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Potassium 3-Anilino-2-phenyl-3*H*-naphtho[1,2-*d*]imidazole-5-sulphonate, $K[C_{23}H_{16}N_3O_3S]$

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Abstract. M_r = 453·57, monoclinic, $P2_1/c$, a = 22·991 (2), b = 10·128 (1), c = 9·283 (2) Å, β = 96·30 (2)°, V = 2148·5 (6) Å^3, D_x = 1·402 g cm^{-3}, Z = 4, T = 298 K, $F(000)$ = 936, Cu $K\alpha$, λ = 1·5418 Å, R = 0·068 for 2319 reflections. The constitution of the molecule is confirmed as that of a naphtho[1,2-*d*]imidazole, a ring whose structure had not previously been studied by X-ray diffraction analysis. The shape of the main molecular skeleton fits very well the models previously proposed for the active sites of bitter and sweet molecules.

Introduction. Neri (1941, and references therein) had shown that the compounds prepared from condensation of various aldehydes with aminonaphthaleneazobenzenesulphonates were characterized by pronounced sapidant properties. Their taste ranged from sweet to bitter to tasteless, depending on the substituents attached to the main ring system. The structure of this molecular skeleton, however, was described as that of a naphthoisotriazine, contrary to previous evidence (Fisher, 1924) that pointed to the presence of a naphthoimidazole ring in the condensation products of aldehydes with 2-aminonaphthalene-1-azobenzene.

We have undertaken the crystal structure analysis of a series of these compounds with the main goal of establishing their consistency with the models of sweet and bitter receptor sites previously proposed in our laboratory (Temussi, Lelj & Tancredi, 1978; Tancredi, Lelj & Temussi, 1979).

Experimental. The title compound (PANIK) was prepared through the condensation of benzaldehyde with 1-amino-2-phenylazonaphthalene-4-sulphonic acid (Neri & Grimaldi, 1937) and recrystallized from aqueous alcoholic solutions. Thin colourless needles, Ni-filtered Cu $K\alpha$ radiation, Enraf–Nonius CAD-4 automated single-crystal diffractometer, ω–θ mode, $2\theta \leq 120°$. 3132 independent reflections collected and corrected for polarization and Lorentz factors; 813 having $I < 3\sigma(I)$ were not considered in the refinement. Structure solved by means of the direct method using the program *MULTAN* (Germain, Main & Woolfson, 1971) included in the Enraf–Nonius structure determination package (SDP) for a PDP-11 computer. The Fourier map, calculated with the set of phases presenting the highest combined figure of merit given by *MULTAN*, revealed all non-hydrogen atoms. Refinement was achieved by least-squares procedures for all except the H atoms; for these, positions were calculated stereochemically and isotropic thermal factors equal to those of the carrier atoms were assigned; these parameters were kept fixed in the refinement. The refinement, with weights $w = 1/\sigma(F)^2$, was ended when the maximum shifts in the atomic coordinates were less than $\frac{1}{5}$ of the corresponding standard deviations. Atomic scattering factors were calculated according to *International Tables for X-ray Crystallography* (1974). The final R = 0·068, R_w = 0·10.

Table 1. *Final positional and thermal parameters with e.s.d.'s, in units of the last significant figure, in parentheses*

	x	y	z	B_{eq}†(Å^2)
K	1·01925 (9)	0·2172 (2)	0·5093 (2)	4·17 (8)
S	0·93825 (8)	0·0269 (2)	0·7228 (2)	3·09 (7)
O(1)	0·9338 (2)	0·0306 (6)	0·5641 (5)	3·7 (2)
O(2)	0·9534 (2)	−0·1030 (6)	0·7758 (6)	4·3 (2)
O(3)	0·9757 (2)	0·1301 (6)	0·7862 (6)	4·2 (2)
N(1)	0·6930 (2)	0·1076 (6)	0·8424 (6)	3·0 (3)
N(2)	0·7137 (2)	0·1089 (6)	0·6133 (6)	3·0 (2)
N(3)	0·7072 (3)	0·1119 (6)	0·4596 (6)	3·0 (3)
C(1)	0·8668 (3)	0·0594 (7)	0·7684 (7)	2·9 (3)
C(2)	0·8555 (3)	0·0616 (8)	0·9214 (7)	2·9 (3)
C(3)	0·9006 (3)	0·0467 (9)	1·0380 (8)	3·4 (3)
C(4)	0·8876 (4)	0·0510 (10)	1·1791 (8)	4·3 (4)
C(5)	0·8299 (4)	0·0686 (11)	1·2089 (8)	4·6 (5)
C(6)	0·7853 (3)	0·0805 (9)	1·1016 (8)	3·9 (4)
C(7)	0·7976 (3)	0·0787 (8)	0·9550 (7)	3·1 (3)
C(8)	0·7525 (3)	0·0922 (8)	0·8385 (7)	2·8 (3)
C(9)	0·7669 (3)	0·0922 (7)	0·6966 (7)	2·8 (3)
C(10)	0·8231 (3)	0·0760 (8)	0·6600 (7)	2·8 (3)
C(11)	0·6701 (3)	0·1139 (7)	0·7045 (7)	3·1 (3)
C(12)	0·6869 (3)	−0·0061 (8)	0·3913 (7)	3·0 (3)
C(13)	0·6501 (3)	0·0070 (9)	0·2595 (8)	3·9 (4)
C(14)	0·6330 (4)	−0·1052 (10)	0·1822 (9)	4·9 (4)
C(15)	0·6489 (4)	−0·2280 (10)	0·2306 (9)	5·9 (5)
C(16)	0·6842 (5)	−0·2405 (9)	0·3621 (10)	5·6 (5)
C(17)	0·7027 (4)	−0·1297 (9)	0·4389 (9)	4·3 (4)
C(18)	0·6072 (3)	0·1255 (8)	0·6599 (8)	3·1 (3)
C(19)	0·5704 (3)	0·0518 (9)	0·7381 (8)	3·7 (4)
C(20)	0·5100 (4)	0·0603 (10)	0·7068 (9)	4·5 (4)
C(21)	0·4863 (3)	0·1429 (10)	0·5970 (9)	4·5 (4)
C(22)	0·5226 (4)	0·2152 (10)	0·5192 (9)	4·6 (4)
C(23)	0·5830 (3)	0·2081 (9)	0·5488 (8)	3·6 (3)

† $B_{eq} = (B_{11}B_{22}B_{33})^{1/3}$ where $B_{11} = 4\beta_{11}/a^{*2}$, $B_{22} = 4\beta_{22}/b^{*2}$ and $B_{33} = 4\beta_{33}/c^{*2}$.

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Discussion. Table 1 contains the final positional parameters and the corresponding equivalent isotropic thermal parameters of PANIK.*

The molecular model of PANIK derived from the crystal structure analysis is shown in Fig. 1, with relevant bond lengths, bond angles and internal rotation angles.

All molecular parameters are consistent with those typical of compounds containing naphthalene and imidazole rings (Trotter, 1960; Macintyre & Zahrobsky, 1963). The molecular packing is characterized by the relative positions of ions and interactions among phenyl groups. Each K^+ ion is surrounded by the six O atoms of four adjacent sulphonates with K^+—O distances in the narrow range from 2·69 to 2·99 Å. Intermolecular distances of the order of 3·4 Å are found between pairs of atoms of the phenyl groups attached to C(11) and N(3) of symmetry-related molecules: *e.g.* C(15)···C(17) = 3·42 (1) Å $(x, -y-\frac{1}{2}, z-\frac{1}{2})$, C(20)···C(21) = 3·49 (1) Å $(-x+1, -y, -z+1)$.

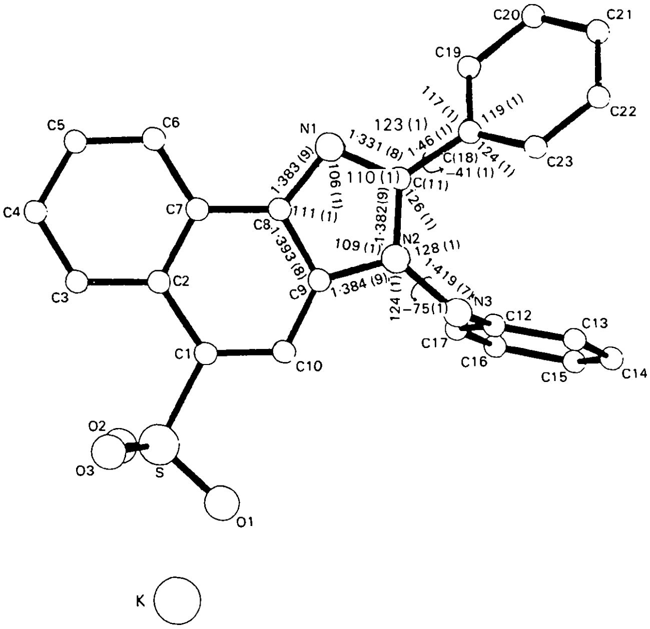

Fig. 1. Molecular model of PANIK. Some relevant internal parameters are reported (Å and °).

A rather short intermolecular distance of 3·05 Å, possibly connected with a hydrogen bond, is also found between N(1) and N(3) of a symmetry-related molecule $(x, \frac{1}{2}-y, z+\frac{1}{2})$. It is interesting, in connection with the characteristics of the models of active sites, to note that the C(11) phenyl ring is not coplanar with the naphthoimidazole ring and that the N(2) anilino substituent projects completely out of this plane. In fact, the rather large value of the C(23)—C(18)—C(11)—N(2) torsion angle may be one of the causes for the lack of taste of this compound, in spite of the similarity of the naphthoimidazole ring to the main part of the model of the sweet-taste receptor site (Temussi, Lelj & Tancredi, 1978). A more complete discussion of the relevance of this structure for the theory of taste is postponed until other structures of similar (sweet) compounds are available.

It may be interesting to note that, to the best of our knowledge, the structure of PANIK is the first reported for a naphtho[1,2-*d*]imidazole.

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* Lists of structure factors and anisotropic thermal parameters, and a table of bond lengths and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38497 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.