compound is long compared with that in 1 -dimethyl-amino-4-nitrobenzene, $1.358 \AA$ (Mak \& Trotter, 1965) and in $p$-dimethylaminobenzaldehyde oxime, $1 \cdot 380 \AA$ (Bachechi \& Zambonelli, 1972). Therefore, the degree of the double-bond character in the title compound is relatively small.

The torsion angles $\mathrm{C}(12)-\mathrm{C}(11)-\mathrm{C}(13)-\mathrm{O}(1)$, $-154 \cdot 2(4)^{\circ}, \quad$ and $\quad \mathrm{C}(11)-\mathrm{C}(12)-\mathrm{C}(16)-\mathrm{O}(3)$, $-142.9(3)^{\circ}$, show that the two carbonyl groups twist from the mean plane of the triazole ring on opposite sides. These directions differ notably in the case of diisopropyl 1-(1-naphthyl)-1 $H-1,2,3$-triazole-4,5-dicarboxylate (Nagawa, Goto, Honda \& Nakanishi, 1988), in which the carbonyl group at the 4-position exists in the triazole plane and at the 5 -position it twists from the triazole plane. The results reflect the requirements of intramolecular contacts of the extra dimethylamino group. The larger temperature factors of $\mathrm{C}(15)$ and $\mathrm{O}(1)$ atoms might be due to the disorder.
The packing of the molecule in the crystal is shown in Fig. 2. The crystal structure is stabilized mainly by van der Waals forces; the shortest intermolecular distance is $3.315(5) \AA$ for $\mathrm{C}(19)$ $(x, y, z) \cdots \mathrm{N}(3)(1-x,-y, 1-z)$.

## References

Alder, R. W., Bowman, P. S., Steele, W. R. S. \& Winterman, D. R. (1968). J. Chem. Soc. Chem. Commun. pp. 723-724.

Bachechi, F. \& Zambonelli, L. (1972). Acta Cryst. B28, 24892492.

Einspahr, H., Robert, J. B., Marsh, R. E. \& Roberts, J. D. (1973). Acta Cryst. B29, 1611-1616.

Honda, K., Nakanishi, H., Nagawa, Y. \& Yabe, A. (1984). J. Chem. Soc. Chem. Commun. pp. 450-451.
International Tables for $X$-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
Johnson, C. K. (1965). ORTEP. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
Main, P., Hull, S. E., Lessinger, L., Germain, G., Declerce, 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.
Mak, T. C. W. \& Trotter, J. (1965). Acta Cryst. 18, 68-74.
Nagawa, Y., Goto, M., Honda, K. \& Nakanishi, H. (1986). Acta Cryst. C42, 478-480.
Nagawa, Y., Goto, M., Honda, K. \& Nakanishi, H. (1987). Acta Cryst. C43, 147-149.
Nagawa, Y., Goto, M., Honda, K. \& Nakanishi, H. (1988). Bull. Chem. Soc. Jpn, 61, 3553-3557.
Nagawa, Y., Honda, K. \& Nakanishi, H. (1987). Synthesis, pp. 905-906.
Sakurai, T. \& Kobayashi, K. (1979). Rep. Inst. Phys. Chem. Res. 55, 69-77.

# Structure of 3-(1-Pyridinio)indole-2-thiolate 

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Abstract. $\mathrm{C}_{13} \mathrm{H}_{10} \mathrm{~N}_{2} \mathrm{~S}, M_{r}=226 \cdot 3$, monoclinic, $P 2_{1} / c$, $a=10.037$ (4), $b=8.076$ (3), $c=14.124$ (4) $\AA, \quad \beta=$ $104.59(3)^{\circ}, V=1107.9(6) \AA^{3}, Z=4, D_{m}=1.34$ (1), $D_{x}=1.36 \mathrm{~g} \mathrm{~cm}^{-3}, \quad \lambda($ Mo $K \alpha)=0.71069 \AA, \quad \mu=$ $2.6 \mathrm{~cm}^{-1}, F(000)=472, T=295 \mathrm{~K}, R=0.039$ for 2057 observed reflexions. Sulfur forms a hydrogen bond to the NH group of the neighbouring molecule symmetrically related by the screw axis along $b$. The phenyl ring is rotated out of the indolyl plane by $57^{\circ}$.

Introduction. X-ray structure analysis of the title compound has been used to confirm the chemical constitution of the product of a new synthetic method for the preparation of indolyl-based com-
pounds (Gonda, Kristian \& Imrich, 1987; Gonda \& Kristian, 1988) and to obtain information about the contributions of the resonance states (I)-(III) to the average crystal structure. This paper is part of a general project on the development of biologically efficient indolyl compounds substituted by different function groups.

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Experimental. Crystals of 3-(1-pyridinio)indole-2thiolate (m.p. $480-482 \mathrm{~K}$ ) were prepared by Gonda, Kristian \& Imrich (1987). A suitable crystal (dimensions $0.6 \times 0.4 \times 0.4 \mathrm{~mm}$ ) was cut from a thick darkblue slab. The crystal density was measured pycnometrically in toluene- $\mathrm{CCl}_{4}$. The intensities were measured with a Syntex $P 2_{1}$ diffractometer using $\theta-2 \theta$ scans at room temperature. 2057 of 2559 independent reflexions $\left[(\sin \theta) / \lambda<0.651 \AA^{-1}, h 0 / 13\right.$, $k 0 / 10, l-18 / 18]$ were classified as observed with $F_{o}$ $>3.92 \sigma_{F}$. Space group $P 2_{1} / c$ was confirmed by Weissenberg photographs and by scanning of systematically extinct reflexions. Unit-cell parameters were determined from 17 reflexions with $15<2 \theta<$ $28^{\circ}$. Three reference intensities measured at intervals of 30 reflexions were stable within $2 \%$ during data collection. Other measurement details are as given in Has̆ek (1985). No corrections for absorption or extinction were made. The structure was solved by MULTAN80 (Main et al., 1980) and refined by SHELX76 (Sheldrick, 1976). Atomic scattering factors were taken from International Tables for X-ray Crystallography (1974). $\quad \sum w\left(\left|F_{o}\right|-\left|F_{c}\right|\right)^{2}$ minimized with $\left.w=\left.\left|\sigma_{F}^{2}+0.015\right| F_{o}\right|^{2}\right]^{-1} ;$ N1-C16 refined with anisotropic temperature parameters and $\mathrm{H} 1-\mathrm{H} 16$ localized from difference map with isotropic temperature parameters until all the parameter shifts dropped below 0.2 of the respective e.s.d.'s. The resulting $R=0.039, w R=0.052$ for 2057 independent reflexions and 185 refined parameters. The highest peak on the final difference map is $0.2 \mathrm{e} \AA^{-3}$ and the minimum height is $-0.32 \mathrm{e}^{-3}$. Atomic coordinates and the $U_{\text {eq }}$ 's for non- H atoms are given in Table 1.* Bond lengths and bond angles are given in Fig. 1. The structure geometry was calculated using XANADU (Roberts \& Sheldrick, 1976), PARST (Nardelli, 1983) and IMC (Hašek, 1981).

Discussion. The average bond length in the benzene ring of the indolyl group is as usual [1.393 (1) $\AA$ ]; however, the $\mathrm{C}-\mathrm{C}$ bond common to both the fiveand six-membered rings is longer, $1 \cdot 417$ (2) $\AA$. The bonds in the pyrrole ring, in the sequence $\mathrm{C}-\mathrm{N}-\mathrm{C}-\mathrm{C}-\mathrm{C}$, are 1.382 (2), 1.369 (2), 1.392 (2) and 1.424 (2) $\AA$, respectively, and none can be considered to be a single or a double bond. The S atom participating in the hydrogen bridge $\mathrm{N}-\mathrm{H} \cdots \mathrm{S}$ is on the opposite side of the indole to the pyridine ring. The angles are $\mathrm{C}-\mathrm{C}-\mathrm{S} \quad 130 \cdot 8(1), \mathrm{N}-\mathrm{C}-\mathrm{S}$ $123.4(1)^{\circ}$, with the corresponding $\mathrm{N}-\mathrm{C}-\mathrm{C}$ angle $105 \cdot 8(1)^{\circ}$.

[^0]Table 1. Final coordinates $\left(\times 10^{5}\right)$ and equivalent isotropic thermal parameters $\left(\times 10^{3} \AA^{2}\right)$ for the non -H atoms with e.s.d.'s in parentheses

| $U_{\text {eq }}=(1 / 3) \sum_{i} \sum_{j} U_{i j} a_{i}{ }^{*} a_{j}{ }^{*} \mathbf{a}_{i} \cdot \mathbf{a}_{j}$. |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  | $x$ | $y$ | $z$ | $U_{\text {eq }}$ |
| N1 | - 15749 (15) | -9730 (19) | 69904 (11) | 39 (1) |
| C2 | -10107 (18) | 3237 (20) | 66021 (12) | 34 (1) |
| C3 | -21077 (17) | 13527 (21) | 61682 (12) | 36 (1) |
| C4 | - 33685 (19) | 6939 (23) | 62927 (13) | 38 (1) |
| C5 | -47549 (19) | 11401 (29) | 60072 (14) | 48 (1) |
| C6 | - 57183 (20) | 895 (34) | 62409 (17) | 58 (1) |
| C7 | -53320 (23) | -13723 (36) | 67613 (17) | 62 (1) |
| C8 | -39576 (22) | -18545 (28) | 70560 (15) | 53 (1) |
| C9 | -29853 (19) | 7997 (25) | 68166 (13) | 41 (1) |
| S10 | 7255 (04) | 5239 (06) | 67065 (03) | 41 (1) |
| N11 | -20067 (14) | 27997 (17) | 56086 (10) | 36 (1) |
| C12 | -14599 (20) | 26815 (24) | 48284 (13) | 43 (1) |
| C13 | - 14173 (23) | 40446 (30) | 42504 (16) | 53 (1) |
| C14 | - 19386 (29) | 55437 (26) | 44688 (18) | 57 (1) |
| C15 | -24769 (29) | 56481 (26) | 52675 (18) | 62 (1) |
| C16 | -25000 (26) | 42670 (26) | 58385 (15) | 51 (1) |


(a)

(b)

Fig. 1. (a) The atom-numbering scheme showing bond distances $(\AA)$, (b) the interbond angles ( ${ }^{\circ}$ ). E.s.d.'s of distances between non-H atoms are $0.002-0.004 \AA$, e.s.d.'s of $\mathrm{C}-\mathrm{H}$ bonds $0.02-$ $0.03 \AA$. Corresponding e.s.d.'s of angles are in the ranges $0 \cdot 1-0.3$ and $1-2^{\circ}$.

The mean $\mathrm{C}-\mathrm{C}$ bond length in the pyridine ring is 1.378 (1) $\AA$ and the pyridine $\mathrm{C}-\mathrm{N}$ bonds are 1.355 (2) and 1.353 (2) $\AA$. The mean endocyclic pyridine angle is $120.0(1)^{\circ}$.

The maxima of electron density of H atoms were refined to the expected distances $0.94-1.06$ (3) $\AA$;


Fig. 2. The molecular packing: $\mathrm{N}-\mathrm{H} \cdot \cdots \mathrm{S}$ bridges are denoted by dotted lines.
only the electron density of H 1 was localized at 0.85 (3) $\AA$ from the indolyl N atom.

The bond distances and uniformly small angles of the indolyl unit show the delocalization of $\pi$ electrons over the whole indolyl moiety; the bond C4-C9 [1.417 (3) $\AA$ ] is elongated in comparison with a typical benzene bond, the bonds C3-C4 [1.424 (3) $\AA$ ], N1-C2 [1.369 (2) $\AA$ ] are shorter than expected for single bonds, and $\mathrm{C}(2)-\mathrm{C}(3)$ [ $1 \cdot 392$ (2) $\AA$ ] cannot be considered as a double bond.

No conjugation between the indolyl and pyridyl ring can be assumed because of a high torsion angle around the $\mathrm{C} 3-\mathrm{N} 11$ bond; $\mathrm{C} 2-\mathrm{C} 3-\mathrm{N} 11-\mathrm{C} 12$ is $55 \cdot 4^{\circ}$ and $\mathrm{C} 4-\mathrm{C} 3-\mathrm{N} 11-\mathrm{Cl} 658 \cdot 3^{\circ}$. The $\mathrm{C} 3-\mathrm{N} 11$
bond deviates slightly from the indolyl plane; the torsion angles are $\mathrm{C} 5-\mathrm{C} 4-\mathrm{C} 3-\mathrm{N} 11-2 \cdot 7^{\circ}$ and $\mathrm{S} 10-\mathrm{C} 2-\mathrm{C} 3-\mathrm{N} 116.5^{\circ}$.

The packing of atoms in the unit cell is shown in Fig. 2. The molecules are paired by two symmetrically equivalent hydrogen bridges $\mathrm{N}-\mathrm{H} \cdots \mathrm{S}^{\mathrm{i}}$, thus forming dimers around the screw axis: $\mathrm{N} 1-\mathrm{Hl}$ 0.85 (2), $\mathrm{N} 1 \cdots \mathrm{~S}^{\mathrm{i}} 3.366$ (2), $\mathrm{Hl} \cdots \mathrm{S}^{\mathrm{i}} 2 \cdot 57$ (2) $\AA$, angle $\mathrm{N} 1-\mathrm{H} 1 \cdots \mathrm{~S}^{\mathrm{i}} 157(1)^{\circ}\left[(\mathrm{i})-x, y-\frac{1}{2}, \frac{3}{2}-z\right]$.

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## References

Gonda, J. \& Kristian, P. (1988). Collect. Czech. Chem. Commun. 53, 1761-1769.
Gonda, J., Kristian, P. \& Imrich, J. (1987). Collect. Czech. Chem. Commun. 52, 2508-2520.
HAŠEK, J. (1981). IMC program package. In Experimental Techniques in $X$-ray and Neutron Structure Analysis (in Czechoslovakian). Institute of Macromolecular Chemistry, Praha, Czechoslovakia.
HaŠek, J. (1985). Acta Cryst. C41, 583-586.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declerce, J.-P. \& Woolfson, M. M. (1980). MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data. Univs. of York, England, and Louvain, Belgium.
Nardelli, M. (1983). Comput. Chem. 3, 95-98.
Roberts, D. \& Sheldrick, G. M. (1976). XANADU. Program for crystallographic calculations. Univ. of Cambridge, England.
Sheldrick, G. M. (1976). SHELX76. Program for crystal structure determination. Univ. of Cambridge, England.

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# Structure of Karanjin* 

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#### Abstract

C}_{18} \mathrm{H}_{12} \mathrm{O}_{4}, M_{r}=292 \cdot 3\), monoclinic, $P 2_{1} / n, a$ $=7 \cdot 196$ (3), $\quad b=11.275$ (3), $c=17.495$ (3) $\AA, \quad \beta=$ 100.70 (2) ${ }^{\circ}, V=1394.8$ (7) $\AA^{3}, D_{m}=1.38$ (2),,$D_{x}=$ $1.39 \mathrm{~g} \mathrm{~cm}^{-3}, \quad Z=4, \quad \lambda(\mathrm{Cu} \mathrm{K} \mathrm{\alpha})=1.5418 \AA, \quad \mu=$ $7.2 \mathrm{~cm}^{-1}, T=293 \mathrm{~K}, F(000)=608, R=0.058, w R=$


[^1]0.066 for 1453 reflections with $I \geq 2 \sigma(I)$. The furan ring is planar while the pyran ring is distorted from planarity. The phenyl ring makes an angle of 28.7 (2) ${ }^{\circ}$ with the pyran ring.

Introduction. The title compound, a naturally occurring furoflavone, extracted from the seed oil of the Indian beech Pongamia glabra (Aneja, Khanna \& Seshadri, 1963), was obtained from commercial sour(c) 1990 International Union of Crystallography


[^0]:    * Lists of H -atom parameters, anisotropic temperature parameters and structure factors, together with a scheme showing torsion angles, have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52230 ( 12 pp .). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

[^1]:    * 3-Methoxy-2-phenyl-4 H -furo[2,3-h][1] benzopyran-4-one. $\dagger$ To whom correspondence should be addressed. $\ddagger$ DCB contribution No. 744.

