JEFFREY, G. A., GHOSE, S. & WARWICKER, J. O. (1961). *Acta Cryst.* **14**, 881.
KARLE, I. L. & KARLE, J. (1963). *Acta Cryst.* **16**,969.
KARLE, I. L., BRITTS, K. & GUM, P. (1964). *Acta Cryst.* **17**, 496.
KIM, S. H. (1964). *Illustrative Example of Beursken's Sign Correlation by the Sayre Equation.* Tech. Rep. The Crystallographic Laboratory, Univ. of Pittsburgh, Pittsburgh 13, Pa., U.S.A.
MATSUDA, H., OSAKI, K. & NITTA, I. (1958). *Bull. Chem. Soc. Japan* **31**, 611.
MULLIKEN, R. S. (1952*a*). *J. Phys. Chem.* **56**, 801.
MULLIKEN, R. S. (1952*b*). *J. Amer. Chem. Soc.* **74**, 811.
PAULING, L. (1960). *The Nature of the Chemical Bond.* Ithaca: Cornell Univ. Press.
PERSON, W. B. & WILLIAMS, D. G. (1957). *J. Phys. Chem.* **61**, 1017.
PREISLER, P.W. & BERGER, L. (1942). *J. Amer. Chem. Soc.* **64**, 67.
RABINOWITZ, I. N. & KRAUT, J. (1964). *Acta Cryst.* **17**, 159.
ROLLETT, J. S. & DAVIES, D. R. (1955). *Acta Cryst.* **8**, 125.
SAKURAI, T. (1965). *Acta Cryst.* **19**, 320.
SAYRE, D. (1952). *Acta Cryst.* **5**, 60.
SCHOMAKER, V., WASER, J., MARSH, R. E. & BERGMAN, G. (1959). *Acta Cryst.* **12**, 600.
SHIONO, R. (1962). *IBM 7070 Programs for Isotropic and Anisotropic Structure Factor Calculations.* Technical Report No. 29, The Crystallographic Laboratory, University of Pittsburgh, Pittsburgh 13, Pa., U.S.A.
SHIONO, R. (1963). *Three-Dimensional Differential Fourier Synthesis Program for IBM 7070 Computer.* Tech. Rep. No. 42, The Crystallographic Laboratory, Univ. of Pittsburgh, Pittsburgh 13, Pa., U.S.A.
SHIONO, R. (1963). *ORFLS PX for IBM* 7090. The Crystallographic Laboratory, Univ. of Pittsburgh, Pittsburgh 13, Pa., U.S.A.
SHIONO, R. (1964). *Analysis of Thermal Vibration Ellipsoids and Rigid Body Translation and Libration Calculation.* Original program by P. K. Gantzel, C. L. Coulter and K. N. Trueblood, and adapted to the Michigan System IBM 7090, by R. Shiono. The Crystallographic Laboratory, Univ. of Pittsburgh, Pittsburgh 13, Pa., U.S.A.
SMITH, G. S. & ALEXANDER, L. E. (1963). *Acta Cryst.* **16**, 462.
SUTTON, L. E. (1958). *Tables of Interatomic Distances.* Special Publication No. 11. London: The Chemical Society.
TROTTER, J. (1960). *Acta Cryst.* **13**, 86.
WONG, C-H., MARSH, R. E. & SCHOMAKER, V. (1964). *Acta Cryst.* **17**, 131.

Acta Cryst. (1965). **19**, 992

Crystal Structures of D, L-Homocysteine Thiolactone Hydrochloride: Two Polymorphic Forms and a Hybrid*

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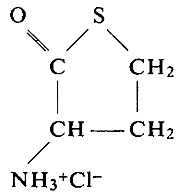
The structures of three different crystalline forms of D,L-homocysteine thiolactone hydrochloride have been determined by X-ray diffraction techniques. Two of the crystal forms are polymorphs: one crystallizes in space group *Pbca* and the other crystallizes in space group $Pbc2_1$. The third form is a hybrid in which both of these polymorphs coexist. The *Pbca* and $Pbc2_1$ domains of the hybrid crystal scatter X-rays independently but have their corresponding unit-cell axes oriented in the same directions.

The structures of the polymorphs were arrived at by conventional heavy-atom Fourier and vector-coincidence methods, and each structure was refined by two different least-squares criteria, one based on reflection amplitudes and the other based on reflection intensities. To verify the structure of the hybrid form, a linear combination of reflection intensities from the *Pbca* and $Pbc2_1$ crystals was scaled by least squares to the reflection intensities of the hybrid crystal; the agreement obtained between the reflection intensities corresponds to a conventional R index of 9 %.

The crystal structures of the two polymorphs are very similar. The five-membered thiolactone ring is in the envelope conformation, with four atoms lying in a plane from which the β carbon atom is displaced by approximately 0·7 Å. In both structures the molecules are packed in layers perpendicular to the unit-cell c axis, and there is a network of hydrogen bonds between the ammonium group and chloride ions. Apparent small differences in bond-lengths and angles between molecules in the two structures are not significant; differences of about the same magnitude were produced by the two alternate methods of refinement for each individual polymorph.

Introduction

The structures of three different crystalline forms of D,L-homocysteine thiolactone hydrochloride (HTL)



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* Most of the material in this communication has been abstracted from a Ph.D. thesis submitted by S.T.F. to the University of Washington in 1964.

will be described in this communication. The structures are very closely related; in fact one of them is a mixture of the other two, with at least the outward appearance of an ordinary single crystal. Crystals of all three forms were grown under similar conditions.

The first crystals we obtained happened to be the hybrid form (but we were not aware of this until much later, after the structures of the other forms had already been determined) with apparent space group *Pbca*, but pseudo $Pbc2_1$. When two plausible trial structures, one in each of these space groups, failed to refine below an R index of 21%, we decided to recrystallize the HTL in the hope of obtaining better data crystals. Instead, a new crystal form with authentic space group symmetry $Pbc2_1$ was discovered. When the new intensity data were used, it then became possible to refine the $Pbc2_1$ trial structure to an acceptably low value for the R index.

However, renewed attempts to solve the structure of the hybrid crystal continued to fail, and so the recrystallization experiments were resumed. Eventually we obtained *Pbca* crystals which were *not* hybrids, and once again a trial structure deduced from the original data, this time the *Pbca* trial structure, was readily refined with data obtained from the new crystal form.

Finally, by comparing reflection intensities from the original crystal form with reflection intensities from the two well-behaved forms, it was possible to demonstrate that the original crystal was actually a hybrid in which the two polymorphs coexist.

The two polymorphic forms of HTL will be referred to collectively as 'polymorphs' and individually as HTL–*Pbca* and HTL–$Pbc2_1$ throughout the rest of this communication. We have adopted the terminology of Ubbelohde & Woodward (1946*b*) in designating the third crystal form 'hybrid' HTL.

Experimental

All crystals were grown at room temperature from solutions in methanol–nonsolvent mixtures. The hybrid and $Pbc2_1$ crystals were obtained with HTL purchased from Mann Research Laboratories, Inc., and the *Pbca* crystals with HTL from the California Corporation for Biochemical Research.

The hybrid crystal form, HTL-hybrid, was crystallized by slow evaporation from a solution of HTL in a mixture of methanol and amyl alcohol. The crystals exhibited a lath-like habit with prominent (100) faces and with the long dimension parallel to the unit-cell c axis. Although most crystals large enough for data collection were severely cracked, there was no evidence of multiple growth. Systematic absence of reflections $0kl$ with k odd, $h0l$ with l odd, and $hk0$ with h odd apparently established the space group as *Pbca*. However, the extreme weakness of most h odd reflections indicated pseudo-$Pbc2_1$ symmetry (with the a axis halved). All reflections were sharp, and there was no indication of streaking. The data crystal, a fragment approximately 0·1 mm on a side, was dipped repeatedly into liquid nitrogen in an attempt to reduce possible extinction effects.

HTL-$Pbc2_1$ crystallized from a methanol solution in vapor equilibrium with methanol-dioxan (1:1). The crystal habit was similar to that of HTL-hybrid. The crystal density and systematic absence of reflections $0kl$ for k odd and $h0l$ for l odd established its space group as $Pbc2_1$ (space group no. 29, $Pca2_1$, for the setting given in *International Tables*). The dimensions of the data crystal were 0·08 × 0·1 × 0·12 mm.

Well-formed large plates, (100) faces prominent, of HTL-*Pbca* crystallized from an evaporating solution in methanol and amyl alcohol. The same systematic absences were observed as for HTL-hybrid, establishing the space group as *Pbca*. Data were collected with a crystal fragment approximately 0·1 mm along each edge.

Unit-cell constants for the three crystal forms are given in Table 1. Lattice parameters for HTL-hybrid were measured by precession photography; uncertainties were estimated from repeated measurement of the precession films. Lattice parameters and their estimated standard deviations for HTL-*Pbca* and HTL-$Pbc2_1$ were determined by least-squares treatment of 2θ angles measured with a General Electric XRD-5 diffractometer. Copper $K\alpha$ radiation was used throughout, for both intensity and lattice parameter data, a wavelength of 1·5418 Å being assumed for the mean of $K\alpha_1$ and $K\alpha_2$, or 1·54051 Å for $K\alpha_1$ where the two components were resolvable in high order reflections; all measurements were made at room temperature. Densities were obtained by free flotation in carbon tetrachloride-bromobenzene. The uncertainties are r.m.s. deviations among six independent measurements for HTL-hybrid and three independent measurements for each of HTL-$Pbc2_1$ and HTL-*Pbca*.

Intensities were collected on the diffractometer by a 2θ-scanning technique; stationary background counts were taken at both the start and finish of the peak scan. All unique reflections within range of the instrument ($2\theta \leq 160°$) were examined; 1452 reflections measured, with 66% observed for HTL-hybrid; 796 reflections measured, with 86% observed for HTL-$Pbc2_1$; and 1413 reflections measured, with 90% observed for HTL-*Pbca*. For HTL-hybrid the criteria of observability were left to the judgment of the diffractometer

Table 1. *Unit-cell constants*

	a	b	c	D_{meas}	D_{calc}	Z
HTL-Hybrid	19·55 ± 0·03 Å	9·29 ± 0·02 Å	7·23 ± 0·02 Å	1·535 ± 0·003 g.cm^{-3}	—	–
HTL-$Pbc2_1$	9·806 ± 0·003	9·321 ± 0·002	7·321 ± 0·002	1·519 ± 0·001	1·525 g.cm^{-3}	4
HTL-*Pbca*	19·512 ± 0·002	9·296 ± 0·003	7·272 ± 0·001	1·543 ± 0·002	1·547	8

operator and intensities of unobserved reflections were not recorded; an estimated minimum observable F_o was assigned to unobserved reflections during data reduction. For HTL-$Pbc2_1$ and HTL-*Pbca*, on the other hand, the intensities of all reflections were recorded and the criterion of observability was based on counting statistics.

Although absorption effects are significant for a compound with the elementary composition of HTL, no correction was applied, and this is probably a source of appreciable error. Nevertheless, since all the intensity data were collected with small and approximately equidimensional crystal fragments, the error is probably not excessive.

Structure determination and initial refinement of HTL-*Pbca* and HTL-$Pbc2_1$

A combination of vector-coincidence and heavy-atom Fourier methods was used to deduce a plausible trial structure in space group *Pbca* from the HTL-hybrid intensity data. However, full-matrix least-squares refinement with a slightly modified version of the Busing & Levy (1959) program failed to reduce the *R* index below 21%. Since only 38% of the *h*-odd reflections for HTL-hybrid were observed, it was decided to begin again, ignoring the *h*-odd reflections entirely, and attempt to solve the structure in space group $Pbc2_1$. A second trial structure, very closely related to the first, was readily obtained, but once more it could not be refined below an *R* index of 21%.

Since neither trial structure could be refined with the HTL-hybrid intensity data, it seemed possible that the original data crystal was disordered in a manner somewhat analogous to azulene (Robertson, Shearer, Sim & Watson, 1962). A difference-Fourier synthesis phased on the *Pbca* trial structure apparently verified this conclusion: the difference map contained regions of negative electron density surrounding the positions of several of the input atoms and positive peaks in locations related to these positions by reflection through a mirror at $z=\frac{1}{4}$. For this reason we suspected that HTL-hybrid was a disordered *Pbca* structure in which alternate molecules were randomly replaced by their enantiomorph. However, trial structures which included the original *Pbca* trial structure, plus its mirror image, as fractional atoms could not be refined. In order to eliminate the possibility that HTL-mixed contained molecules with different conformations of the thiolactone ring, we also tried to refine several trial structures in which only certain atoms were replaced by two fractional atoms. Again, no refinable trial structure was obtained. Finally, in desperation, we decided to recrystallize the HTL and start all over with new data crystals.

The subsequent discovery of two additional crystal forms, one with genuine *Pbca* symmetry and the other with genuine $Pbc2_1$ symmetry, has already been outlined. After these crystals were obtained, we were able to refine each of the above trial structures with newly collected intensity data from the corresponding polymorph. Atomic scattering factors given in *International Tables for X-ray Crystallography* (1962) were used throughout the calculations. For the refinement of both polymorphs a weighting scheme similar to Hughes's (1941) was applied, the weight assigned to each reflection being the smaller of the two quantities $[\sigma(F)]^{-2}$ or $(0{\cdot}05F)^{-2}$, where $\sigma(F)$ was estimated from counting statistics. The quantity minimized was $\Sigma w(F_o-kF_c)^2$. Unobserved reflections for which F_c was less than F_o were omitted from the matrix of normal equations.

Refinement calculations of HTL-$Pbc2_1$ were carried out on an IBM-709 computer with the full-matrix least-squares program of Busing & Levy (1959). Seven cycles reduced the *R* index to 10·8%, at which point difference-Fourier synthesis and bond-length calculations indicated an erroneous placement of C(4). Refinement was then continued, with new C(4) coordinates, to an *R* index of 6·2%. The eight hydrogen atoms of the asymmetric unit were located in a new difference-Fourier synthesis, albeit with some uncertainty, and introduced into the structure with the fixed anisotropic temperature factors of the atoms to which they were covalently bonded. Three final refinement cycles were calculated in which all parameters except hydrogen-atom temperature factors were varied. The last parameter shift was in no case greater than one standard deviation. The final *R* index was 4·9% for 682 equally weighted observed reflections. The estimated standard deviation for an observation of unit weight, $[\Sigma w(\Delta F)^2/(m-s)]^{\frac{1}{2}}$, was 1·28.

In the case of HTL-*Pbca*, refinement calculations were carried out on a CDC-1604 machine with a modified block-diagonal version of the least-squares program of Gantzel, Sparks & Trueblood (1961). Seven cycles of refinement reduced the *R* index to 6·5%. The eight highest peaks (0·55–0·86 e.Å^{-3}) in a difference-Fourier synthesis calculated at this point were in reasonable locations for hydrogen atoms. When these were introduced into the structure, each with the fixed anisotropic temperature factor of the atom to which it was covalently bonded, the *R* index dropped to 4·9%. Nevertheless the parameter shifts on the next cycle were still unreasonably large and further refinement cycles failed to cause convergence. Indeed, during subsequent cycles it became obvious that most of the parameters were oscillating with increasing amplitude about fairly well-defined mean values. Finally each parameter was assigned this mean value and a damping factor of 0·5 was applied to all subsequently calculated shifts. This procedure succeeded in causing convergence in three additional cycles. The mean final shift was 0·2σ, and no shift was larger than σ. The *R* index for 1265 equally weighted observed reflections was 4·2% and the estimated standard deviation for an observation of unit weight was 1·46. At a later date, when a *full-matrix* least-squares program for the CDC-1604 computer became available, it was used to calculate one additional refinement cycle in order to confirm the validity of the block-diagonal treatment. This cycle produced a maximum parameter shift of 0·2σ, and a mean shift of only 0·08σ.

Difference-Fourier syntheses, phased on final parameters for all atoms, were calculated for both polymorphs as a concluding check on the refinement. No interpretable features could be seen.

Deduction of the crystal structure of HTL-hybrid

Even though essentially correct trial structures for both polymorphs had been derived from the intensity data of HTL-hybrid, the structure of this crystal form was as yet unknown. Two possible explanations seemed reasonable: (1) HTL-hybrid was disordered in a way which had not occurred to us, and (2) HTL-hybrid was composed of separate domains of HTL-*Pbca* and HTL-$Pbc2_1$ which scattered X-rays independently but had their unit-cell axes oriented in the same directions. Since several composite trial structures (the calculated structure factors for one of which were equivalent to a linear combination of F_c's of the two polymorphs) designed to allow for certain kinds of random disorder in space group *Pbca* had already failed to refine, we decided to test the second of these hypotheses. The idea that there were independent scattering regions within the HTL-hybrid crystal was further supported when high-order reflections for three freshly grown HTL-hybrid single crystals were found to exhibit pronounced splitting. For example, four distinct peaks, with 2θ values of 147·7°, 147·9°, 149·1°, and 150·2°, were observed for the 24,2,0 reflection. These values correspond reasonably well with Bragg angles calculated for Cu $K\alpha_1$ and α_2 from lattice parameters of HTL-$Pbc2_1$ (146·2° and 147·2°) and HTL-*Pbca* (148·2° and 149·2°).

As a further test of the hybrid-crystal hypothesis, a linear combination of F_o^2 (*Pbca*) and F_o^2 ($Pbc2_1$), each on an absolute scale, was scaled by least-squares to F_o^2 (hybrid), and the agreement index of the resulting 'calculated intensities' for the best linear combination was compared with the corresponding agreement obtained from the intensities for either polymorph alone. Specifically, scale constants k_1 and k_2 were adjusted to minimize $\Sigma\{F_o^2(\text{hybrid}) - [k_1F_o^2(Pbca) + k_2F_o^2(Pbc2_1)]\}^2$, but were otherwise unconstrained. The agreement index was calculated as $R_2 = \Sigma|F_o^2\ (\text{hybrid}) - [k_1F_o^2\ (Pbca) + k_2F_o^2\ (Pbc2_1)]|/\Sigma F_o^2\ (\text{hybrid})$. Only 863 reflections which were sufficiently strong to be considered 'observed' for all crystal forms were included in the summations.

Results were as follows:

	R_2	k_1	k_2
HTL (*Pbca*) only	36·7%	5·15	0
HTL ($Pbc2_1$) only	25·5%	0	23·42
Linear combination	11·2%	2·12	15·10

Comparable results were also obtained when the F_c^2 instead of F_o^2 of the polymorphs were similarly scaled to the F_o^2 of the hybrid crystal; corresponding R_2 values were 35·7% for *Pbca* only, 27·0% for $Pbc2_1$ only, and 13·1% for the best linear combination. The conventional R index, taking F_c (hybrid) to be $[k_1F_o^2\ (Pbca) + k_2F_o^2\ (Pbc2_1)]^{\frac{1}{2}}$, was 8·6% for the 863 'observed' reflections.

We believe that the much smaller value for R_2 obtained with the best linear combination, when compared with the value for R_2 obtained with either polymorph alone, is fairly good verification of the hybrid structure proposed for HTL-hybrid.

Three estimates of the relative number of HTL molecules in *Pbca* and $Pbc2_1$ regions of the hybrid crystal were made. These were based upon (1) the observed densities of the three crystal forms; (2) the least-squares scale constants, k_1 and k_2; and (3) comparison of the ratio $P(\frac{1}{2}, 0, 0)/P(0, 0, 0)$ in the HTL-hybrid and HTL-*Pbca* Patterson maps (the origin peak from the HTL-$Pbc2_1$ portion contributes to $P(\frac{1}{2}, 0, 0)$ in a Patterson map calculated with the HTL-hybrid intensities). The values obtained, expressed as per cent of the molecules in HTL-$Pbc2_1$ regions, are 32%, 64%, and 58%, respectively. Although the estimates vary considerably, it should be noted that the low figure based upon density measurements is probably the most inaccurate. In any case, all three results do indicate that the hybrid crystal form must be composed of roughly equal amounts of the constituent polymorphs.

The arrangement of *Pbca* and $Pbc2_1$ regions within the hybrid crystal remains unknown. As far as our data are concerned, the size of individual *Pbca* and $Pbc2_1$ regions could range from separate randomly intermixed mosaic blocks, on the one hand, to regions so large, on the other hand, that the crystal would be considered a heterogenous twin.

The existence of different subcrystalline domains within a 'single' crystal was first observed by Ubbelohde & Woodward while studying continuous phase transitions of Rochelle salt (1946*a*) and potassium dihydrogen phosphate (1946*b*). Since then, crystals of many other compounds which undergo continuous phase transitions have also been observed to change into crystal hybrids near the transition temperature (Ubbelohde, 1963). It would be of interest to know whether these polymorphs of HTL could exist in equilibrium at room temperature, and whether HTL-hybrid could result from a continuous phase transition. We have no data which would bear on these questions and it is possible that HTL-hybrid may instead result from co-crystallization of the two polymorphs.

F^2 Refinement of HTL-*Pbca* and HTL-$Pbc2_1$

When a full-matrix least-squares program for the CDC 1604 machine became available to us [adapted by Dr R. A. Alden from the program of Busing, Martin & Levy (1962)], we decided to try F^2 full-matrix refinement of HTL-*Pbca* and HTL-$Pbc2_1$. The quantity minimized in this refinement was $\Sigma w(F_o^2 - kF_c^2)^2$, where $w=$

$[1/\sigma(F_o^2)]^2$ with $\sigma(F_o^2)$ determined from counting statistics. This is to be contrasted with the quantity minimized in the refinement procedure previously described, namely $\Sigma w(F_o-kF_c)^2$. No distinction was now made between 'observed' and 'unobserved' reflections. Weak reflections for which background intensity accidentally exceeded peak intensity were assigned $F_o^2=0$ at data reduction time. All reflections except 002 contributed to the matrix of normal equations; the 002 reflection of HTL-*Pbca* exhibited obvious extinction effects and was therefore not included in either refinement or R index calculations. Parameters from the final least-squares cycle of F refinement were used as input to the F^2 refinement of both structures.

The net result of this computational experiment was that the F^2 refinement of both HTL-*Pbca* and HTL-*Pbc*2_1 converged to structures which differed slightly, but significantly, from the structures obtained with the corresponding F refinements. Details of the procedure are outlined in the following paragraphs.

F^2 refinement of HTL-*Pbca* progressed routinely. Two initial cycles were calculated with hydrogen thermal parameters fixed. Most of the refinement was accomplished during these cycles. Hydrogen atoms were then assigned individual isotropic temperature factors and two more cycles were run in which only hydrogen thermal parameters were permitted to vary. Finally, all parameters, both hydrogen and non-hydrogen, were adjusted in two concluding cycles. In the last cycle the maximum parameter shift was 0·28σ and the mean shift was 0·05σ. The estimated standard deviation for an observation of unit weight, $[\Sigma w(\Delta F^2)^2/(m-s)]^{\frac{1}{2}}$ was 3·03.

F^2 refinement of HTL-*Pbc*2_1 did not proceed as smoothly since the hydrogen atoms of this structure were not as well defined. Hydrogen thermal parameters became negative when they were permitted to vary. After several unsuccessful attempts at refinement, individual isotropic temperature factors were assigned to hydrogen atoms (3·1 Å^2 for hydrogen atoms covalently bonded to carbon atoms and 4·8 Å^2 for hydrogen atoms covalently bonded to the nitrogen atom) and were not adjusted during further refinement. Most of the refinement took place during the first two cycles, in which hydrogen positional parameters were also fixed. Finally, four concluding cycles were run, in which all parameters except hydrogen thermal parameters were permitted to vary. It is doubtful that hydrogen positional parameters actually refined significantly since they were observed to shift erratically throughout the refinement. In the last cycle the mean parameter shift was 0·2σ and the maximum shift was 1·3σ (only one parameter, H(2)$-y$, was altered by more than one standard deviation). The estimated standard deviation for an observation of unit weight was 3·54.

Over the course of the F^2 refinement of each polymorph the weighted sum of squares of the F^2 residuals decreased by approximately 50%; and, as would be expected, parameters from the final F^2 cycle produced an *increase* in the weighted sum of squares of the residuals calculated for the F's.

Differences between bond lengths and angles resulting from the two types of refinement are, on the average, of the same magnitude as the estimated standard deviations. Although the mean bond-length difference between the F and F^2 refinement was only 1·2σ (the mean σ is 0·003 Å for HTL-*Pbca* and 0·01 Å for HTL-*Pbc*2_1) for both crystal forms, the important point to be made is that *some* of the refinement-dependent differences were very appreciable, *i.e.* 0·01 Å for HTL-*Pbca*, and 0·04 Å for HTL-*Pbc*2_1. Because of this, no significance can safely be attributed to the small differences apparently observed between molecules in the HTL-*Pbca* and HTL-*Pbc*2_1 structures, even though some of these exceeded 2σ (see Tables 8 and 9). Possibly, elimination of systematic errors in the data, in particular application of absorption corrections, would reduce this effect.

Since it seems preferable from a theoretical point of view to base parameter refinement on quantities proportional to the first power of the data rather than the square root of the data, parameters and calculated structure factors reported for HTL-*Pbca* and HTL-*Pbc*2_1 in this communication are taken from the F^2 refinement. Final R_2 indices, based on F^2 and calculated over all reflections, were 7·4% for HTL-*Pbc*2_1 and 5·0% for HTL-*Pbca*; corresponding R indices, based on the F's, were 6·5% and 4·8%.

Refined positional parameters and their estimated standard deviations are listed in Table 2. Thermal parameters are given in Table 3. Observed reflection amplitudes and calculated structure factors for the two polymorphs are listed in Tables 4 and 5. The corresponding table for the hybrid crystal structure has been omitted since presumably it represents only one of a series of hybrid structures containing varying amounts of the two components.

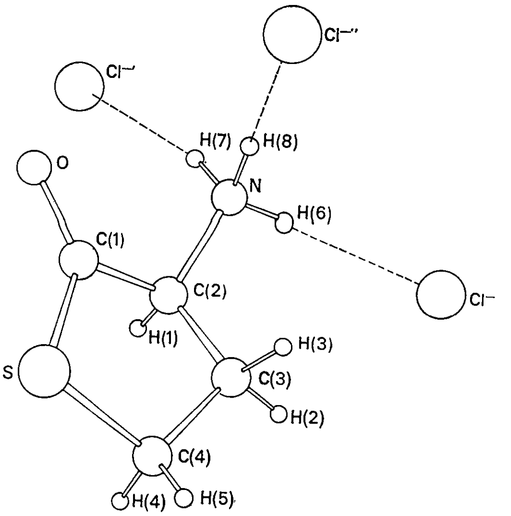

Fig. 1. Computed perspective projection of a single HTL moelcule.

Results and discussion

Fig. 1 is a representation of a single HTL molecule from the HTL-*Pbca* crystal structure. The drawing is a perspective projection from an arbitrary vantage point, chosen to show the thiolactone ring and the arrangement of hydrogen bonds most clearly. Molecular packing of both polymorphs is shown in Figs. 2, 3, and 4. Hydrogen atoms are omitted for clarity. Figs. 2 and 3 are orthographic projections along the *c* axis of HTL-*Pbca* and HTL-$Pbc2_1$ respectively; hydrogen bonds are indicated by dashed lines. Orthographic projections along the *b* axis are shown in Fig. 4 for both crystal forms.

Bond lengths and angles of covalent bonds not involving hydrogen atoms are given in Tables 6 and 7. Covalent bond lengths and angles involving hydrogen atoms are listed in Table 8 for HTL-*Pbca*. Since the hydrogen atoms of the $Pbc2_1$ structure were not well-defined, the corresponding table for this polymorph is omitted; the range of covalent bond lengths to hydrogen atoms for HTL-$Pbc2_1$ was from 0·65 to 1·42 Å. Hydrogen-bond lengths and angles are listed in Tables 9 and 10. Bond lengths and angles involving HTL-$Pbc2_1$ hydrogen atoms are again omitted.

The HTL molecules in the *Pbca* and $Pbc2_1$ crystal structures are nearly identical. Although examination of bond lengths and angles for the two structures does reveal differences, it should be emphasized again that similar differences were obtained when either polymorph was refined by two different methods. Thus, differences in bond lengths and angles of as much as 0·03 Å and 3·5° in these two structures may well be without significance.

The overall shape of the molecules is that of a puckered five-membered ring, four atoms lying nearly

Table 2. *Positional parameters, in fractional coordinates* $\times 10^4$ ($\times 10^3$ *for hydrogen parameters*), *and their estimated standard deviations*

	HTL-*Pbca*			HTL-$Pbc2_1$		
Atom	x/a	y/b	z/c	x/a	y/b	z/c
Cl^-	4066 (1)	760 (1)	2615 (1)	8192 (2)	839 (2)	2615 (*)
S	3114 (1)	6973 (1)	2246 (1)	6160 (2)	6969 (2)	2053 (5)
O	4380 (1)	6970 (2)	0963 (3)	8700 (5)	7020 (5)	0877 (9)
N	4553 (1)	4008 (2)	1786 (4)	9100 (6)	4102 (7)	1743 (12)
C(1)	3950 (1)	6347 (3)	1843 (4)	7842 (7)	6419 (7)	1763 (12)
C(2)	4041 (1)	4889 (3)	2794 (3)	8063 (7)	4953 (6)	2750 (14)
C(3)	3340 (1)	4193 (3)	2911 (4)	6671 (9)	4239 (8)	2778 (17)
C(4)	2855 (1)	5382 (3)	3512 (4)	5633 (9)	5394 (8)	3395 (15)
H(1)	417 (1)	511 (3)	399 (3)	822 (7)	552 (7)	405 (10)
H(2)	331 (1)	333 (3)	371 (4)	652 (10)	384 (9)	348 (12)
H(3)	318 (1)	377 (3)	172 (4)	652 (7)	335 (7)	122 (11)
H(4)	290 (1)	562 (3)	487 (4)	581 (6)	562 (7)	495 (11)
H(5)	237 (1)	517 (3)	307 (4)	454 (6)	517 (7)	292 (12)
H(6)	458 (1)	304 (3)	231 (5)	943 (7)	331 (6)	268 (14)
H(7)	504 (1)	431 (3)	201 (4)	986 (8)	445 (8)	191 (14)
H(8)	451 (2)	398 (3)	059 (5)	936 (8)	425 (9)	034 (12)

Table 3. *Thermal parameters of non-hydrogen atoms and their estimated standard deviations*

β as given here is defined by: $T=\exp\left[-10^{-4}(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)\right]$

HTL-*Pbca*

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl^-	18 (1)	65 (1)	138 (1)	2 (1)	−6 (1)	1 (1)
S	21 (1)	79 (1)	225 (2)	16 (1)	17 (1)	31 (1)
O	22 (1)	65 (2)	208 (5)	0 (1)	16 (1)	23 (3)
N	16 (1)	56 (2)	139 (5)	1 (1)	4 (1)	10 (3)
C(1)	18 (1)	54 (3)	136 (5)	3 (1)	3 (2)	−2 (3)
C(2)	14 (1)	61 (3)	103 (5)	1 (1)	1 (2)	−3 (3)
C(3)	13 (1)	72 (3)	175 (7)	−5 (1)	5 (2)	−2 (4)
C(4)	17 (1)	82 (3)	171 (7)	−1 (1)	11 (2)	1 (4)

HTL-$Pbc2_1$

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl^-	109 (2)	99 (2)	223 (4)	5 (2)	1 (3)	−3 (3)
S	131 (2)	122 (2)	304 (7)	35 (2)	30 (4)	38 (4)
O	134 (7)	99 (7)	309 (17)	−16 (5)	13 (9)	18 (10)
N	95 (7)	91 (7)	221 (15)	4 (6)	21 (9)	20 (11)
C(1)	117 (9)	94 (8)	213 (21)	7 (7)	1 (12)	−9 (12)
C(2)	87 (7)	92 (7)	202 (17)	−5 (6)	27 (13)	−6 (13)
C(3)	98 (7)	104 (9)	294 (24)	0 (8)	33 (15)	5 (15)
C(4)	127 (11)	104 (10)	298 (25)	2 (8)	61 (15)	0 (14)

Table 4. *Observed and calculated structure factors for* HTL-*Pbca*

Within each group of constant k and l, the columns contain from left to right: h, $10F_o$, and $10F_c$. An asterisk designates reflections for which the observed intensity was less than 1σ above background. F_o's followed by E were affected by secondary extinction.

H,0,0		
2	174	199
4	1068	-1081
6	930	-945
8	1470	-1462
10	1052	1049
12	333	300
14	585	-573
16	234	-231
18	94	-75
20	386	361
22	363	352
24	118	-104
H,1,0		
2	488	-473
4	915	929
6	757	-734
8	173	157
10	319	310
12	237	-209
14	641	614
16	107	-95
18	408	-389
20	20*	16
22	200	-200
24	115	112
H,2,0		
0	591	599
2	367	366
4	430	-436
6	942	-942
8	721	705
10	355	326
12	268	254
14	51	50
16	820	-802
18	105	112
20	161	141
22	99	91
24	210	210
H,3,0		
2	1629	1714
4	603	599
6	331	322
8	97	-100
10	805	-768
12	463	441
14	236	217
16	203	-191
18	157	-161
20	346	-336
22	126	114
24	205	196
H,4,0		
0	250	-245
2	428	-419
4	232	218
6	102	108
8	118	-110
10	106	78
12	44	26
14	163	146
16	177	165
18	73	-56
20	142	-128
22	14*	12
H,5,0		
2	705	667
4	489	473
6	357	-346
8	407	-393
10	215	-216
12	388	372
14	250	241
16	83	-66
18	227	-224
20	127	-120
22	171	157
H,6,0		
0	337	-320
2	349	-336
4	275	261
6	240	219
8	101	-79
10	41	31
12	304	-294
14	150	140
16	388	373
18	72	-62
20	28	-22
H,7,0		
2	460	-443
4	143	139
6	560	-549
8	55	30
10	148	141
12	63	-50
14	230	220
16	47	-53
18	42	37
20	73	75
H,8,0		
0	672	-648
2	155	153
4	89	64
6	42	-20
8	431	431
10	273	-268
12	120	-111
14	43	33
16	95	-82
18	154	152
H,9,0		
2	182	-172
4	380	-369
6	323	315
8	219	221
10	129	-125
12	0*	-11
14	392	-392
16	110	109
H,10,0		
0	431	426
2	27	10
4	32	-14
6	85	85
8	354	-347
10	21	12
12	32	20
H,11,0		
2	342	-346
4	70	64
6	67	-64
8	142	152
H,1,1		
1	321	331
2	604	-603
3	355	364
4	754	768
5	259	-249
6	815	-828
7	31	-21
8	542	-529
9	179	-181
10	83	-67
11	23	-22
12	87	82
13	118	-127
14	410	398
15	0*	7
16	180	191
17	70	67
18	99	-88
19	0*	-10
20	179	-178
21	105	95
22	29	34
23	39	-44
24	86	91
H,2,1		
0	1270	-1318
1	127	-123
2	224	226
3	189	-187
4	702	722
5	142	136
6	871	866
7	0*	12
8	222	186
9	129	139
10	1131	-1088
11	110	108
12	231	-215
13	0*	-27
14	157	138
15	50	56
16	84	59
17	76	-78
18	274	265
19	61	-63
20	206	-195
21	70	-69
22	161	-160
23	28	-5
24	197	197
H,3,1		
1	562	-556
2	702	714
3	69	69
4	289	-281
5	23	25
6	487	486
7	441	420
8	135	112
9	78	67
10	345	-335
11	0*	14
12	342	347
13	55	53
14	367	-364
15	100	-89
16	76	-57
17	21	-26
18	151	156
19	60	-58
20	149	-162
21	35	-12
22	191	195
23	18	31
H,4,1		
0	449	437
1	406	397
2	409	-399
3	225	226
4	329	337
5	364	361
6	1008	979
7	155	150
8	719	-716
9	197	-195
10	317	-296
11	27	7
12	262	-250
13	174	-165
14	189	-206
15	56	-53
16	659	629
17	29	15
18	35	10
19	27	-11
20	85	-71
21	50	45
22	79	-86
23	51	41
H,5,1		
1	50	49
2	841	-834
3	48	-48
4	81	84
5	75	72
6	187	-175
7	73	-100
8	721	710
9	181	-183
10	491	477
11	0*	20
12	551	-548
13	47	44
14	42	-27
15	144	149
16	187	-186
17	75	86
18	19*	-2
19	50	-41
20	316	316
21	31	-34
22	211	-214
H,6,1		
0	740	-745
1	25	-25
2	272	262
3	183	-175
4	155	-141
5	135	-133
6	178	-171
7	188	-194
8	582	579
9	35	35
10	160	-147
11	142	138
12	63	61
13	56	52
14	100	86
15	110	107
16	184	-189
17	93	-81
18	122	129
19	22	3
20	27	-7
21	0*	-5
H,7,1		
1	135	-131
2	241	-234
3	60	-64
4	695	-696
5	29	36
6	539	546
7	117	116
8	675	672
9	84	88
10	116	-123
11	30	-7
12	192	-190
13	20	3
14	433	-431
15	56	-52
16	56	-57
17	0*	-13
18	387	383
19	21	20
H,8,1		
0	239	219
1	47	49
2	36	25
3	92	-74
4	246	-246
5	0*	-7
6	165	-150
7	60	35
8	113	-112
9	41	-37
10	307	301
11	40	-36
12	272	265
13	45	-49
14	120	-125
15	48	33
16	33	29
17	38	32
18	155	-157
H,9,1		
1	42	37
2	264	-277
3	0*	10
4	195	-203
5	41	35
6	49	49
7	0*	-24
8	78	70
9	19	-30
10	118	118
11	58	-51
12	159	-156
13	34	-15
14	99	-94
15	21	-4
H,10,1		
0	228	225
1	27	31
2	127	129
3	67	-62
4	139	-146
5	18	8
6	304	-301
7	77	76
8	40	-34
9	31	-7
10	268	273
11	30	-18
12	89	86
H,11,1		
1	33	41
2	25	17
3	14*	12
4	116	115
5	57	57
6	170	-170
7	72	-73
8	163	-164
H,0,2		
0	2493E	-3115
1	58	-19
2	162	148
3	680	-690
4	938	953
5	498	-504
6	327	306
7	492	-491
8	597	577
9	34	10
10	1039	-1056
11	57	52
12	413	-416
13	211	215
14	650	666
15	398	413
16	291	296
17	140	-153
18	204	210
19	50	50
20	279	-291
21	76	-76
22	356	-374
23	74	-77
24	64	72
H,1,2		
1	500	-502
2	61	-54
3	334	340
4	1114	-1150
5	175	170
6	310	324
7	272	271
8	87	79
9	117	125
10	90	-86
11	248	-237
12	379	381
13	38	42
14	413	-414
15	92	-93
16	42	36
17	90	-87
18	270	277
19	20*	-6
20	102	-114
21	50	-40
22	108	122
23	118	123
24	76	-92
H,2,2		
0	536	-538
1	737	731
2	719	-724
3	156	159
4	478	479
5	254	231
6	923	929
7	39	37
8	356	-347
9	398	-380
10	80	-64
11	25	25
12	309	-303
13	65	-58
14	78	-78
15	29	31
16	535	537
17	37	-2
18	114	-124
19	20*	10
20	136	-134
21	62	57
22	46	-52
23	34	45
H,3,2		
1	268	270
2	1161	-1189
3	235	227
4	96	-68
5	368	357
6	96	-90
7	355	-337
8	317	321
9	227	-219
10	502	491
11	275	-273
12	542	-524
13	104	-108
14	313	-298
15	212	194
16	103	110
17	36	43
18	196	203
19	0*	-11
20	291	303
21	23	21
22	55	-63
23	30	29
H,4,2		
0	210	208
1	225	211
2	267	270
3	151	146
4	128	-136
5	191	177
6	191	-180
7	76	-89
8	66	51
9	26	-5
10	43	-34
11	178	178
12	0*	-1
13	29	-19
14	42	-14
15	30	-15
16	139	-139
17	142	-134
18	44	41
19	66	-58
20	84	84
21	0*	15
22	37	-30
H,5,2		
1	82	76
2	574	-566
3	92	-88
4	261	-264
5	114	106
6	201	193
7	139	-138
8	416	413
9	143	145
10	134	133
11	54	-65
12	305	-305
13	56	-55
14	233	-229
15	66	64
16	45	17
17	0*	-23
18	230	234
19	65	61
20	95	95
21	28	-34
H,6,2		
0	398	395
1	133	-134
2	333	336
3	19	-8
4	285	-279
5	113	107
6	311	-299
7	53	9
8	29	-3
9	140	146
10	30	-7
11	0*	2
12	304	298
13	47	-54
14	74	-77
15	0*	-4
16	296	-292
17	53	-40
18	65	58
19	32	-18
20	27	18
H,7,2		
1	187	-183
2	215	215
3	79	-87
4	241	-243
5	21	-28
6	239	254
7	89	95
8	0*	-4
9	206	211
10	84	-91
11	0*	11
12	161	158
13	107	120
14	111	-109
15	74	-69
16	37	37
17	50	-50
18	27	-24
19	34	35
H,8,2		
0	437	422
1	30	34
2	182	-180
3	30	-18
4	112	-99
5	63	67
6	73	73
7	132	130
8	235	-239
9	89	-88
10	296	306
11	47	-51
12	123	117
13	77	-84
14	119	-119
15	50	-45
16	19	4
17	137	136
H,9,2		
1	77	81
2	208	210
3	118	-122
4	447	454
5	124	130
6	213	-221
7	126	-134
8	177	-182
9	72	-77
10	17*	11
11	40	44
12	62	-63
13	34	31
14	291	301
15	86	91
H,10,2		
0	277	-276
1	95	-101
2	112	107
3	18	-6
4	35	14
5	124	-123
6	126	-132
7	163	-168
8	198	203
9	25	32
10	103	-106
11	12*	10
12	28	-14
H,11,2		
1	0*	-15
2	246	260
3	0*	3
4	96	-98
5	17	4
6	20	15
7	18	25
H,1,3		
1	344	-339
2	274	-280
3	242	-242
4	623	-632
5	178	169
6	126	134
7	74	70
8	509	514
9	38	42
10	67	47
11	26	-21
12	19*	11
13	252	257
14	249	-251
15	42	17
16	112	-114
17	36	-27
18	174	176
19	19*	9
20	65	71
21	181	-182
22	28	-6
23	46	53
H,2,3		
0	580	587
1	214	212
2	120	-117
3	105	-99
4	423	-415
5	406	-392
6	286	-287
7	28	-12
8	70	-56
9	187	-184
10	685	689
11	38	35
12	213	208
13	117	121
14	256	-253
15	67	-71
16	133	-130
17	104	104
18	254	-264
19	57	57
20	154	155
21	93	96
22	194	212
23	20	-15
H,3,3		
1	431	420
2	148	-150
3	292	-282
4	619	621
5	103	104
6	198	-195
7	302	-308
8	47	51
9	87	94
10	66	57
11	107	115
12	354	-356
13	219	-213
14	138	133
15	0*	12
16	47	-36
17	45	-30
18	51	-51
19	60	61
20	144	158
21	91	89
22	40	-49
H,4,3		
0	132	115
1	388	-383
2	732	736
3	54	-60
4	319	-319
5	216	-213
6	911	-909
7	111	-112
8	220	232
9	243	236
10	35	10
11	231	-226
12	235	228
13	70	70
14	137	147
15	89	95
16	339	-345
17	28	-11
18	37	28
19	142	142
20	121	114
21	13*	-16
H,5,3		
1	193	195
2	482	472
3	235	238
4	194	-201
5	330	-327
6	39	-43
7	62	-61
8	431	-439
9	173	169
10	242	-232
11	96	-103
12	584	592
13	0*	9
14	123	120
15	188	-182
16	51	55
17	73	-82
18	94	-91
19	114	119
20	328	-336
21	42	43
H,6,3		
0	181	189
1	52	35
2	268	-274
3	35	6
4	53	-45
5	0*	28
6	252	254
7	305	306
8	172	-168
9	42	-44
10	248	242
11	70	-68
12	75	66
13	20	-11
14	230	-217
15	151	-151
16	86	90
17	123	122
18	152	-160
19	71	-73
H,7,3		
1	116	114
2	270	281
3	36	29
4	656	666
5	21	9
6	270	-271
7	143	-132
8	491	-491
9	30	-28
10	0*	14
11	70	64
12	55	35
13	56	-62
14	282	290
15	17*	34
16	58	54
17	44	-41
18	281	-281
H,8,3		
0	293	-285
1	42	-41
2	47	43
3	208	207
4	152	155
5	90	94
6	114	113
7	70	-82
8	77	74
9	34	24
10	284	-293
11	57	53
12	134	-138
13	62	49
14	113	117
15	45	-44
16	59	69
H,9,3		
1	39	-46
2	191	202
3	34	-35
4	57	57
5	62	-54
6	45	-43
7	25	13
8	113	-114
9	83	74
10	86	-77
11	97	94
12	131	137
13	24	28
H,10,3		
0	227	-230
1	33	-34
2	73	-79
3	166	175
4	135	138
5	15*	26
6	261	263
7	156	-158
8	19	-4
9	0*	-10
10	246	-260
H,11,3		
1	11*	-23
2	44	-40
3	11*	-7
4	148	-159
H,0,4		
0	866	863
1	16*	14
2	105	-103
3	180	-181
4	604	-585
5	29	-31
6	140	-125
7	354	351
8	197	-178
9	27	19
10	716	708
11	289	291
12	476	474
13	100	-99
14	408	-420
15	314	-320
16	182	-179
17	154	158
18	257	-272
19	127	-137
20	120	136
21	0*	0
22	247	276
H,1,4		
1	35	38
2	124	127
3	502	-497
4	683	682
5	97	97
6	216	-219
7	25	13
8	249	-236
9	194	185
10	56	63
11	365	366
12	206	-212
13	179	-175
14	257	254
15	63	-54
16	21*	6
17	56	-48
18	195	-201
19	39	-32
20	110	112
21	95	98
22	24	-33
H,2,4		
0	189	197
1	418	-410
2	539	524
3	104	104
4	374	-360
5	198	186
6	586	-569
7	41	43
8	182	179
9	277	273
10	45	30
11	194	-195
12	253	252
13	202	-204
14	0*	5
15	21	-13
16	297	-288
17	20*	28
18	41	41
19	96	103
20	126	131
21	18	2
H,3,4		
1	114	106
2	665	652
3	134	-131
4	44	-49
5	419	-399
6	99	-100
7	51	48
8	456	-457
9	112	108
10	271	-269
11	199	205
12	418	422
13	166	173
14	304	307
15	167	-163
16	0*	-6
17	27	-21
18	144	-156
19	85	88
20	171	-186
21	47	-53
H,4,4		
0	37	-37
1	127	-127
2	49	-49
3	204	-201
4	27	8
5	159	-176
6	165	152
7	80	96
8	29	-30
9	21	-2
10	0*	-19
11	119	-119
12	37	-22
13	36	22
14	116	-123
15	34	41
16	102	103
17	117	121
18	23	-1
19	54	49
20	24	-12
H,5,4		
1	40	23
2	345	346
3	20	29
4	144	135
5	74	-92
6	0*	-25
7	47	42
8	320	-325
9	108	-114
10	73	-66
11	70	62
12	125	137
13	79	82
14	178	177
15	72	-73
16	50	38
17	23	4
18	172	-180
19	21	-24
H,6,4		
0	317	-303
1	168	164
2	160	-153
3	69	-67
4	245	235
5	202	-203
6	274	268
7	52	-70
8	30	-13
9	148	-162
10	128	-133
11	54	65
12	233	-232
13	127	134
14	36	33
15	29	26
16	205	213
17	24	22
18	30	-8
H,7,4		
1	37	47
2	73	-65
3	36	-31
4	141	137
5	140	148
6	21	17
7	41	-44
8	29	11
9	53	-59
10	104	107
11	0*	34
12	155	-154
13	171	-172
14	16*	7
15	37	39
16	30	-32
H,8,4		
0	306	-310
1	29	-11
2	60	66
3	191	207
4	147	133
5	73	66
6	27	14
7	121	-124
8	104	111
9	64	68
10	228	-243
11	84	-73
12	106	-105
13	19	27
14	128	134
H,9,4		
1	25	32
2	104	-111
3	195	201
4	327	-336
5	180	-184
6	154	163
7	27	13
8	108	112
9	0*	9
10	55	57
11	114	-125
12	41	44
H,10,4		
0	152	155
1	54	52
2	138	-144
3	96	-101
4	29	-31
5	25	15
6	79	80
7	154	159
H,1,5		
1	162	153
2	338	333
3	33	15
4	304	304
5	43	-24
6	34	-23
7	115	-108
8	351	-346
9	122	117
10	21*	35
11	63	52
12	82	74
13	175	-176
14	172	184
15	0*	-6
16	19*	5
17	59	-54
18	224	-227
19	0*	1
20	32	-50
H,2,5		
0	485	-473
1	152	-145
2	148	-140
3	254	249
4	187	181
5	317	312
6	198	190
7	70	-71
8	206	204
9	104	111
10	213	-209
11	90	-100
12	166	-165
13	88	-86
14	128	139
15	52	45
16	67	68
17	71	-80
18	143	150
19	0*	-29
20	88	-92
H,3,5		
1	113	-115
2	110	103
3	285	273
4	253	-246
5	105	-112
6	206	199
7	46	55
8	42	-42
9	113	-116
10	106	-95
11	206	-217
12	78	60
13	199	205
14	79	-71
15	60	51
16	59	63
17	46	54
18	78	78
19	25	22
H,4,5		
0	89	-79
1	188	192
2	385	-383
3	58	-53
4	239	238
5	29	-27
6	441	434
7	0*	0
8	196	-184
9	199	-197
10	101	-90
11	273	263
12	148	-152
13	98	98
14	42	41
15	75	-77
16	265	272
17	49	52
18	18	36
19	181	-193
H,5,5		
1	237	-239
2	471	-464
3	280	-285
4	130	-130
5	411	418
6	47	-41
7	117	113
8	215	222
9	75	-77
10	219	218
11	99	94
12	294	-294
13	61	-64
14	65	-70
15	126	129
16	44	40
17	38	33
18	64	69
H,6,5		
0	190	-172
1	89	-83
2	52	52
3	181	170
4	148	144
5	91	84
6	46	-50
7	198	-196
8	108	100
9	79	75
10	161	-158
11	66	-71
12	130	-124
13	40	-27
14	149	142
15	59	61
16	86	-88
H,7,5		
1	64	-58
2	151	-149
3	49	43
4	365	-357
5	20	7
6	148	146
7	87	73
8	266	268
9	81	-81
10	17*	-5
11	139	-132
12	33	-30
13	88	84
14	206	-210
H,8,5		
0	352	346
1	26	-26
2	0*	3
3	176	-188
4	95	-89
5	137	-140
6	110	-114
7	96	99
8	107	-95
9	29	33
10	162	174
11	52	-53
12	53	51
H,9,5		
1	30	-19
2	110	-121
3	29	31
4	25	23
5	47	51
6	34	36
7	42	39
8	116	122
H,0,6		
0	436	-406
1	97	-77
2	97	-89
3	301	319
4	325	309
5	21	20
6	220	218
7	290	-287
8	215	198
9	56	42
10	299	-296
11	171	-178
12	349	-347
13	193	186
14	98	98
15	145	148
16	23	33
17	181	-185
18	151	161
H,1,6		
1	120	-115
2	29	1
3	309	302
4	155	-143
5	98	-96
6	267	259
7	73	87
8	244	244
9	70	-73
10	116	-107
11	250	-252
12	66	-61
13	109	117
14	202	-202
15	0*	16
16	35	-36
17	45	39
18	145	155
H,2,6		
0	51	39
1	242	239
2	182	-162
3	81	81
4	212	211
5	128	-123
6	259	242
7	37	-24
8	188	-183
9	222	-224
10	153	-157
11	78	79
12	148	-149
13	224	226
14	36	38
15	37	-36
16	200	199
17	23	12
18	55	58
H,3,6		
1	155	-147
2	424	-402
3	73	69
4	87	-86
5	238	231
6	101	92
7	36	38
8	382	380
9	105	-97
10	182	182
11	94	-95
12	222	-220
13	105	-109
14	194	-198
15	149	155
16	34	-27
17	38	51
H,4,6		
0	127	-118
1	21	-8
2	47	-42
3	137	123
4	30	19
5	59	71
6	66	-55
7	71	-81
8	57	59
9	28	13
10	47	37
11	32	33
12	54	50
13	24	13
14	108	109
15	28	-22
16	60	-63
H,5,6		
1	72	-63
2	148	-147
3	58	48
4	116	-105
5	61	56
6	20	-10
7	0*	26
8	190	179
9	19	-23
10	48	40
11	57	-54
12	0*	-30
13	50	-55
14	111	-111
15	74	86
H,6,6		
0	139	134
1	160	-161
2	0*	25
3	0*	1
4	178	-173
5	83	88
6	181	-177
7	18	-22
8	66	61
9	124	130
10	207	206
11	30	-29
12	151	158
13	76	-79
14	22	-29
H,7,6		
1	43	-43
2	50	53
3	84	80
4	0*	9
5	121	-129
6	51	-51
7	98	95
8	49	-47
9	0*	-16
10	91	-95
11	28	-33
H,8,6		
0	285	271
1	57	54
2	65	70
3	111	-124
4	113	-119
5	19	-21
6	120	-119
7	88	100
8	84	-83
H,1,7		
1	84	-76
2	261	-252
3	36	47
4	205	-201
5	21	-24
6	35	46
7	140	133
8	176	179
9	97	-105
10	26	17
11	40	-29
12	99	-99
13	52	48
14	130	-131
15	41	-36
16	33	38
H,2,7		
0	303	293
1	131	125
2	126	131
3	132	-131
4	68	-66
5	64	-53
6	106	-114
7	189	185
8	159	-150
9	65	-50
10	36	28
11	30	-1
12	91	90
13	56	59
14	54	-55
15	53	-57
H,3,7		
1	127	122
2	35	-21
3	101	-110
4	60	51
5	20	13
6	80	-78
7	81	-75
8	26	-29
9	36	-34
10	85	77
11	146	154
12	21	25
13	81	-85
14	12*	18
H,4,7		
0	157	158
1	130	-125
2	140	137
3	91	-94
4	141	-143
5	0*	-18
6	198	-203
7	0*	1
8	62	64
9	182	178
10	129	130
11	79	-74
12	85	87
13	68	-73
H,5,7		
1	36	35
2	315	309
3	129	124
4	150	160
5	279	-279
6	53	50
7	16*	11
8	86	-91
9	148	149
10	115	-120
11	0*	22
12	104	109
H,6,7		
0	165	155
1	137	133
2	0*	1
3	71	-75
4	105	-102
5	0*	-10
6	25	-36
7	100	100
8	59	-50
9	96	-106
10	96	97
H,7,7		
1	127	129
2	69	77
3	49	-54
4	146	144
5	71	-76
6	67	-66
H,0,8		
0	132	130
1	26	13
2	26	-1
3	255	-255
4	102	-103
5	30	5
6	115	-115
7	221	219
8	54	-48
9	15*	-7
10	166	161
11	0*	16
12	136	137
H,1,8		
1	155	150
2	62	59
3	113	-112
4	110	95
5	57	53
6	106	-105
7	120	-117
8	159	-156
9	60	-46
10	0*	7
11	95	97
12	41	50
H,2,8		
0	61	62
1	158	-157
2	50	41
3	157	-154
4	85	-74
5	23	5
6	153	-143
7	15*	1
8	0*	37
9	157	156
10	112	119
11	11*	-11
H,3,8		
1	103	104
2	170	168
3	16*	-20
4	97	97
5	112	-118
6	111	-107
7	41	-35
8	195	-198
9	66	69
10	88	-90
H,4,8		
0	101	83
1	61	51
2	0*	1
3	0*	-12
4	14*	4
5	34	8
6	33	37
7	63	57
8	11*	-28
9	10*	-3
H,5,8		
1	77	78
2	29	25
3	50	-49
4	93	86
5	66	-69
6	42	-38
H,1,9		
1	21	1
2	152	154
3	25	-27
4	128	132
5	14	-1
H,2,9		
0	116	-114
1	33	-25
2	21	-31
3	79	84

Table 5. *Observed and calculated structure factors for* HTL-$Pbc2_1$

Within each group of constant k and l, the columns contain from left to right: h, $10F_o$, $|10F_c|$, and the phase angle in millicycles. An asterisk designates reflections for which the observed intensity was less than 1σ above background.

H,0,0			
1	74	87	000
2	453	460	500
3	500	515	500
4	669	677	500
5	478	491	000
6	143	126	000
7	141	143	500
8	101	101	500
9	80	73	500
10	101	100	000
11	88	90	000
12	13	1	000
H,1,0			
1	247	247	500
2	449	461	000
3	335	342	500
4	146	140	000
5	68	72	000
6	99	80	500
7	281	282	000
8	68	57	500
9	115	107	500
10	28	23	500
11	73	73	500
12	59	56	000
H,2,0			
0	273	273	000
1	197	202	000
2	157	153	500
3	364	363	500
4	296	297	000
5	64	46	000
6	133	129	000
7	43	13	500
8	282	285	500
9	64	55	000
10	28	14	000
11	60	60	000
12	57	53	000
H,3,0			
1	840	835	000
2	340	335	000
3	217	224	000
4	68	65	500
5	392	368	500
6	149	152	000
7	94	86	000
8	25	4	000
9	46	57	500
10	125	119	500
11	0*	11	000
12	39	39	000
H,4,0			
0	133	131	500
1	205	201	500
2	144	137	000
3	85	80	000
4	44	41	500
5	12*	7	000
6	36	24	500
7	50	44	000
8	79	69	000
9	14	2	000
10	31	23	500
11	19	7	500
H,5,0			
1	259	247	000
2	170	160	000
3	101	96	500
4	83	77	500
5	45	58	500
6	101	111	000
7	55	47	000
8	29	16	500
9	62	68	500
10	16	19	500
11	20	19	000
H,6,0			
0	181	168	500
1	182	180	500
2	105	99	000
3	115	111	000
4	41	39	000
5	43	46	000
6	150	148	500
7	29	26	000
8	105	109	000
9	0*	14	000
10	18	17	000
H,7,0			
1	246	240	500
2	14*	5	000
3	178	180	500
4	110	118	000
5	62	57	000
6	44	39	500
7	24	28	000
8	33	36	500
9	38	38	000
10	32	33	000
H,8,0			
0	231	239	500
1	65	66	000
2	25	24	500
3	42	29	500
4	158	167	000
5	52	57	500
6	19	2	500
7	0*	14	500
8	21	24	500
9	38	43	000
H,9,0			
1	93	95	500
2	162	160	500
3	97	101	000
4	61	69	000
5	0*	17	500
6	8*	3	500
7	120	128	500
8	41	43	000
H,10,0			
0	172	173	000
1	19	26	000
2	26	30	500
3	25	30	500
4	107	118	500
5	46	47	000
6	12	28	000
H,11,0			
1	80	88	500
2	21	22	000
3	50	49	500
4	16	17	000
H,1,1			
1	315	314	448
2	436	447	083
3	345	345	478
4	241	247	457
5	125	116	543
6	27	21	276
7	191	169	949
8	112	117	978
9	25	11	465
10	90	78	530
11	24	25	376
12	29	25	959
H,2,1			
0	701	698	480
1	99	101	939
2	340	353	946
3	471	479	998
4	113	116	920
5	512	484	487
6	116	101	465
7	0*	13	430
8	68	65	151
9	134	125	000
10	51	49	491
11	46	47	601
12	25	31	900
H,3,1			
1	366	368	860
2	208	206	529
3	270	265	908
4	121	106	201
5	106	103	419
6	112	117	997
7	186	187	457
8	33	31	946
9	43	47	997
10	26	24	580
11	52	48	945
12	44	42	483
H,4,1			
0	461	450	836
1	195	190	547
2	153	141	944
3	451	428	040
4	317	320	417
5	109	90	554
6	163	170	450
7	87	87	547
8	199	200	976
9	14	18	056
10	22	28	904
11	49	50	502
H,5,1			
1	450	422	472
2	50	45	678
3	102	102	374
4	383	378	996
5	218	216	937
6	200	205	511
7	55	61	629
8	116	118	458
9	46	48	151
10	97	103	017
11	53	54	459
H,6,1			
0	256	249	449
1	170	161	053
2	99	100	503
3	80	70	518
4	228	227	922
5	66	67	572
6	57	56	037
7	0*	10	338
8	76	86	406
9	41	44	935
10	12	8	400
H,7,1			
1	91	87	606
2	269	261	535
3	239	235	954
4	222	234	999
5	53	55	334
6	56	57	467
7	147	149	478
8	18	23	587
9	79	83	982
10	24	24	105
H,8,1			
0	125	113	974
1	44	47	118
2	99	102	520
3	88	87	511
4	74	76	439
5	113	121	001
6	114	118	983
7	0*	28	696
8	0*	15	715
9	70	78	502
H,9,1			
1	32	35	441
2	35	34	455
3	0*	22	173
4	14	6	406
5	29	31	965
6	26	35	575
7	14	5	910
8	25	21	985
H,10,1			
0	32	42	015
1	32	40	120
2	42	45	552
3	79	91	527
4	16	6	397
5	74	84	992
6	22	32	045
H,11,1			
1	22	34	054
2	45	50	986
3	55	62	403
4	52	65	504
H,0,2			
0	1413	1496	455
1	260	263	195
2	379	387	006
3	201	195	018
4	362	355	870
5	455	441	513
6	204	203	609
7	197	194	947
8	204	199	136
9	106	97	975
10	100	93	418
11	99	99	527
12	25	27	693
H,1,2			
1	369	368	711
2	534	552	491
3	152	157	912
4	130	130	219
5	165	148	194
6	161	158	927
7	203	197	447
8	46	41	803
9	74	66	925
10	0*	9	536
11	58	60	899
12	47	43	412
H,2,2			
0	599	597	665
1	357	358	424
2	205	209	034
3	402	402	039
4	214	205	325
5	128	126	772
6	159	156	515
7	42	44	663
8	188	173	984
9	43	47	454
10	0*	10	580
11	37	34	476
12	29	33	417
H,3,2			
1	555	541	471
2	92	83	384
3	300	290	286
4	142	152	031
5	232	225	005
6	192	190	541
7	171	155	613
8	25	10	494
9	77	73	017
10	102	105	986
11	20	8	244
H,4,2			
0	175	165	891
1	155	153	987
2	97	93	511
3	142	133	431
4	56	55	728
5	29	20	722
6	81	82	160
7	36	30	187
8	73	64	398
9	31	32	706
10	25	22	790
11	6*	5	782
H,5,2			
1	226	216	452
2	105	95	540
3	79	75	138
4	113	121	910
5	84	95	150
6	67	74	470
7	70	66	587
8	0*	8	668
9	57	60	940
10	24	22	134
11	12	6	378
H,6,2			
0	202	188	064
1	163	156	920
2	121	120	576
3	120	116	488
4	47	55	572
5	70	80	279
6	135	136	027
7	20	15	409
8	82	82	481
9	14	18	632
10	21	14	437
H,7,2			
1	148	143	945
2	35	35	582
3	99	100	873
4	88	90	554
5	53	50	397
6	62	63	946
7	64	65	232
8	31	29	981
9	35	30	483
H,8,2			
0	142	138	924
1	72	73	474
2	33	28	773
3	49	50	945
4	107	114	380
5	57	63	964
6	0*	21	169
7	16	12	561
8	40	36	758
H,9,2			
1	108	117	063
2	174	177	946
3	82	86	379
4	61	72	578
5	43	50	659
6	0*	15	507
7	90	97	988
H,10,2			
0	120	129	421
1	18	19	856
2	38	50	146
3	0*	18	156
4	85	86	866
5	66	69	535
6	29	35	640
H,11,2			
1	48	57	962
2	30	38	499
3	29	32	863
4	19	14	569
H,1,3			
1	171	175	621
2	334	326	572
3	61	67	844
4	211	211	991
5	78	71	030
6	80	74	781
7	121	122	385
8	73	71	474
9	35	39	071
10	0*	57	105
11	33	28	833
H,2,3			
0	266	266	952
1	205	191	259
2	199	187	404
3	215	215	593
4	33	34	417
5	294	282	924
6	96	85	003
7	48	51	389
8	90	85	619
9	95	100	480
10	44	41	954
11	74	72	103
H,3,3			
1	264	255	224
2	285	279	928
3	144	135	346
4	131	130	727
5	33	26	542
6	132	132	359
7	98	86	890
8	15*	27	463
9	30	27	667
10	25	28	939
11	32	29	285
H,4,3			
0	363	348	208
1	306	288	967
2	145	128	430
3	368	352	514
4	143	140	801
5	130	121	232
6	138	140	893
7	57	65	935
8	92	91	465
9	43	40	685
10	38	38	225
11	40	37	107
H,5,3			
1	229	207	000
2	246	242	251
3	77	69	679
4	221	215	516
5	91	96	395
6	195	194	955
7	93	93	122
8	54	60	876
9	73	73	608
10	88	94	502
H,6,3			
0	49	49	741
1	132	123	463
2	24	30	922
3	130	131	896
4	111	115	282
5	72	65	966
6	29	24	499
7	57	53	425
8	48	58	830
9	55	57	349
10	16	20	822
H,7,3			
1	116	122	068
2	247	247	006
3	118	116	376
4	154	165	508
5	50	52	667
6	31	31	239
7	88	92	959
8	25	30	084
9	43	53	517
H,8,3			
0	116	117	531
1	90	86	739
2	63	70	074
3	86	87	116
4	37	33	917
5	94	107	495
6	47	53	467
7	37	32	121
8	34	38	084
H,9,3			
1	24	19	984
2	19	18	445
3	22	24	687
4	21	27	666
5	29	2	357
6	38	40	070
7	7*	4	219
H,10,3			
0	53	54	524
1	53	61	658
2	30	44	098
3	85	88	055
4	13	8	778
5	55	58	482
H,11,3			
1	25	33	567
2	44	50	454
H,0,4			
0	343	333	972
1	82	88	241
2	234	224	547
3	225	212	670
4	94	94	345
5	241	240	947
6	238	244	115
7	127	134	367
8	136	137	636
9	91	94	430
10	58	55	831
11	68	63	015
H,1,4			
1	187	192	144
2	331	329	866
3	76	70	490
4	148	140	610
5	53	52	656
6	168	173	276
7	102	99	953
8	25	28	174
9	46	37	525
10	29	31	788
11	30	33	329
H,2,4			
0	260	248	152
1	272	259	851
2	168	151	538
3	197	190	462
4	63	55	823
5	169	170	215
6	115	106	020
7	36	38	711
8	87	77	534
9	32	36	754
10	29	26	121
11	24	22	142
H,3,4			
1	285	259	030
2	121	109	222
3	165	159	709
4	187	184	555
5	123	122	575
6	117	122	981
7	154	153	104
8	24	25	078
9	51	44	517
10	60	60	428
H,4,4			
0	95	95	308
1	55	65	346
2	0*	20	947
3	106	111	866
4	32	30	189
5	0*	13	517
6	67	66	616
7	54	47	526
8	40	44	913
9	44	36	155
10	25	20	137
H,5,4			
1	97	95	954
2	34	42	059
3	38	38	742
4	84	80	421
5	70	70	666
6	0*	14	922
7	58	67	090
8	21	15	071
9	41	30	453
10	8*	16	642
H,6,4			
0	159	148	565
1	83	85	312
2	109	100	078
3	84	83	965
4	15*	29	081
5	100	106	648
6	94	96	542
7	25	6	873
8	54	53	003
9	26	31	118
H,7,4			
1	55	52	430
2	65	57	701
3	58	61	175
4	49	45	055
5	43	43	978
6	57	60	356
7	58	61	661
8	15	21	419
H,8,4			
0	62	58	433
1	53	54	788
2	50	38	149
3	40	45	269
4	43	49	822
5	39	53	344
6	39	35	641
7	12*	18	893
H,9,4			
1	55	64	561
2	120	125	361
3	53	48	891
4	38	52	094
5	52	53	089
6	25	32	722
H,10,4			
0	68	69	966
1	52	48	298
2	49	52	641
3	57	56	679
4	35	35	293
H,1,5			
1	150	148	063
2	122	119	043
3	39	42	168
4	127	134	538
5	21	6	445
6	57	57	209
7	56	60	896
8	35	25	092
9	61	51	549
10	45	42	616
H,2,5			
0	163	147	476
1	183	180	642
2	60	66	943
3	156	172	117
4	64	68	958
5	72	79	332
6	75	72	545
7	14*	29	793
8	54	53	125
9	51	48	986
10	26	22	437
H,3,5			
1	116	109	698
2	128	121	306
3	82	70	914
4	58	70	201
5	0*	11	360
6	104	106	691
7	34	26	329
8	22	19	961
9	33	28	096
10	0*	25	256
H,4,5			
0	170	174	670
1	125	126	406
2	79	79	963
3	123	128	981
4	67	63	289
5	126	125	671
6	53	55	380
7	37	44	184
8	57	54	977
9	59	59	154
H,5,5			
1	176	159	526
2	258	252	661
3	55	54	225
4	108	102	057
5	71	62	967
6	75	72	386
7	72	71	649
8	23	20	255
9	41	44	107
H,6,5			
0	53	35	284
1	75	71	734
2	33	30	058
3	72	76	266
4	63	58	765
5	46	48	293
6	9*	13	589
7	37	31	861
8	26	31	387
H,7,5			
1	53	65	612
2	98	97	477
3	23	41	842
4	69	76	060
5	25	26	182
6	56	55	710
7	51	47	488
H,8,5			
0	136	135	040
1	67	67	186
2	43	42	583
3	97	96	613
4	27	29	482
5	51	55	010
6	14	17	998
H,9,5			
1	23	22	564
2	28	30	854
3	9*	6	253
4	29	34	121
H,10,5			
0	46	45	047
H,0,6			
0	95	89	476
1	100	118	638
2	141	140	089
3	149	153	125
4	72	71	833
5	62	70	435
6	163	165	594
7	0*	14	797
8	85	80	177
9	45	42	922
H,1,6			
1	112	118	672
2	78	86	229
3	69	68	882
4	96	98	072
5	54	50	261
6	86	88	644
7	43	46	437
8	22	20	637
9	35	26	998
H,2,6			
0	140	132	714
1	48	51	288
2	91	89	080
3	46	41	996
4	64	58	318
5	101	108	626
6	58	56	599
7	28	42	131
8	37	34	003
9	35	34	137
H,3,6			
1	146	134	547
2	82	83	647
3	72	69	149
4	131	131	051
5	63	64	047
6	38	41	446
7	103	95	601
8	19	18	513
9	29	24	179
H,4,6			
0	42	19	407
1	25	27	669
2	15	4	195
3	36	33	351
4	25	28	750
5	0*	17	043
6	28	40	040
7	35	29	025
8	20	25	431
H,5,6			
1	38	24	653
2	25	12	493
3	0*	11	252
4	30	34	044
5	18	27	161
6	21	10	923
7	44	45	588
8	0*	9	531
H,6,6			
0	93	93	092
1	24	23	684
2	60	62	551
3	49	49	506
4	37	27	699
5	68	80	056
6	52	56	045
7	16	7	258
H,7,6			
1	21	21	897
2	55	60	122
3	54	52	620
4	0*	21	477
5	29	31	499
6	19	18	812
H,8,6			
0	40	37	861
1	28	34	116
2	28	30	582
3	29	28	575
4	27	28	260
H,9,6			
1	43	40	168
H,1,7			
1	81	87	541
2	46	57	494
3	25	29	676
4	70	71	090
5	18	8	101
6	24	20	567
7	26	26	474
8	28	23	721
H,2,7			
0	58	57	929
1	75	84	081
2	38	34	635
3	74	83	609
4	43	44	335
5	0*	13	298
6	49	43	095
7	7*	1	084
8	36	40	612
H,3,7			
1	60	61	149
2	14*	17	661
3	19	22	322
4	18	30	596
5	33	34	763
6	37	49	107
7	15	13	605
H,4,7			
0	104	112	105
1	36	28	999
2	38	38	556
3	50	47	563
4	48	46	681
5	57	66	112
6	21	15	129
7	20	19	580
H,5,7			
1	71	67	991
2	105	113	101
3	40	57	705
4	50	50	629
5	15	21	423
6	15	12	060
H,6,7			
0	56	54	746
1	29	35	158
2	16	19	504
3	0*	17	658
4	36	37	211
5	17	24	739
H,7,7			
1	59	57	164
2	36	33	064
3	11*	10	200
H,0,8			
0	29	34	216
1	54	57	174
2	13*	64	638
3	62	69	638
4	27	25	195
5	40	29	068
6	59	59	091
H,1,8			
1	54	66	118
2	18	5	753
3	0*	33	253
4	47	43	530
5	26	33	665
6	31	27	059
H,2,8			
0	75	80	157
1	12*	9	298
2	36	37	629
3	33	24	595
4	34	34	687
5	39	46	082
6	18	25	177
H,3,8			
1	37	47	090
2	39	45	124
3	15	34	533
4	50	52	553
5	18	21	528
H,4,8			
0	31	34	732
1	0*	1	324
2	0*	3	043
3	15	13	014
4	8*	18	175
H,5,8			
1	38	31	252
2	15	13	045
3	8*	9	511
H,6,8			
0	48	50	585
1	0*	6	804
H,1,9			
1	26	34	994
2	23	24	981
3	17	3	318
H,2,9			
0	20	15	596
1	14	22	573
2	19	26	169
H,3,9			
1	8*	20	558

Table 6. *Bond lengths of covalent bonds, and their estimated standard deviations*

	Length	
Bond	HTL-*Pbca*	HTL-$Pbc2_1$
S–C(1)	1·756 ± 0·003 Å	1·740 ± 0·007 Å
S–C(4)	1·814 ± 0·003	1·840 ± 0·009
O–C(1)	1·204 ± 0·003	1·201 ± 0·009
N–C(2)	1·486 ± 0·003	1·485 ± 0·010
C(1)–C(2)	1·532 ± 0·003	1·561 ± 0·010
C(2)–C(3)	1·515 ± 0·004	1·519 ± 0·011
C(3)–C(4)	1·520 ± 0·004	1·549 ± 0·012

Table 7. *Bond angles for covalent bonds, and their estimated standard deviations*

Angle	HTL-*Pbca*	HTL-$Pbc2_1$
C(1)–S–C(4)	94·3 ± 0·1°	95·5 ± 0·4°
O–C(1)–S	125·3 ± 0·2	126·3 ± 0·5
O–C(1)–C(2)	125·8 ± 0·2	124·1 ± 0·6
S–C(1)–C(2)	109·0 ± 0·2	109·4 ± 0·5
N–C(2)–C(1)	110·1 ± 0·2	109·4 ± 0·7
N–C(2)–C(3)	113·5 ± 0·2	112·8 ± 0·6
C(1)–C(2)–C(3)	107·4 ± 0·2	105·4 ± 0·6
C(2)–C(3)–C(4)	105·5 ± 0·2	106·8 ± 0·6
S–C(4)–C(3)	105·8 ± 0·2	102·4 ± 0·6

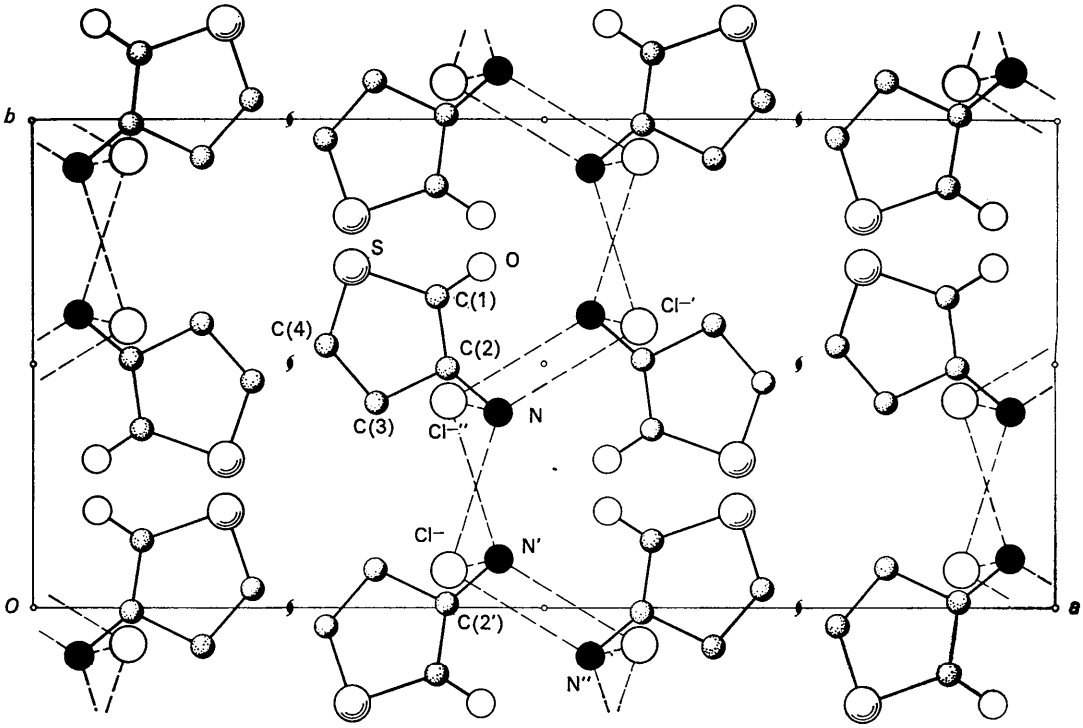

Fig. 2. Orthographic projection along the *c* axis of HTL-*Pbca*.

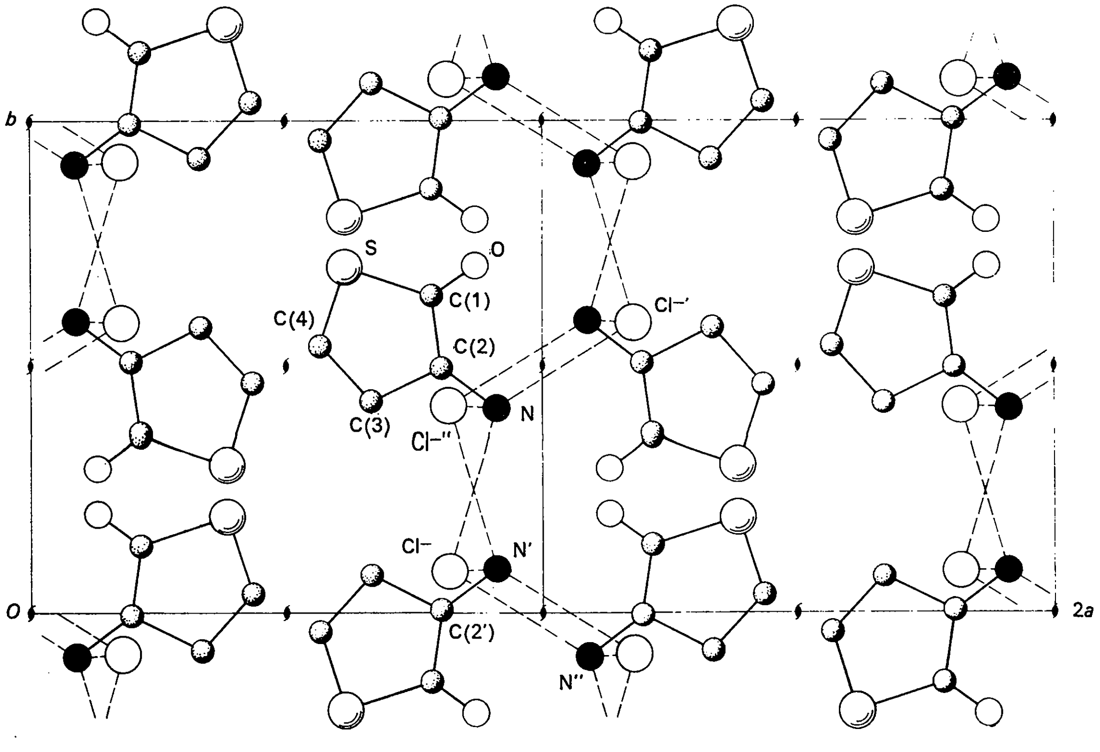

Fig. 3. Orthographic projection along the *c* axis of HTL-$Pbc2_1$.

Table 8. *Covalent bond lengths and angles involving hydrogen atoms and their estimated standard deviations for* HTL-*Pbca*

Bond	Length
H(1)–C(2)	0·93 ± 0·03 Å
H(2)–C(3)	1·00 ± 0·03
H(3)–C(3)	1·00 ± 0·03
H(4)–C(4)	1·02 ± 0·03
H(5)–C(4)	1·02 ± 0·03
H(6)–N	0·98 ± 0·03
H(7)–N	1·00 ± 0·03
H(8)–N	0·88 ± 0·04

Angle	Degrees
H(1)–C(2)–C(1)	104·9 ± 1·6°
H(1)–C(2)–N	113·3 ± 1·5
H(1)–C(2)–C(3)	107·2 ± 1·5
H(2)–C(3)–C(2)	116·0 ± 1·5
H(2)–C(3)–C(4)	112·2 ± 1·6
H(2)–C(3)–H(3)	99·8 ± 2·2
H(3)–C(3)–C(2)	113·9 ± 1·4
H(3)–C(3)–C(4)	109·5 ± 1·4
H(4)–C(4)–C(3)	112·8 ± 1·4
H(4)–C(4)–S	106·7 ± 1·5
H(4)–C(4)–H(5)	115·6 ± 2·1
H(5)–C(4)–C(3)	110·3 ± 1·6
H(5)–C(4)–S	104·8 ± 1·6
H(6)–N–C(2)	110·2 ± 1·8
H(6)–N–H(7)	98·4 ± 2·3
H(6)–N–H(8)	111·9 ± 2·9
H(7)–N–C(2)	113·9 ± 1·6
H(7)–N–H(8)	105·3 ± 2·7
H(8)–N–C(2)	115·8 ± 2·1

Table 9. *Hydrogen-bond lengths and their estimated standard deviations*

Lengths involving hydrogen atoms of HTL–*Pbc*2_1 are omitted because of the uncertainty of these positional parameters.

Bond	HTL–*Pbca*	HTL–*Pbc*2_1
N–Cl$^-$	3·222 ± 0·003 Å	3·233 ± 0·007 Å
N–Cl$^{-\prime}$	3·178 ± 0·002	3·175 ± 0·006
N–Cl$^{-\prime\prime}$	3·185 ± 0·003	3·151 ± 0·008
Cl$^-$–H(6)	2·36 ± 0·03	—
Cl$^{-\prime}$–H(7)	2·22 ± 0·03	—
Cl$^{-\prime\prime}$–H(8)	2·34 ± 0·04	—
Cl$^-$–C(2′)	3·558 ± 0·003	3·640 ± 0·010
Cl$^-$–H(1′)	2·77 ± 0·03	—

Table 10. *Hydrogen-bond angles and their estimated standard deviations*

Angles involving HTL–*Pbc*2_1 hydrogen atoms are omitted because of the uncertainty of these positional parameters.

Angle	HTL–*Pbca*	HTL–*Pbc*2_1
N–Cl$^-$–N′	91·5 ± 0·1	95·5 ± 0·2
N–Cl$^-$–N″	104·8 ± 0·1	102·1 ± 0·2
N′–Cl$^-$–N″	69·6 ± 0·1	88·0 ± 0·2
Cl$^-$–N–Cl$^{-\prime}$	134·8 ± 0·1	132·1 ± 0·2
Cl$^-$–N–Cl$^{-\prime\prime}$	98·8 ± 0·1	97·3 ± 0·2
Cl$^{-\prime}$–N–Cl$^{-\prime\prime}$	110·4 ± 0·1	114·8 ± 0·2
H(6)–N–Cl$^-$	23·1 ± 1·7	—
H(7)–N–Cl$^{-\prime}$	14·7 ± 1·5	—
H(8)–N–Cl$^{-\prime\prime}$	12·7 ± 2·1	—
H(1′)–C(2′)–Cl$^-$	27·6 ± 1·5	—

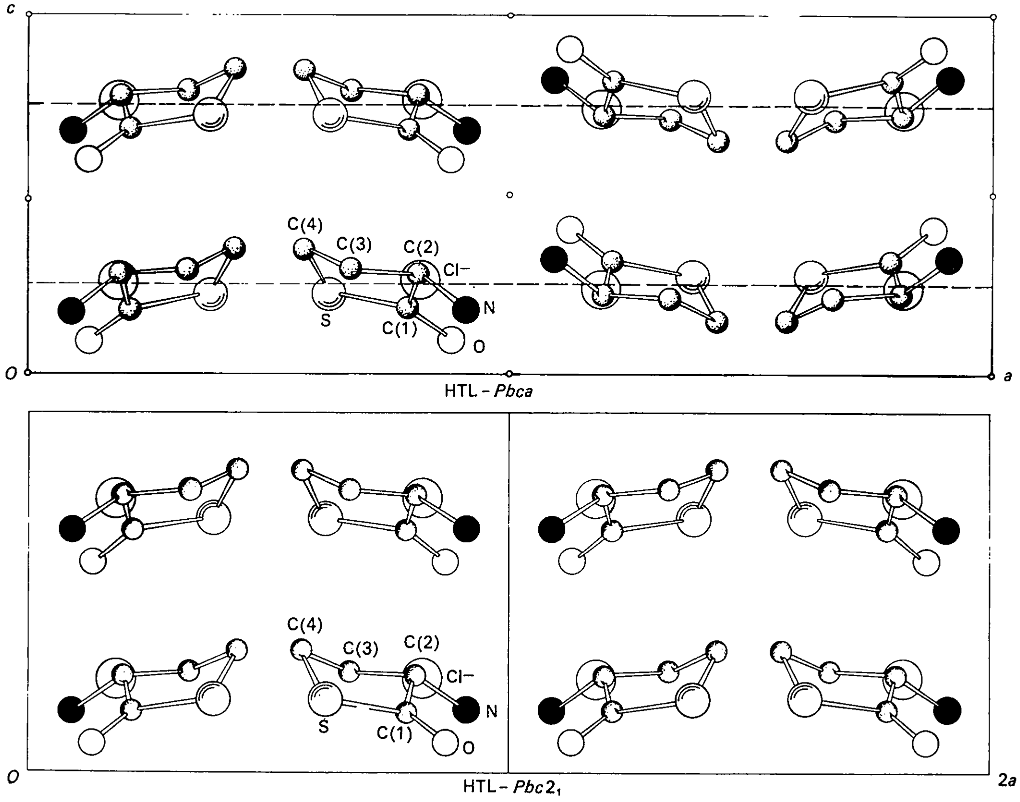

Fig. 4. Orthographic projections along the *b* axis of HTL-*Pbca* and HTL-*Pbc*2_1.

in a plane and the fifth atom, C(3), displaced approximately 0·7 Å from this plane. For both HTL-*Pbca* and HTL-$Pbc2_1$ the r.m.s. deviation of S, O, C(1), C(2), and C(4) from their least-squares plane is 0·02 Å; the maximum deviation is 0·026 Å. The thiolactone group exhibits the same characteristic planarity, and the associated shortening of the bond between the hetero atom and the C=O group, as has been found for lactones (McConnell, Mathieson & Schoenborn, 1964). Bond lengths and angles for HTL are similar to those found in other amino acids.

Molecular packing of the two crystal forms is very similar. Indeed, the [*c*] projections of the *Pbca* and $Pbc2_1$ structures are almost indistinguishable (Figs. 2 and 3). In both polymorphs the molecules lie in layers at $z=\frac{1}{4}$ and $\frac{3}{4}$, with the plane of the thiolactone ring approximately normal to the unit-cell *c* axis. The principal packing difference is apparent in Fig. 4: the O,N ends of adjacent molecules are staggered on opposite sides of the a glide plane in HTL-*Pbca*, while they are directly opposed in HTL-$Pbc2_1$. This produces slightly tighter packing in the *Pbca* polymorph, accounting for its slightly greater density and perhaps for its lower mean temperature factor (mean $B=2\cdot79$ Å^2 for HTL-*Pbca* and 4·45 Å^2 for HTL-$Pbc2_1$).

The prominent feature of the molecular arrangement in both polymorphic crystal structures is an extensive hydrogen-bonding network between the ammonium groups and chloride ions. The three protons of the ammonium group participate in hydrogen-bond formation with three chloride ions. Since there is but one chloride ion in the asymmetric unit, each chloride ion must accept hydrogen bonds from three NH_3^+ donor groups. In both polymorphs the chloride ion and its three hydrogen-bonded ammonium groups form a distorted triangular pyramid. One clear difference between the two structures is that the pyramid is more regular in HTL-$Pbc2_1$, the three N–Cl^-–N angles at the Cl^- vertex being more nearly equal in this structure. This may be seen in the first three entries of Table 10, although it is not evident in the projections shown in Figs. 2, 3 and 4.

There is possibly a weak hydrogen bond between the chloride ion and C(2′) in HTL-*Pbca* (atom designations correspond to those in Fig. 2). The Cl^-- -H(1′) distance is approximately 0·2 Å shorter than the normal van der Waals contact of 3·0 Å. However, the Cl^-–C(2′)–H(1′) angle of 27·6° is rather large and places the existence of such a hydrogen bond only on the verge of credibility.

Thermal ellipsoids were calculated for both polymorphs but are not listed here because of their dubious accuracy. It is probable that the thermal parameters were strongly affected by neglect of absorption corrections. All atoms, however, had significant anisotropy according to the criteria proposed by Kraut & Jensen (1963). In general the direction of greatest vibration for the ring atoms was approximately normal to the plane of the ring. Bond lengths were not corrected for librational motions of the entire molecule, since molecular libration is evidently not an important mode of thermal motion.

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References

Busing, W. R. & Levy, H. A. (1959). *A Crystallographic Least-Squares Refinement Program for the IBM-*704. U.S. Atomic Energy Commission Publication ORNL 59-4-37.

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *A Fortran Crystallographic Least-Squares Program.* U.S. Atomic Energy Commission Publication ORNL-TM-305.

Gantzel, P. K., Sparks, R. A. & Trueblood, K. N. (1961). Private communication.

Hughes, E. W. (1941). *J. Amer. Chem. Soc.* **63**, 1737.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham, Kynoch Press.

Kraut, J. & Jensen, L. H. (1963). *Acta Cryst.* **16**, 79.

McConnell, J. F., Mathieson, A. McL. & Schoenborn, B. P. (1964). *Acta Cryst.* **17**, 472.

Robertson, J. M., Shearer, H. M. M., Sim, G. A., & Watson, D. G. (1962). *Acta Cryst.* **15**, 1.

Ubbelohde, A. R. (1963). *Z. Phys. Chem.* (*Frankfurt*), **37**, 183.

Ubbelohde, A. R. & Woodward, I. (1946*a*). *Proc. Roy. Soc.* A, **185**, 448.

Ubbelohde, A. R. & Woodward, I. (1946*b*). *Proc. Roy. Soc.* A, **188**, 358.