$S = 0.78$
6093 reflections
484 parameters
H atoms treated by a mixture of independent and constrained refinement
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = −0.06 (6)

Table 1. *Selected geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| C1A—F1A | 1.365 (5) | C16A—C17A | 1.368 (6) |
| C1B—F1B | 1.366 (5) | C16A—O1A | 1.384 (5) |
| C4A—C7A | 1.518 (6) | C16B—C17B | 1.383 (6) |
| C4B—C7B | 1.518 (5) | C16B—O1B | 1.392 (5) |
| C7A—C11A | 1.537 (5) | C17A—O2A | 1.375 (5) |
| C7A—C8A | 1.541 (5) | C17B—O2B | 1.370 (4) |
| C7B—C8B | 1.538 (5) | C19A—O1A | 1.417 (6) |
| C7B—C11B | 1.539 (5) | C19A—O2A | 1.445 (5) |
| C8A—C9A | 1.517 (6) | C19B—O2B | 1.418 (5) |
| C8B—C9B | 1.516 (5) | C19B—O1B | 1.452 (5) |
| C9A—N1A | 1.496 (5) | Cl1···H1O4$^{i}$ | 2.35 (5) |
| C9B—N1B | 1.490 (5) | Cl2···H2N2 | 1.94 (5) |
| C10A—N1A | 1.475 (5) | Cl2···H1N1 | 2.18 (4) |
| C10A—C11A | 1.523 (6) | N1A—H1N1 | 0.89 (4) |
| C10B—N1B | 1.483 (5) | N1A—H2N1 | 1.12 (5) |
| C10B—C11B | 1.542 (5) | N1B—H1N2 | 0.84 (4) |
| C11A—C12A | 1.524 (5) | N1B—H2N2 | 1.22 (5) |
| C11B—C12B | 1.501 (5) | O4—H1O4 | 0.79 (5) |
| C12A—O3A | 1.428 (4) | O4—H2O4 | 0.99 (7) |
| C12B—O3B | 1.428 (4) | O4···H2N1 | 1.69 (5) |
| C13A—O3A | 1.381 (4) | O4···N1A | 2.772 (6) |
| C13B—O3B | 1.371 (4) | | |
| C4A—C7A—C11A | 114.5 (4) | C16A—C17A—O2A | 110.0 (4) |
| C4A—C7A—C8A | 111.3 (3) | C18A—C17A—O2A | 127.1 (4) |
| C4B—C7B—C8B | 112.5 (3) | O2B—C17B—C18B | 128.3 (4) |
| C4B—C7B—C11B | 109.7 (3) | O2B—C17B—C16B | 109.9 (3) |
| O3A—C12A—C11A | 105.8 (3) | O1A—C19A—O2A | 107.2 (4) |
| O3B—C12B—C11B | 108.7 (3) | O2B—C19B—O1B | 107.0 (3) |
| O3A—C13A—C14A | 115.7 (4) | H1N1—N1A—H2N1 | 112 (4) |
| O3A—C13A—C18A | 122.8 (4) | H1N2—N1B—H2N2 | 114 (4) |
| O3B—C13B—C14B | 123.3 (4) | H1O4—O4—H2O4 | 94 (5) |
| O3B—C13B—C18B | 115.2 (4) | N1A—H1N1···Cl2 | 174 (4) |
| C15A—C16A—O1A | 128.4 (4) | N1A—H2N1···O4 | 159 (4) |
| C17A—C16A—O1A | 109.7 (4) | N1B—H2N2···Cl2 | 152 (3) |
| C15B—C16B—O1B | 128.7 (4) | O4—H1O4···Cl1$^{ii}$ | 164 (4) |
| C17B—C16B—O1B | 109.2 (4) | O4—H2O4···Cl1 | 143 (6) |

Symmetry codes: (i) $1 - x, y - \frac{1}{2}, 1 - z$; (ii) $1 - x, \frac{1}{2} + y, 1 - z$.

The positional and isotropic displacement parameters of the H atoms on the piperidinium N atoms and on the water molecule were refined. Other H atoms were placed at calculated positions and were refined with a riding model. All non-H atoms were refined anisotropically.

Data collection: *SMART* (Bruker, 1997). Cell refinement: *SMART*. Data reduction: *SAINT-Plus* (Bruker, 1997). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXTL/PC* (Sheldrick, 1997). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXTL/PC*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1162). Services for accessing these data are described at the back of the journal.

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# Fromm's methylphenyldithiodimethylketuret

JOHN S. DAVIDSON,[a] STEVEN J. RETTIG[b] AND JAMES TROTTER[b]

[a]*Crosslaw, Ballplay Road, Moffat, Dumfriesshire DG10 9JU, Scotland, and* [b]*Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada V6T 1Z1. E-mail: jtrt@xray4.chem.ubc.ca*

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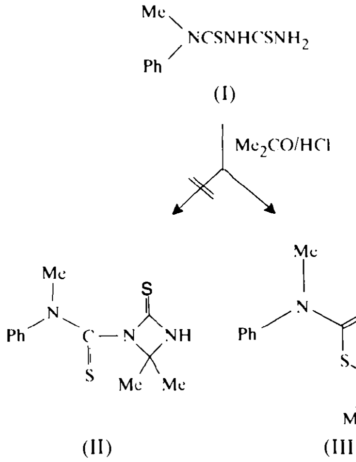
## Abstract

The 'keturet' obtained by reacting 1-methyl-1-phenyldithiobiuret with acetone is shown to be 6,6-dimethyl-2-methylanilino-5,6-dihydro-4*H*-1,3,5-thiadiazine-4-thione, $C_{12}H_{15}N_3S_2$. The molecule contains a six-membered thiadiazine ring with a distorted half-chair conformation, rather than a previously proposed four-membered ring structure. Molecular dimensions are normal, and the molecules (two per asymmetric unit) are linked by two N—H···S hydrogen bonds, one fairly strong [H···S 2.39 (3) Å] and one weaker [H···S 2.65 (4) Å].

## Comment

Condensation of 1-aryldithiobiurets with ketones, under the influence of dry hydrogen chloride, gives compounds called 'keturets' (Fromm, 1893), some of which can be formulated as hexahydrotriazine derivatives (Fairfull & Peak, 1955). Reaction of 1-methyl-1-phenyldithiobiuret, (I), with acetone gives a keturet which cannot be a hexahydrotriazine (since the disubstitution on N1 of the dithiobiuret blocks its formation). The compound was originally formulated as a diazacyclobutane, (II) (Fromm & Junius, 1895), but Fairfull & Peak (1955) point out that the structure has not been established conclusively, and that alternative structures, 'even' (III), might be postulated; compounds with such a structure have been synthesized, and characterized by spectroscopic methods (Goerdeler & Lüdke, 1970; Kristian *et al.*, 1973). To solve this long-standing problem, the structure of the condensation product of (I) and acetone has now been determined by X-ray methods, and proves to be (III).



There are two molecules per asymmetric unit (Fig. 1), with structures which are similar, but which differ in the details of their conformation (the conformations of the two independent molecules shown in Fig. 1 are mirror images, but the mirror-image conformation of each molecule is also present in the $P\bar{1}$ unit cell). The two independent molecules are related by a very rough pseudo-inversion center near $(\frac{1}{2},\frac{1}{4},0.21)$; the positions of the pseudo-related atoms differ by about 0.75 Å for S and by more than 2 Å for some of the outer atoms of the molecules, and there are very significant differences in the strengths of the two (pseudo-related) hydrogen bonds (see below). The molecule contains a six-membered thiadiazine ring [(III) and Fig. 1]. The C=N double bond (C2=N2 and C14=N5) constrains the S—C=N—C(S) grouping to be nearly planar [torsion angles 0.7 (5) and −6.8 (5)° in the two molecules; maximum displacements from four-atom planes 0.004 (3) and 0.032 (3) Å]. The other two atoms of the ring are displaced from this plane in the same direction, the C atom [0.874 (3) and 0.967 (3) Å] by considerably more than the N(H) atom [0.293 (2) and 0.335 (2) Å]; the conformation may be described as a distorted half-chair. Molecular dimensions are close to normal, with the C2=N2 [1.307 (4) Å] and C14=N5 [1.307 (4) Å] distances indicating double bonds.

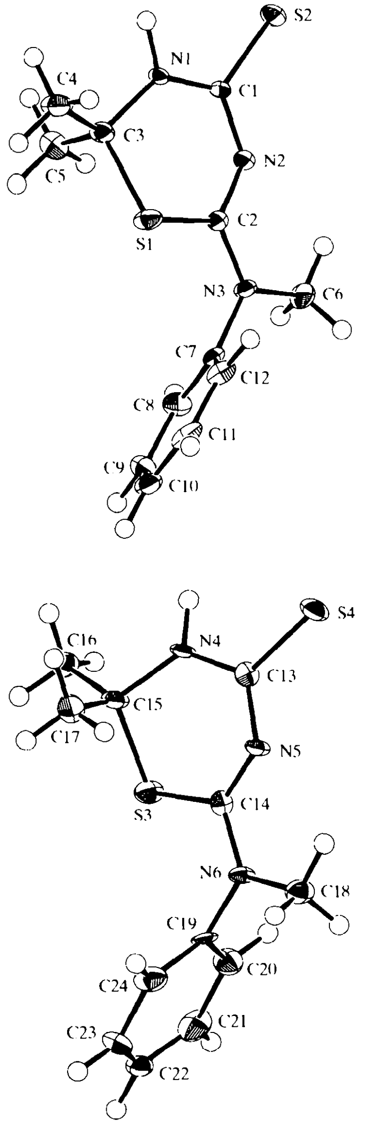


Fig. 1. Views of the two independent molecules of (III), with 50% probability displacement ellipsoids.

The molecules are linked by two N—H···S hydrogen bonds (Table 2); one is fairly strong [N1H···S4 2.39 (3) Å], and the other much weaker [N4H···S2 2.65 (4) Å]. There are also a few possibly significant C—H···S intermolecular interactions. The very different strengths of the two N—H···S bonds appear to cause some minor differences in related bond lengths between the two independent molecules (Table 1). Atom N1, which is the donor in the stronger hydrogen bond, presumably has a higher partial negative charge than N4, and this results in more extensive electron delocalization over the N1—C1=S2 system, relative to N4—C13=S4. Thus, N1—C1 is shortened to 1.324 (4) Å [N4—C13 1.350 (4) Å], and S2=C1 is lengthened to 1.711 (3) Å [S4=C13 1.689 (3) Å].

## Experimental

The 'keturet' was prepared from 1-methyl-1-phenyldithiobiuret and acetone, and crystallized from ethanol, using the procedure previously described by Fromm & Junius (1895) and Fairfull & Peak (1955) (yield 69%, m.p. 424–425 K).

*Crystal data*

$C_{12}H_{15}N_3S_2$
$M_r = 265.39$
Triclinic
$P\bar{1}$
$a = 9.871\,(2)$ Å
$b = 11.044\,(2)$ Å
$c = 13.117\,(3)$ Å
$\alpha = 87.403\,(8)°$
$\beta = 89.625\,(4)°$
$\gamma = 67.3872\,(11)°$
$V = 1318.6\,(4)$ Å$^3$
$Z = 4$
$D_x = 1.337$ Mg m$^{-3}$
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 5212 reflections
$\theta = 2–30°$
$\mu = 0.385$ mm$^{-1}$
$T = 180$ K
Plate
0.35 × 0.20 × 0.05 mm
Colorless

*Data collection*

Rigaku/ADSC CCD diffractometer
CCD scans
Absorption correction: multi-scan (*d*TREK*; Molecular Structure Corporation, 1997*a*)
$T_{\min} = 0.85$, $T_{\max} = 0.98$
12 370 measured reflections

5927 independent reflections
2257 reflections with $I > 3\sigma(I)$
$R_{\rm int} = 0.050$
$\theta_{\max} = 30.07°$
$h = -11 \rightarrow 13$
$k = -11 \rightarrow 15$
$l = -15 \rightarrow 18$

*Refinement*

Refinement on $F^2$
$R(F) = 0.040$
$wR(F^2) = 0.077$
$S = 1.020$
5927 reflections
315 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2)]$
$(\Delta/\sigma)_{\max} = 0.005$

$\Delta\rho_{\max} = 1.00$ e Å$^3$ (0.8 Å from H10, bonded to C6)
$\Delta\rho_{\min} = -0.90$ e Å$^3$ (0.4 Å from H8, bonded to C6)
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| S1—C2 | 1.774 (3) | S3—C14 | 1.775 (3) |
| S1—C3 | 1.822 (4) | S3—C15 | 1.842 (3) |
| S2—C1 | 1.711 (3) | S4—C13 | 1.689 (3) |
| N1—C1 | 1.324 (4) | N4—C13 | 1.350 (4) |
| N2—C2 | 1.307 (4) | N5—C14 | 1.307 (4) |
| C2—S1—C3 | 96.7 (2) | C14—S3—C15 | 95.7 (2) |

Table 2. *Hydrogen-bonding geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H1···S4$^{\rm i}$ | 1.02 (3) | 2.39 (3) | 3.353 (3) | 157 (2) |
| N4—H16···S2$^{\rm ii}$ | 0.96 (3) | 2.65 (4) | 3.522 (3) | 152 (3) |

Symmetry codes: (i) $1 + x, y - 1, z$; (ii) $x - 1, 1 + y, z$.

The $U_{ij}$ values are quite small (low-temperature data), but physically very reasonable, with atoms near the centers of the molecules having the lowest displacement parameters and those on the periphery the highest. The highest correlation coefficient in the refinement is 0.51, for $U_{22}$ and $U_{12}$ of atom C12 (see *Comment* for a discussion of the pseudosymmetry). The higher than usual value of $R_{\rm int}$ resulted from lower than usual crystal quality. All parameters were refined for the two H atoms bonded to N; the other H atoms were placed on calculated sites, with C—H = 0.98 Å and *U*(H) equal to 1.2 times *U* of the C atom to which they were bonded. Methyl group H atoms were placed from a difference synthesis.

Data collection: *d*TREK* (Molecular Structure Corporation, 1997*a*). Cell refinement: *d*TREK*. Data reduction: *d*TREK*. Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993). Program(s) used to refine structure: *TEXSAN* (Molecular Structure Corporation, 1997*b*). Software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1159). Services for accessing these data are described at the back of the journal.

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# Two dioxane derivatives of anthraquinone

Richard C. Cambie, Rachel M. Lorimer, Clifton E. F. Rickard and P. Stewart Rutledge

*Department of Chemistry, University of Auckland,*
*Private Bag 92019, Auckland, New Zealand. E-mail:*
*c.rickard@auckland.ac.nz*

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## Abstract

The structures of 1-methoxy-4-(2-methylprop-2-enyloxy)-2-[(2*R*,6*R*)-4,4,6-trimethyl-1,3-dioxan-2-yl]anthraquinone, $C_{26}H_{28}O_6$, and 4-hydroxy-3-(2-methylprop-2-