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Order–Disorder Phenomena in Structures of Carboxylic Acids: The Structures of Fluoromalonic Acid and Hydroxymalonic Acid at 20 and −150 °C

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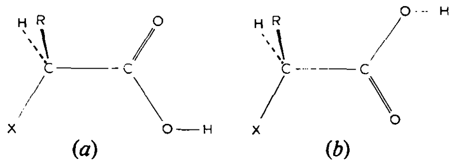
Fluoromalonic acid ($C_3H_3FO_4$) crystallizes in space group *Pnam* ($Z = 4$) with $a = 4{\cdot}593$ (1), $b = 8{\cdot}329$ (2), $c = 11{\cdot}219$ (2) Å at room temperature, and $a = 4{\cdot}576$ (1), $b = 7{\cdot}874$ (1), $c = 11{\cdot}321$ (2) Å at liquid-nitrogen temperature. At room temperature the carboxyl group is disordered (C—O 1·253 and 1·257 Å; C—C—O 116·6 and 116·8°), and this is associated with a splitting of the electron density of the carboxylic H atom. This disorder markedly decreases on cooling (C—O 1·292, C=O 1·221 Å; C—C—O 113·6, C—C=O 119·8°) and the electron-density splitting diminishes. At liquid-nitrogen temperature the C=O bond is antiplanar with the C—F bond. Hydroxymalonic acid (tartronic acid, $C_3H_4O_5$) crystallizes in space group $P2_12_12_1$ ($Z = 4$) with $a = 4{\cdot}494$ (1), $b = 8{\cdot}819$ (2), $c = 10{\cdot}882$ (3) Å at room temperature and $a = 4{\cdot}399$ (1), $b = 8{\cdot}731$ (2), $c = 10{\cdot}905$ (3) Å at liquid-nitrogen temperature. The molecular geometries of the structures at both temperatures are equal within experimental error. The C=O bonds are synplanar with the aliphatic C—O bond.

Introduction

As a result of crystallographic study, the C—O distances and C—C—O angles in fluoromalonic acid at room temperature (RT) were found to be equal within experimental error (Roelofsen, Kanters, Kroon & Vliegenthart, 1971). The equality of C—O distances and C—C—O angles has been found in many free carboxylic acids (*e.g.* Manojlović & Speakman, 1967; Housty, 1968; Filipakis, Leiserowitz, Rabinovich & Schmidt, 1972). These findings suggest that the packing of the carboxyl groups is disordered and imply that at least two conformations (syn- and antiplanar) are present (Leiserowitz, 1976). From an analysis of X-ray data on carboxylic acids (Jeffrey & Parry, 1952; Kanters, Kroon, Peerdeman & Schoone, 1967) the stability of the approximately coplanar arrangement of the α substituent with the non-hydrogen atoms of the acetic acid group (C—COOH), such that the C=O bond is in a *syn* position with respect to that α substituent (Fig. 1), could be inferred. In crystals of unsubstituted saturated monocarboxylic acids the synplanar C^{β}—C^{α}—C=O arrangement is adopted without any known exceptions.

On the other hand, from IR studies of unsubstituted monocarboxylic acids at different temperatures Hayashi, Hara & Kimura (1968) and Hayashi & Umemura (1972, 1974, 1975) deduced that in odd-membered acids the crystal contains the *syn* form at lower temperatures, whereas (lower members excepted) crystals of the even-membered acids contain the *anti* form. They also pointed out that by assuming the difference in energy between the *syn* and *anti* forms to be small, it may be expected that they coexist in crystals of carboxylic acids in various temperature-dependent statistical proportions.

This concept of temperature-dependent disordering in crystals of organic acids prompted us to look into the change of carboxyl group geometry at liquid-nitrogen temperature (LNT) in crystalline fluoromalonic acid. A preliminary account has been given (Kanters, Roelofsen & Kroon, 1975). A more thorough study of the disorder necessitated a redetermination of the structure of fluoromalonic acid at RT. The structure of hydroxymalonic acid (van Eijck, Kanters & Kroon, 1965), which is isotypic with that of fluoromalonic acid (Roelofsen, Kanters, Kroon & Vliegenthart, 1971) and in which at RT no disorder was detected, was also determined at LNT. For comparison a RT structure analysis of the same crystal was carried out.



(*a*) (*b*)

Fig. 1. (*a*) Antiplanar and (*b*) synplanar conformations in α-substituted carboxylic acids.

Experimental

Crystals of fluoromalonic acid were obtained by sublimation *in vacuo*. The highly hygroscopic crystal was sealed in a capillary tube. 660 reflexions [$397 > 3\sigma(I)$] were measured at RT and 624 reflexions [$509 > 3\sigma(I)$] were collected at LNT with the ω-scan technique. Crystals of tartronic acid were grown by slow evaporation from an isobutanol solution. 741 reflexions [$697 > 3\sigma(I)$] were obtained at LNT and 768 reflexions [$690 > 3\sigma(I)$] were collected at RT from a crystal, sealed in a capillary tube, with the ω–2θ scan technique. All cell dimensions and intensities were measured on a Nonius CAD-4 diffractometer. Crystal data are summarized in Table 1.

Lorentz and polarization corrections were applied, but no correction for absorption was made.

Refinement of the structures

The positional parameters obtained from earlier studies (van Eijck, Kanters & Kroon, 1965; Roelofsen, Kanters, Kroon & Vliegenthart, 1971) were used as the starting point for the refinement. The structures were refined by full-matrix least squares, first isotropically, then anisotropically.

Table 1. *Crystal data for fluoromalonic acid and tartronic acid at RT and LNT*

	Fluoromalonic acid ($C_3H_3FO_4$, FW 122·05)		Tartronic acid ($C_3H_4O_5$, FW 120·06)	
	RT	LNT	LNT	RT
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
a (Å)	4·593 (1)	4·576 (1)	4·399 (1)	4·494 (1)
b (Å)	8·329 (2)	7·874 (1)	8·731 (2)	8·819 (2)
c (Å)	11·219 (2)	11·321 (2)	10·905 (3)	10·882 (3)
V (Å^3)	429·2	407·9	418·8	431·3
Systematic absences	$0kl$, $k+l=2n+1$	$0kl$, $k+l=2n+1$	$h00$, $h=2n+1$	$h00$, $h=2n+1$
	$h0l$, $h=2n+1$	$h0l$, $h=2n+1$	$0k0$, $k=2n+1$	$0k0$, $k=2n+1$
			$00l$, $l=2n+1$	$00l$, $l=2n+1$
Space group	*Pnam*	*Pnam*	$P2_12_12_1$	$P2_12_12_1$
Z	4	4	4	4
D_c (g cm^{-3})	1·89	1·99	1·90	1·85
μ(Mo $K\alpha$; λ=0·71069 Å) (cm^{-1})	2·20	2·31	2·05	1·99
Crystal dimensions (mm)	0·5 × 0·3 × 0·2	0·5 × 0·3 × 0·2	0·7 × 0·3 × 0·2	0·7 × 0·3 × 0·2
$(\sin\theta/\lambda)_{\max}$ (Å^{-1})	0·703	0·703	0·703	0·703

A difference synthesis computed with the RT data of fluoromalonic acid showed two maxima (0·3 e Å^{-3}, 0·6 Å apart) near the O···O′ axis of the hydrogen bond; each maximum was occupied by a half H atom.

In the final cycles all parameters were refined except the isotropic temperature factors of the H atoms, which were set equal to those of the carrier atoms; the occupancy parameters of the hydroxyl group H atoms in the RT analysis of fluoromalonic acid were also kept constant.

The function minimized was $\sum w(F_o - F_c)^2$ and the weights were proportional to $\sigma^{-1}(F_o)$. All calculations were performed with the XRAY system (1972). The scattering factors of Stewart, Davidson & Simpson (1965) were used for H; all other scattering factors were from Cromer & Mann (1968). Table 2 shows details of the course of the refinement; Tables 3 and 4 contain positional and thermal parameters of the structures.[*]

Discussion

Bond lengths and angles are given in Table 5, torsion angles in Table 6. The atomic numbering and the

Table 2. *Refinement information*

Expressions for R, R_w and goodness of fit are given in the XRAY system.

	Fluoromalonic acid		Tartronic acid	
	RT	LNT	LNT	RT
Number of variables	48	45	85	85
Number of observations	660	624	741	768
Number of observations $>3\sigma(I)$	397	509	697	690
Type of refinement	Full matrix	Full matrix	Full matrix	Full matrix
R	0·034	0·036	0·035	0·038
R_w	0·033	0·037	0·040	0·042
Goodness of fit	0·45	0·54	0·53	0·27
Average shift/error	0·03	0·08	0·01	0·03
Maximum shift/error	0·17	1·10	0·05	0·26
Maximum density in the final difference syntheses (e Å^{-3})	0·2	0·3	0·3	0·1

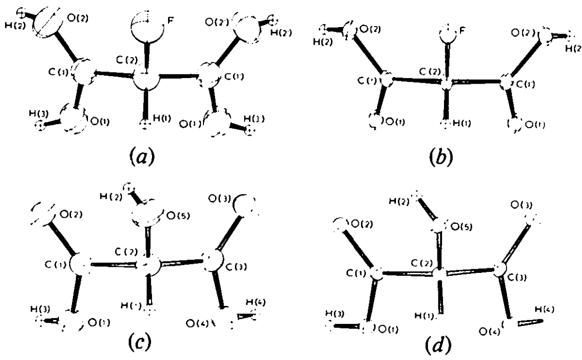


Fig. 2. Molecular conformation and atomic numbering of fluoromalonic acid (*a*) at RT, (*b*) at LNT, and of tartronic acid (*c*) at RT, (*d*) at LNT. C, O and F atoms are represented by thermal ellipsoids at the 50% level (Johnson, 1965).

Table 3. *Fractional atomic coordinates and thermal parameters* ($\times 10^4$, *for* H $\times 10^3$, *except the isotropic thermal parameters*) *for fluoromalonic acid*

The upper lines refer to RT and the lower to LNT. E.s.d.'s are given in parentheses and refer to the last decimal positions. The anisotropic temperature factor is of the form $\exp[-2\pi^2(a^{*2}h^2U_{11}+\ldots+2b^*c^*klU_{23})]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
F	−1243 (4)	1067 (2)	2500	325 (10)	475 (11)	430 (10)	101 (9)	0	0
	−1183 (3)	1182 (2)	2500	156 (7)	191 (7)	121 (6)	42 (6)	0	0
O(1)	4334 (4)	−1215 (2)	1204 (1)	457 (9)	427 (9)	312 (8)	111 (8)	58 (8)	−4 (8)
	4543 (3)	−1145 (2)	1211 (1)	182 (6)	186 (6)	102 (5)	28 (5)	11 (5)	0 (5)
O(2)	2260 (4)	1129 (2)	711 (1)	467 (10)	439 (9)	376 (9)	49 (9)	46 (8)	119 (8)
	2083 (3)	1205 (2)	691 (1)	192 (6)	184 (6)	103 (5)	11 (5)	24 (5)	30 (5)
C(1)	2621 (4)	−69 (2)	1377 (2)	307 (9)	301 (9)	253 (8)	−36 (9)	−36 (8)	−22 (9)
	2706 (3)	−48 (2)	1383 (1)	142 (7)	141 (6)	84 (6)	−33 (6)	−19 (6)	−12 (6)
C(2)	758 (6)	−148 (4)	2500	280 (14)	300 (14)	310 (14)	34 (14)	0	0
	821 (5)	−109 (3)	2500	142 (10)	144 (10)	79 (9)	7 (9)	0	0

	x	y	z	B (Å^2)	Occupancy
H(1)	−25 (7)	−128 (4)	250	2·34	
	−19 (8)	−120 (5)	250	0·96	
H(2)	298 (12)	136 (7)	24 (5)	3·38	0·5
	334 (6)	120 (3)	21 (2)	1·26	1·0
H(3)	514 (12)	−136 (6)	66 (4)	3·15	0·5

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[*] Lists of structure factors for both compounds at RT and LNT have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33524 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. *Fractional atomic coordinates and thermal parameters* (× 10^4, *for* H × 10^3, *except the isotropic thermal parameters*) *for tartronic acid*

The upper lines refer to RT and the lower to LNT. E.s.d.'s are given in parentheses and refer to the last decimal positions. The anisotropic temperature factor is of the form $\exp[-2\pi^2(a^{*2}h^2U_{11}+\ldots+2b^*c^*klU_{23})]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	1299 (5)	−1391 (2)	3604 (2)	439 (13)	233 (8)	276 (9)	81 (9)	94 (9)	10 (8)
	1341 (5)	−1401 (2)	3605 (2)	200 (10)	96 (7)	111 (7)	23 (8)	33 (8)	5 (6)
O(2)	−249 (5)	928 (2)	3070 (2)	448 (13)	277 (8)	283 (8)	88 (10)	73 (10)	80 (7)
	−356 (5)	928 (2)	3042 (2)	181 (9)	117 (7)	110 (7)	21 (8)	8 (8)	22 (6)
O(3)	148 (5)	1155 (2)	6629 (1)	443 (13)	238 (8)	291 (9)	27 (10)	−41 (10)	−57 (7)
	118 (5)	1188 (2)	6626 (1)	184 (9)	98 (7)	115 (7)	−2 (8)	−5 (8)	−19 (6)
O(4)	1303 (5)	−1282 (2)	6281 (2)	443 (13)	235 (8)	280 (9)	61 (9)	−95 (9)	−18 (7)
	1354 (5)	−1278 (2)	6264 (2)	184 (9)	99 (7)	123 (7)	23 (8)	−30 (8)	−3 (7)
O(5)	−4276 (5)	979 (2)	4897 (2)	352 (10)	316 (10)	378 (10)	94 (9)	47 (10)	72 (8)
	−4386 (4)	1012 (2)	4879 (2)	162 (8)	119 (7)	140 (8)	25 (7)	25 (8)	39 (7)
C(1)	−225 (7)	−154 (2)	3760 (2)	275 (13)	212 (9)	208 (9)	3 (11)	−13 (10)	−18 (8)
	−273 (7)	−156 (3)	3748 (2)	141 (11)	110 (9)	88 (9)	−20 (11)	−7 (10)	−13 (8)
C(2)	−2119 (5)	−152 (3)	4923 (2)	267 (10)	207 (9)	240 (10)	−7 (9)	7 (10)	10 (9)
	−2188 (6)	−141 (3)	4915 (2)	148 (10)	89 (9)	108 (9)	−5 (9)	−4 (10)	−8 (9)
C(3)	−99 (7)	−16 (3)	6042 (2)	280 (13)	224 (10)	207 (9)	−18 (11)	26 (10)	11 (8)
	−99 (7)	7 (3)	6031 (2)	136 (11)	113 (10)	96 (9)	−18 (10)	19 (9)	12 (8)

	x	y	z	B (Å^2)		x	y	z	B (Å^2)
H(1)	−332 (6)	−112 (3)	496 (3)	1·97	H(3)	237 (8)	−138 (4)	310 (3)	2·49
	−288 (7)	−119 (3)	498 (3)	0·84		227 (8)	−145 (4)	293 (3)	1·02
H(2)	−395 (8)	149 (4)	456 (3)	2·70	H(4)	271 (7)	−120 (4)	680 (3)	2·46
	−361 (8)	171 (4)	447 (3)	1·08		261 (8)	−117 (4)	691 (3)	1·03

Table 5. *Bond lengths* (Å) *and angles* (°)

E.s.d.'s are given in parentheses.

	Fluoromalonic acid		Tartronic acid		
	RT	LNT	LNT	RT	
C(1)–O(1)	1·253 (3)	1·221 (2)	1·221 (3)	1·215 (3)	C(1)–O(2)
			1·222 (3)	1·219 (3)	C(3)–O(3)
C(1)–O(2)	1·257 (3)	1·292 (2)	1·308 (3)	1·300 (3)	C(1)–O(1)
			1·316 (3)	1·309 (3)	C(3)–O(4)
C(1)–C(2)	1·524 (3)	1·531 (2)	1·527 (3)	1·524 (3)	C(1)–C(2)
			1·531 (3)	1·524 (3)	C(2)–C(3)
C(2)–F	1·367 (4)	1·369 (3)	1·396 (3)	1·391 (3)	C(2)–O(5)
C(2)–H(1)	1·05 (3)	0·98 (4)	0·97 (3)	1·01 (3)	C(2)–H(1)
O(2)–H(2)	0·65 (5)	0·79 (3)	0·84 (3)	0·73 (3)	O(1)–H(3)
			0·90 (3)	0·86 (3)	O(4)–H(4)
O(1)–H(3)	0·73 (5)				
			0·83 (3)	0·60 (3)	O(5)–H(2)
C(2)–C(1)–O(1)	116·6 (2)	119·8 (2)	120·2 (2)	120·5 (2)	C(2)–C(1)–O(2)
			122·7 (2)	122·7 (2)	C(2)–C(3)–O(3)
C(2)–C(1)–O(2)	116·8 (2)	113·6 (2)	114·0 (2)	113·8 (2)	C(2)–C(1)–O(1)
			111·9 (2)	112·2 (2)	C(2)–C(3)–O(4)
O(1)–C(1)–O(2)	126·6 (2)	126·6 (2)	125·9 (2)	125·7 (2)	O(1)–C(1)–O(2)
			125·4 (2)	125·1 (2)	O(3)–C(3)–O(4)
C(1)–C(2)–C(1′)	111·5 (2)	111·3 (2)	109·4 (2)	109·3 (2)	C(1)–C(2)–C(3)
C(1)–C(2)–F	110·2 (2)	110·7 (1)	111·4 (2)	111·9 (2)	C(1)–C(2)–O(5)
			112·1 (2)	112·0 (2)	C(3)–C(2)–O(5)
C(1)–C(2)–H(1)	107 (1)	107 (1)	103 (2)	109 (2)	C(1)–C(2)–H(1)
			102 (2)	111 (2)	C(3)–C(2)–H(1)
H(1)–C(2)–F	112 (2)	110 (2)	118 (2)	103 (2)	H(1)–C(2)–O(5)
C(1)–O(2)–H(2)	130 (5)	105 (2)	114 (2)	116 (3)	C(1)–O(1)–H(3)
			111 (2)	115 (2)	C(3)–O(4)–H(4)
C(1)–O(1)–H(3)	125 (4)				
			105 (2)	113 (4)	C(2)–O(5)–H(2)

Symmetry code: (′) $x, y, -z+\frac{1}{2}$.

Table 6. *Torsion angles* (°)

The torsion angle $A(1)$–$A(2)$–$A(3)$–$A(4)$ is viewed along $A(2)$–$A(3)$, with a clockwise rotation of $A(1)$ to $A(4)$ taken to be positive.

Fluoromalonic acid	RT	LNT	Tartronic acid LNT	RT	
O(1)–C(1)–C(2)–F	−172·6	−177·3	13·9	15·4	O(2)–C(1)–C(2)–O(5)
			−17·7	−19·5	O(5)–C(2)–C(3)–O(3)

Table 7. *Hydrogen-bond geometry*

Fluoromalonic acid	RT	LNT	Tartronic acid LNT	RT	
O(2)···O(1′)	2·659 (2) Å	2·651 (2) Å	2·667 (3) Å	2·685 (3) Å	O(1)···O(3″)
			2·636 (3)	2·652 (3)	O(2)···O(4″)
O(2)–H(2)	0·65 (5)	0·79 (3)	0·84 (3)	0·73 (3)	O(1)–H(3)
			0·90 (3)	0·86 (3)	O(4″)–H(4″)
O(1′)–H(3′)	0·73 (5)				
O(1′)···H(2)	2·04 (5)	1·88 (3)	1·84 (3)	1·96 (3)	O(3″)···H(3)
			1·74 (3)	1·80 (3)	O(2)···H(4″)
O(2)···H(3′)	1·95 (5)				
O(2)–H(2)···O(1′)	159 (3)°	164 (3)°	166 (3)°	172 (3)°	O(1)–H(3)···O(3″)
			174 (3)	170 (3)	O(2)···H(4″)–O(4″)
O(1′)–H(3′)···O(2)	163 (3)				

Symmetry code: superscripts: (′) $1-x, -y, -z$; (″) $\frac{1}{2}-x, -y, \frac{1}{2}+z$.

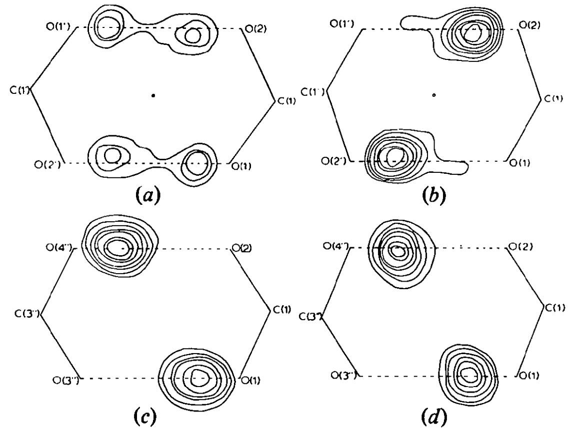

Fig. 3. Difference syntheses in the plane of the carboxyl group dimers of fluoromalonic acid (*a*) at RT, (*b*) at LNT, and of tartronic acid (*c*) at RT, (*d*) at LNT. Contours are on an arbitrary scale.

orientation of the thermal ellipsoids (*ORTEP*, Johnson, 1965) are shown in Fig. 2.

After termination of the refinements, difference syntheses in the least-squares plane of the carboxyl group dimers, based on F_c computed with all atoms except the contributions of the H atoms of the carboxyl groups, show two distinct peaks of height 0·42 e Å^{-3} in the O···O hydrogen-bond region for the RT structure of fluoromalonic acid and one unsplit peak of height 0·65 e Å^{-3} for the LNT structure of fluoromalonic acid (Fig. 3). The analogous difference syntheses for tartronic acid reveal two unsplit peaks for the independent carboxylic H atoms (0·60 and 0·55 e Å^{-3}) for the RT structure and also for the LNT structure (0·62 and 0·70 e Å^{-3}) (Fig. 3). The electron-density splitting in the RT structure of fluoromalonic acid, which experimentally appeared to be a reversible phenomenon, can be accounted for if it is assumed that the *syn* and *anti* conformations coexist in temperature-dependent ratios. Such a static disorder implies that the temperature factors of the carboxyl group O atoms, which are approximately 0·2 Å apart in the two distinct conformations, become artificially high. It is of interest to compare the U's of the RT structures of fluoromalonic and tartronic acids. In particular, the U_{22}'s of O(1) and O(2) of fluoromalonic acid (0·043 and 0·044 Å^2) are considerably greater than those of the corresponding atoms of tartronic acid (0·026 and 0·023 Å^2); upon cooling, these values in fluoromalonic acid decrease significantly more than in tartronic acid.

Another possibility would be that the proton is centrally situated on a locally symmetric O—H···O bond and that the C—O bonds of the carboxyl groups are in a state of resonance. However, the length of the hydrogen bond (Table 7), the significant electron-density splitting and the behaviour of the thermal parameters are not in favour of such a view. Evidently packing and conformational energy differences in tartronic acid are large so that the synplanar carboxyl group conformation also persists at RT. In fluoromalonic acid these differences are small so that the entropy effect manifests itself by the occurrence of conformational disorder at RT, while at LNT the anti-planar conformation is favoured (Table 6), either by dominant intramolecular or decisive packing conditions.

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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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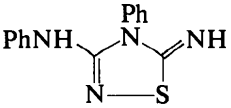
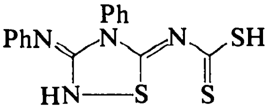
The 1:1 adduct of Hector's base and carbon disulphide crystallizes as a hydrate, $C_{15}H_{12}N_4S_3.0{\cdot}7H_2O$, in the orthorhombic system, space group $P2_12_12_1$, with $a = 20{\cdot}297$ (3), $b = 10{\cdot}355$ (2), $c = 7{\cdot}797$ (2) Å, $Z = 4$. The structure was solved by direct methods from diffractometer data and refined to $R = 0{\cdot}0376$. 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

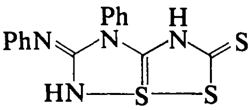
The oxidation of 1-phenylthiourea with H_2O_2 yields a heterocyclic base, $C_{14}H_{12}N_4S$ (Hector, 1889), generally known as Hector's base, whose constitution is 5-imino-4-phenyl-3-phenylamino-4*H*-1,2,4-thiadiazoline (I) (Glidewell & Liles, 1978). With CS_2 Hector's base forms a 1:1 adduct (Fromm & 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



(I)



(II)



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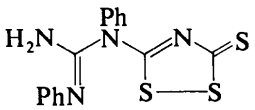

(IV)

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