

acridine moiety, Table 3, somewhat less pronounced in the (Z) derivative, is of the same order as found in other acridines considered to be planar: for both compounds the best planes of the two outer rings are roughly parallel to one another and also parallel to the central ring in (Z) while in (E) they are rotated with respect to the best plane of the central ring by $1.4(1)^\circ$.

As far as the geometry of the ethylenic C(15)=C(16) bond is concerned, the distortion about the double bond is given in terms of the *trans* torsion angle in the (E) and the *cis* torsion angle in the (Z) derivative, reported in Table 2. The puckering value for the *cis*, greater than that of the *trans* compound, reflects the mutual steric interaction of the xylyl and the acridinyl groups.

The packing is consistent with van der Waals interactions.

References

- BELLETTI, D., UGOZZOLI, F., CANTONI, A. & PASQUINELLI, G. (1979). *Gestione on line di Difrattometro a Cristallo Singolo Siemens AED con Sistema General Automation Jumbo 220*. Internal Report 1-3/79. Centro di Studio per la Strutturistica Difrattometrica del CNR, Parma, Italy.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- JONES, A. & NEIDLE, S. (1975). *Acta Cryst.* B31, 1324-1333.
- LEHMANN, M. S. & LARSEN, F. K. (1974). *Acta Cryst.* A30, 580-589.
- MAIN, P., WOOLFSON, M. M. & GERMAIN, G. (1971). *MULTAN. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- PHILLIPS, D. C. (1956). *Acta Cryst.* 9, 237-250.
- PHILLIPS, D. C., AHMED, F. R. & BARNES, W. H. (1960). *Acta Cryst.* 13, 365-377.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Acta Cryst. (1989). C45, 1580-1583

Structure of 7,14,15,17-Tetraoxa-10-azapentacyclo[10.2.1.1^{2,11}.1^{5,8}.0^{3,9}]-heptadeca-3,9-dien-2-ol, a Pentacyclic Alcohol Prepared from Levoglucosenone

BY V. KETTMANN

Department of Analytical Chemistry, Faculty of Pharmacy, Comenius University, Odbojárov 10, CS-83232 Bratislava, Czechoslovakia

AND S. BYSTRICKÝ, T. STICZAY AND M. KOÓŠ

Institute of Chemistry, Centre for Chemical Research, Slovak Academy of Sciences, Dúbravská cesta, CS-84238 Bratislava, Czechoslovakia

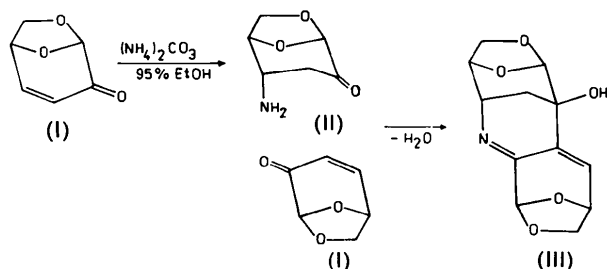
(Received 27 January 1988; accepted 17 February 1989)

Abstract. C₁₂H₁₃NO₅, *M_r* = 251.2, orthorhombic, *P*2₁2₁2₁, *a* = 9.294 (3), *b* = 10.714 (3), *c* = 10.846 (3) Å, *V* = 1080.0 (6) Å³, *Z* = 4, *D_m* = 1.55, *D_x* = 1.55 Mg m⁻³, λ(Cu Kα) = 1.54178 Å, μ = 1.04 mm⁻¹, *F*(000) = 528, *T* = 293 K, *R* = 0.039 for 800 unique observed reflections. The crystal structure consists of helical chains of the title molecule, the principal intrachain interaction being hydrogen bonding between the hydroxyl and imine groups. The structure previously assigned on the basis of chemical and spectroscopic evidence is confirmed. The conformation of the pyranose ring is ¹C₄ distorted towards a mixture of *E*₀ and ¹H₀, and that of the anhydro rings is between ⁰E and ⁰T₄. The inherent rigidity of the pentacyclic skeleton of the title alcohol forces N=C and C=C bonds of the α,β-unsaturated imine moiety, —N=C—C=C—, to

be coplanar but there is no crystallographic evidence for any conjugation within this moiety.

Introduction. The title compound (III) was prepared by reaction of glycoside precursor (I), 1,6-anhydro-3,4-dideoxy-β-D-glycero-hex-3-enopyranos-2-ulose (levoglucosenone) (Bhaté & Horton, 1983), with ammonium carbonate in refluxing 95% ethanol. Spectroscopic and analytical data (Bystrický, Sticzay, Koóš, Kettmann, 1986) were consistent with the structure (III), *i.e.* the reaction was found to proceed in a different way from that observed in pyrones, which, under the same reaction conditions, prefer substitution of the ring oxygen by nitrogen to give pyridones (Kaiser, Work, Wolfe & Hauser, 1967). The carbohydrate product (III) must thus have arisen by a novel sequential reaction, the

sequence involving the conjugate attack of ammonium carbonate from the *exo* face of the cyclic enone system followed by condensation of the resulting 1,6-anhydro-3,4-dideoxy-4-*exo*(axial)-amino- β -D-hexopyranos-2-ulose (II) with another molecule of levoglucosenone.



The structure (III), however, especially whether or not the central cyclization had taken place, could not be established unambiguously from spectroscopic data. To resolve this ambiguity and determine the detailed stereochemistry of this compound, an X-ray diffraction study of (III) was undertaken.

Experimental. Crystals of (III) suitable for X-ray analysis recrystallized from ethanol, crystal used: $0.4 \times 0.4 \times 0.5$ mm; D_m by flotation in bromoform/cyclohexane; systematic absences $h00$ for h odd, $0k0$ for k odd and $00l$ for l odd, from Weissenberg photographs; Syntex $P2_1$ diffractometer; accurate unit-cell parameters by least-squares refinement of 15 reflections, $12 < \theta < 45^\circ$; intensity data ($h = 0$ to 9, $k = 0$ to 11, $l = 0$ to 11) by $\theta/2\theta$ scans, variable rate 4.9 to $29.3^\circ \text{ min}^{-1}$ in 2θ , background-to-scan-time ratio = 1.0, scan width 2° plus α_1 - α_2 dispersion, Cu $K\alpha$ radiation filtered by graphite monochromator; two standards measured every 98 reflections, no appreciable trends; 811 unique reflections, $5 < \theta \leq 55^\circ$, 800 with $l \geq 2\sigma(I)$ considered observed and included in the refinement; L_p correction but none for absorption or extinction; structure solved by direct methods using *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and *MAGIC* (Declercq, Germain & Woolfson, 1979) and refined by block-diagonal least squares, $\Delta\rho$ map showed positions of all H atoms, refinement continued on positional parameters, anisotropic thermal parameters for non-H atoms and isotropic thermal parameters for H atoms fixed equal to those of covalently bonded atoms; in final cycle $R = 0.039$, $wR = 0.045$ for observed reflections only, $S = 1.8$, max. shift/e.s.d. 0.16, function minimized $\sum w(\Delta F)^2$, where $w = 1$ if $|F_o| < 25$ and $w = 25/|F_o|$ if $|F_o| \geq 25$, max. and min. heights in final $\Delta\rho$ synthesis 0.19 and $0.17 \text{ e } \text{\AA}^{-3}$, scattering factors for uncharged atoms from *International Tables for X-ray Crystallography* (1974); all calculations except *MULTAN* and

MAGIC performed with local version of the *NRC* system (Ahmed, Hall, Pippy & Huber, 1973).

Discussion. Final atomic coordinates of non-H atoms and equivalent isotropic B 's for the title alcohol (III) are listed in Table 1,* bond distances and angles in Table 2. A perspective drawing of the molecule and numbering of the atoms are shown in Fig. 1. The absolute configuration at chiral centres of adduct (III) was determined from stereochemical arguments, from ^1H and ^{13}C NMR data, and from circular dichroism spectra (Bystrický, Sticzay, Koš & Kettmann, 1986). These results are now unambiguously confirmed and extended by this crystal structure determination, Fig. 1 giving the correct enantiomorphic form. As shown in Fig. 1, the derived alcohol (III) may be considered as being composed of two 1,6-anhydropyranose subunits, one saturated and the other unsaturated, linked to each other by an imine nitrogen bridge and *via* the C(2)—C(3') bond; the unsaturated ('primed') subunit can be interpreted alternatively as levoglucosenone substituted at C(2'), having a C=N instead of a C=O bond. Thus, the product (III) must be formed by the chemical transformations depicted in the reaction scheme above.

The corresponding bonding and torsional parameters for the chemically equivalent portions of the two subunits, *i.e.* the anhydro rings, agree within the limits of experimental error, with the exception of the C(1)—O(1) and C(1')—O(1') bonds which differ by a significant amount (9σ). Similar observations have also been reported for two symmetry-independent molecules in the structure of 1,6-anhydro- β -D-mannopyranose (Maluszynska, Kinoshita & Jeffrey, 1982) and explained as being due to the involvement of the O atom of the longer C—O bond in a hydrogen-bonding interaction. In the present structure such an explanation has been discarded in view of the fact that both O(1) and O(1') have a very similar crystal-field environment [neither O(1) nor O(1') is involved in any hydrogen-bonding interaction] and the reason for the discrepancy remains unclear.

The bond distances within the saturated 1,6-anhydropyranose moiety show typical features of similar structures reported in the literature (*e.g.* Maluszynska, Kinoshita & Jeffrey, 1982, and references therein; Shelling, Dolphin, Wirz, Cobbledick & Einstein, 1984), *i.e.* the geometry of the parent 1,6-anhydropyranose system is not significantly per-

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, least-squares planes and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51959 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final atomic coordinates ($\times 10^4$) with e.s.d.'s in parentheses and equivalent isotropic thermal parameters

| | x | y | z | $B_{eq}(\text{\AA}^2)$ |
|-------|-----------|----------|----------|------------------------|
| C(1) | 3890 (3) | 2516 (2) | 7729 (2) | 2.64 |
| C(2) | 3178 (3) | 1499 (2) | 6920 (2) | 2.12 |
| C(3) | 3777 (3) | 238 (2) | 7308 (2) | 2.44 |
| C(4) | 3487 (3) | 151 (2) | 8711 (2) | 2.64 |
| C(5) | 4116 (3) | 1306 (2) | 9361 (2) | 2.91 |
| C(6) | 5623 (3) | 1612 (3) | 8953 (3) | 3.55 |
| O(1) | 5396 (2) | 2333 (2) | 7828 (2) | 3.03 |
| O(2) | 3535 (2) | 1813 (1) | 5681 (1) | 2.74 |
| O(5) | 3351 (2) | 2401 (1) | 8950 (1) | 2.72 |
| N(4) | 1935 (2) | 106 (2) | 8972 (2) | 2.67 |
| C(1') | -476 (3) | 732 (3) | 8458 (3) | 3.40 |
| C(2') | 1112 (3) | 741 (2) | 8252 (2) | 2.52 |
| C(3') | 1604 (3) | 1479 (2) | 7160 (2) | 2.24 |
| C(4') | 581 (3) | 2057 (2) | 6521 (2) | 2.75 |
| C(5') | -966 (3) | 1986 (2) | 6908 (2) | 3.05 |
| C(6') | -1625 (3) | 752 (3) | 6563 (3) | 3.97 |
| O(1') | -1158 (2) | -62 (2) | 7553 (2) | 4.23 |
| O(5') | -1037 (2) | 1937 (2) | 8231 (1) | 3.17 |

Table 2. Interatomic distances (\AA) and valence angles ($^\circ$) with e.s.d.'s in parentheses

| | | | |
|-----------------|-----------|-------------------|-----------|
| C(1)—C(2) | 1.548 (3) | C(6)—O(1) | 1.459 (3) |
| C(1)—O(1) | 1.418 (3) | C(1')—C(2') | 1.492 (4) |
| C(1)—O(5) | 1.421 (3) | C(1')—O(1') | 1.445 (3) |
| C(2)—C(3) | 1.521 (3) | C(1')—O(5') | 1.414 (3) |
| C(2)—O(2) | 1.424 (3) | C(2')—C(3') | 1.496 (3) |
| C(2)—C(3') | 1.486 (3) | C(2')—N(4) | 1.288 (3) |
| C(3)—C(4) | 1.548 (4) | C(3')—C(4') | 1.330 (3) |
| C(4)—C(5) | 1.540 (4) | C(4')—C(5') | 1.500 (4) |
| C(4)—N(4) | 1.470 (3) | C(5')—O(5') | 1.437 (3) |
| C(5)—O(5) | 1.442 (3) | C(5')—C(6') | 1.504 (4) |
| C(5)—C(6) | 1.504 (4) | C(6')—O(1') | 1.450 (4) |
| O(5)—C(1)—C(2) | 108.4 (2) | C(1)—O(1)—C(6) | 106.3 (2) |
| O(1)—C(1)—C(2) | 111.6 (2) | C(4)—N(4)—C(2') | 116.6 (2) |
| O(1)—C(1)—O(5) | 105.4 (2) | O(5')—C(1')—C(2') | 109.4 (2) |
| C(1)—C(2)—C(3) | 108.2 (2) | O(1')—C(1')—C(2') | 109.6 (2) |
| C(1)—C(2)—O(2) | 105.6 (2) | O(1')—C(1')—O(5') | 104.9 (2) |
| C(1)—C(2)—C(3') | 109.4 (2) | C(1')—C(2')—C(3') | 115.1 (2) |
| C(3)—C(2)—O(2) | 112.7 (2) | C(1')—C(2')—N(4) | 119.5 (2) |
| C(3)—C(2)—C(3') | 107.4 (2) | C(3')—C(2')—N(4) | 125.3 (2) |
| C(3')—C(2)—O(2) | 113.4 (2) | C(2')—C(3')—C(4') | 116.1 (2) |
| C(2)—C(3)—C(4) | 105.1 (2) | C(2')—C(3)—C(2) | 116.6 (2) |
| C(3)—C(4)—C(5) | 109.6 (2) | C(4')—C(3')—C(2) | 127.3 (2) |
| C(3)—C(4)—N(4) | 111.3 (2) | C(3')—C(4')—C(5') | 121.1 (2) |
| C(5)—C(4)—N(4) | 108.1 (2) | C(4')—C(5')—O(5') | 109.0 (2) |
| C(4)—C(5)—O(5) | 108.9 (2) | C(4')—C(5')—C(6') | 111.4 (2) |
| C(4)—C(5)—C(6) | 113.2 (2) | O(5')—C(5')—C(6') | 101.4 (2) |
| O(5)—C(5)—C(6) | 113.2 (2) | O(5')—C(5')—C(6') | 101.4 (2) |
| C(1)—O(5)—C(5) | 100.7 (2) | C(1')—O(1')—C(6') | 106.3 (2) |
| C(5)—C(6)—O(1) | 103.1 (2) | C(1')—O(5')—C(5') | 101.0 (2) |

turbed by the presence of the cyclic imine structure, as far as bond lengths are concerned. Significant differences, however, appear among valence and torsion angles. The central cyclization has caused a considerable puckering of the pyranose ring at the C(3) side, *i.e.* the ring is less flattened at C(3) compared with the parent, unperturbed 1,6-anhydropyranoses. This is reflected in the angular distortions at C(2), C(3) and C(4), *e.g.* the endocyclic angle at C(3) is 5–7° smaller than in the corresponding parent molecules; similarly, the torsion angles at C(3)

[C(1)—C(2)—C(3)—C(4) = 55.3 (2), C(2)—C(3)—C(4)—C(5) = -53.9 (2)°] are 10–20° larger than in 1,6-anhydropyranose derivatives.

The conformations of the rings can also be expressed in terms of Cremer & Pople (1975) ring-puckering parameters with e.s.d.'s according to Norrestam (1981). The pyranose ring in the title compound is characterized by $Q = 0.684$ (4) \AA , $\varphi_2 = 195$ (1) and $\theta = 171$ (1)°, showing that the ring is ¹C₄ chair distorted toward a conformation which is midway between sofa *E*₀ and half-chair ¹H₀. The corresponding *Q* values for unperturbed 1,6-anhydropyranose so far investigated vary in the range 0.61–0.64 \AA with the conformation limited to the range *E*₀–⁵H₀ (Jeffrey & Yates, 1979), thus showing again a larger overall puckering amplitude for the pyranoid ring of the present structure as well as its different distortion mode from the ¹C₄ form. As expected, the conformation of the anhydro rings is between ⁰T₄ and ⁰E, similar to those of related 1,6-anhydropyranoses; the values of the ring-

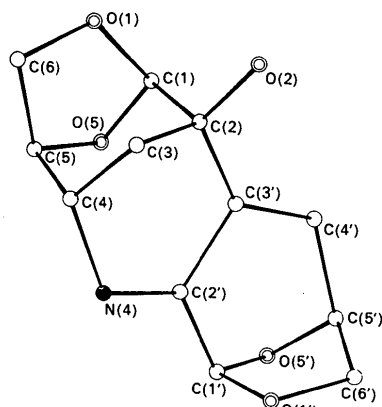


Fig. 1. The molecular structure of the title compound (III) and labelling of the atoms.

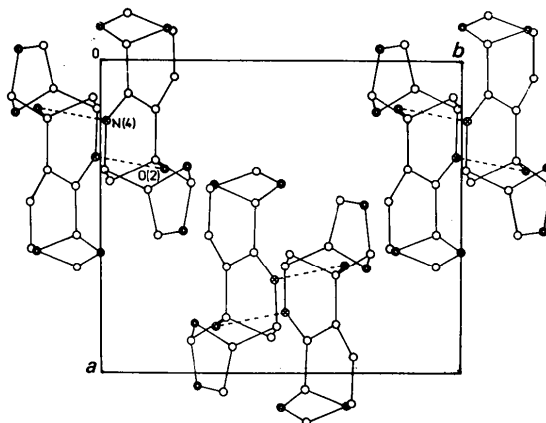


Fig. 2. The crystal structure as seen along the *c* axis. The broken lines represent hydrogen bonds. Only atoms of the reference molecule involved in the independent hydrogen bond are numbered.

puckering coordinates are $Q = 0.446(3) \text{ \AA}$, $\varphi_2 = 351(2)^\circ$ for the sequence O(5), C(1), O(1), C(6), C(5) and $Q = 0.445(4) \text{ \AA}$, $\varphi_2 = 350(2)^\circ$ for the sequence O(5'), C(1'), O(1'), C(6'), C(5'). The newly formed six-membered heterocycle has an envelope conformation with C(3) displaced $0.781(2) \text{ \AA}$ from the mean plane through the remaining five atoms.

The central part of the molecule [formed by the atoms N(4), C(2'), C(3'), C(4'), C(1'), C(4), C(2) and C(5')] is planar to within $\pm 0.016(3) \text{ \AA}$ with the exception of C(5') which is $0.027(3) \text{ \AA}$ out of the least-squares plane of this eight-atom fragment. The twist angle about the central C(2')—C(3') bond as measured by the angle between the planes [N(4), C(2'), C(1')] and [C(2), C(3'), C(4')] is only $1.1(2)^\circ$. On the other hand, the pattern of bond lengths within the alkylideneimine grouping, $-\text{N}=\text{C}=\text{C}-$, is entirely consistent with integer bond orders: the N(4)—C(2') and C(3')—C(4') bond distances of $1.288(3)$ and $1.330(3) \text{ \AA}$ are in good agreement with the values reported for pure $\text{C}=\text{N}$ (Schenetti, Taddei, Greci, Marchetti, Milani, Andreotti, Bocelli & Sgarabotto, 1980) and $\text{C}=\text{C}$ (Bartell, Roth, Hollowell, Kuchitsu & Young, 1965) double bonds, and the C(2')—C(3') bond has a length [$1.496(3) \text{ \AA}$] which is slightly larger than the value of $1.487(5) \text{ \AA}$ normally accepted for a $\text{C}(sp^2)\text{—C}(sp^2)$ single bond (Shmueli, Shanan-Atidi, Horwitz & Shvo, 1973). The latter bond length compares quite well with the central bond length in 2,2'-bipyrimidine [$1.497(4) \text{ \AA}$; Fernholt, Rømming & Samdal, 1981] where conjugation is hindered by repulsion. There is, therefore, no evidence for any π -electron delocalization between N(4)=C(2') and C(3')=C(4'). Thus it may be concluded that the planarity of the central portion of the molecule results from rigidity of the polycyclic skeleton rather than from conjugation within the α,β -unsaturated imine function.

The crystal structure of the compound is shown in Fig. 2. Molecules are linked by hydrogen bonds, $\text{O}(2)\text{—H}\cdots\text{N}(4)(\frac{1}{2}-x, -y, -\frac{1}{2}+z)$ [$\text{O}\cdots\text{N} = 2.802(3)$, $\text{O—H} = 0.78(3)$, $\text{H}\cdots\text{N} = 2.03(3) \text{ \AA}$, $\text{O—H}\cdots\text{N} = 176(3)^\circ$], to form infinite chains running along 2_1 screw axes [$(\frac{1}{4}, 0, z)$ and $(\frac{3}{4}, \frac{1}{2}, z)$]. The chains are packed by van der Waals forces only.

References

- AHMED, F. R., HALL, S. R., PIPPY, M. E. & HUBER, C. P. (1973). NRC crystallographic programs for the IBM/360 system. Accession Nos. 133–147 in *J. Appl. Cryst.* (1973), **6**, 309–346.
- BARTELL, L. S., ROTH, E. A., HOLLOWELL, C. D., KUCHITSU, K. & YOUNG, J. E. (1965). *J. Chem. Phys.* **42**, 2683–2686.
- BHATÉ, P. & HORTON, D. (1983). *Carbohydr. Res.* **122**, 189–199.
- BYSTRICKÝ, S., STICZAY, T., KOÓŠ, M. & KETTMANN, V. (1986). *Chem. Pap.* **40**, 79–87.
- CREMER, D. & POPLÉ, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
- DECLERCQ, J.-P., GERMAIN, G. & WOOLFSON, M. M. (1979). *Acta Cryst.* **A35**, 622–626.
- FERNHOLT, L., RØMMING, C. & SAMDAL, S. (1981). *Acta Chem. Scand. Ser. A*, **C35**, 707–715.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- JEFFREY, G. A. & YATES, J. H. (1979). *Carbohydr. Res.* **74**, 319–322.
- KAISER, E. M., WORK, S. D., WOLFE, J. F. & HAUSER, C. R. (1967). *J. Org. Chem.* **32**, 1483–1487.
- MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- MALUSZYNKA, H., KINOSHITA, Y. & JEFFREY, G. A. (1982). *Carbohydr. Res.* **100**, 17–28.
- NORRESTAM, R. (1981). *Acta Cryst.* **A37**, 764–765.
- SCHENETTI, M. L., TADDEI, F., GRECI, L., MARCHETTI, L., MILANI, G., ANDREOTTI, G. D., BOCELLI, G. & SGARABOTTO, P. (1980). *J. Chem. Soc. Perkin Trans. 2*, pp. 421–426.
- SHELLING, J. G., DOLPHIN, D., WIRZ, P., COBBLEDICK, R. E. & EINSTEIN, F. W. B. (1984). *Carbohydr. Res.* **132**, 241–259.
- SHMUELI, U., SHANAN-ATIDI, H., HORWITZ, H. & SHVO, Y. (1973). *J. Chem. Soc. Perkin Trans. 2*, 657–662.

Acta Cryst. (1989). **C45**, 1583–1585

Structure of Phenacyl Pentamethylenedithiocarbamate

BY U. BAUMEISTER, W. DÖLLING, H. HARTUNG* AND H. OLA

Sektion Chemie, Martin-Luther-Universität Halle-Wittenberg, Postfach, DDR-4010 Halle, German Democratic Republic

(Received 12 September 1988; accepted 27 February 1989)

Abstract. $\text{C}_{14}\text{H}_{17}\text{NOS}_2$, $M_r = 279.4$, monoclinic, $P2_1/n$, $a = 15.186(2)$, $b = 9.510(2)$, $c = 9.765(2) \text{ \AA}$, $\beta = 95.71(2)^\circ$, $V = 1403.3(5) \text{ \AA}^3$, $Z = 4$, $D_x = 1.32$, $D_m = 1.33 \text{ Mg m}^{-3}$, $\lambda(\text{Mo K}\alpha) = 0.71069 \text{ \AA}$, $\mu =$

0.32 mm^{-1} , $F(000) = 592$, $T = 293 \text{ K}$, final $R = 0.043$ for 1150 observed reflections. The molecule of the title substance (1) has normal bond lengths and angles. The nearly planar phenacyl group is approximately perpendicular to the dithiocarbamate group. The conformation of (1) is discussed with regard to

* To whom correspondence should be addressed.