

entropy effect manifests itself by the occurrence of conformational disorder at RT, while at LNT the antiplanar conformation is favoured (Table 6), either by dominant intramolecular or decisive packing conditions.

References

- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A24, 321–324.
- ELJCK, B. P. VAN, KANTERS, J. A. & KROON, J. (1965). *Acta Cryst.* 19, 435–439.
- FILIPAKIS, S. E., LEISEROWITZ, L., RABINOVICH, D. & SCHMIDT, G. M. J. (1972). *J. Chem. Soc. Perkin Trans. 2*, pp. 1750–1758.
- HAYASHI, S., HARA, H. & KIMURA, N. (1968). *Bull. Inst. Chem. Res. Kyoto Univ.* 46, 213–218.
- HAYASHI, S. & UMEMURA, J. (1972). *Acta Cryst.* A28, S239.
- HAYASHI, S. & UMEMURA, J. (1974). *J. Chem. Phys.* 60, 2630–2633.
- HAYASHI, S. & UMEMURA, J. (1975). *J. Chem. Phys.* 63, 1732–1740.
- HOUSTY, J. (1968). *Acta Cryst.* B24, 486–494.
- JEFFREY, G. A. & PARRY, G. S. (1952). *Nature (London)*, 169, 1105–1106.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- KANTERS, J. A., KROON, J., PEERDEMAN, A. F. & SCHOONE, J. C. (1967). *Tetrahedron*, 23, 4027–4033.
- KANTERS, J. A., ROELOFSEN, G. & KROON, J. (1975). *Nature (London)*, 257, 625–626.
- LEISEROWITZ, L. (1976). *Acta Cryst.* B32, 775–802.
- MANOJLOVIĆ, L. & SPEAKMAN, J. C. (1967). *J. Chem. Soc. A*, pp. 971–979.
- ROELOFSEN, G., KANTERS, J. A., KROON, J. & VliegENTHART, J. A. (1971). *Acta Cryst.* B27, 702–705.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* 42, 3175–3187.
- XRAY system (1972). Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland; implemented and extended by the Dutch XRAY System Group, 1973.

Acta Cryst. (1978). B34, 2570–2574

The Constitution of the 1:1 Adduct of Hector's Base and Carbon Disulphide: The Crystal and Molecular Structure of 5-(1,2-Diphenylguanidino)-3*H*-1,2,4-dithiazole-3-thione

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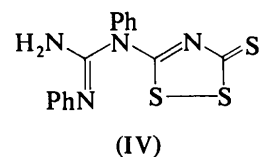
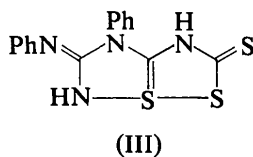
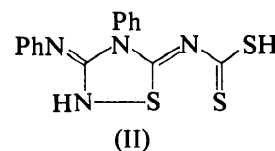
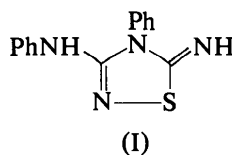
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The 1:1 adduct of Hector's base and carbon disulphide crystallizes as a hydrate, $\text{C}_{15}\text{H}_{12}\text{N}_4\text{S}_3 \cdot 0.7\text{H}_2\text{O}$, in the orthorhombic system, space group $P2_12_12_1$, with $a = 20.297$ (3), $b = 10.355$ (2), $c = 7.797$ (2) Å, $Z = 4$. The structure was solved by direct methods from diffractometer data and refined to $R = 0.0376$. The adduct is 5-(1,2-diphenylguanidino)-3*H*-1,2,4-dithiazole-3-thione in which S(1)–S(2) is 2.121 and S(1)⋯N(3) 2.324 Å.

Introduction

The oxidation of 1-phenylthiourea with H_2O_2 yields a heterocyclic base, $\text{C}_{14}\text{H}_{12}\text{N}_4\text{S}$ (Hector, 1889), generally known as Hector's base, whose constitution is 5-imino-4-phenyl-3-phenylamino-4*H*-1,2,4-thiadiazoline (I) (Glidewell & Liles, 1978). With CS_2 Hector's base forms a 1:1 adduct (Fromm & Heyder, 1909) for which the alternative structures (II) and (III) have been suggested (Butler, 1978). The structure analysis reported in the present paper shows that the constitution of



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the adduct is in fact (IV), 5-(1,2-diphenylguanidino)-3*H*-1,2,4-dithiazole-3-thione.

Experimental

The adduct was prepared by reaction of Hector's base with excess CS₂ in ethanol, and recrystallized from ethanol. Crystals suitable for X-ray examination were grown from ethanol-acetone; the structure analysis showed that these were partially hydrated, C₁₅H₁₂N₄S₃·0.7H₂O. Composition found: C 49.85, H 3.65, N 15.49%; C₁₅H₁₂N₄S₃ requires: C 52.30, H 3.51, N 16.27%; C₁₅H₁₂N₄S₃·0.7H₂O requires: C 50.45, H 3.78, N 15.69%.

Data collection

The intensities of 2667 unique reflections with $3 \leq \theta \leq 30^\circ$ were measured on a Philips PW 1100 automatic four-circle diffractometer with graphite-monochromatized Mo *K*α radiation, the $\omega-2\theta$ scan mode, a scan speed of 0.05° s⁻¹ in ω , a scan width of (0.8 + 0.05 tan θ)° in ω , and a maximum of two scans per reflection. Backgrounds were measured at each end of the scan range for a time = (scan time/2)√(*I*_{BK}/*I*_{INT}), or a minimum of 10 s, where *I*_{BK} = the background intensity scaled from an initial 10 s measurement, and *I*_{INT} = integrated peak intensity. Three standard reflections were measured every six hours, and showed only small random deviations from their means. Lorentz and polarization corrections were applied to the data, but no corrections for absorption were made.

Crystal data

C₁₅H₁₂N₄S₃·0.7H₂O, *M*_r = 357.08, orthorhombic, space group *P*2₁2₁2₁, *a* = 20.297 (3), *b* = 10.355 (2), *c* = 7.797 (2) Å, *U* = 1638.7 Å³, *Z* = 4, *D*_c = 1.447 kg dm⁻³, *F*(000) = 740, Mo *K*α radiation, λ = 0.71069 Å, μ(Mo *K*α) = 4.04 cm⁻¹.

The space group was determined uniquely from the systematic absences: *h*00, *h* ≠ 2*n*; 0*k*0, *k* ≠ 2*n*; 00*l*, *l* ≠ 2*n*.

Structure solution and refinement

The structure was solved by direct methods and refined with *SHELX* 76 (Sheldrick, 1976). 304 reflections with *E* > 1.40 giving 7021 unique triple-phase relations were used to calculate a convergence map. The reflections 0, 11, 1, 605 and 15, 3, 0 were each assigned phases of 90° to define the origin. The enantiomorph was fixed by assigning phases of 45 and 135° to reflection 352.

Reflections 122 and 14, 4, 1 were each assigned phases of 45, 135, 225 and 315° to give 32 starting phase permutations. The best solution from the multi-solution tangent refinement yielded an *E* synthesis from which positions were found for all non-hydrogen atoms, except phenyl atoms C(4) to C(9) and C(11) to C(14). A weighted difference synthesis was calculated which gave the positions of all the C atoms not previously found.

Full-matrix least-squares refinement with 1781 reflections having $F_o \geq 6\sigma(F_o)$, individual isotropic temperature factors for all non-hydrogen atoms and a weighting scheme $w = [\sigma(F_o)]^{-2}$ yielded *R* (= $\sum \Delta / \sum F_o$, $\Delta = |F_o - F_c|$) = 0.1487 and *R*_G [= $(\sum w\Delta^2 / \sum wF_o^2)^{1/2}$] = 0.1980. The introduction of anisotropic temperature factors for the S atoms reduced *R*_G to 0.1358. Refinement with anisotropic temperature factors for all non-hydrogen atoms reduced *R*_G to 0.1205. At this stage a difference synthesis showed an isolated electron density peak which could only be ascribed to the O atom of a water molecule of crystallization. The site-occupation factor

Table 1. *Atom coordinates*

The site-occupation factor for O(1) is 0.70 (1).

| | <i>x</i> | <i>y</i> | <i>z</i> |
|-------|------------|------------|-------------|
| S(1) | 0.3142 (0) | 0.6635 (1) | 0.3845 (1) |
| S(2) | 0.2913 (0) | 0.5246 (1) | 0.2040 (2) |
| S(3) | 0.3599 (0) | 0.4283 (1) | -0.0859 (1) |
| N(1) | 0.4015 (1) | 0.6054 (3) | 0.1363 (4) |
| N(2) | 0.4354 (2) | 0.7620 (4) | 0.3279 (5) |
| N(3) | 0.3692 (2) | 0.8168 (3) | 0.5483 (4) |
| N(4) | 0.4726 (2) | 0.9176 (5) | 0.5200 (6) |
| C(1) | 0.3537 (2) | 0.5240 (4) | 0.0854 (5) |
| C(2) | 0.3888 (2) | 0.6741 (4) | 0.2733 (5) |
| C(3) | 0.4244 (2) | 0.8374 (5) | 0.4748 (5) |
| C(4) | 0.4946 (2) | 0.7800 (5) | 0.2253 (6) |
| C(5) | 0.4924 (2) | 0.8647 (6) | 0.0895 (7) |
| C(6) | 0.5504 (3) | 0.8858 (6) | -0.0035 (7) |
| C(7) | 0.6071 (2) | 0.8229 (6) | 0.0385 (7) |
| C(8) | 0.6080 (2) | 0.7396 (6) | 0.1762 (8) |
| C(9) | 0.5513 (2) | 0.7157 (5) | 0.2696 (7) |
| C(10) | 0.3483 (2) | 0.8781 (4) | 0.6995 (5) |
| C(11) | 0.3532 (2) | 1.0107 (4) | 0.7265 (6) |
| C(12) | 0.3293 (2) | 1.0649 (5) | 0.8767 (9) |
| C(13) | 0.2992 (2) | 0.9910 (5) | 0.9984 (7) |
| C(14) | 0.2927 (2) | 0.8590 (5) | 0.9703 (6) |
| C(15) | 0.4173 (2) | 0.8035 (4) | 0.8235 (6) |
| H(1) | 0.510 (3) | 0.910 (5) | 0.475 (6) |
| H(2) | 0.467 (2) | 0.967 (5) | 0.602 (7) |
| H(5) | 0.453 (2) | 0.913 (5) | 0.057 (6) |
| H(6) | 0.545 (2) | 0.949 (5) | -0.090 (7) |
| H(7) | 0.647 (2) | 0.840 (5) | -0.023 (6) |
| H(8) | 0.644 (3) | 0.695 (5) | 0.200 (6) |
| H(9) | 0.549 (3) | 0.662 (5) | 0.361 (7) |
| H(11) | 0.369 (2) | 1.067 (5) | 0.637 (6) |
| H(12) | 0.333 (2) | 1.154 (5) | 0.892 (7) |
| H(13) | 0.288 (2) | 1.019 (5) | 1.104 (7) |
| H(14) | 0.275 (2) | 0.809 (5) | 1.055 (7) |
| H(15) | 0.311 (3) | 0.719 (5) | 0.802 (7) |
| O(1) | 0.5122 (3) | 1.1366 (7) | -0.2664 (9) |

(s.o.f.) of the O atom was allowed to refine with its temperature factor fixed at 0.08 \AA^2 . R_G decreased to 0.0611, and the s.o.f. refined to 0.70 (1). A further difference synthesis gave the positions of all the H atoms except those of the water molecule. Refinement with a common isotropic temperature factor for the two amine H atoms and a second common temperature factor for the phenyl H atoms, and with the s.o.f. for the O atom fixed at 0.70 and its isotropic temperature factor allowed to refine, yielded $R = 0.0384$, $R_w (= \sum w^{1/2} \Delta / \sum w^{1/2} F_o) = 0.0394$ and $R_G = 0.0437$. [At each stage in the refinement the reduction in R_G was significant at the 99.5% level (Hamilton, 1965).] The alternative enantiomorph yielded $R = 0.0376$, $R_w = 0.0386$, and $R_G = 0.0429$, significant at the 99.9% level. The chirality is imposed upon the molecule by the twisting of the phenyl rings from the plane of the skeleton and has no chemical significance.

Complex neutral-atom scattering factors (Cromer & Mann, 1968; Doyle & Turner, 1968) were employed for all atoms. In the final refinement 242 parameters were varied, comprising 105 positional coordinates, 132 anisotropic temperature factor components, three isotropic temperature factors, one site occupation factor, and one overall scale factor; all parameter shifts were $< 0.50\sigma$. A final difference synthesis revealed no electron density $> 0.25 \text{ e \AA}^{-3}$.

The results of the final cycle are given in Table 1. These, together with the full covariance matrix, were used to calculate the bond lengths and angles which are given in Tables 2 and 3. Least-squares planes are given in Table 4. Fig. 1 shows the molecule and the

numbering scheme for atoms and bonds: H atoms bonded to C are given the numbers of the corresponding C atoms. Fig. 2 shows the unit cell.*

Results and discussion

This determination indicates that the adduct of Hector's base and carbon disulphide has the constitution (IV), rather than either of those previously suggested (Butler, 1978). The dimensions of the heterocycle are similar to those reported for 3-acetamido-1,2,4-dithiazole-5-thione (V) (Eide, Hordvik & Sæthre, 1972) and for xanthan hydride (VI) (Hordvik, 1963). The exocyclic fragment exhibits bond distances, bond angles and torsion angles similar to those of the analogous adduct (VII) of Hector's base with an aryl cyanamide (Akiba, Tsuchiya, Inamoto, Onuma, Nagashima & Nakamura, 1976).

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33514 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. *Least-squares planes and distances ($\text{\AA} \times 10^3$) of atoms from these planes*

Least-squares planes are defined in orthogonal coordinates in ångströms by the equation $Ax + By + Cz + 1 = 0$.

| | A | B | C | | | |
|---|---------|---------|---------|-------|--------|-------|
| Plane 1: S(1), S(2), N(1), C(1), C(2) S(1) 5.9; S(2) -8.9; N(1) -5.7; C(1) 14.0; C(2) -4.9; S(3) 12.3; N(2) -66.7 | 0.4251 | -0.8238 | 0.6525 | | | |
| Plane 2: S(1), C(2), N(2), C(3), N(3) S(1) -0.7; C(2) 6.2; N(2) -29.7; C(3) -9.6; N(3) 40.4; N(4) -18.4 | 0.5623 | -1.034 | 0.8400 | | | |
| Plane 3: C(4), C(5), C(6), C(7), C(8), C(9) C(4) -2.1; C(5) 0.2; C(6) -3.1; C(7) 7.4; C(8) -9.4; C(9) 7.1; N(2) -64.2 | -0.0252 | -0.0785 | -0.0642 | | | |
| Plane 4: C(10), C(11), C(12), C(13), C(14), C(15) C(10) -7.7; C(11) 11.5; C(12) -5.8; C(13) -6.6; C(14) 8.1; C(15) -1.2; N(3) 54.6 | -0.1200 | 0.0199 | -0.0612 | | | |
| Dihedral angles ($^\circ$) | | | | | | |
| Planes | 1, 2 | 1, 3 | 1, 4 | 2, 3 | 2, 4 | 3, 4 |
| Angles | 1.10 | 84.16 | -45.96 | 85.04 | -44.92 | 67.74 |

Table 2. *Bond distances (\AA)*

The mean H-C (aryl) distance is $0.93 (3) \text{ \AA}$.

| | | | | | | | |
|---|-----------|---|-----------|---|-----------|---|-----------|
| a | 2.121 (2) | h | 1.404 (5) | o | 1.400 (7) | v | 1.387 (7) |
| b | 1.736 (4) | i | 1.331 (5) | p | 1.361 (8) | w | 1.363 (8) |
| c | 1.667 (4) | j | 1.275 (5) | q | 1.377 (8) | x | 1.391 (7) |
| d | 1.345 (4) | k | 0.84 (5) | r | 1.385 (7) | y | 1.374 (6) |
| e | 1.309 (5) | l | 0.83 (5) | s | 1.373 (6) | z | 1.389 (6) |
| f | 1.749 (4) | m | 1.455 (5) | t | 1.404 (5) | | |
| g | 1.379 (5) | n | 1.375 (7) | u | 1.393 (6) | | |

Table 3. *Bond angles ($^\circ$)*

| | | | | | |
|----|-----------|----|-----------|----|-----------|
| ab | 95.1 (2) | hj | 114.4 (4) | sm | 119.4 (4) |
| bc | 119.5 (2) | ik | 119 (4) | sn | 122.0 (4) |
| bd | 116.8 (3) | il | 119 (4) | jt | 124.6 (4) |
| cd | 123.7 (3) | kl | 121 (5) | tu | 123.4 (4) |
| de | 116.1 (3) | gm | 120.6 (3) | uv | 120.1 (5) |
| ef | 122.7 (3) | hm | 118.7 (3) | vw | 121.2 (5) |
| fa | 89.2 (1) | mn | 118.6 (4) | wx | 119.0 (5) |
| eg | 118.4 (3) | no | 118.1 (5) | xy | 120.5 (5) |
| fg | 118.8 (3) | op | 120.7 (5) | yz | 120.8 (4) |
| gh | 120.6 (3) | pq | 120.0 (5) | zt | 118.0 (4) |
| hi | 116.5 (4) | qr | 120.6 (5) | zu | 118.4 (4) |
| ij | 129.1 (4) | rs | 118.6 (5) | | |

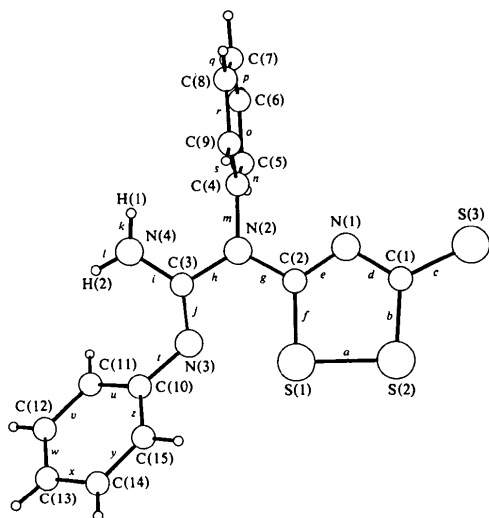
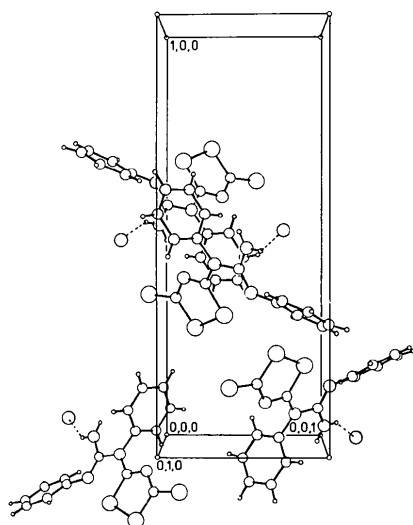
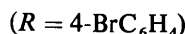
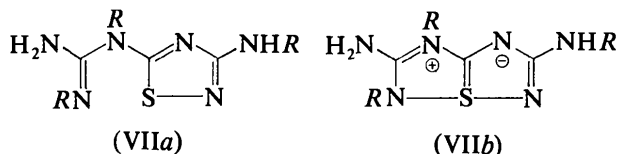
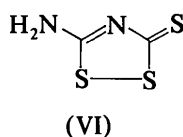
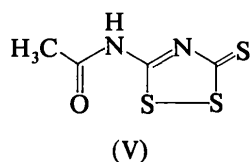
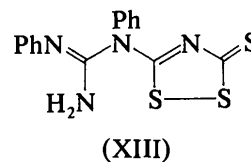
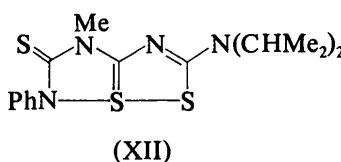
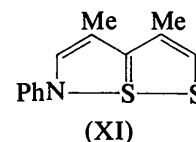
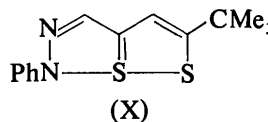
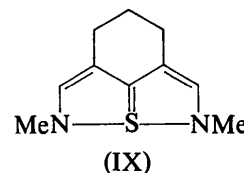
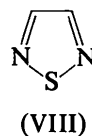


Fig. 1. The molecule showing the labelling of atoms and bonds.

Fig. 2. The unit-cell contents viewed down *b*.

In the present adduct the exocyclic S(1)···N(3) distance is 2.324 Å, shorter than the 2.538 Å observed in (VII), in which the S···N distance and the planarity of the skeleton were regarded as indicative of a strong

interaction involving S^{IV}, e.g. (VIIb) (Akiba *et al.*, 1976), but very much longer than the S—N bond in 1,2,5-thiadiazole (VIII) (1.632 Å) (Momany & Bonham, 1964). A correlation has been presented of S—N distance with S—N bond order (Glemser, Müller, Böhler & Krebs, 1968) which suggests that the S—N bond order becomes zero at an interatomic distance of *ca* 2.0 Å. If this correlation is valid, there are no grounds for suggesting any significant S···N interaction either in (IV), or *a fortiori* in (VII). It is noteworthy that in (IX), which does contain a S^{IV} atom as the central atom in an N—S—N chain, the N—S distances are 1.901 and 1.948 Å (Hordvik & Julshamn, 1972); other similar examples are (X), (XI) and (XII), in which the N—S distances are 1.841 (Hansen & Tomren, 1977), 1.774 (Darmo & Hansen, 1977) and 1.863 Å (Hansen, 1977) respectively.



The planarity of the skeleton in (IV) [and in (VII)] can be ascribed to an extensive π system embracing all the N atoms and all the non-benzenoid C atoms; in particular the sums of angles at both N(2) and N(4) are 360° within experimental uncertainty. Given the planarity of the skeleton, the only other likely configurations are (XIII), derived from (IV) by a rotation of 180° about N(2)—C(3), and a further pair derived from (IV) and (XIII) respectively by a rotation of 180° about C(2)—N(2). In the reaction of Hector's base (I) with CS₂ one such rotation about N(2)—C(3) must occur to yield (IV): the driving force for this rotation is not immediately apparent.

As crystallized from ethanol–acetone the adduct (IV) is hydrated by 0.7H₂O per molecule. The isotropic vibrational parameter for the O atom refined to a fairly high value, 91 (2) × 10⁻³ Å², and the H atoms of the water could not be placed: possibly they are disordered.

The O atom engages in a hydrogen bond with H(2), with the interatomic distances H(2)···O(1) 2.23 and N(4)···O(1) 2.926 Å, and an NHO angle of 141°. There are no other significant intermolecular interactions.

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References

- AKIBA, K., TSUCHIYA, T., INAMOTO, N., ONUMA, K., NAGASHIMA, N. & NAKAMURA, A. (1976). *Chem. Lett.* pp. 723–726.
- BUTLER, A. R. (1978). *J. Chem. Res. (S)*, p. 50; *J. Chem. Res. (M)*, pp. 855–864.
- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
- DARMO, L. P. & HANSEN, L. K. (1977). *Acta Chem. Scand. Ser. A*, **31**, 412–416.
- DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* **A24**, 390–397.
- EIDE, G., HORDVIK, A. & SÆTHRE, L. J. (1972). *Acta Chem. Scand.* **26**, 2140.
- FROMM, E. & HEYDER, R. (1909). *Chem. Ber.* **42**, 3804–3807.
- GLEMSE, O., MÜLLER, A., BÖHLER, D. & KREBS, B. (1968). *Z. Anorg. Chem.* **357**, 184–189.
- GLIDEWELL, C. & LILES, D. C. (1978). Unpublished.
- HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502–510.
- HANSEN, L. K. (1977). *Acta Chem. Scand. Ser. A*, **31**, 855–860.
- HANSEN, L. K. & TOMREN, K. (1977). *Acta Chem. Scand. Ser. A*, **31**, 292–296.
- HECTOR, D. S. (1889). *Chem. Ber.* **22**, 1176–1180.
- HORDVIK, A. (1963). *Acta Chem. Scand.* **17**, 2575–2592.
- HORDVIK, A. & JULSHAMN, K. (1972). *Acta Chem. Scand.* **26**, 343–354.
- MOMANY, F. A. & BONHAM, R. A. (1964). *J. Am. Chem. Soc.* **86**, 162–164.
- SHELDRIK, G. M. (1976). Personal communication.

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The Crystal Structures of the α Form of *p*-Chlorobenzamide at Room Temperature and -120°C

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Crystal structures at room temperature and -120°C have been investigated by X-rays for the α form of *p*-chlorobenzamide. Crystal data are: (room temperature) $a = 15.027$ (7), $b = 5.481$ (4), $c = 14.486$ (7) Å, $\alpha = 97.84$ (5), $\beta = 111.99$ (5), $\gamma = 95.17$ (5)°; (-120°C) $a = 14.95$, $b = 5.42$, $c = 14.23$ Å, $\alpha = 97.0$, $\beta = 111.5$, $\gamma = 95.0^\circ$; $Z = 6$, triclinic with space group $P\bar{1}$. Intensity data were collected by the equi-inclination Weissenberg technique. The structures were refined by block-diagonal least-squares calculations. The R values for the room- and low-temperature structures based on 3090 and 3112 reflexions were 0.110 and 0.108 respectively. The crystal structures are composed of one centrosymmetric and two asymmetric dimeric units consisting of independent molecules, *A*, *B* and *C*. These units are linked by hydrogen bonds to form an endless chain along *a*. Dihedral angles between the planes of the amide group and the benzene ring for molecules *A*, *B* and *C* are 20.3, 30.3 and 33.8° (17.9, 29.1 and 33.7°) respectively, where the values in parentheses are those for the low-temperature structure. Molecules *B* and *C* are approximately parallel to each other, but the plane of the benzene ring for *A* makes angles of 34.0 and 37.8° (40.0 and 44.4°) with those for *B* and *C* respectively. A marked movement of molecules occurring gradually over a range of temperatures below the transition point (*ca* 44°C) can be described approximately in terms of rotations of molecules about the long axes of the dimeric units. The sense of rotation is the same as that of the rotation occurring drastically during the transition.

Introduction

p-Chlorobenzamide, $\text{C}_7\text{H}_6\text{ClNO}$, exhibits two polymorphs at room temperature (Harada, Taniguchi, Takaki & Sakurai, 1969). They are triclinic with space group $P\bar{1}$ or $P1$ (α form) and monoclinic with $P2_1/a$ (β form). Harada, Taniguchi, Takaki & Sakurai found

that crystals of the α form undergo a reversible solid-phase transformation at about 44°C to the high-temperature disordered form (γ form, space group $P\bar{1}$), the *a* axis being one third that of the α form. They obtained an 'averaged structure' for the γ form by means of sharp reflexions only, but gave no solutions for the structures of the α and β forms.