

C11—C12	1.390 (6)	C32—O34	1.178 (6)	Cluzeau, P., Nguyen, H. T., Destrade, C., Isaert, N., Barois, P. & Babeau, A. (1995). <i>Mol. Cryst. Liq. Cryst.</i> In the press.
C12—C13	1.383 (6)	O33—C35	1.469 (6)	Cotrait, M., Destrade, C. & Gasparoux, H. (1977). <i>Mol. Cryst. Liq. Cryst.</i> <b>39</b> , 159–172.
C13—C14	1.396 (6)	C35—C36	1.503 (8)	Davies, K. (1983). <i>SNOOPI. Program for Drawing Crystal and Molecular Diagrams</i> . Chemical Laboratory, University of Oxford, England.
C13—C16	1.453 (6)	C35—C37	1.497 (8)	Enraf–Nonius (1977). <i>CAD-4 Operations Manual</i> . Enraf–Nonius, Delft, The Netherlands.
C14—C15	1.364 (6)	C37—C38	1.521 (9)	Gilmore, C. J. (1984). <i>J. Appl. Cryst.</i> <b>17</b> , 42–46.
C16—C17	1.170 (6)	C38—C39	1.40 (1)	Hori, K. & Endo, K. (1993). <i>Bull. Chem. Soc. Jpn.</i> <b>66</b> , 46–50.
C17—C20	1.442 (6)	C39—C40	1.53 (1)	Hori, K., Kawahara, S. & Ito, K. (1993). <i>Ferroelectrics</i> , <b>147</b> , 91–94.
O18—C19	1.423 (5)	C40—C41	1.40 (1)	Hori, K. & Ohashi, Y. (1991). <i>J. Mater. Chem.</i> <b>1</b> , 667–672.
O18—C23	1.364 (5)	C41—C42	1.53 (1)	Hori, K. & Ohashi, Y. (1993). <i>Mol. Cryst. Liq. Cryst.</i> <b>203</b> , 171–176.
C2—C1—C6	119.5 (4)	C17—C20—C21	120.2 (4)	Sheldrick, G. M. (1976). <i>SHELX76. Program for the Solution of Crystal Structures</i> . University of Cambridge, England.
C2—C1—C32	118.6 (4)	C17—C20—C25	121.7 (4)	
C6—C1—C32	121.9 (4)	C21—C20—C25	118.1 (4)	
C1—C2—C3	121.1 (4)	C20—C21—C22	120.8 (4)	
C2—C3—C4	118.2 (4)	C21—C22—C23	120.1 (4)	
C3—C4—C5	123.2 (4)	O18—C23—C22	116.1 (4)	
C3—C4—O7	120.6 (4)	O18—C23—C24	123.9 (4)	
C5—C4—O7	116.2 (4)	C22—C23—C24	119.9 (4)	
C4—C5—C6	118.4 (4)	C23—C24—C25	119.6 (4)	
C1—C6—C5	119.7 (4)	C20—C25—C24	121.4 (4)	
C4—O7—C8	117.5 (3)	C19—C26—C27	110.2 (3)	
O7—C8—O9	123.5 (4)	C26—C27—C28	114.2 (3)	
O7—C8—C10	112.1 (3)	C27—C28—C29	111.6 (3)	
O9—C8—C10	124.4 (4)	C28—C29—C30	113.2 (4)	
C8—C10—C11	122.7 (4)	C29—C30—C31	113.8 (4)	
C8—C10—C15	117.5 (3)	C1—C32—O34	123.2 (4)	
C11—C10—C15	119.9 (4)	C1—C32—O33	113.9 (4)	
C10—C11—C12	119.5 (4)	C32—O33—C35	117.1 (4)	
C11—C12—C13	120.5 (4)	O33—C35—C36	108.3 (4)	
C12—C13—C14	119.5 (4)	O33—C35—C37	107.1 (4)	
C12—C13—C16	122.6 (4)	O34—C32—O33	122.9 (4)	
C14—C13—C16	117.9 (4)	C36—C35—C37	110.7 (5)	
C13—C14—C15	120.0 (4)	C35—C37—C38	110.1 (5)	
C10—C15—C14	120.6 (4)	C37—C38—C39	121.9 (6)	
C13—C16—C17	176.8 (5)	C38—C39—C40	117.6 (7)	
C16—C17—C20	178.0 (5)	C39—C40—C41	111.0 (7)	
C19—O18—C23	118.4 (3)	C40—C41—C42	109.8 (7)	
O18—C19—C26	108.9 (3)			
C3—C4—O7—C8	−63.2 (4)	C32—O33—C35—C36	−92.9 (4)	
C5—C4—O7—C8	118.5 (4)	C32—O33—C35—C37	147.6 (4)	
C23—O18—C19—C26	175.9 (3)	O33—C35—C37—C38	−70.7 (5)	
C19—O18—C23—C22	−175.3 (4)	C36—C35—C37—C38	171.4 (5)	

The structure was solved by direct methods, which led to the positions of almost all non-H atoms; the remaining atoms appeared after successive Fourier syntheses. The atomic parameters of non-H atoms were refined with full-matrix least squares. H atoms were located in their theoretical positions (refined isotropically) and followed the C atoms to which they are attached.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1977). Cell refinement: *CAD-4 Software*. Data reduction: *SDP* (B. A. Frenz & Associates Inc., 1982). Program(s) used to solve structure: *MITHRIL* (Gilmore, 1984). Program(s) used to refine structure: *SHELX76* (Sheldrick, 1976). Molecular graphics: *SNOOPI* (Davies, 1983). Software used to prepare material for publication: local programs.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, and complete geometry have been deposited with the IUCr (Reference: PA1193). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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 B. A. Frenz & Associates Inc. (1982). *SDP Structure Determination Package*. College Station, Texas, USA.  
 Bideau, J. P., Bravic, G., Cotrait, M., Destrade, C. & Nguyen, H. T. (1991). *Liq. Cryst.* **10**, 379–388.

*Acta Cryst.* (1996). **C52**, 444–447

## A 5,18:9,14-Di-*o*-benzeno-6,17:7,16:8,15-trimethanobenzo[1'',2'':3,4;4'',5'':3',4']dicyclobuta[1,2-*b*:1',2'-*b'*]dianthracene Derivative

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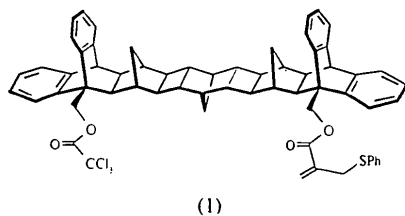
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## Abstract

The phenylthiomethyl and trichloroacetyl groups of the title compound, 2-phenylthiomethyl-2-propenoic acid (5a $\alpha$ ,6 $\beta$ ,6a $\alpha$ ,6b $\beta$ ,7 $\alpha$ ,7a $\beta$ ,7b $\alpha$ ,8 $\beta$ ,8a $\alpha$ ,14a $\alpha$ ,15 $\beta$ ,15a $\alpha$ ,15b $\beta$ ,16 $\alpha$ ,16a $\beta$ ,16b $\alpha$ ,17 $\beta$ ,17a $\alpha$ )[6,6a,6b,7,7a,7b,8,8a,9,14,14a,15,15a,15b,16,16a,16b,17,17a,18-icosahydro-9-(trichloroacetoxymethyl)-5,18:9,14-di-*o*-benzeno-6,17:7,16:8,15-trimethanobenzo[1'',2'':3,4;4'',5'':3',4']dicyclobuta[1,2-*b*:1',2'-*b'*]dianthracen-5(5aH)-yl]methyl ester hemihydrate, C<sub>63</sub>H<sub>55</sub>Cl<sub>3</sub>O<sub>4</sub>S.0.5H<sub>2</sub>O, adopt a *cis* orientation with respect to each other about the hydrocarbon skeleton of the template. The average bond distances in the hydrocarbon skeleton are: Csp<sup>3</sup>—Csp<sup>3</sup> 1.54 (1), Csp<sup>3</sup>—Csp<sup>2</sup> 1.52 (1) and C—C aromatic 1.39 (1) Å.

## Comment

The main objective of the crystal analysis described in this paper was to ascertain the molecular structure and conformation of the title compound, (1). The crystal structure is composed of independent molecules of (1) separated by normal van der Waals distances. The asymmetric unit also contains a half molecule of water, lying close to an inversion centre and disordered.



An ORTEPII (Johnson, 1976) drawing of (1) with numbering scheme is presented in Fig. 1. The molecular dimensions in the hydrocarbon skeleton of the template are unexceptional with average bond distances:  $Csp^3-Csp^3$  1.54 (1),  $Csp^3-Csp^2$  1.52 (1) and C—C aromatic 1.39 (1) Å. The phenylthiomethyl and trichloroacetate groups adopt a *cis* orientation with respect to each other. The molecules are packed in a highly efficient manner in the unit cell (Fig. 2) and are arranged as centrosymmetric pairs with the substituent groups of one pointing to the hydrocarbon backbone of the other, thus forming more-or-less rectangular blocks.

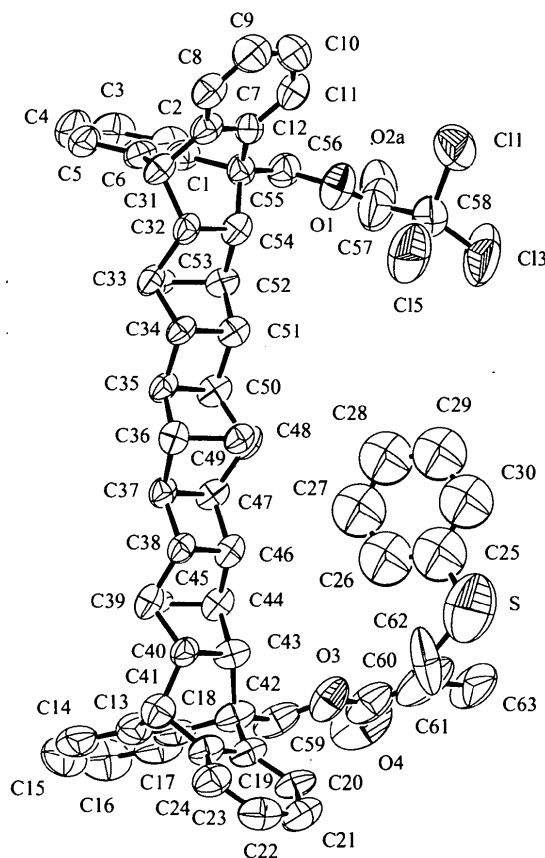


Fig. 1. ORTEPII (Johnson, 1976) drawing of the title compound with crystallographic numbering scheme; the displacement ellipsoids are plotted at the 50% probability level. H atoms have been ignored for clarity and only three of the six sites of disordered Cl atoms have been included. The large thermal motion of the SPh C atoms is not shown.

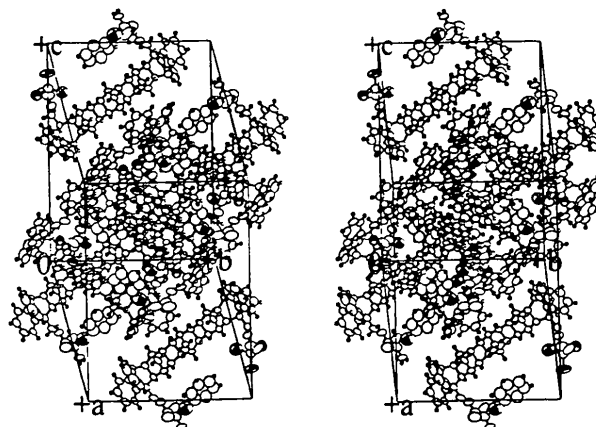


Fig. 2. Stereoview of the unit cell showing the molecular packing.

## Experimental

The synthesis of the title compound was reported by Feldman, Bobo, Ensel, Lee & Weinreb (1990).

### Crystal data

$C_{63}H_{55}Cl_3O_4S \cdot 0.5H_2O$

$M_r = 1023.55$

Monoclinic

$C2/c$

$a = 28.103$  (4) Å

$b = 18.370$  (3) Å

$c = 23.755$  (6) Å

$\beta = 123.58$  (1)°

$V = 10217$  (3) Å<sup>3</sup>

$Z = 8$

$D_x = 1.33$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation

$\lambda = 0.71069$  Å

Cell parameters from 25 reflections

$\theta = 10-15^\circ$

$\mu = 0.271$  mm<sup>-1</sup>

$T = 293$  (1) K

Block

$0.45 \times 0.42 \times 0.35$  mm

Colourless

### Data collection

Enraf-Nonius CAD-4 diffractometer

$\omega/2\theta$  scans

Absorption correction:

refined from  $\Delta F$

(DIFABS; Walker & Stuart, 1983)

$T_{min} = 0.480$ ,  $T_{max} = 0.910$

7706 measured reflections

5697 independent reflections

3176 observed reflections

$[I > 3\sigma(I)]$

$R_{int} = 0.029$

$\theta_{max} = 23^\circ$

$h = -30 \rightarrow 30$

$k = 0 \rightarrow 19$

$l = 0 \rightarrow 25$

3 standard reflections

frequency: 120 min

intensity decay: none

### Refinement

Refinement on  $F$

$R = 0.098$

$wR = 0.112$

$S = 3.42$

3176 reflections

Blocks, 415 and 382

parameters

H-atom parameters not

refined

$w = 1/[\sigma^2(F) + 0.014F^2]$

$(\Delta/\sigma)_{max} = <0.2$

$\Delta\rho_{max} = 0.80$  e Å<sup>-3</sup>

$\Delta\rho_{min} = -0.62$  e Å<sup>-3</sup>

Extinction correction: none

Atomic scattering factors

from Cromer & Mann

(1968) and Stewart,

Davidson & Simpson

(1965)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)
$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	U <sub>eq</sub>
S(1)	0.2749 (2)	-0.1334 (4)	0.3184 (3)	0.180 (5)
Cl(1)†	0.2980 (10)	-0.6124 (8)	0.6089 (11)	0.140 (10)
Cl(2)†	0.2799 (4)	-0.4521 (6)	0.5851 (4)	0.153 (8)
Cl(3)†	0.3289 (7)	-0.4489 (6)	0.5682 (5)	0.197 (11)
Cl(4)†	0.3332 (6)	-0.5361 (10)	0.5312 (5)	0.195 (12)
Cl(5)†	0.3658 (5)	-0.5873 (5)	0.5550 (5)	0.131 (7)
Cl(6)†	0.2885 (7)	-0.5754 (12)	0.6007 (10)	0.156 (12)
O(1)	0.3849 (3)	-0.5032 (4)	0.7148 (4)	0.088 (5)
O(2a)†	0.4395 (7)	-0.5515 (11)	0.6855 (8)	0.161 (14)
O(2b)†	0.4162 (14)	-0.4662 (18)	0.6603 (15)	0.161 (10)
O(3)	0.3837 (3)	0.0384 (5)	0.4191 (4)	0.099 (6)
O(4)	0.4435 (5)	0.0081 (6)	0.3889 (5)	0.176 (10)
O(5)†	0.2605 (11)	0.2858 (13)	0.0240 (12)	0.190 (9)
C(1)	0.4631 (3)	-0.4333 (5)	0.8931 (4)	0.052 (5)
C(2)	0.5177 (4)	-0.4580 (5)	0.9252 (5)	0.062 (6)
C(3)	0.5565 (4)	-0.4379 (6)	0.9933 (6)	0.077 (7)
C(4)	0.5422 (5)	-0.3965 (6)	1.0273 (5)	0.075 (7)
C(5)	0.4856 (4)	-0.3714 (5)	0.9954 (4)	0.068 (6)
C(6)	0.4474 (3)	-0.3897 (5)	0.9289 (4)	0.054 (5)
C(7)	0.3511 (3)	-0.4361 (5)	0.8596 (4)	0.054 (5)
C(8)	0.3100 (4)	-0.4594 (6)	0.8707 (5)	0.071 (7)
C(9)	0.2848 (4)	-0.5261 (7)	0.8486 (5)	0.087 (8)
C(10)	0.2994 (4)	-0.5687 (6)	0.8122 (6)	0.080 (7)
C(11)	0.3392 (4)	-0.5457 (5)	0.7989 (4)	0.063 (6)
C(12)	0.3656 (3)	-0.4804 (5)	0.8236 (4)	0.052 (5)
C(13)	0.4278 (4)	0.2217 (6)	0.5891 (5)	0.071 (7)
C(14)	0.4651 (5)	0.2661 (6)	0.6424 (6)	0.086 (8)
C(15)	0.5229 (6)	0.2721 (7)	0.6619 (7)	0.099 (10)
C(16)	0.5409 (5)	0.2348 (9)	0.6304 (9)	0.120 (12)
C(17)	0.5036 (5)	0.1881 (7)	0.5734 (7)	0.112 (10)
C(18)	0.4466 (4)	0.1812 (6)	0.5545 (5)	0.076 (7)
C(19)	0.3489 (3)	0.1787 (5)	0.4537 (4)	0.065 (6)
C(20)	0.3174 (4)	0.1837 (5)	0.3835 (4)	0.068 (6)
C(21)	0.2703 (4)	0.2275 (6)	0.3487 (5)	0.081 (7)
C(22)	0.2532 (4)	0.2692 (5)	0.3832 (5)	0.071 (7)
C(23)	0.2841 (4)	0.2637 (5)	0.4524 (5)	0.083 (7)
C(24)	0.3320 (3)	0.2206 (5)	0.4889 (4)	0.057 (6)
C(25)	0.3246 (7)	-0.1855 (7)	0.3872 (6)	0.112 (11)
C(26)	0.3681 (5)	-0.1515 (6)	0.4448 (8)	0.124 (11)
C(27)	0.4002 (6)	-0.1919 (9)	0.5051 (6)	0.173 (17)
C(28)	0.3861 (7)	-0.2647 (8)	0.5066 (7)	0.20 (2)
C(29)	0.3346 (8)	-0.2924 (7)	0.4529 (9)	0.22 (2)
C(30)	0.3033 (7)	-0.2519 (10)	0.3931 (8)	0.25 (3)
C(31)	0.3848 (3)	-0.3671 (5)	0.8869 (4)	0.057 (5)
C(32)	0.3732 (3)	-0.3239 (4)	0.8239 (4)	0.053 (5)
C(33)	0.4067 (3)	-0.2531 (4)	0.8352 (4)	0.054 (5)
C(34)	0.3741 (3)	-0.2128 (4)	0.7677 (3)	0.048 (4)
C(35)	0.4017 (3)	-0.1482 (5)	0.7568 (4)	0.049 (5)
C(36)	0.3622 (3)	-0.0899 (4)	0.7092 (4)	0.053 (5)
C(37)	0.3983 (3)	-0.0388 (4)	0.6964 (4)	0.048 (5)
C(38)	0.3666 (4)	0.0186 (5)	0.6379 (4)	0.059 (5)
C(39)	0.3950 (4)	0.0898 (5)	0.6439 (4)	0.065 (6)
C(40)	0.3603 (4)	0.1241 (5)	0.5728 (4)	0.057 (5)
C(41)	0.3668 (4)	0.2067 (5)	0.5640 (4)	0.067 (6)
C(42)	0.4009 (4)	0.1306 (5)	0.5001 (4)	0.074 (6)
C(43)	0.3789 (4)	0.0787 (5)	0.5331 (4)	0.062 (5)
C(44)	0.4195 (3)	0.0224 (5)	0.5855 (4)	0.060 (5)
C(45)	0.4501 (3)	0.0656 (5)	0.6524 (4)	0.065 (6)
C(46)	0.3827 (3)	-0.0284 (5)	0.5958 (4)	0.055 (5)
C(47)	0.4127 (3)	-0.0842 (5)	0.6543 (4)	0.057 (5)
C(48)	0.3810 (3)	-0.1558 (5)	0.6444 (4)	0.056 (5)
C(49)	0.3274 (3)	-0.1308 (5)	0.6412 (4)	0.052 (5)
C(50)	0.4147 (3)	-0.1943 (5)	0.7133 (4)	0.056 (5)
C(51)	0.3866 (3)	-0.2606 (4)	0.7229 (4)	0.053 (5)
C(52)	0.4269 (3)	-0.3211 (5)	0.7722 (4)	0.057 (5)
C(53)	0.4613 (3)	-0.2789 (5)	0.8394 (4)	0.055 (5)
C(54)	0.3885 (3)	-0.3726 (5)	0.7819 (4)	0.055 (5)
C(55)	0.4139 (3)	-0.4487 (4)	0.8188 (4)	0.054 (5)
C(56)	0.4331 (4)	-0.4938 (5)	0.7847 (4)	0.067 (6)
C(57)	0.3922 (7)	-0.5247 (10)	0.6696 (7)	0.139 (13)
C(58)	0.3347 (8)	-0.5334 (7)	0.6002 (6)	0.135 (12)

C(59)	0.4247 (5)	0.0906 (6)	0.4660 (6)	0.092 (8)
C(60)	0.3998 (8)	0.0003 (8)	0.3835 (7)	0.114 (11)
C(61)	0.3550 (9)	-0.0500 (11)	0.3363 (8)	0.142 (14)
C(62)	0.3063 (9)	-0.0582 (11)	0.3407 (9)	0.22 (2)
C(63)	0.3585 (8)	-0.0884 (7)	0.2893 (8)	0.182 (18)

† Occupancies are 0.49 (1) for Cl(1), Cl(3) and Cl(5), 0.51 (1) for Cl(2), Cl(4) and Cl(6), 0.63 (1) for O(2a), 0.37 (1) for O(2b), and 0.50 for O(5).

Table 2. Selected geometric parameters (Å, °)

C(25)—S(1)	1.74 (1)	C(60)—O(4)	1.17 (3)
C(62)—S(1)	1.57 (2)	C(55)—C(54)	1.59 (1)
C(56)—O(1)	1.46 (1)	C(56)—C(55)	1.45 (2)
C(57)—O(1)	1.26 (1)	C(58)—C(57)	1.55 (2)
C(57)—O(2a)	1.26 (3)	C(61)—C(60)	1.46 (2)
C(57)—O(2b)	1.35 (4)	C(57)—C(61)	1.44 (4)
C(59)—O(3)	1.44 (1)	C(63)—C(61)	1.37 (3)
C(60)—O(3)	1.35 (2)		
Average C—C distances			
C(1)—C(6) ring	1.38 (2)		
C(7)—C(12) ring	1.38 (2)		
C(13)—C(18) ring	1.40 (2)		
C(19)—C(24) ring	1.38 (2)		
C(25)—C(30) ring	1.40 (constrained)		
C(31)—C(55) template	1.54 (1)		
C(sp <sup>2</sup> )—C(sp <sup>3</sup> )	1.52 (1)		
C—Cl	1.52 (3)—2.03 (2)		
C(62)—S(1)—C(25)	99.1 (7)	C(58)—C(57)—O(2a)	125.7 (18)
C(57)—O(1)—C(56)	121.3 (10)	C(58)—C(57)—O(2b)	103.2 (16)
C(60)—O(3)—C(59)	115.2 (12)	O(4)—C(60)—O(3)	124.2 (13)
C(26)—C(25)—S(1)	119.6 (9)	C(61)—C(60)—O(3)	111.2 (19)
C(30)—C(25)—S(1)	114.1 (10)	C(61)—C(60)—O(4)	124.6 (20)
C(55)—C(56)—O(1)	107.6 (8)	C(52)—C(61)—C(60)	117.5 (19)
O(2a)—C(57)—O(1)	120.4 (13)	C(63)—C(61)—C(60)	122.2 (22)
O(2b)—C(57)—O(1)	102.7 (21)	C(63)—C(61)—C(62)	120.4 (17)
C(58)—C(57)—O(1)	111.9 (17)	C(61)—C(62)—S(1)	116.7 (17)

## Range of C—C—C angles

C(1)—C(6) ring	118 (1)—123 (1)
C(7)—C(12) ring	118 (1)—122 (1)
C(13)—C(18) ring	117 (2)—122 (1)
C(19)—C(24) ring	119 (1)—123 (1)
C(25)—C(30) ring	120 (constrained)
C(31)—C(55) template	88.5 (6)—119.7 (6)
C atoms at junctions	112.7 (8)—128.3 (10)

The Cl atoms of the trichloroacetyl group are disordered over six sites with occupancy factors of between 0.49 (1) and 0.51 (1). The carbonyl O atom of the trichloroacetyl group is also disordered over two sites. The C atoms in the phenyl ring of the phenylthiomethyl group exhibit large thermal motions indicating gross disorder in this part of the molecule as well. As a result of this gross disorder in the bulky parts of the molecule, the *R* factor could not be improved further. Since the data were collected several years ago on a sample that is no longer available, a more accurate absorption correction could not be applied to the data.

Space group *C2/c* or *Cc* from the systematic absences:  $hkl = 2n + 1$  and  $00l, l = 2n + 1$ ; the former was chosen and confirmed by successful analysis. Lorentz—polarization corrections were applied. The structure was solved by direct methods using *SAPI91* (Fan, 1991) and refined by block-diagonal least squares using *SHELX76* (Sheldrick, 1976). Non-H atoms were allowed anisotropic temperature factors except the O atom of the water molecule and O(2b) (the smaller fraction of the disordered carbonyl O atom), which were allowed isotropic temperature factors. H atoms were included at geometrically idealized positions (C—H 0.95 Å) except for the H atoms of the water molecule which were

ignored. Corrections were made for anomalous dispersion (Cromer & Liberman, 1970). A difference map calculated at the conclusion of the refinement had no chemically significant features.

The author thanks Dr Feldman for providing the crystals of the title compound.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the IUCr (Reference: BR1035). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## 5-(*p*-Anisidino)-4-cyano-2,3-dihydro-3-pyrazolone Hemihydrate, C<sub>11</sub>H<sub>10</sub>N<sub>4</sub>O<sub>2</sub>·0.5H<sub>2</sub>O

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## Abstract

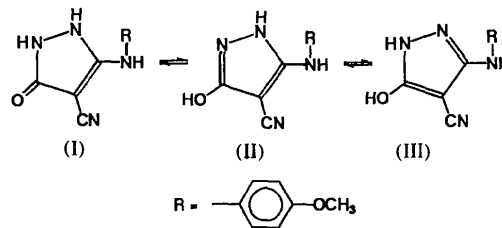
The title compound exists entirely in the keto form in the solid state, although NMR spectroscopy indicates that in solution the enol form is present. The asymmetric unit contains two structurally similar independent molecules and a water molecule of solvation. There is an extensive three-dimensional network of intermolecular hydrogen bonds of types N—H···O, N—H···N and OW—H···O.

## Comment

Pyrazole derivatives have been found to have moderate antimalarial activity (Garg, Singhal & Mathur, 1973). A number of derivatives of pyrazoles and several other heterocycles were synthesized and tested during a research project aimed at finding new antimalarial drugs which are more active or less toxic than those currently in use (Charris, 1993). The title compound, (I), was prepared as a part of that project, but was found to have no antimalarial activity.

The structure analysis showed that the asymmetric unit contains two independent molecules of (I) and a water molecule of solvation. The two organic molecules (labelled *a* and *b*) are structurally similar and only three bond distances differ by more than three e.s.d.'s: O2—C7 (3.3σ), N1—N2 (3.8σ) and N2—C1 (5.8σ).

In solution, the keto form (I) can exist in tautomeric equilibrium with enol forms (II) and (III). Indeed, the NMR spectrum in solution (see *Experimental*) shows an absorption corresponding to an OH group. However, in the crystal structure, the molecules are in the keto form, as shown by the bond length pattern of the five-membered ring, the C=O distance, the positions of the H atoms and the hydrogen-bonding scheme. In addition, the solid-state IR spectrum (see *Experimental*) shows an absorption assigned to a C=O stretch.



The bond lengths in the five-membered rings (mean values N1—N2 1.405, N1—C3 1.346, N2—C1 1.369, C1—C2 1.426, C2—C3 1.397 Å) are similar to those observed in several other pyrazolones (Mogensen & Simonsen, 1991, and references therein) and are significantly different from the values observed in pyrazole rings (Allen *et al.*, 1987). Moreover, the endo- and exocyclic bond angles do not follow the rules described by Bonati & Bovio (1990) for pyrazole rings. The C=O distances (mean value 1.255 Å) are also comparable to those found in pyrazolones (Mogensen & Simonsen, 1991, and references therein) and are significantly shorter than the value of 1.333 Å expected for enols (Allen *et al.*, 1987).

The N3—C3 distances (mean 1.343 Å) are significantly shorter than the N3—C4 bond lengths (mean 1.437 Å). Since N3 is planar, the former values can be compared with the value of 1.339 Å tabulated for planar C=C—NH—C moieties (Allen *et al.*, 1987), but the N3—C4 distances are too long when compared with the value of 1.353 Å for planar C<sub>aryl</sub>—NH—C moieties (Allen *et al.*, 1987).