

Fig. 2. Hydrogen-bonding scheme and packing of the molecules. Projection is onto the yz plane.

molecules form a relatively thick layer parallel to the yz plane [~ 6.6 Å elevation between O(2) and its centrosymmetrically related atom] and the molecular arrangement is relatively open as indicated by the 'hole' in the center of the cell, Fig. 2.

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Structure of 4-Formylamino- Δ^2 -1,2,4-triazoline-5-thione

BY C. GORS, F. BAERT AND M. FOULON

Laboratoire de Dynamique des Cristaux Moléculaires, associé au CNRS (ERA 465), Université des Sciences et Techniques de Lille I, BP 36, 59650 Villeneuve d'Ascq, France

AND J. P. HENICHART AND R. HOUSSIN

Institut de Chimie Pharmaceutique, rue du Professeur Laguesse, 59045 Lille CEDEX, France

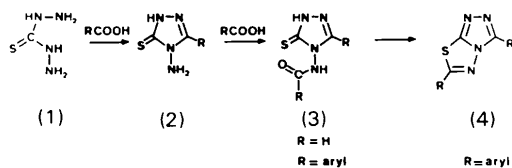
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Abstract. $C_3H_4N_4OS$, orthorhombic, $Pna2_1$, $a = 8.508$ (17), $b = 6.599$ (13), $c = 10.382$ (21) Å, $V = 582.9$ Å³, $Z = 4$, $D_x = 1.47$, $D_m = 1.44$ Mg m⁻³, $\lambda(Mo K\alpha) = 0.7107$ Å; final $R = 5.1\%$. The molecule has a non-planar structure which explains the non-cyclization to 3-triazolo[3,4-*b*]thiadiazole.

References

- ADOLPH, H. G. & KAMLET, M. J. (1966). *J. Am. Chem. Soc.* **88**, 4761–4763.
- ADOLPH, H. G. & KAMLET, M. J. (1969). *J. Org. Chem.* **34**, 45–50.
- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
- GALLAHER, K. L., YOKOZEKI, A. & BAUER, S. H. (1974). *J. Phys. Chem.* **78**, 2389–2395.
- GILLIGAN, W. H. & ADOLPH, H. G. (1974). US Patent 3,846,493.
- GRIFFITH, R. C. & ROBERTS, J. D. (1974). *Tetrahedron Lett.* pp. 3499–3502.
- HAGEN, K. & HEDBERG, K. (1973). *J. Am. Chem. Soc.* **95**, 8263–8266.
- HOLDEN, J. R. & DICKINSON, C. (1969). *J. Phys. Chem.* **73**, 1199–1204.
- IMMIRZI, A. & PERINI, B. (1977). *Acta Cryst.* **A33**, 216–218.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- KAPLAN, L. A. & BURLINSON, N. E. (1972). *J. Org. Chem.* **37**, 3932–3937.
- LIPCZYŃSKA-KOCHANY, E. & URBAŃSKI, T. (1977). *Can. J. Chem.* **55**, 2504–2509.
- MARR, H. E., KRUGER, G. J. & STEWART, J. M. (1977). *Acta Cryst.* **B33**, 2886–2887.
- SICKMAN, D. V., KAMLET, M. J., RICH, R. D., HELLER, H. & KAPLAN, L. A. (1973). US Patent 3,745,076.
- STEWART, J. M. (1972). The XRAY system – version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

crystallization of the crude product gives a second compound identified as 4-formylamino- Δ^2 -1,2,4-triazoline-5-thione (3) in small amount (10%). The deshielding of the proton of the formyl group ($\delta = 8.6$ p.p.m. in Me_2SO) could correspond to the existence of an intermolecular or intramolecular hydrogen bond. An intramolecular hydrogen bond could give the molecule a planar structure which could assist further cyclization to the unknown 3-triazolo[3,4-*b*]thiadiazole (4). Nevertheless, in the presence of catalysts, the cyclization has not occurred. The structure of (3) was investigated in an attempt to explain its nonreactivity.



Single crystals were obtained by evaporation of an ethanolic solution. Intensities were collected on a Philips PW 1100 diffractometer by the θ - 2θ scan technique. Of the 1352 independent reflexions, 1327 had $F > 6\sigma(F)$. The systematic extinctions ($0kl$, for $k + l = 2n + 1$ and $h0l$, for $h = 2n + 1$) are consistent with $Pna2_1$. The intensities were corrected for Lorentz and polarization effects, but not for absorption or extinction. The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971). The *E* map showed only the position of the S atom, which was used to phase a Fourier synthesis. Refinement was carried out with *ORION* (André, Fourme & Renaud, 1971). The final *R* was 5.1%. The final positional parameters are listed in Table 1.*

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33993 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Positional parameters ($\times 10^4$, for H $\times 10^3$)

	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	8592 (3)	4099 (4)	9908 (23)
C(2)	8931 (3)	6734 (4)	8578 (22)
C(3)	10583 (3)	2431 (5)	7589 (22)
N(1)	7497 (2)	5537 (4)	10053 (23)
N(2)	7687 (3)	7169 (4)	9241 (23)
N(3)	9525 (2)	4901 (3)	8956 (23)
N(4)	10816 (2)	3942 (3)	8434 (23)
O	9310 (3)	1947 (4)	7169 (23)
S	8771 (1)	1868 (1)	10647 (22)
H(N4)	1173	417	906
H(C2)	938	727	781
H(C3)	1148	151	726
H(N1)	660	553	1062

Discussion. Bond lengths and angles are given in Figs. 1 and 2. The deviation of the triazole ring from planarity is negligible (0.004 Å). The short bond distances are evidence for appreciable delocalization of the π electrons (Goldstein, Ladell & Abowitz, 1969). The delocalization also affects the formylamino group and can explain the short N(4)–C(3) bond. Furthermore, C(1)–S (1.67 Å) is intermediate between a C=S double bond (1.61 Å) and a C–S single bond (1.81 Å), as in derivatives of thiourea and thiocarbazon (Iwasaki, 1974; Lecomte, Aubry, Protas, Boussard & Marraud, 1974*a,b*).

The Newman projection (Fig. 3) shows the non-planar structure of the molecules. The non-conjugation of the amide group with the ring does not favour the enolate form and therefore the subsequent closure.

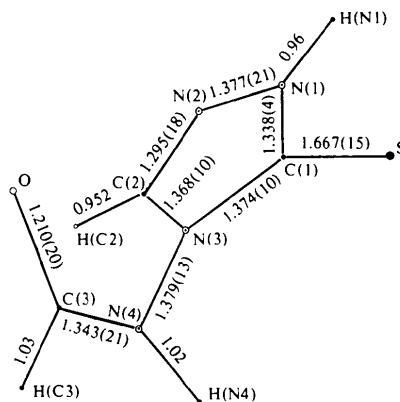


Fig. 1. Bond distances (Å) with e.s.d.'s in parentheses.

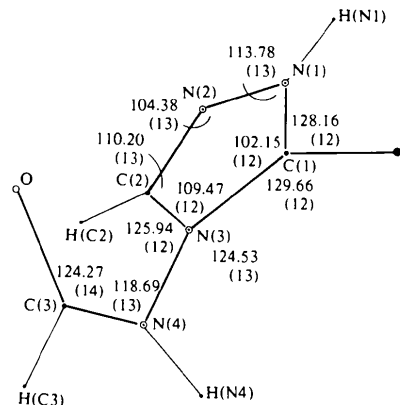


Fig. 2. Bond angles ($^\circ$) with e.s.d.'s in parentheses.

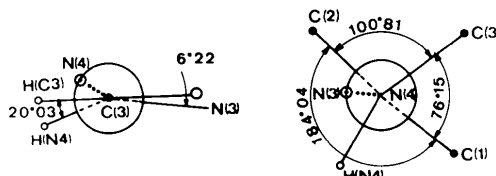


Fig. 3. Newman projections along N(3)–N(4) and C(3)–N(4).

Table 2. *Interatomic distances* (Å)

For the hydrogen bond $A-H \cdots B$, the distance $H \cdots B$ is in parentheses.

Symmetry code

(I) $x + \frac{1}{2}, \frac{3}{2} - y, z$	(IV) $2 - x, -y, z - \frac{1}{2}$
(II) $x + \frac{1}{2}, \frac{1}{2} - y, z$	(V) $2 - x, 1 - y, z - \frac{1}{2}$
(III) $\frac{3}{2} - x, y - \frac{1}{2}, z + \frac{1}{2}$	(VI) $x - \frac{1}{2}, \frac{3}{2} - y, z$

N(4)–H(N4)···N(2) ^I	3.134 (2.55)
N(4)–H(N4)···S ^{II}	3.448 (2.49)
N(1)–H(N1)···O ^{III}	2.838 (2.01)
C(3)–H(C3)···S ^{IV}	3.524 (2.79)
N(2)···C(2) ^{VI}	3.348
C(3)···O ^{VI}	3.277
C(3)···N(1) ^V	3.376

The molecules are connected by hydrogen bonds and van der Waals contacts (Table 2 and Fig. 4).

The S atom is engaged in an intermolecular hydrogen bond. This analysis removes any ambiguity about the nature of the hydrogen bonding involving H(C3).

References

- ANDRÉ, D., FOURME, R. & RENAUD, M. (1971). *Acta Cryst.* B27, 2371–2380.
- BEYER, H. & KRÖGER, C. F. (1960). *Ann. Chem. (Warsaw)*, 637, 126–134.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A27, 368–376.
- GOLDSTEIN, P., LADELL, J. & ABOWITZ, G. (1969). *Acta Cryst.* B25, 135–143.
- IWASAKI, F. (1974). *Acta Cryst.* B30, 2503–2505.
- LECOMTE, C., AUBRY, A., PROTAS, J., BOUSSARD, G. & MARRAUD, M. (1974a). *Acta Cryst.* B30, 1992–1996.
- LECOMTE, C., AUBRY, A., PROTAS, J., BOUSSARD, G. & MARRAUD, M. (1974b). *Acta Cryst.* B30, 2343–2348.

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cis-Dibromo-2,4 Bicyclo[3.2.1]octanone-3

PAR M. VAN MEERSCHE, G. GERMAIN ET J. P. DECLERCQ*

Laboratoire de Chimie physique et de Cristallographie de l'Université de Louvain, Bâtiment Lavoisier, 1 place Pasteur, B-1348 Louvain-la-Neuve, Belgique

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Abstract. $C_8H_{10}Br_2O$, triclinic, $P\bar{1}$, $a = 12.877$ (5), $b = 7.041$ (3), $c = 10.829$ (4) Å, $\alpha = 105.07$ (2), $\beta = 89.10$ (2), $\gamma = 99.47$ (2)°, $Z = 4$, $D_x = 2.00$ Mg m⁻³. The structure has been solved by direct methods from three-dimensional X-ray data. The molecules possess m symmetry. The Br and ethano bridge substituents occupy axial positions in a cyclohexanone ring with a flattened-chair conformation.

Introduction. Le composé globulaire qui fait l'objet de la présente analyse cristallise avec deux molécules dans

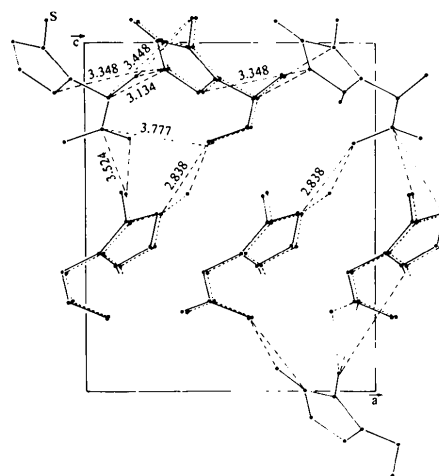


Fig. 4. Projection along b with the hydrogen bonds. Between the molecules shown by full lines and those by dashed lines, the translation vector is b .

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l'unité asymétrique. Sa configuration exacte s'étant avérée difficile à préciser par les méthodes spectroscopiques habituelles, une investigation par diffraction de rayons X a été jugée préférable. La structure a été déterminée par le système *MULTAN* (Main, Lessinger, Woolfson, Germain & Declercq, 1976) et affinée par les programmes XRAY 72 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) par moindres carrés dans l'approximation des blocs diagonaux avec constantes d'agitation thermique anisotropes. L'analyse repose sur un spectre de 1707 réflexions considérées comme observées qui ont, parmi les 2771 réflexions indépendantes mesurées, des intensités qui dépassent 2,5 fois l'écart-type des mesures d'intensité.