$C_{29}H_{33}N_2O_2PS$

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Structural Investigations of Benzo[c]cinnoline Derivatives. III. Structure of 2-Fluorobenzo[c]cinnoline

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Abstract. $C_{12}H_7N_2F$, $M_r = 198.20$, monoclinic, $C2/c$, $a = 11.296\,(4)$, $b = 8.471\,(3)$, $c = 18.889\,(2)$ Å, $\beta = 98.83\,(2)°$, $V = 1786.0\,(2)$ Å^3, $Z = 8$, $D_m = 1.45$, $D_x = 1.474$ g cm^{-3}, λ(Cu $K\alpha$) $= 1.54180$ Å, μ(Cu $K\alpha$) $= 8.284$ cm^{-1}, $F(000) = 816$, $T = 293$ K, $R = 0.051$ for 1378 observed unique reflections $[I \ge 3\sigma(I)]$. The rings in the benzo[c]cinnoline skeleton are close to planar with dihedral angles of $0.45\,(7)$–$1.17\,(8)°$. The F atom is located $0.004\,(3)$ Å from the least-squares plane of the benzenoid ring.

Introduction. Benzo[c]cinnoline and some of its derivatives have mutagenic (Leary, Lafleur, Liber & Blemann, 1983), antirheumatic (Matter, 1957; Erlenmeyer, 1958) and carcinogenic (Ashby, Styles & Paton, 1980) physiological activities. They have also been used as bleach catalysts in the processing of photograph silver-dye bleach materials (Jan, 1980). The structures of benzo[c]cinnoline (van der Meer, 1972), 1-morpholinobenzo[c]cinnoline (Hökelek, Watkin, Kılıç & Tüzün, 1990), 1- and 3-piperidinobenzo[c]cinnoline (Hökelek, Kılıç & Tüzün, 1991a) and 2- and 4-pyrrolidinobenzo[c]cinnoline (Hökelek, Kılıç & Tüzün, 1991b) have previously been reported. The structure determination of the title compound was undertaken to study the effects of changing the types and positions of the substituents.

Experimental. The title compound was dissolved in ethanol. The clear solution was cooled slowly at room temperature. In about two days, yellow rod-shaped crystals were obtained. Experimental data, the method used to solve the structure and other related data and procedures are given in Table 1. Non-H atoms were included with anisotropic displacement parameters. Since difference syntheses did not clearly show the positions of the H atoms they were placed in calculated positions at a distance of 1.079 Å from the corresponding C atoms with coordinates and isotropic displacement parameters taken as 1.3 times the corresponding displacement parameters of the connecting non-H atoms.

Discussion. The final coordinates and equivalent isotropic thermal parameters are given in Table 2.* The molecular structure with the atom-numbering scheme is shown in Fig. 1. Bond lengths and angles are given in Table 3. The benzo[c]cinnoline skeleton is close to, but not exactly, planar, as can be seen from the dihedral angles α—$\beta = 1.17\,(8)$, α—$\gamma = 0.50\,(7)$ and β—$\gamma = 0.45\,(7)°$ between rings α (C8, C9, C10, C11, C12, C13), β (C5, N6, N7, C8, C13, C14) and γ (C1, C2, C3, C4, C5, C14) in Fig. 1.

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* Lists of observed and calculated structure factors, anisotropic thermal parameters, H-atom parameters, and bond distances and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53665 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Experimental data and structure-refinement parameters*

Method of measuring D_m	Flotation in aqueous KI
Crystal shape and size (mm)	Rod-shaped, 0·33 × 0·37 × 0·55
Diffractometer used and data-collection technique	Four-circle diffractometer (Enraf-Nonius CAD-4), ω–2θ scan
Number and θ range (°) of reflections used for measuring lattice parameters	25 reflections with $18 \le 2\theta \le 36$
Absorption correction applied, max. and min. values	Semi-empirical (North, Phillips & Mathews, 1968), 1·31 and 1·18
Maximum value of $(\sin\theta)/\lambda$ reached in intensity measurement (Å^{-1})	0·617
Range of h, k and l	$-1 \le h \le 13$, $-1 \le k \le 10$, $-23 \le l \le 23$
Standard reflections and their intensity variation (%) throughout experiment	$22\bar{5}$, $\bar{1}\bar{1}3$, $\bar{2}20$, 1
Number of reflections measured	4963
Number of unique reflections	1746
Number of unobserved reflections	368
Number of reflections used in the refinement	1378
Criterion for recognizing unobserved reflections	$I \le 3\sigma(I)$
Method used to solve structure	Direct methods (see below)
Use of F or F^2 magnitudes in least-squares refinement	F
Parameters refined	Coordinates and anisotropic temperature factors of non-H atoms, 136
Values of R, wR	0·051, 0·051
Method used to calculate w	$w = 1$
Final residual electron densities ($e\ \text{Å}^{-3}$) for max. and min. peaks	+0·28 and −0·34
Max. Δ/σ	0·003
Source of atomic scattering factors	*International Tables for X-ray Crystallography* (1974, Vol. IV)
Computer programs used	*SHELXS*86 (Sheldrick, 1990), *SHELX*76 (Sheldrick, 1976), *CRYSTALS* (Watkin, Carruthers & Betteridge, 1985), *SNOOPI* (Davies, 1983)

Table 2. *Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{Å}^2 \times 10^4$) with e.s.d.'s in parentheses*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
C1	9806 (3)	2142 (4)	5578 (2)	438 (17)
C2	9829 (3)	1556 (4)	6248 (2)	504 (19)
C3	9085 (3)	361 (4)	6430 (2)	549 (20)
C4	8269 (3)	−287 (4)	5897 (2)	508 (19)
C5	8195 (2)	292 (3)	5192 (2)	413 (16)
N6	7327 (2)	−404 (3)	4683 (1)	495 (16)
N7	7208 (2)	35 (3)	4022 (1)	485 (15)
C8	7930 (2)	1219 (3)	3810 (2)	401 (16)
C9	7737 (3)	1626 (4)	3078 (2)	479 (18)
C10	8405 (3)	2788 (4)	2829 (2)	518 (19)
C11	9285 (3)	3591 (4)	3307 (2)	505 (19)
C12	9489 (2)	3210 (3)	4023 (2)	424 (16)
C13	8812 (2)	2007 (3)	4289 (1)	365 (14)
C14	8956 (2)	1505 (3)	5022 (1)	366 (14)
F15	643 (2)	2165 (3)	6786 (1)	780 (15)

Table 3. *Bond lengths (Å) and bond angles (°) with e.s.d.'s in parentheses*

C1—C2	1·355 (4)	N7—C8	1·390 (4)
C1—C14	1·417 (4)	C8—C9	1·408 (4)
C2—C3	1·392 (5)	C8—C13	1·408 (4)
C2—F15	1·364 (3)	C9—C10	1·367 (4)
C3—C4	1·370 (4)	C10—C11	1·411 (4)
C4—C5	1·410 (4)	C11—C12	1·375 (4)
C5—C14	1·408 (4)	C12—C13	1·412 (4)
C5—N6	1·394 (4)	C13—C14	1·434 (4)
N6—N7	1·290 (3)		
C2—C1—C14	117·7 (3)	N7—C8—C13	123·1 (3)
C1—C2—C3	124·9 (3)	C9—C8—C13	120·2 (3)
C1—C2—F15	118·1 (3)	C8—C9—C10	120·2 (3)
C3—C2—F15	117·0 (3)	C9—C10—C11	119·9 (3)
C2—C3—C4	118·3 (3)	C10—C11—C12	120·8 (3)
C3—C4—C5	119·3 (3)	C11—C12—C13	120·1 (3)
N6—C5—C14	122·8 (3)	C8—C13—C12	118·8 (3)
C4—C5—N6	116·0 (3)	C8—C13—C14	116·4 (2)
C4—C5—C14	121·3 (3)	C12—C13—C14	124·8 (2)
C5—N6—N7	120·2 (3)	C1—C14—C5	118·5 (3)
N6—N7—C8	120·5 (2)	C1—C14—C13	124·5 (3)
N7—C8—C9	116·7 (3)	C5—C14—C13	117·0 (2)

The dihedral angle between the benzenoid rings is 2·5° in benzo[c]cinnoline (van der Meer, 1972), 11·7° in 1-morpholinobenzo[c]cinnoline (Hökelek, Watkin, Kılıç & Tüzün, 1990), 14·32 (6), 3·4 (1)° (molecule *A*) and 1·8 (1)° (molecule *B*) in 1- and 3-piperidinobenzo[c]cinnoline (Hökelek, Kılıç & Tüzün, 1991*a*), 1·32 (6) and 4·95 (7)° in 2- and 4-pyrrolidinobenzo[c]cinnoline (Hökelek, Kılıç & Tüzün, 1991*b*), respectively.

The values of these dihedral angles depend on the steric interactions between the benzo[c]cinnoline skeleton and the substituents. The interaction is greatest with the substituents in the 1-position. These steric interactions are also clearly seen from the dihedral angles between ring β and the substituent group depending on the types and position of the substituents (van der Meer, 1972; Hökelek, Watkin, Kılıç & Tüzün, 1990; Hökelek, Kılıç & Tüzün, 1991*a,b*).

The steric interactions between the H atoms at C12 and C1 generates enlarged C12—C13—C14 and C13—C14—C1 angles and smaller angles at the opposite side of the benzo[c]cinnoline group (see
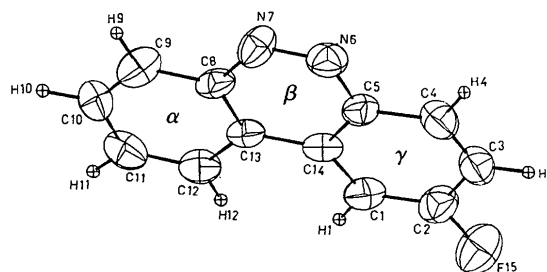

Fig. 1. A *SNOOPI* (Davies, 1983) drawing of the title molecule with the atom-numbering scheme. The thermal ellipsoids are drawn at the 50% probability level.

Table 3). This effect is in accordance with what was found in benzo[c]cinnoline, 1-morpholinobenzo-[c]cinnoline, 1- and 3-piperidinobenzo[c]cinnoline and 2- and 4-pyrrolidinobenzo[c]cinnoline. The F atom is located 0·004 (3) Å from the least-squares plane of the benzenoid ring.

The bond lengths C1—C2, C3—C4, C9—C10 and C11—C12 are generally shorter than the other bonds, as can be expected from theorectical calculations (Mulliken, 1955; Hoffman, 1963). This has also been determined experimentally in the above-mentioned benzo[c]cinnolines.

As the most electronegative substituent, the F atom withdraws electrons from the γ ring and affects the bond lengths and angles of the ring, causing short bonds: C1—C2 = 1·355 (4), C2—C3 = 1·392 (5) and C3—C4 = 1·370 (4) Å; small angles: C2—C1—C14 = 117·7 (3), C2—C3—C4 = 118·3 (3), C3—C4—C5 = 119·3 (3) and C1—C14—C5 = 118·5 (3)°; and large angles: C1—C2—C3 = 124·9 (3) and C4—C5—C14 = 121·3 (3)°.

A general conclusion based on the above results is that the type and position of the substituent determines the shape of the benzo[c]cinnoline skeleton.

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Structure of Two Complex Salts Formed by Diethylamine and Quinol

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Abstract. (I), Bis(diethylammonium) 1,4-benzene-diolate(2−)–1,4-benzenediol (1/1), $2C_4H_{12}N^+$.$C_6H_4O_2^{2-}$.$C_6H_6O_2$, 2DEAH$^+$.Q^{2-}.Q (DEA = diethylamine, Q = quinol), $M_r = 366·5$, monoclinic, $C2/c$, $a = 12·55$ (1), $b = 11·87$ (1), $c = 16·69$ (1) Å, $\beta = 119·15$ (8)°, $V = 2171$ Å^3, $Z = 4$, $D_x = 1·12$ Mg m^{-3}, Mo $K\alpha$ radiation, $\lambda = 0·71069$ Å, $\mu = 0·084$ mm^{-1}, $F(000) = 800$, room temperature, $R = 0·148$, $wR = 0·207$ for 513 reflections $[I > 2·5\sigma(I)]$. (II), Diethyl-ammonium 1,4-benzenediolate(1−)–1,4-benzenediol (1/1), $C_4H_{12}N^+$.$C_6H_5O_2^-$.$C_6H_6O_2$, DEAH$^+$.Q$^-$.Q, $M_r = 293·36$, triclinic, $P\bar{1}$, $a = 8·77$ (1), $b = 7·09$ (1), $c = 14·32$ (1) Å, $\alpha = 91·0$ (1), $\beta = 101·2$ (2), $\gamma = 114·2$ (1)°, $V = 792$ Å^3, $Z = 2$, $D_m = 1·20$ (3), $D_x = 1·23$ Mg m^{-3}, Mo $K\alpha$ radiation, $\lambda = 0·71069$ Å, $\mu = 0·095$ mm^{-1}, $F(000) = 316$, room temperature, $R = 0·076$, $wR = 0·095$ for 2121 reflections $[I > 3\sigma(I)]$. Both structures are extensively hydrogen bonded. (I) has chains of Q, Q^{2-}, Q′, DEAH$^+$, Q^{2-}, DEAH$^+$, Q, in which Q^{2-} ions link pairs of successive chains in the b direction and Q molecules link chains in the c direction. (II) has two independent Q molecules, a Q$^-$ ion, and DEAH$^+$ ions hydrogen bonded together in a three-dimensional manner.

Introduction. As part of a series of studies of complexes of quinol (1,4-dihydroxybenzene) with nitrogen bases (*cf.* Mahmoud & Wallwork, 1979), crystals were prepared by adding diethylamine to solutions of quinol in ether. In different preparations, two types of crystal were obtained, the first (I) having a 1:1

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