

Structure of *N*-(4-Methoxysalicylidene)-2-thienylmethylamine*

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Abstract. $C_{13}H_{13}NO_2S$, $M_r = 247.3$, monoclinic, $P2_1$, $a = 8.406$ (3), $b = 5.798$ (1), $c = 12.984$ (4) Å, $\beta = 98.85$ (3)°, $V = 625.3$ (6) Å³, $Z = 2$, $D_x = 1.31$, $D_m = 1.31$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 2.03$ cm⁻¹, $F(000) = 260$, $T = 293$ K, $R = 0.0369$ for 1067 observed reflections. The benzene and thiophene rings are planar with dihedral angle of 104 (1)°. A very strong intramolecular H bond (1.76 Å) locks the salicylaldimino moiety in the planar geometry. The thiophene ring shows statistical disorder with two orientations.

Introduction. Crystalline *N*-salicylideneanilines are either thermochromic or photochromic. The above behaviour has been attributed to the conformation, planar or non-planar respectively, of the molecules in the crystals (Cohen & Schmidt, 1962). By choosing *ortho* and *meta* aminopyridines for the amino part of the molecule, planar or nearly planar conformations have been imposed on the molecules. As a result, this class of compounds shows only thermochromic behaviour (Moustakali-Mavridis, Hadjoudis & Mavridis, 1978, 1980). In our search to modify the chromo-behaviour of the Schiff bases of substituted salicylaldehydes we have found compounds that are simultaneously photochromic and thermochromic (Hadjoudis, Vittorakis & Moustakali-Mavridis, 1986). The title compound is one of these and its crystal structure was determined in order to correlate the structural characteristics with the above behaviour.

Experimental. The title compound was prepared by condensation of the corresponding aldehyde and amine in ethanol. Crystals in the form of needles were grown by evaporation of cyclohexane solutions. The systematic absences $0k0$, $k = 2n$ and the crystal class established the space group. Density measured by flotation in aqueous $ZnCl_2$. A summary of data collection and structure refinement is given in Table 1. Intensities were corrected for Lorentz and polarization effects.

Scattering factors for neutral atoms taken from *International Tables for X-ray Crystallography* (1974).

* Preferred IUPAC name: 2-[(2-thienyl)methyliminomethyl]-5-methoxyphenol.

Table 1. Summary of data collection and structure refinement

Data collection*	Mo $K\alpha$ (Zr-filtered)
Radiation	θ -2 θ scan.
Mode	1.8° plus α_1 - α_2 divergence in 2 θ
Scan range	1.0–10.0
Scan rate (° min ⁻¹)	$\frac{1}{4}$ of scan time at start and end of each scan
Background	2.5–50.0
2 θ range (°)	0.0, –15
Range in hkl , min.	max.
	10.6, 15
Total reflections measured	1217
Crystal dimensions (mm)	0.1 × 0.5 × 0.1
Absorption correction	none
Structure refinement	
Reflections used ($F > 4\sigma_F$)	1067
Number of variables	182
Goodness of fit, S	2.8
R_wR	0.0369, 0.0345
R for all data	0.0437
Max. density in difference map (e Å ⁻³)	0.18
Min. density in difference map (e Å ⁻³)	–0.18

* Unit-cell parameters were obtained by least-squares refinement of the setting angles of 14 reflections with $14.4 < 2\theta < 22.9^\circ$. Syntax *P2*, autodiffractometer. Crystal stability and X-ray damage were monitored by measurement of three check reflections every 67 reflections. No damage to the crystal was observed.

Structure solved and refined with *SHELX76* (Sheldrick, 1976). Best E map ($E > 1.2$) revealed 12 non-hydrogen atoms. The remaining five atoms were found by difference Fourier map. H atoms were initially located at the end of isotropic refinement in a difference map. Full-matrix least-squares refinement [$\sum w(F_o - F_c)^2$ minimized], $w = 1$. Refinement of the positional and anisotropic thermal parameters for non-hydrogen atoms, fixed positional and isotropic thermal parameters (1.25 times those of the corresponding non-hydrogen atoms) for the H atoms terminated with $R = 0.0854$. The bond distances and thermal parameters of the thiophene-ring atoms indicate disorder for that part of the molecule involving 180° rotation of the ring around the C(8)–C(9) bond. As a result, in a fraction of the molecules in the crystal the S atom is positioned very close to the C(10) atom site. This was reflected in the residual positive electron density at the vicinity of that atom, the long C(9)–C(10) and

C(10)–C(11) bond distances (1.55 and 1.57 Å respectively), as well as in its small U_{eq} indicating partial occupation of the C(10) site by S.

An additional full-matrix unit-weight refinement was therefore carried out with partial occupancies for two orientations of the thiophene ring according to the assumed disorder. The starting occupancy ratio was 9:1 and the thermal parameters of the thiophene C atoms of the minor conformer were kept isotropic during this refinement. Best agreement was obtained for a 64.7% occupancy of the major thiophene conformation ($R = 0.0369$, mean shift/e.s.d. = 0.062, max shift/e.s.d. = 0.10 for the non-disordered atoms and 0.35 and 0.98 respectively for the disordered ones). The refinement on the disordered structure was also carried out with weighted least-squares refinement and led approximately to the same results but the convergence was slower and the shift/e.s.d. ratios higher. The alternative enantiometric structure was refined separately and converged to $R = 0.0370$ and $wR = 0.0354$ (Hamilton, 1964).

Discussion. The geometry and atom labelling of the structure with two conformations of the thiophene ring are shown in Fig. 1. Final coordinates and equivalent isotropic temperature factors are listed in Table 2* and bond lengths in Table 3. The distances in the salicylaldimino part of the molecule indicate a contribution of a quinoid form as major valence bond structure. The short C(3)–C(4), C(5)–C(6) and C(2)–O(1) bond lengths compare very well both with salicylic acid (Sundaralingam & Jensen, 1965) and *N*-salicylidene-2-aminopyridines (Moustakali-Mavridis *et al.*, 1978). The bond distances and angles of the major orientation of the thiophene ring altered in the expected direction

when its disorder was taken into account (Harshbarger & Bauer, 1970).

Both the salicylaldimino moiety and the thiophene ring are planar. The dihedral angle between the phenyl ring and the plane of the atoms C(1), C(7), N(1) and O(1) is 1(1)°. The molecule as a whole is non-planar due to the methylene group [the dihedral angle between the two rings is 104 (1)°]. The non-planarity gives rise to the characteristic crystal structure of the photo-

Table 2. Coordinates for refined atoms ($\times 10^4$) and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^3$)

	x	y	z	U_{eq}
C(1)	3332 (4)	7734	3913 (3)	48 (2)
C(2)	2459 (4)	9749 (8)	4005 (3)	49 (2)
C(3)	1894 (4)	10278 (9)	4943 (3)	53 (2)
C(4)	2247 (4)	8799 (9)	5771 (3)	52 (2)
C(5)	3112 (4)	6785 (9)	5695 (3)	59 (2)
C(6)	3626 (4)	6260 (9)	4772 (3)	55 (2)
C(7)	3956 (4)	7176 (10)	2962 (3)	60 (2)
C(8)	4402 (5)	7685 (11)	1242 (3)	85 (3)
C(9)	3118 (32)	6651 (59)	429 (22)	55 (8)*
C(10)	2648 (26)	7290 (37)	−541 (15)	105 (14)*
C(11)	1434 (15)	5865 (22)	−1118 (7)	52 (4)*
C(12)	1083 (32)	4219 (53)	−483 (19)	76 (8)*
C(13)	714 (6)	11048 (11)	6826 (3)	85 (3)
N	3698 (4)	8432 (9)	2150 (2)	67 (2)
O(1)	2111 (4)	11224 (8)	3203 (2)	72 (2)
O(2)	1796 (3)	9186 (9)	6722 (2)	74 (2)
S	2187 (6)	4191 (11)	662 (3)	74 (2)*
NC(9)	3283 (54)	6671 (97)	413 (38)	68 (10)†
NC(10)	2367 (46)	4637 (79)	546 (29)	105 (19)†
NC(11)	1231 (56)	4092 (105)	−602 (34)	74 (9)†
NC(12)	1112 (39)	6141 (75)	−1240 (24)	118 (15)†
NS	2716 (9)	7848 (17)	−729 (6)	65 (3)†
HO	2589 (46)	10641 (81)	2643 (31)	86

* Atom of thiophene ring; site occupancy 0.647 (8).

† Atom of thiophene ring; site occupancy 0.353 (8).

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and bond angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43845 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

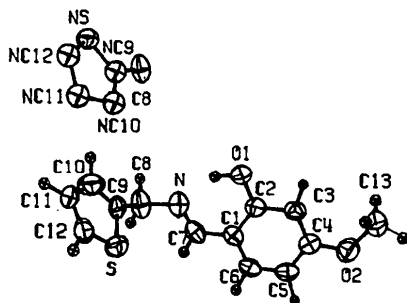


Fig. 1. ORTEP (Johnson, 1965) drawing of the molecule showing the atomic labelling. The minor orientation of the thiophene ring is shown displaced from its actual location.

Table 3. Bond lengths (\AA) with e.s.d.'s in parentheses

C(1)–C(2)	1.395 (5)	C(9)–C(10)	1.32 (3)
C(1)–C(6)	1.397 (5)	C(10)–C(11)	1.43 (2)
C(1)–C(7)	1.451 (5)	C(11)–C(12)	1.32 (3)
C(2)–C(3)	1.408 (5)	C(9)–S	1.68 (3)
C(2)–O(1)	1.344 (4)	C(12)–S	1.63 (3)
C(3)–C(4)	1.372 (5)	C(13)–O(2)	1.431 (6)
C(4)–C(5)	1.387 (5)	NC(9)–C(8)	1.44 (6)
C(4)–O(2)	1.366 (4)	NC(9)–NC(10)	1.43 (6)
C(5)–C(6)	1.368 (5)	NC(9)–NS	1.64 (5)
C(7)–N	1.273 (5)	NC(11)–NC(10)	1.67 (6)
C(8)–N	1.463 (5)	NC(11)–NC(12)	1.44 (6)
C(8)–C(9)	1.51 (3)	NS–NC(12)	1.72 (4)

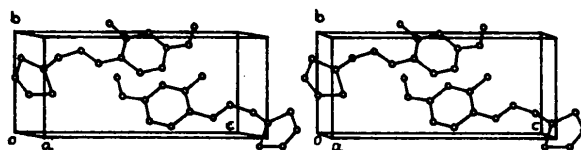


Fig. 2. Stereoscopic view of the molecular packing as viewed along *a* (ORTEP, Johnson, 1965).

chromic 2-chloro-*N*-salicylideneaniline (Bregman, Leiserowitz & Osaki, 1964) with no close intermolecular contacts. The molecular packing is shown in Fig. 2.

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Structure du [Diéthylamino-3 propyl-1)-1 diméthyl-2,6 dihydro-1,4 pyridinylidène-4]-2 Indanedione-1,3

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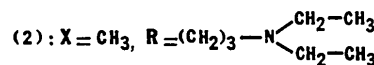
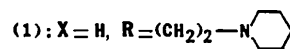
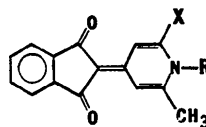
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Abstract. $C_{23}H_{28}N_2O_2$, $M_r = 364.5$, monoclinic, $P2_1/c$, $a = 7.948$ (1), $b = 17.917$ (2), $c = 14.321$ (2) Å, $\beta = 99.90$ (1)°, $V = 2009.0$ Å³, $Z = 4$, $D_x = 1.205$ g cm⁻³, $\lambda(\text{Cu K}\alpha) = 1.54178$ Å, $\mu = 11.1$ cm⁻¹, $F(000) = 784$, room temperature, final $R = 0.059$ for 1657 observed reflections. The bond lengths and angles are normal. The pyridinylidene and indanedione rings are coplanar. In the crystal, the molecules are associated in dimers with overlap of the pyridinylidene rings and a very short interplanar distance (3.33 Å). The partial atomic charges, calculated using the INDO method, show several strong dipoles, particularly for the carbonyl groups.

Introduction. Dans de précédents travaux, nous avons décrit les modes d'accès et les activités anti-inflammatoire, antihistaminique et anticoagulante de (*N*- ω aminoalkyl dihydro-1,4 pyridinylidène-4)-2 indanedione-1,3 (Clairc, Le Baut, Ploquin, Petit & Welin, 1981; Ploquin, Le Baut, Floc'h, Leblois, Welin & Petit, 1982). L'étude du mécanisme de l'action anti-inflammatoire de la (pipéridinyléthyl-1 méthyl-2 dihydro-1,4 pyridinylidène-4)-2 indanedione-1,3 (1) a permis de constater que ces pyrophthalones réduisent la production de prostaglandines, mais à l'inverse de nom-

breux autres anti-inflammatoires non stéroïdiens, elles n'ont aucun effet sur la prostaglandine synthétase. Elles pourraient entraîner une diminution du taux de substrat disponible pour l'enzyme par le biais de l'inhibition de la libération des acides gras polyinsaturés, à partir des lipides de la membrane cellulaire, sous l'action de la phospholipase lysosomale (Henry, Petit & Welin, 1977).



Diverses méthodes d'analyse structurale nous ont conduit à interpréter les propriétés physico-chimiques très particulières de ces pyrophthalones comme résultant de leur caractère bétaïnique et de leur état d'association marqué (Ploquin, Sparfel, Le Baut & Floc'h, 1974), cependant, l'étude radiocristallographique s'imposait pour étayer cette hypothèse. Le choix s'est porté sur la (diéthylaminopropyl-1 diméthyl-2,6 dihydro-1,4 pyridinylidène-4)-2 indanedione-1,3 (2); car bien qu'elle manifeste une activité anti-inflammatoire légèrement