<td>3200</td>
<td>3200</td>
<td>$B_{3u}$ + $B_{3u}$</td>
</tr>
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<td>~2500, vb</td>
<td>~2500, vb</td>
<td>vOH</td>
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<td>1705</td>
<td>$B_{2u}$ + $B_{3u}$</td>
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<td>1700</td>
<td>1705</td>
<td>$B_{2u}$ + $B_{3u}$</td>
</tr>
<tr>
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<td>1631</td>
<td>$B_{2u}$ + $B_{3u}$</td>
</tr>
<tr>
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<td>1610, vw</td>
<td>1615, vw</td>
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</tr>
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<td>1436</td>
<td>1435</td>
<td>$B_{2u}$ + $B_{3u}$</td>
</tr>
<tr>
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<td>1377</td>
<td>$B_{2u}$ + $B_{3u}$</td>
</tr>
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<td>556</td>
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<tr>
<td>525, sh</td>
<td>529</td>
<td>534</td>
<td>$B_{2u}$ + $B_{3u}$</td>
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</table>

* vb=very broad, vw=very weak, sh=shoulder, v=stretch, r=out-of-plane bend, τ=twist, δ=in-plane bend, ρ=rock, w=wag, ip=in-phase, op=out-of-phase, combi=combination
bands could be assigned easily to fundamental vibrations, since their frequencies coincide with the well known group frequencies of vinyl and carboxyl groups.

Some of the assignments of the liquid spectrum are completely different from those made by Feairheller and Katon. They have assigned the bands at 1046, 628, and 525 cm\(^{-1}\) to the Raman-active \(a_\nu\) modes of the CH\(_2\) rocking, CO\(_2\) bending, and CO\(_2\) rocking vibrations, respectively. They have considered that the dimer possesses \(C_{2z}\) symmetry, but that the selection rule does not hold rigorously because the coupling between monomer units is by hydrogen bonds rather than by the stronger chemical bonds. Such a degradation of the selection rule is not a common occurrence in the dimeric fatty acids. In the infrared and Raman spectra of propionic acid, for example, the selection rule holds rigorously. In the present paper, the bands mentioned above are assigned to the fundamentals of the trans isomer, as mentioned before.

The 1808-cm\(^{-1}\) band of crystalline CH\(_2=\text{CHCOOH}\), which shows the narrowing of band width and apparent increase in intensity on cooling, may be assigned to the combination band of the infrared active (\(a_\nu\)) and the Raman active (\(b_\sigma\)) O–H out-of-plane bending vibrations, as in the case of saturated fatty acids.

The OH out-of-plane bending vibration shows a large frequency shift from 925 cm\(^{-1}\) (liquid) to 886 cm\(^{-1}\) (crystal at \(-20^\circ\text{C}\)) on crystallization. It is well known that the frequency of this vibration in saturated fatty acids is very sensitive to the intermolecular forces. The above frequency shift in acrylic acid may be also due to the change in the intermolecular forces on crystallization.

The 864-cm\(^{-1}\) band of liquid CH\(_2=\text{CHCOOH}\) has been assigned to the \(b_\sigma\) mode of the OH out-of-plane bending vibration by Feairheller and Katon. It is apparent, from the dichroism of the corresponding band at 875 cm\(^{-1}\) in Fig. 5, that the band is due to the in-plane vibration. We assigned the 864-cm\(^{-1}\) band to the C–C–O in-phase stretching vibration.

Feairheller and Katon have observed a shoulder at 512 cm\(^{-1}\) and assigned it to the CO\(_2\) wagging vibration in liquid CH\(_2=\text{CHCOOH}\). We could not observe it in the liquid and crystal spectra. It is not certain whether it is due to the weakness of the band or the CO\(_2\) wagging vibration occurs below the lowest limit of frequency, 500 cm\(^{-1}\), in the present measurement.

In the infrared spectra of CH\(_2=\text{CHCOOD}\) shown in Fig. 6, bands due to undeuterated species appear weakly at 1815, 1685, 1679, 1444, 1395, 1306, 1260, 1256, 1075, and 910 cm\(^{-1}\). Bands due to the unremovable CH\(_3\)OD are also observed weakly in Fig. 6. These are the bands at 2431, 1057, 1050, 932, and 928 cm\(^{-1}\). These five bands have strong intensities in the spectrum of the pure CH\(_3\)OD crystal. All of the bands described above were not listed in Table II, for simplicity.

DISCUSSIONS

For the cis-trans isomerism shown in Fig. 1, the following two processes can be considered. One is the simultaneous proton transfer along two hydrogen bonds of a dimer by the tunneling effect. From the microwave study of the hydrogen-bonded bimolecule CF\(_3\)COOH–CH\(_3\)COOD, Costain and Srivastava have speculated
that the proton transfer occurs at a rate faster than the pure rotational frequency in
the gas phase. Another possible process is the internal rotation of the carboxyl group
about the C—C bond. Through the microwave investigation of the gaseous monomer
of acrylic acid, Bolton and coworkers have estimated the barrier heights to the internal
rotation as 3.8±1.4 kcal/mol which is low enough for the transformation between
cis and trans isomers. The barrier height to the internal rotation in the gaseous
dimer would be similar to that of the monomer, and the cis-trans isomerism may occur
also through the internal rotation about the C—C bond.

In the liquid phase, these two processes seem to occur simultaneously. In the
crystalline phase, however, the internal rotation may be strongly restricted, as the bar-
rier to internal rotation will become very higher by the intermolecular forces. Ac-
cording to the results of X-ray analyses of the crystalline acrylic acid, the molecular
planes of dimers are piled, in parallel, on each other with a distance of about 3.2 Å.
The abrupt decrease in intensity of the band due to the trans isomer at the temperature
of transition from liquid to crystal seems to be reflected by the restriction of the internal
rotation in the crystal. Therefore, it seems likely that the cis-trans isomerism in the
crystalline phase is predominantly due to the simultaneous proton transfer along
hydrogen bonds.

In Fig. 1, only two types of dimers, that is, the cis dimer (cis monomer-cis monomer)
and the trans dimer (trans monomer-trans monomer) are shown. In the liquid phase,
however, the other dimer of the type, cis monomer-trans monomer, may be also pre-
sent, since the internal rotation of the ethyl group about the C—C bond can occur.
This dimer may show a mixed spectrum of those of the cis and trans dimer. This dimer
can not exist in the crystal because of the restriction of the internal rotation and of the
unsuitableness for the crystal packing.

Our conclusion that the cis isomer is the more stable isomer in the crystalline acrylic
acid is consistent with the results of the microwave study and the semi-empirical
calculation for the monomeric acrylic acid. Through microwave analysis, it has
been shown that the cis isomer is more stable than the trans isomer, with the energy
difference of 0.17±0.06 kcal/mol. According to the semi-empirical calculations,
the energy of the cis isomer is lower than that of the trans isomer by 0.89 kcal/mol
(the CNDO/2 method), and by 0.15 kcal/mol (the extended Huckel method).

Kanters and coworkers have examined the existent results of the structure deter-
minations of some aliphatic carboxylic acids by means of the X-ray diffraction, and
pointed out a common feature that the C=O bond is in an eclipsed position with
the C—C bond, i.e., the configuration is the cis form. They have speculated that
the configuration of the molecule is governed chiefly by intramolecular interactions
predominating over intermolecular interactions, on the ground that the cis form of
aliphatic carboxylic acids is compatible with the most stable configuration expected
from the Pauling's bent bond idea of the double bond. Contrary to their speculation,
we have given the infrared evidences to show that the cis isomer is not always a most
stable one. In the case of acrylic acid, this point becomes clear. The Pauling's
cent bond idea of the double bond predicts that the most stable isomer of acrylic
acid is the trans isomer, as in the cases of other conjugated molecules. If we accept
the speculation made by Kanters and coworkers, therefore, the stable isomer of acrylic
acid in the crystal should be the trans isomer. As described before, however, the infrared and X-ray data show that the cis isomer is present as the stable isomer in the crystal.

ACKNOWLEDGMENT

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