# Topochemistry. Part XVII.[1] The Crystal Structures of Two Modifications of *trans*-β-2-Thienylacrylic Acid

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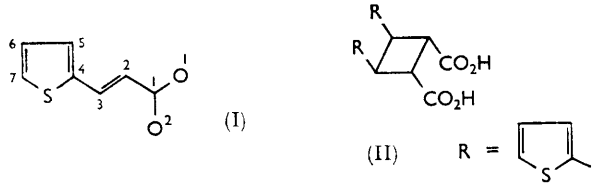
The partial three-dimensional analyses of two crystal modifications of *trans*-β-2-thienylacrylic acid are reported. The C–C bond lengths have been determined with an e.s.d. of about 0·02 Å; the differences in bond lengths and angles measured independently in the two packing arrangements are not significantly greater than the standard deviations of their measurements.

According to their cell dimensions as well as the geometry of contact of exocyclic >C=C< groups the two modifications belong, respectively, to the β- and γ-type of the cinnamic acid series. The photochemistry of the two forms is discussed in terms of their packing arrangements.



ACCORDING to current work in this laboratory[2] the two modifications of *trans*-β-2-thienylacrylic acid (I) undergo different photo-reactions: whereas the metastable




β-2-*Thienylacrylic acid* (I). The numbering of atoms used in the present analysis.

form gives the cyclobutane (II) in high yield together with small quantities of polymer the stable form polymerises exclusively and affords no dimeric material whatever. This variation in photo-behaviour with packing arrangement has led us to analyse the two crystal structures of the monomer. Since we were primarily interested in the crystal structures rather than exact molecular dimensions only partial three-dimensional data were collected.

## EXPERIMENTAL

The acid (I) was prepared from thiophen-2-aldehyde by condensation with malonic acid in pyridine solution in the presence of piperidine. The crystals obtained from slowly cooled solutions in ethanol or acetic acid had m. p. 147° (lit.,[3] 147°); they are colourless monoclinic laths elongated along [010]. This form, the cell dimensions of which are listed in Table 1, is designated γ in accordance with the nomenclature of Part III.[4] A second, also monoclinic, modification has been grown from solutions in dimethylformamide by evaporation; slowly heated on a microscope hot-stage the crystals of this modification transform into the γ-modification between 130 and 135° without actually melting, and liquefy at 147°, the m. p. of the stable form. According to its cell dimensions (Table 1) this (metastable) modification belongs to the β-type. Cell dimensions were measured from high-angle reflections on zero-level Weissenberg photographs calibrated for film shrinkage; densities were measured by flotation in liquids of calibrated density (carbon tetrachloride–toluene mixtures).

TABLE 1

Cell constants of the two forms of thienylacrylic acid, $C_7H_6O_2S$, $M$, 154·2

γ-*Modification:* $a = 11{\cdot}41_2$, $b = 5{\cdot}04_0$, $c = 13{\cdot}00_5$ Å; $\beta = 98{\cdot}2°$. *Absences:* $h0l$ for $l$ odd, $0k0$ for $k$ odd; *space group:* $P2_1/c$; $V = 740$ Å$^3$; $d$ (flotation): 1·37; $d$ (calc.) ($n = 4$): 1·384 g./cm.$^3$. $F$ (000) = 320.

β-*Modification:* $a = 9{\cdot}58_5$, $b = 3{\cdot}91_1$, $c = 20{\cdot}19_2$ Å; $\beta = 109{\cdot}5_1°$. *Absences:* $h0l$ for $l$ odd; $0k0$ for $k$ odd; *space group:* $P2/c$; $V = 714$ Å$^3$; $d$ (flotation): 1·45; $d$ (calc.) ($n = 4$): 1·436 g./cm.$^3$. $F$ (000) = 320.

The $h0l$ and $h1l$ reflections of each modification were recorded on Weissenberg photographs with Ni-filtered Cu $K_\alpha$ radiation. Absorption was not allowed for; spotshape corrections according to Phillips[5] were applied to the $h1l$ intensities. The number of measured and "unobserved" reflections were $F(h0l)$: (168 + 28) and (225 + 16); $F(h1l)$: (304 + 57) and (383 + 29), for the γ and β modifications, respectively. Both $h0l$ zones were solved by means of sharpened Patterson projections which showed the S · · · S space-group vectors as well as the vectors between sulphur and all other atoms. After the short-axis projections had been refined by a full-matrix programme on the CDC 1604 installation to acceptable agreement factors (γ-form: $r[= \Sigma w(k^2F_o^2 - F_c^2)^2/\Sigma wk^4F_o^4] = 0{\cdot}019$; $R[= \Sigma|kF_o - |F_c||/\Sigma kF_o] = 0{\cdot}075$; β-form: $r = 0{\cdot}040$; $R = 0{\cdot}093$) the $y$ co-ordinates were derived from approximate molecular models projected onto the ($xz$) co-ordinates; the refinement of the $h1l$ reflections was carried out first separately and later combined with their $h0l$ reflections. In the absence of experimental scale factors connecting $F(h0l)$ and $F(h1l)$ the scale factors of the levels $k = 1$ were included as parameters in the least-squares procedure. Hydrogen co-ordinates were derived by means of the usual assumptions and introduced into the anisotropic refinement of all the atoms, the thermal parameters of the hydrogens being treated as isotropic throughout. Iterations were stopped when the shifts in all parameters had become random and reached about a third of their standard deviations. At this stage the agreement factors for the combined $h0l$ and $h1l$ reflections stood at $r = 0{\cdot}011$, $R = 0{\cdot}062$ (γ-form) and $r = 0{\cdot}032$ and $R = 0{\cdot}085$ (β-form). The following scattering factor curves were used: $f_{C,O}$, Berghuis *et al.*,[6] $f_S$, Dawson.[7]

[1] Part XVI, S. E. Filippakis and G. M. J. Schmidt, preceding Paper.
[2] M. Lahav and G. M. J. Schmidt, Part XVIII, following Paper.
[3] C. C. Price and E. A. Dudley, *J. Amer. Chem. Soc.*, 1956, **78**, 68.
[4] G. M. J. Schmidt, *J. Chem. Soc.*, 1964, 2014.
[5] D. C. Phillips, *Acta Cryst.*, 1954, **7**, 746.
[6] J. Berghuis, IJ. M. Haanappel, M. Potters, B. O. Loopstra, C. H. MacGillavry, and A. L. Veenendaal, *Acta Cryst.*, 1955, **8**, 478.
[7] B. Dawson, *Acta Cryst.*, 1960, **13**, 403.

TABLE 2(a)

Structure factors, $\gamma$-modification

| h k l | $F_o$ | $F_c$ | h k l | $F_o$ | $F_c$ | h k l | $F_o$ | $F_c$ | h k l | $F_o$ | $F_c$ | h k l | $F_o$ | $F_c$ | h k l | $F_o$ | $F_c$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 0 2 | 14.74 | 15.95 | | -12 | 6.93 | -7.38 | | -9 | 3.71 | -4.50 | | 8 | 24.69 | 25.63 | | 2 | 5.47 | 4.85 |
| 4 | 19.83 | -20.24 | 7 3 0 | | 14.72 | -12.57 | | -10 | 6.82 | 5.82 | | 9 | 3.31 | 4.13 | | 3 | 9.94 | 9.17 |
| 6 | 40.57 | -39.64 | | 2 | 6.22 | 5.63 | | -11 | 7.47 | 7.40 | | 10 | 3.36 | 3.50 | | 4 | 3.29u | 1.48 |
| 8 | 9.27 | -11.06 | | 4 | 9.81 | 10.12 | | -12 | 3.34u | -.14 | | 11 | 6.15 | -5.24 | | 5 | 10.84 | -10.24 |
| 10 | 3.71 | -2.81 | | 6 | 4.72 | -3.89 | | -13 | 10.42 | 10.99 | | 12 | 3.08u | -.28 | | 6 | 4.75 | 4.80 |
| 12 | 8.82 | 8.41 | | 8 | 3.95u | -3.86 | | -14 | 4.14 | -4.25 | | 13 | 3.86 | -4.51 | | 7 | 6.20 | -5.23 |
| 14 | 7.42 | -7.88 | | 10 | 4.44 | -4.56 | | 1 | 10.18 | -10.03 | 5 1 -1 | | 8.89 | 9.05 | | 8 | 3.19 | -2.79 |
| 16 | 2.76 | -1.49 | 7 0 12 | | 8.37 | 7.26 | | 2 | 18.59 | 18.31 | | -2 | 2.29u | .20 | | 9 | 6.68 | -6.95 |
| 1 0 -2 | 24.29 | 24.96 | 8 0 -2 | | 12.06 | -11.91 | | 3 | 10.03 | 9.60 | | -3 | 8.15 | 7.89 | | 10 | 5.02 | -4.04 |
| -4 | 5.33 | -6.07 | | -4 | 3.57u | -.77 | | 4 | 1.94 | -.68 | | -4 | 27.02 | 25.84 | | 11 | 2.23 | 2.23 |
| -6 | 18.86 | -17.28 | | -6 | 3.75 | -3.07 | | 5 | 11.09 | -9.87 | | -5 | 11.57 | 11.78 | 9 1 -1 | | 11.95 | 11.97 |
| -8 | 9.21 | 6.84 | | -8 | 13.00 | 13.15 | | 6 | 5.89 | -6.90 | | -6 | 4.74 | -4.78 | | -2 | 21.95 | -22.34 |
| -10 | 4.52 | 4.02 | | -10 | 7.30 | 7.89 | | 7 | 19.22 | 18.81 | | -7 | 13.47 | 14.31 | | -3 | 3.28u | -1.48 |
| -12 | 17.21 | 15.46 | 8 0 0 | | 25.22 | 23.95 | | 8 | 13.93 | -13.35 | | -8 | 3.08 | -2.85 | | -4 | 5.20 | -5.93 |
| 1 0 0 | 7.46 | -7.88 | | 2 | 26.76 | 24.54 | 1 1 9 | | 8.46 | 8.36 | | -9 | 3.94 | -4.13 | | -5 | 3.32 | -3.32 |
| 2 | 92.75z | 123.74 | | 4 | 3.81 | -3.93 | | 10 | 7.65 | 7.13 | | -10 | 3.32 | -2.41 | | -6 | 9.76 | 11.03 |
| 4 | 19.36 | -18.93 | | 6 | 19.52 | -19.04 | | 11 | 8.21 | 7.53 | | -11 | 14.63 | -14.68 | | -7 | 8.56 | -9.08 |
| 6 | 14.27 | 14.57 | | 8 | 10.12 | -9.99 | | 12 | 11.74 | 11.77 | 5 1 0 | | 12.75 | 13.56 | | -8 | 3.34u | -.90 |
| 8 | 5.15 | 3.50 | | 10 | 3.29u | 1.23 | | 13 | 8.88 | -9.28 | | 1 | 20.98 | -19.87 | | -9 | 6.10 | 6.91 |
| 10 | 20.80 | 22.09 | | 12 | 5.98 | 5.91 | | 14 | 5.24 | 5.03 | | 2 | 8.36 | -10.57 | 9 1 0 | | 4.01 | -3.72 |
| 12 | 3.93u | 2.24 | 9 0 -2 | | 3.75u | -.97 | 2 1 -1 | | 63.62z | 82.47 | | 3 | 6.93 | 7.08 | | 1 | 3.29u | 1.03 |
| 14 | 4.18 | -4.67 | | -4 | 22.55 | -22.26 | | -2 | 81.59z | 102.46 | 5 1 4 | | 6.57 | 7.66 | | 2 | 9.68 | 9.71 |
| 16 | 2.03 | -1.78 | | -6 | 9.16 | -8.57 | | -3 | 36.40 | 36.14 | | 5 | 7.51 | 7.44 | | 3 | 3.34u | .01 |
| 2 0 -2 | 65.38z | 74.86 | | -8 | 3.95u | -2.21 | | -4 | 16.62 | -17.89 | | 6 | 7.05 | 7.01 | | 4 | 10.36 | 10.07 |
| -4 | 8.94 | -8.81 | | -10 | 3.75u | 3.41 | | -5 | 12.82 | 12.55 | | 7 | 3.16u | -2.22 | | 5 | 7.83 | -8.05 |
| -6 | 14.01 | -13.55 | | -12 | 3.93 | 4.72 | | -6 | 22.78 | -20.20 | | 8 | 3.29u | -.29 | | 6 | 3.28u | 2.34 |
| -8 | 24.23 | -24.66 | 9 0 0 | | 5.96 | 5.44 | | -7 | 7.98 | -6.65 | | 9 | 11.62 | -12.38 | | 7 | 3.14u | -2.43 |
| -10 | 7.40 | 6.06 | | 2 | 9.83 | 8.65 | | -8 | 4.89 | -4.55 | | 10 | 8.80 | -8.82 | | 8 | 4.14 | -4.51 |
| 2 0 0 | 25.06 | -26.22 | | 4 | 9.65 | -9.56 | | -9 | 3.03u | -3.33 | | 11 | 5.00 | -5.85 | 9 1 9 | | 2.63u | 1.25 |
| 2 | 4.74 | -4.68 | | 6 | 3.89u | 1.52 | | 10 | 3.23u | .21 | 6 1 -1 | | 25.41 | -22.02 | | 10 | 2.24u | -2.12 |
| 4 | 53.10 | -53.69 | | 8 | 3.55u | .90 | | -11 | 5.27 | -4.11 | | -2 | 2.54u | -1.07 | | 11 | 4.51 | 4.61 |
| 6 | 4.85 | -4.86 | | 10 | 6.85 | 5.81 | 2 1 0 | | 36.75 | 40.45 | | -3 | 3.67 | 2.70 | 10 1 -1 | | 3.36u | -2.04 |
| 8 | 13.46 | 13.28 | 10 0 -2 | | 21.49 | 21.23 | | 1 | 27.50 | -26.01 | | -4 | 9.64 | 11.25 | | -2 | 3.36u | 2.90 |
| 10 | 27.21 | 26.95 | | -4 | 7.38 | -8.08 | | 2 | 20.87 | 16.79 | | -5 | 4.82 | -4.24 | | -3 | 3.36 | 2.23 |
| 12 | 7.79 | -8.09 | | -6 | 9.65 | -8.94 | | 3 | 52.91 | -48.90 | | -6 | 5.84 | -6.31 | | -4 | 5.82 | -5.73 |
| 14 | 2.31 | -3.00 | | -8 | 3.83u | -3.35 | | 4 | 2.54 | -.98 | | -7 | 9.89 | 10.46 | | -5 | 3.36 | -3.96 |
| 3 0 -2 | 52.13z | 57.18 | | -10 | 6.97 | 6.72 | | 5 | 22.33 | -20.37 | | -8 | 10.08 | -9.94 | | -6 | 5.77 | 5.10 |
| -4 | 26.73 | 26.78 | 10 0 0 | | 10.40 | 9.60 | | 6 | 19.87 | -19.71 | | -9 | 5.22 | 6.14 | | -7 | 4.22 | -3.15 |
| -6 | 23.66 | 22.55 | | 2 | 5.58 | 5.84 | | 7 | 2.74 | -3.93 | | -10 | 7.66 | -6.19 | | -8 | 5.05 | 5.06 |
| -8 | 32.91 | -33.34 | | 4 | 13.48 | -12.54 | | 8 | 9.36 | -8.68 | | -11 | 4.72 | -5.98 | | -9 | 3.06 | 2.59 |
| -10 | 19.44 | -19.06 | | 6 | 5.15 | -5.79 | | 9 | 6.70 | 7.01 | | -12 | 7.17 | 5.68 | 10 1 0 | | 14.83 | 14.66 |
| -12 | 3.95u | -.37 | | 8 | 3.10u | -.36 | | 10 | 8.75 | 8.54 | | -13 | 5.12 | -3.88 | | 1 | 3.36 | 3.21 |
| 14 | 9.33 | 8.28 | | 10 | 5.01 | 5.22 | | 11 | 3.36u | .11 | | -14 | 3.66 | 4.55 | | 2 | 3.36u | .86 |
| 3 0 0 | 1.83u | -.52 | 11 0 -2 | | 8.76 | 8.42 | | 12 | 3.28u | -1.84 | 6 1 0 | | 20.73 | -18.57 | | 3 | 7.80 | -6.75 |
| 2 | 10.97 | -10.55 | | -4 | 15.81 | 15.39 | | 13 | 3.04u | -.06 | | 1 | 3.67 | -3.98 | | 4 | 3.28u | -1.06 |
| 4 | 2.49u | -.88 | | -6 | 3.79u | -2.35 | | 14 | 4.99 | -4.40 | | 2 | 26.34 | -26.94 | | 5 | 5.49 | -5.34 |
| 6 | 33.66 | 32.26 | | -8 | 7.54 | -7.16 | 3 1 -1 | | 14.37 | -14.62 | | 3 | 21.65 | 22.41 | | 6 | 6.40 | -6.41 |
| 8 | 11.35 | 11.32 | | -10 | 4.85 | 4.57 | | -2 | 4.22 | -5.59 | | 4 | 5.04 | -5.53 | | 7 | 2.79u | -.51 |
| 10 | 17.64 | -17.23 | 11 0 0 | | 3.91u | -.97 | | -3 | 47.40 | 45.92 | | 5 | 9.88 | 11.03 | | 8 | 5.02 | -5.04 |
| 12 | 17.76 | -17.49 | | 2 | 9.37 | -9.18 | | -4 | 32.46 | -29.15 | | 6 | 11.69 | 13.10 | | 9 | 6.70 | 6.58 |
| 4 0 -2 | 3.51 | -2.89 | | 4 | 9.57 | -9.05 | | -5 | 8.60 | 8.37 | | 7 | 6.17 | -7.05 | 11 1 -1 | | 4.04 | 3.98 |
| -4 | 3.51 | -2.42 | | 6 | 3.20u | -2.24 | | -6 | 14.51 | -16.32 | | 8 | 9.19 | 9.94 | | -2 | 4.67 | -4.69 |
| -6 | 8.66 | 7.56 | | 8 | 7.28 | 6.65 | | -7 | 4.97 | -3.79 | | 9 | 3.34u | -3.42 | | -3 | 8.06 | 8.94 |
| -8 | 3.35u | 2.95 | 12 0 -2 | | 8.21 | -8.57 | | -8 | 6.42 | 7.73 | | 10 | 3.94 | 4.06 | | -4 | 8.94 | -9.29 |
| -10 | 5.37 | -7.20 | | -4 | 3.61u | 1.51 | | -9 | 14.75 | -15.54 | | 11 | 2.98u | -1.79 | | -5 | 3.23 | -3.22 |
| 4 0 0 | 36.47 | -37.36 | | -6 | 3.45 | -3.06 | | -10 | 13.95 | 12.94 | | 12 | 2.61 | -2.85 | | -6 | 5.49 | -5.72 |
| 2 | 57.52 | -64.07 | | -8 | 5.37 | -5.57 | | -11 | 3.34u | .83 | 7 1 -1 | | 27.72 | -25.73 | | -7 | 4.34 | -4.31 |
| 4 | 6.12 | 5.80 | 12 0 0 | | 4.44 | 4.75 | | -12 | 3.34 | 3.90 | | -2 | 2.81u | 2.44 | | -8 | 4.14 | 4.77 |
| 6 | 15.31 | 16.62 | | 2 | 4.89 | -6.50 | | -13 | 3.19u | .32 | | -3 | 12.55 | -13.42 | | -9 | 4.74 | -5.13 |
| 8 | 8.58 | 8.73 | | 4 | 3.12u | -.75 | | -14 | 4.11 | 4.56 | | -4 | 12.17 | 13.25 | 11 1 0 | | 3.28u | -.19 |
| 10 | 3.95u | -1.50 | | 6 | 6.89 | 4.91 | 3 1 0 | | 27.57 | -27.86 | | -5 | 5.99 | -6.56 | | 1 | 6.50 | 6.56 |
| 12 | 5.25 | 4.28 | 13 0 -2 | | 5.52 | 5.51 | | 1 | 24.46 | -24.82 | | -6 | 15.80 | 16.37 | | 2 | 3.19u | 1.33 |
| 5 0 -2 | 6.20 | 5.81 | | -4 | 7.32 | 6.67 | | 2 | 19.85 | 19.45 | | -7 | 9.61 | 10.63 | | 3 | 7.63 | -8.15 |
| -4 | 31.53 | 32.22 | | -6 | 5.01 | 4.62 | | 3 | 19.89 | -19.10 | | -8 | 5.70 | 5.72 | | 4 | 4.24 | 4.91 |
| -6 | 40.49 | 40.66 | 13 0 0 | | 3.10u | .12 | 3 1 4 | | 3.56 | -4.77 | | -9 | 6.27 | 6.84 | | 5 | 2.83u | -.14 |
| -8 | 6.55 | 6.70 | | 2 | 9.67 | -8.89 | | 5 | 25.21 | 24.27 | | -10 | 7.10 | -6.66 | | 6 | 3.18 | -3.30 |
| -10 | 17.58 | -19.39 | 14 0 -2 | | 2.45u | -.98 | | 6 | 23.16 | -22.59 | | -11 | 6.10 | 4.53 | | 7 | 3.64 | 2.50 |
| -12 | 6.75 | -5.43 | | -4 | 2.37u | .47 | | 7 | 7.32 | 7.14 | | -12 | 9.48 | -9.74 | 12 1 -1 | | 3.03u | 1.05 |
| 5 0 0 | 51.70 | -48.97 | | -6 | 3.20 | 2.58 | | 8 | 7.83 | 8.12 | 7 1 0 | | 19.49 | -18.64 | | -2 | 4.31 | 3.89 |
| 2 | 17.38 | -17.37 | 14 0 0 | | 6.69 | -6.88 | | 9 | 9.99 | 9.76 | | 1 | 8.08 | 7.49 | | -3 | 4.79 | 4.23 |
| 4 | 39.98 | 41.95 | 0 1 1 | | 29.93 | 30.84 | | 10 | 9.46 | 9.90 | | 2 | 8.03 | 8.73 | | -4 | 2.99u | 1.76 |
| 6 | 11.86 | 12.32 | | 2 | 27.50 | 28.73 | | 11 | 5.79 | -5.92 | | | | | | -5 | 4.14 | 3.77 |
| 8 | 5.39 | -5.46 | | 3 | 6.83 | -7.78 | 4 1 -1 | | 29.56 | -29.60 | 7 1 3 | | 13.68 | 12.82 | | -6 | 4.90 | -5.97 |
| 10 | 6.81 | -7.26 | | 4 | 4.59 | -6.09 | | -2 | 33.75 | 34.99 | | 4 | 8.28 | 8.13 | | -7 | 3.29 | -2.04 |
| 12 | 6.55 | -6.90 | | 5 | 21.65 | -19.58 | | -3 | 17.03 | -15.90 | | 5 | 3.23u | -1.40 | | -9 | 2.78 | -2.46 |
| 6 0 -2 | 23.26 | -23.33 | | 6 | 7.58 | -6.07 | | -4 | 26.50 | 24.20 | | 6 | 8.11 | 8.39 | 12 1 0 | | 7.03 | 6.91 |
| -4 | 31.63 | -30.59 | | 7 | 8.94 | -9.76 | | -5 | 6.37 | 6.58 | | 7 | 4.75 | -3.36 | | 1 | 4.64 | 4.66 |
| -6 | 3.31u | .17 | | 8 | 3.99 | -4.31 | | -6 | 21.90 | -22.65 | | 8 | 5.27 | -5.11 | | 2 | 2.84u | 2.96 |
| -8 | 16.58 | 16.84 | | 9 | 4.31u | -.39 | | -7 | 9.79 | 10.46 | | 9 | 3.23u | .66 | 12 1 3 | | 3.82 | -4.51 |
| -10 | 3.93u | -1.77 | | 10 | 4.57u | -1.40 | | -8 | 11.66 | -11.77 | | 10 | 6.72 | -6.56 | | 4 | 4.01 | -4.50 |
| -12 | 6.06 | -4.77 | | 11 | 14.76 | 14.61 | | -9 | 10.87 | -11.83 | | 11 | 2.66u | .61 | | 5 | 2.29u | .83 |
| 6 0 0 | 8.76 | -6.90 | | 12 | 3.34u | -2.29 | | -10 | 3.28u | -.65 | | 12 | 3.52 | -3.41 | | 6 | 3.96 | -4.38 |
| 2 | 36.90 | 35.51 | | 13 | 3.19u | -3.67 | | -11 | 3.36u | 1.80 | 8 1 -1 | | 13.45 | 14.51 | | 7 | 3.09 | 3.23 |
| 4 | 24.69 | 27.62 | | 14 | 2.88u | 1.36 | | -12 | 3.32u | 1.13 | | -2 | 5.70 | -4.63 | 13 1 -1 | | 2.58 | -1.26 |
| 6 | 6.33 | -7.14 | | 15 | 3.42 | -3.27 | | -13 | 5.47 | 5.24 | | -3 | 10.44 | -10.81 | | -2 | 2.59 | .85 |
| 8 | 8.76 | -9.34 | 1 1 -1 | | 57.68 | 57.24 | 4 1 0 | | 23.33 | 20.73 | | -4 | 3.13u | 2.77 | | -3 | 2.58u | -.66 |
| 10 | 8.15 | -8.85 | | -2 | 50.05 | -48.04 | | 1 | 25.70 | -24.85 | | -5 | 6.77 | -6.87 | | -4 | 2.53u | .46 |
| 12 | 3.93 | -3.35 | | -3 | 57.91 | -59.29 | | 2 | 27.47 | -27.76 | | -6 | 3.26u | 1.28 | | -5 | 6.70 | 5.07 |
| 7 0 -2 | 23.90 | -24.71 | | -4 | 69.23 | -72.32 | | 3 | 2.29u | -1.70 | | -7 | 3.31u | -2.44 | | 1 | 4.88 | -6.35 |
| -4 | 6.59 | 6.42 | | -5 | 8.53 | -7.87 | | 4 | 33.99 | -34.21 | | -8 | 3.36u | -3.03 | | 2 | 2.29u | -1.80 |
| -6 | 6.63 | -6.91 | | -6 | 13.07 | 12.46 | | 5 | 20.33 | 19.84 | | -9 | 5.80 | 5.75 | | 3 | 2.99u | -.71 |
| -8 | 14.76 | 14.25 | | -7 | 26.20 | -25.42 | | 6 | 3.46 | -3.16 | | -10 | 6.13 | 5.93 | | 4 | 3.64 | -4.40 |
| -10 | 3.95u | .32 | | -8 | 25.95 | 26.45 | | 7 | 12.97 | 13.72 | 8 1 0 | | 12.82 | -12.50 | 14 1 -1 | | 1.86u | -1.21 |
| | | | | | | | | | | | | 1 | 19.27 | 18.69 | | -2 | 4.66 | 4.69 |

TABLE 2(b)

Structure factors, β-modification

| h k l | $F_o$ | $F_c$ | h k l | $F_o$ | $F_c$ | h k l | $F_o$ | $F_c$ | h k l | $F_o$ | $F_c$ | h k l | $F_o$ | $F_c$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 0 2 | 24.53 | -24.89 | 16 | 2.46 | 2.73 | -10 | 2.52 | -2.11 | -14 | 12.70 | -12.23 | -24 | 5.51 | -5.12 |
| 4 | 48.02 | -49.47 | 18 | 13.26 | -12.55 | -12 | 3.88 | 3.47 | -15 | 1.35 | 1.12 | -25 | 4.42 | 4.67 |
| 6 | 6.89 | -6.18 | 20 | 7.30 | 6.78 | -14 | 8.90 | 8.07 | -16 | 29.34 | 29.74 | 4 1 0 | 47.21 | 52.71 |
| 8 | 72.89 | -72.54 | 5 0 -2 | 47.65 | -44.30 | -16 | 2.16 | -2.12 | -17 | 13.24 | -14.21 | 1 | 1.43 | -.29 |
| 10 | 22.27 | 19.93 | -4 | 26.48 | 24.61 | -18 | 3.30 | -3.16 | -18 | 15.51 | -15.53 | 2 | 1.47 | 1.24 |
| 12 | 29.07 | 28.00 | -6 | 17.02 | -16.79 | -20 | 5.27 | 4.80 | -19 | 6.83 | -6.14 | 3 | 3.43 | 7.13 |
| 14 | 13.08 | -11.23 | -8 | 19.46 | -17.81 | 10 0 0 | 6.07 | -6.37 | -20 | 2.32 | -2.50 | 4 | 4.75 | .83 |
| 16 | 16.10 | -14.79 | -10 | 10.17 | -9.99 | 2 | 8.38 | 8.44 | -21 | 1.26u | .68 | 5 | 4.51 | -5.45 |
| 18 | 5.91 | -4.61 | -12 | 7.15 | -8.30 | 4 | 5.21 | -4.27 | -22 | 6.33 | 5.89 | 6 | 23.83 | 24.88 |
| 20 | 3.10 | -3.66 | -14 | 6.55 | 6.77 | 11 0 -2 | 5.75 | 4.86 | -23 | 6.92 | 6.86 | 7 | 12.80 | -13.34 |
| 22 | 17.62 | 16.83 | -16 | 10.56 | 10.57 | -4 | 5.76 | -5.13 | -24 | 8.53 | -8.70 | 8 | 27.06 | -28.93 |
| 24 | 3.72 | 4.15 | -18 | 3.03 | 3.70 | -6 | 1.07u | -.56 | 2 1 0 | 7.18 | 7.12 | 9 | 10.37 | 10.40 |
| 1 0 -2 | 24.45 | 25.03 | -20 | 1.32u | .10 | -8 | 7.53 | -6.37 | 1 | 4.44 | 4.69 | 10 | 2.40 | 2.98 |
| -4 | 47.26 | 43.98 | -22 | 1.17u | 1.19 | -10 | 2.12 | -2.67 | 2 | 18.56 | 19.61 | 11 | 5.63 | 4.88 |
| -6 | 30.67 | -28.97 | -24 | 8.73 | -8.66 | -12 | 5.49 | 5.59 | 3 | 20.04 | -22.09 | 12 | 9.82 | 9.13 |
| -8 | 31.40 | 34.20 | 5 0 0 | 31.88 | 30.92 | 11 0 0 | 8.94 | 8.75 | 4 | 23.01 | -25.16 | 13 | 7.02 | -6.71 |
| -10 | 2.80 | -.14 | 2 | 29.57 | 30.38 | 12 0 -4 | 9.81 | 9.58 | 5 | 1.31u | -1.77 | 14 | 16.03 | -16.52 |
| -12 | 19.65 | -18.85 | 4 | 26.76 | -25.06 | -6 | 8.00 | -7.55 | 6 | 23.13 | 22.19 | 15 | 7.16 | 7.26 |
| -14 | 28.72 | 27.37 | 6 | 23.65 | 28.28 | -8 | 1.81 | -2.19 | 7 | 20.07 | -18.54 | 16 | 5.59 | 4.65 |
| -16 | 39.08 | -37.80 | 8 | 9.29 | -10.50 | -10 | 6.86 | 6.66 | 8 | 2.70 | -2.22 | 17 | 5.33 | -4.73 |
| -18 | 3.59 | -3.81 | 10 | 16.56 | -16.14 | 0 1 2 | 32.64 | 36.10 | 9 | 3.08 | -3.07 | 18 | .97u | -.88 |
| -20 | 12.24 | 12.04 | 12 | 17.29 | 16.60 | 3 | 9.54 | -10.09 | 10 | 4.75 | -4.99 | 19 | 3.78 | -3.56 |
| -22 | 8.61 | -8.97 | 14 | 3.32 | -3.87 | 4 | 32.17 | -32.37 | 11 | 19.29 | 16.60 | 5 1 -1 | 1.10u | -1.43 |
| -24 | 8.24 | 8.42 | 16 | 7.41 | -6.16 | 5 | 1.51 | -1.13 | 12 | 31.30 | 26.81 | -2 | 28.91 | 30.22 |
| 1 0 0 | 11.27 | -11.37 | 18 | 2.98 | 3.26 | 6 | 1.64 | -1.03 | 13 | 1.38 | -1.49 | -3 | 9.65 | -6.57 |
| 2 | 59.81 | 54.70 | 6 0 -2 | 45.38 | 42.99 | 7 | 39.15 | -34.96 | 14 | 1.41u | -.19 | -4 | 11.12 | 11.40 |
| 4 | 18.41 | -17.58 | -4 | 22.80 | -22.09 | 8 | 24.37 | -24.15 | 15 | 6.95 | 6.18 | -5 | 1.09 | 1.16 |
| 6 | 53.10 | -58.12 | -6 | 16.68 | -15.79 | 9 | 1.77 | -.35 | 16 | 7.27 | -6.98 | -6 | 21.28 | -19.23 |
| 8 | 15.32 | 13.41 | -8 | 7.90 | 8.05 | 10 | 37.19 | -30.06 | 17 | 1.35 | -2.11 | -7 | 21.36 | -22.44 |
| 10 | 33.26 | -28.63 | -10 | 20.83 | -21.50 | 11 | 28.97 | 23.31 | 18 | 1.28u | .63 | -8 | 16.57 | 17.11 |
| 12 | 1.16u | -.51 | -12 | 10.89 | 11.77 | 12 | 30.62 | 23.72 | 19 | 7.46 | -6.77 | -9 | 10.48 | 10.73 |
| 14 | 22.86 | 18.49 | -14 | 5.40 | 5.47 | 13 | 2.87 | -2.15 | 20 | 10.11 | -10.54 | -10 | 4.78 | -4.58 |
| 16 | 1.91u | .96 | -16 | 19.54 | -23.22 | 14 | 1.34u | .16 | 21 | 6.12 | 5.79 | -11 | 4.50 | 4.41 |
| 18 | 5.16 | 4.60 | -18 | 8.54 | 8.58 | 15 | 12.21 | -11.32 | 3 1 -1 | 34.08 | -37.52 | -12 | 17.66 | -18.12 |
| 20 | 1.19u | 1.32 | -20 | 1.28u | -1.16 | 16 | 9.98 | 9.25 | -2 | 17.86 | -17.02 | -13 | 10.01 | -10.53 |
| 22 | 2.49 | -3.28 | -22 | 1.96 | -2.27 | 17 | 9.92 | 9.05 | -3 | 19.00 | 20.19 | -14 | 10.00 | 9.82 |
| 2 0 -2 | 84.99z | 110.12 | -24 | 9.90 | 10.58 | 18 | 11.34 | 11.40 | -4 | 14.79 | -15.09 | -15 | 6.37 | 6.87 |
| -4 | 22.19 | -21.50 | 6 0 0 | 3.63 | 2.68 | 19 | 7.84 | -8.06 | -5 | .86u | .14 | -16 | 11.63 | -12.33 |
| -6 | 21.71 | 21.43 | 2 | 8.99 | 7.47 | 20 | 8.75 | -9.74 | -6 | 21.17 | -20.48 | -17 | 1.42u | 1.51 |
| -8 | 42.61 | -40.82 | 4 | 28.23 | 27.88 | 21 | 1.15u | 1.43 | -7 | 13.29 | -13.96 | -18 | 5.80 | -5.90 |
| -10 | 14.67 | 13.62 | 6 | 33.63 | -39.32 | 22 | 1.01u | -.20 | -8 | 18.21 | 18.07 | -19 | 7.02 | -8.08 |
| -12 | 51.67 | 52.17 | 8 | 1.35u | 1.74 | 23 | 8.25 | 7.68 | -9 | 3.72 | -2.73 | -20 | 8.70 | 9.59 |
| -14 | 14.24 | -12.29 | 10 | 5.69 | 5.85 | 1 1 -1 | 49.35z | 66.69 | -10 | 26.05 | -26.35 | 5 1-21 | 5.17 | 5.20 |
| -16 | 2.90 | 2.73 | 12 | 9.73 | -10.75 | -2 | 60.02z | 78.44 | -11 | 3.77 | 3.63 | -22 | 4.32 | -4.14 |
| -18 | 11.27 | -9.82 | 14 | 9.78 | 8.42 | -3 | 31.71 | 33.10 | 3 1-12 | 3.78 | -3.45 | -23 | 1.03u | .33 |
| -20 | 22.39 | -22.60 | 7 0 -2 | 12.28 | -12.57 | -4 | 6.41 | -6.29 | -13 | 8.64 | 8.64 | -24 | 3.41 | 2.95 |
| -22 | 5.68 | 5.64 | -4 | 3.26 | -.75 | 1 1 -5 | 27.73 | -27.62 | -14 | 18.40 | 18.54 | 5 1 0 | 17.86 | -18.49 |
| -24 | 5.86 | 6.69 | -6 | 12.32 | 11.84 | -6 | 15.21 | 14.67 | -15 | 11.29 | 11.74 | 1 | 21.20 | 22.79 |
| 2 0 0 | 5.88 | -5.40 | 7 0 -8 | 15.20 | -15.04 | -7 | 29.86 | -30.21 | -16 | 9.91 | -9.71 | 2 | 23.92 | 25.30 |
| 2 | 62.97 | -61.39 | -10 | 37.73 | 36.00 | -8 | 29.46 | 27.63 | -17 | 8.23 | -7.58 | 3 | 1.21 | -.68 |
| 2 0 4 | 24.86 | -23.25 | -12 | 16.51 | -15.60 | -9 | 18.29 | 17.20 | -18 | 15.05 | 14.35 | 4 | 8.20 | 8.25 |
| 6 | 50.87 | -55.43 | -14 | 21.20 | -20.01 | -10 | 28.91 | -25.24 | -19 | 2.79 | -2.37 | 5 | 7.40 | 6.82 |
| 8 | 4.82 | -4.58 | -16 | 9.20 | 10.01 | -11 | 2.97 | -2.99 | -20 | 5.58 | 5.41 | 6 | 27.81 | -29.25 |
| 10 | 42.19 | 43.37 | -18 | 11.21 | -11.19 | -12 | 22.77 | 19.29 | -21 | 1.28u | .17 | 7 | 8.71 | -8.72 |
| 12 | 8.10 | 8.17 | -20 | 1.73 | 2.57 | -13 | 9.61 | 9.33 | -22 | 9.38 | -8.01 | 8 | 10.13 | 11.25 |
| 14 | 23.51 | -22.95 | -22 | 7.05 | 7.20 | -14 | 10.80 | 9.59 | -23 | 7.07 | -5.99 | 9 | 11.63 | -12.51 |
| 16 | 24.71 | 23.09 | -24 | 4.08 | -3.68 | -15 | 18.19 | 15.51 | -24 | 5.38 | 5.28 | 10 | 13.74 | -14.26 |
| 18 | 8.09 | -8.57 | 7 0 0 | 23.92 | 22.63 | -16 | 3.70 | -3.51 | 3 1 0 | 16.67 | -17.57 | 11 | 3.15 | 3.81 |
| 20 | 1.08u | -.09 | 2 | 3.22 | 2.22 | -17 | 20.77 | -20.43 | 1 | 22.81 | 22.87 | 12 | 2.38 | -2.41 |
| 22 | 12.01 | 12.52 | 4 | 1.34 | 1.20 | -18 | 2.82 | 1.87 | 2 | 11.00 | 11.46 | 13 | 8.89 | 9.61 |
| 3 0 -2 | .69u | -1.23 | 6 | 6.07 | -5.91 | -19 | 3.38 | -3.82 | 3 | 1.64 | -2.21 | 14 | 8.66 | 8.89 |
| -4 | 23.20 | 22.93 | 8 | 13.96 | -17.29 | -20 | 10.19 | -9.91 | 4 | 29.71 | 31.50 | 15 | 4.61 | -4.10 |
| -6 | 42.37 | -49.62 | 10 | 1.23u | -2.81 | -21 | 1.22u | -.52 | 5 | 29.88 | -31.37 | 16 | 5.26 | -4.08 |
| -8 | 13.32 | -2.12 | 12 | 14.55 | 13.50 | -22 | 7.06 | -6.98 | 6 | 11.15 | 11.11 | 17 | 2.32 | 1.62 |
| -10 | 55.65 | 53.38 | 14 | 1.63 | -2.75 | -23 | 1.91 | 2.51 | 7 | 26.79 | 26.85 | 18 | 3.13 | 3.38 |
| -12 | 8.19 | -7.81 | 8 0 -2 | 19.62 | 17.94 | -24 | 3.80 | 4.19 | 8 | 10.64 | 10.59 | 6 1 -1 | 17.72 | 16.08 |
| -14 | 18.75 | 18.81 | -4 | 2.66 | 2.36 | 1 1 0 | 69.18z | 107.55 | 9 | 7.87 | -7.40 | -2 | 10.86 | 7.08 |
| -16 | 24.65 | 24.86 | -6 | 17.42 | -17.99 | 1 | 20.00 | -20.35 | 10 | 6.43 | -5.59 | -3 | 2.73 | -1.84 |
| -18 | 36.86 | -36.92 | -8 | 14.37 | 14.55 | 2 | 47.23 | -52.56 | 11 | 1.36u | -.60 | -4 | 21.45 | -21.00 |
| -20 | 1.33u | 2.34 | -10 | 4.85 | 4.24 | 3 | 9.45 | 8.62 | 12 | 23.49 | -21.47 | -5 | 13.67 | -13.98 |
| -22 | 3.17 | -3.05 | -12 | 3.32 | -2.53 | 4 | 19.30 | 19.40 | 13 | 8.25 | 6.73 | -6 | 20.20 | 20.71 |
| 3 0 0 | 53.46 | -51.45 | -14 | 16.98 | 17.32 | 5 | 37.73 | -37.58 | 14 | 20.26 | 19.08 | -7 | 6.06 | 5.01 |
| 2 | 40.10 | 40.96 | -16 | 9.18 | -9.84 | 6 | 32.30 | -28.96 | 15 | 1.39u | 1.27 | -8 | 2.50 | -3.00 |
| 4 | 35.06 | -34.64 | -18 | 8.41 | -9.15 | 7 | 22.85 | -19.78 | 16 | 8.43 | -6.75 | -9 | 9.36 | 9.10 |
| 6 | 15.42 | -14.64 | -20 | 1.12u | 2.03 | 8 | 33.12 | 27.09 | 17 | 1.26u | -1.65 | -10 | 18.17 | 19.66 |
| 8 | 20.91 | 19.53 | -22 | 6.98 | -6.32 | 9 | 15.23 | 10.97 | 18 | 4.63 | -4.33 | -11 | 15.78 | -16.10 |
| 10 | 18.27 | -16.63 | -24 | 6.39 | 5.69 | 10 | 27.32 | 21.54 | 19 | 1.02u | -.89 | -12 | 7.99 | 7.90 |
| 12 | 28.80 | 25.66 | 8 0 0 | 12.48 | -12.74 | 11 | 1.72 | -.17 | 20 | 5.74 | 5.58 | -13 | 11.43 | 11.28 |
| 14 | 17.38 | 16.47 | 2 | 6.37 | 7.43 | 12 | 26.66 | -22.18 | 21 | 1.76 | -1.98 | -14 | 19.21 | -21.47 |
| 16 | 13.16 | -13.41 | 4 | 8.59 | -9.01 | 13 | 25.88 | 22.48 | 4 1 -1 | 10.48 | 13.86 | -15 | 1.41u | -1.32 |
| 18 | 3.73 | 3.78 | 6 | 12.22 | -13.93 | 14 | 3.37 | 2.21 | -2 | 30.15 | -29.61 | -16 | 3.47 | -3.34 |
| 20 | 6.18 | -6.80 | 8 | 10.71 | 9.86 | 15 | 15.16 | -14.37 | -3 | 12.73 | 13.04 | -17 | 7.04 | -7.78 |
| 4 0 -2 | .84u | -1.51 | 9 0 -2 | 7.50 | -6.69 | 16 | 18.96 | 18.64 | -4 | 11.45 | -10.87 | -18 | 3.48 | -3.76 |
| -4 | 52.22 | -54.24 | -4 | 17.29 | -15.62 | 17 | 4.86 | -4.54 | -5 | 21.73 | -21.39 | -19 | 6.17 | 6.78 |
| -6 | 10.54 | -9.36 | -6 | 6.21 | 5.62 | 18 | 6.22 | -6.29 | -6 | 15.60 | 15.02 | -20 | 2.87 | -1.85 |
| -8 | .93u | -1.40 | -8 | 8.68 | -8.09 | 19 | 5.58 | 5.50 | -7 | 4.08 | -3.31 | -21 | 4.33 | -4.51 |
| -10 | 29.86 | -28.98 | -10 | 3.02 | 2.55 | 20 | 8.50 | 7.50 | -8 | 16.31 | -16.72 | -22 | 6.60 | 6.98 |
| -12 | 37.73 | 36.59 | -12 | 29.22 | 27.30 | 21 | 3.31 | -3.35 | -9 | 27.29 | -28.48 | -23 | 2.93 | 2.39 |
| -14 | 11.44 | 11.29 | -14 | 10.50 | -11.23 | 22 | 3.04 | -3.64 | -10 | 9.52 | -9.65 | -24 | .81u | 1.38 |
| -16 | 3.99 | -4.28 | -16 | 1.24u | -.40 | 2 1 -1 | 52.56z | 75.18 | -11 | 15.15 | 16.31 | 6 1 0 | 17.80 | 17.45 |
| -18 | 11.75 | 11.83 | -18 | 1.60 | -1.41 | -2 | 48.30z | -65.76 | -12 | 3.89 | 3.06 | 1 | 5.59 | -5.38 |
| -20 | 10.70 | -9.81 | -20 | 6.88 | -7.22 | -3 | 32.42 | -35.33 | -13 | 17.87 | 19.38 | 2 | 15.43 | -15.22 |
| -22 | 1.20u | -.01 | -22 | 8.82 | 7.86 | -4 | 5.85 | -5.65 | -14 | 18.35 | -19.22 | | | |
| -24 | 5.83 | 6.16 | 9 0 0 | 15.97 | 18.82 | -5 | 19.88 | -20.51 | -15 | 9.55 | -10.12 | 6 1 3 | 6.12 | 5.47 |
| 4 0 0 | 24.10 | 21.21 | 2 | 1.29u | -.52 | -6 | 3.61 | -3.46 | 4 1-16 | 1.40 | 1.90 | 4 | 9.72 | 9.82 |
| 2 | 30.45 | -28.95 | 4 | 10.41 | -12.48 | -7 | 2.32 | -2.84 | -17 | 10.96 | 11.89 | 5 | 3.67 | 3.52 |
| 4 | 19.87 | 19.47 | 6 | 8.18 | 7.53 | 2 1 -8 | 27.58 | -29.45 | -18 | 14.03 | 15.02 | 6 | 11.91 | -13.40 |
| 6 | 19.65 | 18.69 | 8 | 12.52 | -11.06 | -9 | 13.18 | -13.64 | -19 | 3.35 | -0.97 | 7 | 12.74 | -14.43 |
| 8 | 12.64 | -12.90 | 10 0 -2 | 1.73 | 1.22 | -10 | 45.61 | 45.65 | -20 | 2.33 | -3.03 | 8 | 13.87 | -15.22 |
| 10 | 24.10 | 24.02 | -4 | 4.36 | 4.74 | -11 | 22.74 | 23.70 | -21 | 7.93 | -8.17 | 9 | 4.20 | 4.61 |
| 4 0 12 | 16.73 | -15.84 | -6 | 13.90 | -13.37 | -12 | 4.40 | 3.80 | -22 | 8.44 | 8.36 | 10 | 11.39 | 11.99 |
| 14 | 5.99 | 6.86 | -8 | 1.28u | 1.71 | -13 | 13.95 | 13.57 | -23 | 5.40 | 4.99 | 11 | 4.18 | -4.16 |

TABLE 2 (b) (*Continued*)

| h k l | $F_o$ | $F_c$ | h k l | $F_o$ | $F_c$ | h k l | $F_o$ | $F_c$ | h k l | $F_o$ | $F_c$ | h k l | $F_o$ | $F_c$ | h k l | $F_o$ | $F_c$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 12 | 1.25u | 1.30 | 2 | 11.71 | 12.42 | -17 | 6.39 | -6.95 | -16 | 6.75 | 6.86 | -16 | 5.34 | -5.03 | | | |
| 13 | 4.02 | 3.82 | 3 | 4.46 | -5.13 | -18 | 6.12 | 6.74 | -17 | 4.55 | 4.25 | -17 | 5.87 | -5.54 | | | |
| 14 | 1.05u | -2.03 | 4 | 17.64 | -19.32 | -20 | 8.91 | -7.99 | -18 | 2.93 | -2.84 | -18 | 3.81 | 3.17 | | | |
| 15 | 4.47 | 4.19 | 5 | 8.14 | -8.33 | 8 1 0 | 6.50 | 6.01 | -19 | 6.16 | -5.61 | -19 | 3.07 | -2.54 | | | |
| 16 | 7.48 | 7.20 | 6 | 3.44 | 4.36 | 1 | 1.41u | 1.00 | 9 1-20 | 4.15 | 3.84 | 10 1 0 | 3.44 | -2.42 | | | |
| 7 1 -1 | 7.45 | 7.38 | 7 | 1.38 | -1.55 | 2 | 8.44 | -7.73 | -21 | 1.14 | 1.15 | 1 | 5.71 | 5.54 | | | |
| -2 | 11.68 | -11.49 | 8 | 10.34 | 9.55 | 3 | 13.86 | 13.92 | | 1.91 | 1.83 | 2 | 6.26 | -5.46 | | | |
| -3 | 11.46 | -11.38 | 9 | 8.18 | -7.67 | 4 | 1.37u | -.15 | 1 | 3.75 | 3.71 | 3 | 2.39 | -2.75 | | | |
| -4 | 22.51 | 20.99 | 10 | 10.31 | -9.41 | 5 | 15.48 | -16.11 | 2 | 5.47 | 5.99 | 4 | 11.77 | 10.96 | | | |
| -5 | 4.81 | 4.45 | 11 | 8.94 | 7.87 | 6 | 3.66 | .65 | 3 | 4.32 | -4.46 | 5 | 1.93 | -2.15 | | | |
| -6 | 12.53 | -11.66 | 12 | 6.26 | 5.61 | 7 | 1.23 | -.85 | 4 | 2.08 | -2.85 | 6 | 7.72 | -8.00 | | | |
| -7 | 6.29 | -6.02 | 13 | 5.95 | 5.01 | 8 | 4.19 | -3.28 | 5 | 2.53 | 3.06 | 11 1 -1 | 6.36 | 6.53 | | | |
| -8 | 5.23 | 4.79 | 1 14 | 5.25 | 4.80 | 9 | 4.30 | 3.57 | 6 | 9.88 | 8.38 | -2 | 8.46 | -7.37 | | | |
| -9 | 1.36u | -.43 | 8 1 -1 | 2.01u | -.94 | 10 | 11.23 | 10.86 | 7 | 5.47 | -4.90 | -3 | 2.87 | -2.59 | | | |
| -10 | 16.39 | 16.84 | -2 | 8.49 | 7.77 | 9 1 -1 | 6.26 | 6.26 | 10 1 -1 | 1.68 | -.96 | -4 | 6.64 | 5.24 | | | |
| -11 | 11.03 | 10.88 | -3 | 6.32 | 5.31 | -2 | 12.41 | -11.74 | -2 | 10.93 | 11.69 | -5 | 3.79 | -2.86 | | | |
| -12 | 11.31 | -11.88 | -4 | 17.89 | -19.58 | -3 | 5.72 | -5.05 | -3 | 8.03 | 7.81 | -6 | 3.09 | 1.93 | | | |
| -13 | 1.41u | -1.23 | -5 | 15.62 | -13.62 | -4 | 5.75 | 4.70 | -4 | 3.08 | -3.34 | -7 | 2.08 | 1.49 | | | |
| -14 | 10.31 | 10.30 | -6 | 1.99u | .05 | -5 | 1.98 | -2.59 | -5 | 6.95 | -7.41 | -8 | 6.23 | -5.49 | | | |
| -15 | 1.41 | -.19 | -7 | 2.00 | -1.38 | -6 | 1.98 | -2.52 | -6 | 3.37 | -4.01 | -9 | 3.58 | -3.49 | | | |
| -16 | 4.43 | 4.64 | -8 | 3.99 | 1.91 | -7 | 2.42 | -3.61 | -7 | 7.98 | -7.69 | -10 | 8.10 | 7.62 | | | |
| -17 | 4.13 | -4.12 | -9 | 2.83 | 2.79 | -8 | 7.26 | -5.99 | -8 | 2.55 | 2.67 | -11 | 1.41 | -.62 | | | |
| -18 | 10.02 | -11.38 | -10 | 12.83 | -11.96 | -9 | 5.57 | -4.86 | -9 | 5.52 | 5.98 | -12 | 7.47 | -5.86 | | | |
| -19 | 3.84 | -3.39 | -11 | 10.13 | 9.54 | -10 | 3.91 | 3.70 | -10 | 8.14 | -8.00 | -13 | 7.43 | 7.21 | | | |
| -20 | 3.20 | 3.18 | -12 | 27.40 | 27.71 | -11 | 14.93 | 13.54 | -11 | 5.11 | -4.50 | -14 | 3.08 | -3.52 | | | |
| -21 | 2.24 | 1.62 | -13 | 4.45 | 3.93 | -12 | 3.04 | -2.79 | -12 | 2.11 | -2.07 | | | | | | |
| -22 | 3.91 | -4.04 | -14 | 1.40u | -.69 | -13 | 2.68 | -2.49 | -13 | 7.95 | 6.60 | 11 1-15 | 4.06 | -4.24 | | | |
| 7 1 0 | 13.66 | -13.16 | -15 | 3.64 | -3.50 | -14 | 1.86 | -.49 | -14 | 8.44 | 7.22 | -16 | 4.50 | 4.02 | | | |
| 1 | 14.21 | 15.59 | -16 | 7.37 | -8.10 | -15 | 1.81 | -1.72 | -15 | 4.93 | 3.94 | 11 1 0 | 5.68 | 5.44 | | | |

"u": "Unobserved" reflections; "z" reflections given zero weight

The structure factors corresponding to the set of co-ordinates listed in Table 3(a) and (b), are given in Table 2(a) and (b). Little significance is attached to the values of the thermal parameters, in particular of $u_{22}$, and these are not listed.

TABLE 3

Atomic co-ordinates and standard deviations (Å)

(a) γ-Modification

| Atom | $x$ | σ | $y$ | σ | $z$ | σ |
|---|---|---|---|---|---|---|
| C(1) * ..... | 4·472 | (6) | 1·318 | (13) | 0·449 | (7) |
| C(2) ..... | 3·515 | (6) | 2·361 | (14) | 0·746 | (7) |
| C(3) ..... | 3·677 | (6) | 3·087 | (14) | 1·842 | (7) |
| C(4) ..... | 2·766 | (6) | 4·105 | (13) | 2·222 | (7) |
| C(5) ..... | 2·926 | (7) | 4·855 | (14) | 3·340 | (6) |
| C(6) ..... | 1·836 | (7) | 5·764 | (16) | 3·387 | (8) |
| C(7) ..... | 0·878 | (8) | 5·611 | (16) | 2·351 | (7) |
| S ..... | 1·237 | (2) | 4·425 | (5) | 1·232 | (2) |
| O(1) ..... | 4·148 | (5) | 0·642 | (10) | −0·643 | (5) |
| O(2) ..... | 5·563 | (4) | 1·119 | (9) | 1·210 | (4) |

(b) β-Modification

| | | | | | | |
|---|---|---|---|---|---|---|
| C(1) ..... | 1·124 | (5) | 0·439 | (12) | 1·901 | (5) |
| C(2) ..... | 2·054 | (6) | 0·793 | (12) | 3·350 | (5) |
| C(3) ..... | 1·711 | (5) | 0·384 | (13) | 4·473 | (5) |
| C(4) ..... | 2·553 | (5) | 0·599 | (12) | 5·934 | (5) |
| C(5) ..... | 2·171 | (6) | 0·232 | (13) | 7·104 | (5) |
| C(6) ..... | 3·270 | (7) | 0·577 | (13) | 8·399 | (6) |
| C(7) ..... | 4·404 | (7) | 1·132 | (13) | 8·195 | (6) |
| S ..... | 4·216 | (1) | 1·305 | (4) | 6·448 | (1) |
| O(1) ..... | 1·635 | (5) | 0·818 | (9) | 0·915 | (4) |
| O(2) ..... | −0·007 | (4) | −0·131 | (9) | 1·661 | (4) |

* Refer to diagram for numbering of atoms.

## DISCUSSION

*Molecular Dimensions.*—Bond lengths and angles, which must be regarded as approximate in view of the necessarily incomplete refinement of the $y$ parameters, are shown in Figures 1 and 2. The e.s.d. of the C–C and C–S bonds are 0·02 and 0·01 Å in both structures; the e.s.d. of the bond angles are 1°. Since these are of the order of the differences in length of equivalent bonds in the two structures we do not wish to attribute significance to these differences. The C–C and C–S bond lengths averaged between the two structures are given in Table 4, as are also the averaged bond angles within the thiophen ring. Comparison with the comparable bond

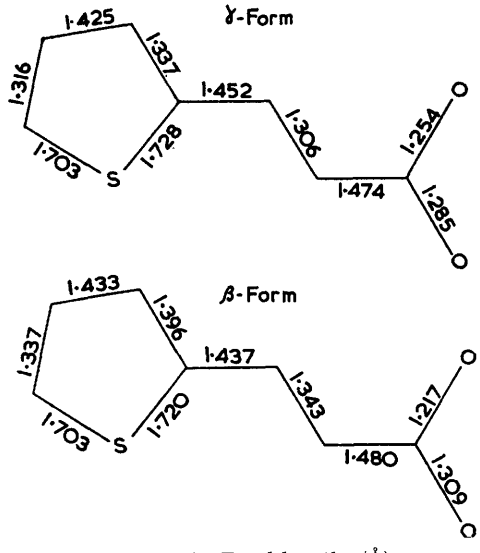



FIGURE 1 Bond lengths (Å)

lengths and angles of thiophen-2-carboxylic acid derived from a three-dimensional analysis [8] shows fair agreement. On the other hand a recent three-dimensional analysis of thiophen-3-carboxylic acid [9] reports unexpectedly large variations in the hetero-ring compared with the thiophen derivatives substituted in the 2-position. Evidently, the bond lengths of substituted thiophens merit further work.

The best planes of the four-carbon chain C(4—7),

[8] M. Nardelli, G. Fava, and G. Giraldi, *Acta Cryst.*, 1962, **15**, 737; P. Hudson and J. H. Robertson, *ibid.*, p. 913.
[9] P. Hudson and J. H. Robertson, *Acta Cryst.*, 1964, **17**, 497.

the thiophen ring [C(4—7), S], the ethylenic C(1—4), and carboxylic [C(2), C(1), O(1), O(2)] groups and the deviations of the atoms from these planes are listed in Table 5 (a) and (b). The hetero-ring is planar in both structures. The angles of twist between the thiophen rings and the ethylenic groups are 3° 10′ (γ) and 0° (β),

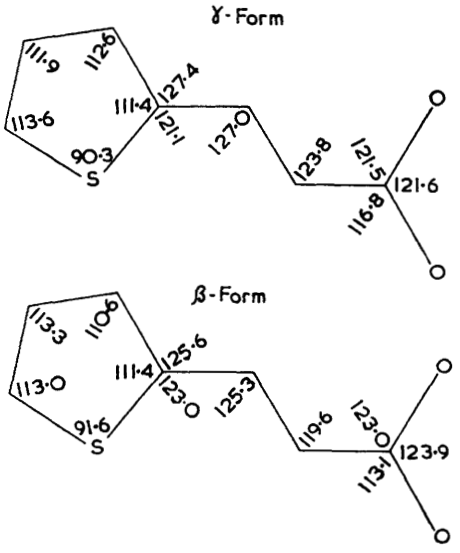



FIGURE 2 Bond angles (degrees)

and between the ethylene and carboxylic groups 1° 50′ (γ) and 4° 25′ (β).

As in furylacrylic acid [1] the exocyclic and endocyclic [C(4)—C(5)] double bonds are in the *trans*-position; the

TABLE 4

Comparison of bond lengths and angles

| | Thienylacrylic acid (averaged) | Thiophen-2-carboxylic acid [8] | Thiophen-3-carboxylic acid [9] |
|---|---|---|---|
| C(1)–C(2) | 1·47$_7$ Å | | |
| C(2)=C(3) | 1·32$_5$ | | |
| C(3)–C(4) | 1·44$_9$ | | |
| C(4)=C(5) | 1·36$_7$ | 1·362 | 1·406 |
| C(5)–C(6) | 1·42$_9$ | 1·414 | 1·437 |
| C(6)=C(7) | 1·32$_7$ | 1·363 | 1·508 |
| C(7)–S | 1·70$_3$ | 1·701 | 1·699 |
| C(4)–S | 1·72$_4$ | 1·693 | 1·708 |
| SC(4)C(5) | 111·4° | 111·8° | 110·4° |
| C(4)C(5)C(6) | 111·6 | 112·4 | 112·5 |
| C(5)C(6)C(7) | 112·6 | 111·9 | 113·3 |
| C(6)C(7)S | 113·3 | 111·8 | 106·0 |
| C(7)SC(4) | 91·0 | 92·0 | 98·0 |

*cis*-conformation of the exocyclic >C=C< and the carboxylic >C=O groups follows the rule established in Part XI.[10]

*Packing Arrangement.*—No abnormally short intermolecular contacts have been found; distances less than 3·6 Å are given in Tables 6 (a) and (b). OH · · · O distances of 2·57 Å (γ) and 2·64 Å (β) are normal.

The packing arrangements of the two forms follow the pattern established in the cinnamic acid series. The stable form consists of two stacks of centrosymmetric, nearly planar, hydrogen-bonded molecule pairs arranged in parallel along the *b* axis, the two sets being related by the twofold screw axis parallel to *b*. The mean molecular plane is inclined at 62° to the stack axis; as a result of this steep inclination intrastack contacts between carbon atoms C(2) and C(3) of the exocyclic double bond are too long for interaction; consequently,

TABLE 5

(a) γ-Modification

(i) Equations of best planes *

| | $m_1$ | $m_2$ | $m_3$ | $d$ |
|---|---|---|---|---|
| Plane A: | | | | |
| C(4),C(5),C(6),C(7) ... | 5·9906 | 3·4961 | −7·3230 | 3·0385 |
| Plane B: | | | | |
| C(4),C(5),C(6),C(7),S | −5·9715 | −3·4874 | 7·3735 | −3·0144 |
| Plane C: | | | | |
| C(1),C(2),C(3),C(4) ... | 6·4322 | 3·4570 | −6·9706 | 3·1929 |
| Plane D: | | | | |
| C(1),C(2),O(1),O(2)... | 6·1451 | 3·3733 | −7·5890 | 3·0357 |

(ii) Deviations (Å) from best planes

| Atom | Plane A | Atom | Plane B | Atom | Plane C | Atom | Plane D |
|---|---|---|---|---|---|---|---|
| C(4) | 0·010 | C(4) | −0·013 | C(1) | −0·009 | C(1) | −0·008 |
| C(5) | −0·016 | C(5) | 0·018 | C(2) | 0·008 | C(2) | 0·002 |
| C(6) | 0·016 | C(6) | −0·014 | C(3) | 0·010 | O(1) | 0·003 |
| C(7) | −0·010 | C(7) | 0·006 | C(4) | −0·009 | O(2) | 0·003 |
| | | S | 0·004 | | | | |
| S | −0·014 | C(3) | −0·002 | O(1) | −0·070 | C(3) | −0·064 |
| C(3) | −0·004 | | | O(2) | 0·062 | | |

(b) β-Modification

(i) Equations of best planes *

| | $m_1$ | $m_2$ | $m_3$ | $d$ |
|---|---|---|---|---|
| Plane A: | | | | |
| C(4),C(5),C(6),C(7) ... | 4·1075 | −3·5333 | −2·7053 | −0·2377 |
| Plane B: | | | | |
| C(4),C(5),C(6),C(7),S | −4·1039 | 3·5340 | 2·6982 | 0·2363 |
| Plane C: | | | | |
| C(1),C(2),C(3),C(4) ... | −5·0566 | 3·3209 | 3·0865 | 0·0871 |
| Plane D: | | | | |
| C(1),C(2),O(1),O(2)... | 4·4883 | −3·4443 | −1·8058 | −0·0346 |

(ii) Deviations (Å) from best planes

| Atom | Plane A | Atom | Plane B | Atom | Plane C | Atom | Plane D |
|---|---|---|---|---|---|---|---|
| C(4) | −0·004 | C(4) | 0·005 | C(1) | −0·017 | C(1) | 0·004 |
| C(5) | 0·007 | C(5) | −0·007 | C(2) | 0·015 | C(2) | −0·001 |
| C(6) | −0·007 | C(6) | 0·007 | C(3) | 0·021 | O(1) | −0·002 |
| C(7) | 0·004 | C(7) | −0·004 | C(4) | −0·018 | O(2) | −0·002 |
| | | S | −0·000 | | | | |
| S | 0·001 | C(3) | −0·024 | O(1) | −0·116 | | |
| C(3) | 0·024 | | | O(2) | 0·059 | C(3) | 0·097 |

* Computed according to V. Schomaker, J. Waser, R. E. Marsh, and E. Bergman, *Acta Cryst.*, 1959, **12**, 600.

this form of the acid belongs to the γ-type and should be light-stable. We report elsewhere [2] that, in accordance with these crystallographic results, this form does not yield dimer. However, the material forms a photopolymer: if we admit, here as in the instance of furylacrylic acid,[1] that the excited exocyclic >C=C< group can react with the double bonds of the hetero-ring, and

[10] L. Leiserowitz and G. M. J. Schmidt, *Acta Cryst.*, 1965, **18**, 1058.

postulate further that polymerisation is initiated by an attack of the exocyclic on an endocyclic double bond, the crystal structure must show sufficiently close contacts (<4·3 Å) between C(2) or C(3) and the carbon atoms of the hetero-ring. That such contacts indeed exist is shown by Table 7(a).

TABLE 6

Short intermolecular contacts <3·6 Å

| (a) γ-Form | | | (b) β-Form | | |
|---|---|---|---|---|---|
| $A_{000}$ | $A_{0\bar{1}0}$ | | $A_{000}$ | $A_{010}$ | |
| C(1) | C(4) | 3·46 | O(1) | O(2) | 3·58 |
| C(3) | C(6) | 3·49 | O(1) | O(2) | 3·51 |
| | $\bar{A}_{110}$ | | | $A_{0\bar{1}0}$ | |
| C(1) | O(2) | 3·48 | C(4) | S | 3·57 |
| C(2) | O(2) | 3·60 | C(6) | C(7) | 3·57 |
| | $\bar{A}_{020}$ | | | $B_{000}$ | |
| S | S | 3·46 | C(6) | O(2) | 3·51 |
| | | | C(5) | O(2) | 3·30 |
| | $B_{100}$ | | | $\bar{B}_{000}$ | |
| C(5) | O(2) | 3·49 | C(6) | O(1) | 3·56 |
| | $\bar{B}_{010}$ | | | $B_{1\bar{1}0}$ | |
| C(5) | O(1) | 3·36 | C(2) | S | 3·54 |
| C(6) | O(1) | 3·34 | | | |

| Co-ordinates of equivalent positions | Symbol |
|---|---|
| $xyz$ | A |
| $\bar{x}\bar{y}\bar{z}$ | $\bar{A}$ |
| $\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$ | B |
| $x, \frac{1}{2}-y, \frac{1}{2}+z$ | $\bar{B}$ |

$A_{pqr}$ denotes fractional co-ordinates $p+x, q+y, r+z$.

The metastable form can be described as consisting of two stacks of nearly planar hydrogen-bonded molecules arranged in parallel along the short $b$ axis, the two stacks being related by the twofold screw axis parallel to $b$. The mean molecular plane is inclined at 27° to the stack axis. As a result of this arrangement, and by analogy with the cinnamic acids crystallising in the 4 Å packing-type, the exocyclic >C=C< groups should, on irradiation, give the dimer of symmetry $m$ (II), which has indeed been isolated in high yield.

However, the β-modification also yields polymer, though in small amounts. It has so far not been possible to establish unambiguously whether the polymer arises indirectly from the thermodynamically stable modification *via* a (thermal) phase transformation or whether it is formed in the β-lattice. Analysis of the distances from C(2) and C(3) to the carbon atoms of the hetero-ring shows in the β-, as in the γ-form, sufficiently numerous and short distances (Table 7b) to permit initiation of polymerisation by the mechanism postulated above, so that direct polymerisation in the β-structure is geometrically at least possible. The modification is thus seen to resemble in its packing arrangement and photo-behaviour the furylacrylic acid analysed in Part XVI.

In conclusion we draw attention to the somewhat unusual situation whereby the metastable modification is significantly denser than the stable form (Table 1). This problem will be discussed in detail elsewhere; here we note that in the β-form each sulphur atom is close-packed to four other sulphurs: of these two make contact of 3·91 Å along the $b$ translation while two other contacts of 3·89 Å are generated by the twofold screw axis along $b$. The stable but less dense form shows only one rather short contact of 3·46 Å between sulphur atoms related by a centre of symmetry.

TABLE 7

Intermolecular contacts (<4·3 Å) between carbon atoms of exocyclic and endocyclic double bonds

| (a) γ-Form | | | (b) β-Form | | |
|---|---|---|---|---|---|
| $A_{000}$ * | $A_{0\bar{1}0}$ | | $A_{000}$ | $A_{010}$ | |
| C(2) | C(4) | 3·73 | C(2) | C(3) | 3·73 |
| C(2) | C(5) | 3·74 | C(4) | C(5) | 3·79 |
| C(2) | C(6) | 3·71 | | | |
| C(2) | C(7) | 3·73 | | $A_{0\bar{1}0}$ | |
| C(3) | C(4) | 4·15 | C(3) | C(4) | 3·96 |
| C(3) | C(5) | 3·72 | C(4) | C(7) | 4·14 |
| C(3) | C(6) | 3·49 | C(5) | C(6) | 3·83 |
| C(3) | C(7) | 3·85 | C(5) | C(7) | 3·69 |
| C(4) | C(6) | 3·74 | C(6) | C(7) | 3·57 |
| C(4) | C(7) | 4·02 | | | |
| C(5) | C(6) | 4·27 | | $\bar{A}_{101}$ | |
| | | | C(6) | C(6) | 3·90 |
| | $\bar{B}_{000}$ | | C(6) | C(7) | 3·86 |
| C(6) | C(7) | 3·76 | C(7) | C(7) | 4·27 |
| C(7) | C(7) | 3·69 | | | |
| | | | | $\bar{A}_{111}$ | |
| | $B_{0\bar{1}0}$ | | C(6) | C(7) | 4·11 |
| C(6) | C(7) | 3·96 | C(7) | C(7) | 3·98 |
| C(7) | C(7) | 3·69 | | | |
| | | | | $B_{000}$ | |
| | $\bar{B}_{01\bar{1}}$ | | C(3) | C(5) | 4·08 |
| C(2) | C(5) | 3·88 | | | |
| C(2) | C(6) | 4·03 | | $B_{0\bar{1}0}$ | |
| | | | C(3) | C(5) | 4·23 |
| | | | | $B_{1\bar{1}0}$ | |
| | | | C(2) | C(7) | 4·17 |

* For definition of symbols see Table 6.

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