uent to the desired position in the benzene ring. The results of the calculations are depicted in Figs. 2(*a*) and 2(*b*) for compounds (1) and (2), respectively.

Independent of the alkylation position, the general profiles of the $E=f(\varphi)$ curves are similar in both diagrams. Therefore, the conformers corresponding to a planar arrangement of the benzene and thiohydantoin rings (φ about 0 and 180°) are in energy maxima. The two absolute minima-energy conformations are those in which the benzene ring is inclined to the thiohydantoin ring at almost 90° for all analyzed compounds. As is clearly visible, the effect of *para* and *meta* substitution is similar and both energy minima have similar heights. The heights of maxima in *ortho*-substituted compounds are different; those at φ about 180° being much greater. The corresponding planar arrangement of both molecules with an *ortho* substituent is especially unfavourable.

The differences in the conformational analysis results also depend on the dialkylation position (1,2- or 2,3-). The energy differences in 1,2-dialkylation products (Fig. 2*a*) are much bigger and also the positions of the extremes are slightly shifted in comparison with 2,3-analogues (Fig. 2*b*).

Summarizing, the energy differences between the conformers and the profiles of the curves suggest that the non-planar conformations for free molecules are preferred for all 1,2-dialkylated compounds. The *para* and *meta* substitutions in 2,3-dialkylated compounds generate no restrictions in the preferences of the conformations while for *ortho* substitution a planar molecule ($\varphi = 180°$) is not favoured. The planar conformation for (2*p*) in the solid state should therefore be a consequence of molecular packing in the crystal.

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Structure of a Carcinogenic Agent: 1-Formyl-3-thiosemicarbazide

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Abstract. $C_2H_6N_3OS$, $M_r = 120{\cdot}15$, monoclinic, $P2_1/c$, $a = 7{\cdot}261$ (1), $b = 7{\cdot}428$ (2), $c = 9{\cdot}589$ (2) Å, $\beta = 98{\cdot}62$ (1)°, $V = 511{\cdot}3$ (2) Å^3, $Z = 4$, $D_m = 1{\cdot}544$ (2), $D_x = 1{\cdot}560$ (2) Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, μ(Cu $K\alpha$) = 4·61 mm^{-1}, $F(000) = 252$, $T = 298$ K, $R = 0{\cdot}077$ for 946 observed reflections [$I \geq 3\sigma(I)$]. The thiosemicarbazide moiety of the molecule is planar with N—C—N—N in a *cis* and S—C—N—N in a *trans* conformation. The conformation of the thiosemicarbazide moiety is similar in thiosemicarbazide and its derivatives but is reversed in its metal complexes.

Introduction. Thiosemicarbazides, thiosemicarbazones, and their derivatives have shown metal-complexing ability in various oxidation states

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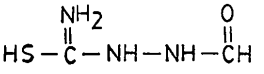
(Nandi, Chaudhuri, Mazumdar & Ghosh, 1984*a*,*b*; Cavalca, Nardelli & Fava, 1962). These compounds have exhibited antibacterial, antiviral, carcinostatic or carcinogenic activities (Johnson, Joyner & Perry, 1952; French & Blanz, 1965, 1966; Williams, 1972; Erturk, Morris, Cohen, Von Esch, Crovetti, Price & Bryan, 1971; Jensen & Jensen, 1952). It has been suggested that the biological activities of these compounds are due to their capability to form metal complexes (Kirschner, Wei, Francis & Bergman, 1966; Palenik, Rendle & Carter, 1974). This has a generated much interest in the study of these compounds (Agarwal, Cushley, McMurray & Sartorelli, 1970; Agarwal, Booth & Sartorelli, 1973; Kuroda, Neidle & Wilman, 1984; Sinha, Ram & Lamba, 1988). 1-Formyl-3-thiosemicarbazide (FTSC) has been found to induce solitary mammary tumours in different species of rats (Erturk, Morris, Cohen, Von Esch, Crovetti, Price & Bryan, 1971). It appears that substitution at the hydrazinic terminal nitrogen reduces its metal-chelating ability. The structures of thiosemicarbazide and its derivatives formed through amino-terminal nitrogen (Chattopadhyay, Banerjee, Mazumdar, Ghosh & Kuroda, 1987) and its metal complexes (Cavalca, Nardelli & Fava, 1962; Cavalca, Nardelli & Branchi, 1960) are available in the literature. Since the metal-chelating property is an important feature of thiosemicarbazide, it is of interest to determine the structure of derivatives of thiosemicarbazide with substitution at the hydrazinic terminal nitrogen. We report here the crystal and molecular structure FTSC (I).



(I)

Experimental. FTSC was synthesized using the procedure described by Mashima (1964). Colourless irregular-shaped crystals were grown from a solution of the compound in ethanol and water. Density measured by flotation in CCl_4 and benzene. A crystal of dimensions 0·75 × 0·47 × 0·15 mm was used for intensity-data collection on an Enraf–Nonius CAD-4 automatic diffractometer, ω–2θ scan mode with $1 \le 2\theta \le 150°$, h −9→9, k 0→9, l 0→12, Cu $K\alpha$ radiation. Data corrected for Lorentz, polarization and absorption effects. 946 unique observed reflections [$I \ge 3\sigma(I)$] out of 3786 measured reflections. The unit-cell parameters were refined for 25 high-angle ($20 \le \theta \le 25°$) individually centred reflections. The intensities of two standard reflections ($\bar{8}12$ and $\bar{7}16$) were measured at regular intervals and no significant variations were observed. A semi-empirical ψ-scan technique was used to correct for absorption (the maximum and minimum correction factors were 0·99 and 0·44). R_{int} for merged data was 0·011 where $R_{int} = \sum(I - \langle I \rangle)/\sum(I)$. Structure solved by direct methods using *SHELXS*86 (Sheldrick, 1986), full-matrix least-squares refinement procedure on $|F|$ for non-hydrogen atoms with anisotropic thermal parameters using *SHELX*76 (Sheldrick, 1976), hydrogen atoms located from a difference map were given the isotropic thermal parameters of the atoms to which they are attached and were included in structure-factor calculations but not refined. Final $R = 0·077$ and $wR = 0.094$ using 946 observed reflections [$I \ge 3\sigma(I)$], full-matrix refinement minimized $\sum w(|F_o| - |F_c|)^2$, $w = k/[\sigma^2(F_o) + 0·002(F_o)^2]$, where σ is the standard deviation of observed amplitude based on counting statistics. $\Delta/\sigma_{max} = 0.14$ and $\Delta\rho_{min,max} = -0.12$, 0.16 e Å^{-3}. The atomic scattering factors for non-hydrogen atoms were taken from Cromer & Mann (1968) and for hydrogen atoms from Stewart, Davidson & Simpson (1965). All calculations were performed on a MicroVAX II system. The atomic coordinates and equivalent isotropic thermal parameters are given in Table 1.*

Table 1. *Positional parameters* ($\times 10^4$) *and equivalent isotropic thermal parameters* (Å$^2 \times 10^3$)

$U_{eq} = (1/24\pi^2)\sum_i\sum_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
S(1)	7192·4 (10)	1890·4 (12)	4589·7 (9)	15 (6)
C(2)	5150 (4)	2932 (4)	3975 (3)	8 (15)
N(3)	5077 (3)	4450 (4)	3283 (3)	17 (15)
N(4)	3543 (3)	2160 (4)	4219 (3)	12 (15)
N(5)	1833 (3)	2963 (3)	3734 (3)	12 (15)
C(6)	841 (4)	2410 (5)	2502 (3)	9 (16)
O(7)	1397 (3)	1337 (4)	1699 (2)	17 (15)

Table 2. *Bond lengths* (Å), *bond angles* (°) *and selected torsion angles* (°)

S(1)—C(2)	1·698 (3)	N(4)—N(5)	1·393 (4)
C(2)—N(3)	1·306 (5)	N(5)—C(6)	1·352 (4)
C(2)—N(4)	1·351 (4)	C(6)—O(7)	1·219 (4)

S(1)—C(2)—N(3)	122·4 (3)	N(4)—N(5)—C(6)	119·5 (3)
S(1)—C(2)—N(4)	118·6 (2)	C(2)—N(4)—N(5)	120·7 (3)
N(4)—C(2)—N(3)	118·9 (3)	N(5)—C(6)—O(7)	124·5 (3)

S(1)—C(2)—N(4)—N(5)	−179·9 (2)	C(6)—N(5)—N(4)—C(2)	96·6 (4)
N(3)—C(2)—N(4)—N(5)	0·4 (5)	N(4)—N(5)—C(6)—O(7)	−6·2 (5)

Discussion. The bond lengths, bond angles and selected torsion angles are given in Table 2. The *ORTEP* drawing and numbering scheme in the molecule are shown in Fig. 1. Crystal packing is shown in Fig. 2. The C(2)—N(3) and C(6)—O(7) distances correspond to the double-bond lengths while S(1)—C(2), N(4)—N(5) and N(5)—C(6) are partial double

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54246 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

bonds as a result of delocalization in a planar environment adjacent to the double bonds. These values are similar to those observed in 3-hydroxy-2-butanone thiosemicarbazone (Nandi, Chaudhuri, Mazumdar & Ghosh, 1984*a*,*b*), thiosemicarbazide (Andreetti, Domiano, Gasparri, Nardelli & Sgarabotto, 1970) and 4-(4-methoxyphenyl)thiosemicarbazide (Chattopadhyay, Banerjee, Mazumdar, Ghosh & Kuroda, 1987). The molecular dimensions differ significantly from those observed in metal complexes of thiosemicarbazides such as bis-(thiosemicarbazidato)nickel(II) (Cavalca, Nardelli & Fava, 1962), mono(thiosemicarbazide)zinc chloride (Cavalca, Nardelli & Branchi, 1960) and nickel(II) dithiosemicarbazide sulfate trihydrate (Gronbaek & Rasmussen, 1962). The segments S(1)—C(2)—N(4)—N(5) and N(3)—C(2)—N(4)—N(5) are essentially planar. S(1)—C(2)—N(4)—N(5) is *trans* whereas N(3)—C(2)—N(4)—N(5) is in a *cis* conformation, similar to the conformations observed in 4-(4-methoxyphenyl)thiosemicarbazide. In metal complexes where the terminal hydrazinic nitrogen and the sulfur atom coordinate to a metal atom the conformations of N(3)—C(2)—N(4)—N(5) and S(1)—C(2)—N(4)—N(5) are reversed. However, in the mono(thiosemicarbazide)silver complex where silver is bonded to the sulfur atom alone, the conformation of the thiosemicarbazide moiety is similar to those observed in thiosemicarbazide and its derivatives. This shows that substitutions at the amino terminal nitrogen, at the hydrazinic nitrogen or interaction through the sulfur atom do not perturb the conformation of the thiosemicarbazide but that metallic coordination through both sulfur and the hydrazinic nitrogen changes it drastically. Torsion angles of the thiosemicarbazide moiety in thiosemicarbazide, its derivatives and their metal complexes are given in the supplementary data. Molecules are arranged in the unit cell very compactly and are held together by intermolecular hydrogen bonds: N(3)···O(7) $(1-x,\ 0{\cdot}5+y,\ 0{\cdot}5-z) = 2{\cdot}916$; H(1,N3)···O(7) = 2·540 Å; N(3)—H(1,N3)···O(7) = 103·39°; N(5)···O(7) $(x,\ 0{\cdot}5-y,\ 0{\cdot}5+z) = 2{\cdot}954$; H(1,N5)···O(7) = 2·350 Å; N(5)—H(1,N5)···O(7) = 127·76°.

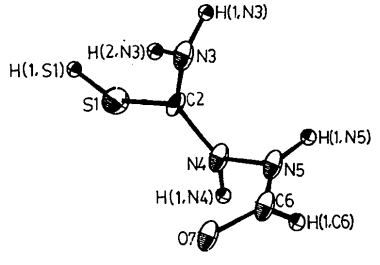


Fig. 1. An *ORTEP*II drawing (Johnson, 1976) showing the numbering scheme for FTSC.

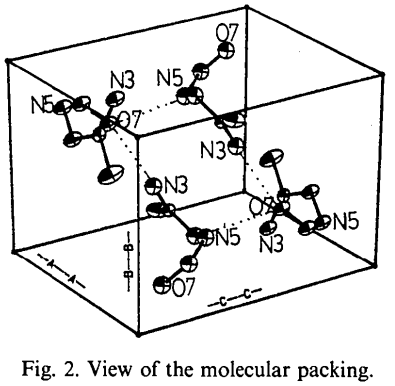


Fig. 2. View of the molecular packing.

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