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Structure of 5-Amino-1-diphenylmethylimidazole-4-carboxamide

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Abstract. $C_{17}H_{16}N_4O$, $M_r = 292{\cdot}34$, monoclinic, $P2_1/a$, $a = 12{\cdot}325$ (1), $b = 22{\cdot}303$ (2), $c = 11{\cdot}3682$ (9) Å, $\beta = 100{\cdot}015$ (7)°, $V = 3077{\cdot}3$ (5) Å^3, $Z = 8$, $D_m = 1{\cdot}283$ (by flotation in benzene–bromoform), $D_x = 1{\cdot}262$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, μ(Cu $K\alpha$) = 6·230 cm^{-1}, $R = 0{\cdot}045$ for 3876 observed reflections. The conformation of the molecule is stabilized by extensive conjugation of the 5-aminoimidazole-4-carboxamide moiety and intramolecular hydrogen bonding. The conformation of the phenyl rings of the diphenylmethyl group is different in the two crystallographically independent molecules. The phenyl rings stand almost perpendicular to each other as found in many active antihistamines.

Introduction. Theophylline and its derivatives have been used as bronchodilators in the treatment of asthma owing to their ability to inhibit the enzyme cyclic adenosine monophsphate (cAMP) phosphodiesterase which regulates the cellular level of cAMP nucleotide under normal conditions. These antihistamines possess an extended planar heterocyclic structure associated with a C=O moiety and a substituent of a basic or neutral character. Higher activity has been observed when the heterocyclic ring-system is capable of being transformed by hydrogen bonding into a more extended aromatic system (Lunt, 1982). The presence of bulky groups like diphenylmethyl and similar dicyclic moieties in well known antihistamines like chloropheniramine, bromopheniramine, promethazine and related compounds, indicates that these groups play important roles in interaction at the receptor site. To achieve a synergistic effect we attempted to combine these two structural features in a single compound and have synthesized a series of 1-substituted-5-aminoimidazole-4-carboxamides. The synthesis and crystal structure analysis of 5-amino-1-diphenylmethylimidazole-4-carboxamide is presented here. This compound is expected to possess an extended planar structure through hydrogen bonding.

Experimental. The title compound was synthesized by heating a mixture of 2-amino-2-cyanoacetamide (1 g, 10 mmol) and ethyl orthoformate (1·6 g, 11 mmol) in acetonitrile (20 ml) under reflux for 45 min, affording ethyl *N*-(carbamoylcyanomethyl)formimidate (Sen, Ray & Chattopadhyay, 1977), followed by addition of diphenylmethylamine (2 g, 11 mmol) and heating under reflux for 1 h; yield 65%, melting point 480–481 K. The compound was characterized by UV, ^{1}H and ^{13}C NMR spectroscopy. UV (EtOH): λ_{max} 270, 210 (log ε 4·14, 4·18 respectively) 230 nm and λ_{min} (log ε 3·66); the ^{1}H NMR singlets at δ 6·74 and 6·69 correspond to C(2)—H of the imidazole ring and $(Ph)_2$—H, respectively; the ^{13}C NMR signal assignments at δ 166·90 (H_2N—C=O), 128·93, 112·58, 143·40 [C(2), C(4) and C(5), respectively of the imidazole ring], 60·08 [$C(Ph)_2$—H], 138·75 (quaternary C of phenyl rings), 128·5, 128·19 (*o*-, *m*- and *p*-C—H carbons of the phenyl rings) were assigned considering the shifting influence of —$CONH_2$, NH_2 and $C(H)Ph_2$ on the imidazole C atoms (Pugmire & Grant, 1968).

Colourless crystals from ethanolic solution, density by flotation (benzene–bromoform mixture); crystal size 0·25 × 0·28 × 0·28 mm; Rigaku AFC-5 rotating-anode four-circle diffractometer; Ni-filtered Cu $K\alpha$ radiation; accurate cell parameters from

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least-squares fit of setting angles for 20 reflections ($18 < \theta < 32°$); 4560 reflections ($-13 < h < 13$, $0 < k < 24$, $0 < l < 12$, $3 < 2\theta < 120°$) measured, ω–2θ scans, reflections $2\bar{3}0$, $23\bar{1}$ and 141 monitored every 97 reflections; variation in standard intensities ±1·9%; scan speed 6° min^{-1} in ω; scan angle (1·2 + 0·15tanθ)°; background measured for 4 s on either side of the peak; correction for Lp, absorption ignored; structure solved by direct methods using *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978); all non-H atoms located from the best *E* map; full-matrix refinement using *SHELX*76 (Sheldrick, 1976) with 3876 'observed' [$I > 2{\cdot}5\sigma(I)$] reflections; non-H atoms anisotropic and H atoms (located from ΔF synthesis) isotropic, $R = 0{\cdot}0447$, $wR = 0{\cdot}0609$, $S = 1{\cdot}20$, $w = 1/[\sigma^2(|F_o|) + 0{\cdot}01185(|F_o|)^2]$; scattering factors from *SHELX*76; $(\Delta/\sigma)_{max} < 0{\cdot}04$; $\Delta\rho$ in final ΔF synthesis in the range $-0{\cdot}24$ to $0{\cdot}25$ e Å^{-3}.

Discussion. The two crystallographically independent molecules constituting the asymmetric unit have been designated as molecules *A* and *B*. These two molecules form hydrogen-bonded dimers; the amino group N(5) of the carboxamide moiety of molecule *A* forms a hydrogen bond with the carbonyl oxygen O(1) of molecule *B* and *vice versa*. Fig. 1 shows a thermal-ellipsoid drawing of molecule *A* together with the numbering scheme of the non-H atoms. The fractional atomic coordinates and the equivalent isotropic thermal parameters are listed in Table 1.* The interatomic bond distances and angles are given tabulated in Table 2.

The difference in bond lengths between the chemically equivalent bonds is not significant.

The molecular conformation is stabilized by extensive conjugation and intramolecular hydrogen bonding. The conjugation of the carboxamide group with the imidazole ring results in near planarity of this group with the ring; the dihedral angle between this group and the imidazole ring is 4·69 (9)° in molecule *A* and 6·40 (1)° in molecule *B*. The carboxamide group is orientated in such a way that the carbonyl oxygen O(1) forms a six-membered hydrogen-bonded chelate ring with the amino nitrogen N(4) at position 5 of the imidazole ring; this hydrogen-bonded ring makes a dihedral angle of 8·52 (7)° in molecule *A* and 9·17 (9)° in molecule *B* with the plane of the imidazole ring. The heterocyclic ring thus forms an extended quasiplanar hydrogen-bonded system and fulfils the important structural requirements for antihistaminic and antiasthmatic activity (Lunt, 1982). The angular asymmetry in the

Table 1. *Fractional atomic coordinates with e.s.d.'s in parentheses*

	x	*y*	*z*	U_{eq}(Å^2)
Molecule *A*				
O(1)	0·0495 (1)	0·1558 (1)	0·7933 (1)	0·0520 (5)
N(1)	0·0566 (1)	0·2768 (1)	1·0770 (1)	0·0381 (5)
N(3)	0·2126 (1)	0·2465 (1)	1·0235 (1)	0·0458 (5)
N(4)	−0·0800 (1)	0·2284 (1)	0·9307 (1)	0·0477 (5)
N(5)	0·2342 (1)	0·1704 (1)	0·8258 (2)	0·0529 (6)
C(2)	0·1694 (1)	0·2786 (1)	1·0979 (2)	0·0465 (6)
C(4)	0·1234 (1)	0·2203 (1)	0·9488 (2)	0·0380 (6)
C(5)	0·0273 (1)	0·2389 (1)	0·9815 (1)	0·0349 (5)
C(6)	0·1329 (1)	0·1806 (1)	0·8504 (2)	0·0408 (6)
C(7)	−0·0181 (1)	0·3057 (1)	1·1471 (2)	0·0394 (6)
C(8)	−0·0499 (2)	0·2648 (1)	1·2424 (2)	0·0455 (6)
C(9)	−0·1294 (2)	0·2846 (1)	1·3061 (2)	0·0633 (9)
C(10)	−0·1632 (2)	0·2494 (2)	1·3923 (2)	0·0820 (11)
C(11)	−0·1185 (3)	0·1936 (2)	1·4151 (2)	0·0797 (12)
C(12)	−0·0397 (3)	0·1729 (1)	1·3546 (2)	0·0830 (11)
C(13)	−0·0046 (2)	0·2088 (1)	1·2668 (2)	0·0628 (8)
C(14)	0·0322 (1)	0·3650 (1)	1·1952 (2)	0·0427 (6)
C(15)	0·0922 (2)	0·3703 (1)	1·3097 (2)	0·0529 (7)
C(16)	0·1434 (2)	0·4240 (1)	1·3480 (2)	0·0667 (8)
C(17)	0·1330 (2)	0·4725 (1)	1·2727 (3)	0·0711 (10)
C(18)	0·0738 (3)	0·4680 (1)	1·1604 (3)	0·0745 (9)
C(19)	0·0224 (2)	0·4143 (1)	1·1205 (2)	0·0591 (17)
Molecule *B*				
O(1)	0·2601 (1)	0·1130 (1)	0·5989 (1)	0·0579 (5)
N(1)	0·2439 (1)	−0·0097 (1)	0·3134 (2)	0·0483 (5)
N(3)	0·0978 (1)	0·0088 (1)	0·3969 (2)	0·0587 (6)
N(4)	0·3835 (1)	0·0508 (1)	0·4322 (2)	0·0581 (7)
N(5)	0·0862 (1)	0·0801 (1)	0·5972 (2)	0·0529 (6)
C(2)	0·1347 (2)	−0·0201 (1)	0·3142 (2)	0·0601 (8)
C(4)	0·1868 (2)	0·0414 (1)	0·4559 (2)	0·0437 (6)
C(5)	0·2781 (1)	0·0298 (1)	0·4040 (2)	0·0404 (6)
C(6)	0·1803 (2)	0·0809 (1)	0·5553 (2)	0·0438 (6)
C(7)	0·3118 (2)	−0·0394 (1)	0·2349 (2)	0·0467 (7)
C(8)	0·2485 (2)	−0·0380 (1)	0·1073 (2)	0·0483 (7)
C(9)	0·2286 (2)	−0·0885 (1)	0·0372 (2)	0·0570 (8)
C(10)	0·1686 (2)	−0·0860 (1)	−0·0772 (2)	0·0715 (9)
C(11)	0·1296 (2)	−0·0322 (1)	−0·1248 (2)	0·0786 (11)
C(12)	0·1496 (3)	0·0188 (1)	−0·0579 (3)	0·0907 (12)
C(13)	0·2096 (3)	0·0163 (1)	0·0564 (3)	0·0782 (10)
C(14)	0·3488 (2)	−0·1009 (1)	0·2815 (2)	0·0467 (6)
C(15)	0·2739 (2)	−0·1432 (1)	0·3105 (2)	0·0624 (8)
C(16)	0·3096 (2)	−0·2000 (1)	0·3512 (2)	0·0745 (11)
C(17)	0·4210 (3)	−0·2144 (1)	0·3645 (2)	0·0779 (10)
C(18)	0·4927 (2)	−0·1735 (1)	0·3359 (3)	0·0827 (11)
C(19)	0·4576 (2)	−0·1175 (1)	0·2953 (2)	0·0665 (8)

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, distances and angles involving H atoms, and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53430 (33 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

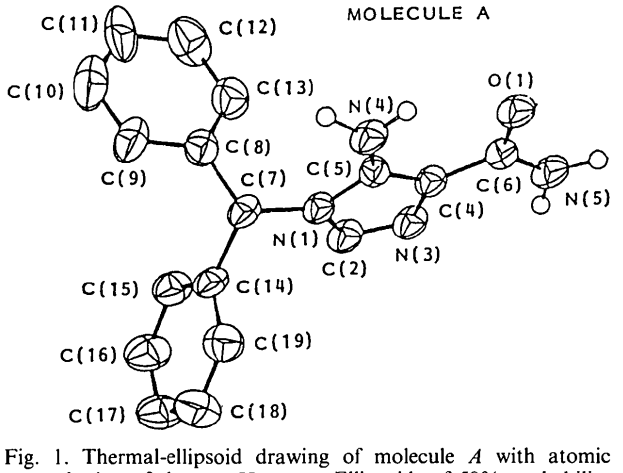

Fig. 1. Thermal-ellipsoid drawing of molecule *A* with atomic numbering of the non-H atoms. Ellipsoids of 50% probability are drawn for the non-H atoms; the H atoms attached to N atoms are represented as spheres equivalent to $B = 1{\cdot}0$ Å^2.

Table 2. *Bond distances* (Å), *bond angles* (°) *and hydrogen-bond distances* (Å) *with e.s.d.'s in parentheses*

	Molecule *A*	Molecule *B*
O(1)—C(6)	1·246 (2)	1·247 (3)
C(6)—N(5)	1·345 (2)	1·328 (3)
C(6)—C(4)	1·447 (3)	1·446 (3)
C(4)—C(5)	1·366 (2)	1·383 (3)
C(5)—N(4)	1·368 (2)	1·366 (2)
C(5)—N(1)	1·374 (2)	1·365 (3)
N(1)—C(2)	1·370 (2)	1·367 (3)
C(2)—N(3)	1·292 (3)	1·286 (3)
N(3)—C(4)	1·395 (2)	1·388 (3)
N(1)—C(7)	1·467 (2)	1·482 (3)
C(7)—C(8)	1·519 (3)	1·523 (3)
C(8)—C(9)	1·388 (4)	1·377 (3)
C(9)—C(10)	1·375 (4)	1·381 (3)
C(10)—C(11)	1·369 (6)	1·369 (3)
C(11)—C(12)	1·372 (5)	1·367 (3)
C(12)—C(13)	1·405 (4)	1·380 (4)
C(13)—C(8)	1·376 (3)	1·391 (3)
C(7)—C(14)	1·521 (3)	1·512 (3)
C(14)—C(15)	1·386 (3)	1·399 (3)
C(15)—C(16)	1·388 (3)	1·393 (3)
C(16)—C(17)	1·372 (3)	1·392 (4)
C(17)—C(18)	1·359 (4)	1·349 (4)
C(18)—C(19)	1·393 (3)	1·375 (3)
C(19)—C(14)	1·382 (3)	1·374 (3)
O(1)—C(6)—N(5)	121·9 (2)	122·8 (2)
O(1)—C(6)—C(4)	120·3 (1)	120·9 (2)
N(5)—C(6)—C(4)	117·8 (1)	116·3 (2)
C(6)—C(4)—N(3)	124·4 (1)	123·4 (2)
C(6)—C(4)—C(5)	125·9 (1)	127·4 (2)
N(3)—C(4)—C(5)	109·6 (2)	109·2 (2)
C(4)—C(5)—N(1)	106·3 (1)	106·0 (2)
C(4)—C(5)—N(4)	130·8 (1)	130·3 (2)
N(4)—C(5)—N(1)	122·7 (1)	123·7 (2)
C(5)—N(1)—C(2)	105·9 (1)	106·2 (2)
C(5)—N(1)—C(7)	126·6 (1)	127·6 (2)
C(2)—N(1)—C(7)	127·3 (2)	126·0 (2)
N(1)—C(2)—N(3)	113·1 (1)	113·2 (2)
C(2)—N(3)—C(4)	105·1 (1)	105·4 (2)
N(1)—C(7)—C(8)	112·8 (2)	108·4 (2)
N(1)—C(7)—C(14)	108·8 (1)	111·2 (2)
C(8)—C(7)—C(14)	113·9 (2)	115·2 (2)
C(7)—C(8)—C(9)	118·3 (2)	123·0 (2)
C(7)—C(8)—C(13)	122·9 (2)	119·8 (2)
C(9)—C(8)—C(13)	118·8 (2)	117·2 (2)
C(8)—C(9)—C(10)	121·3 (2)	121·6 (2)
C(9)—C(10)—C(11)	119·9 (2)	120·1 (2)
C(10)—C(11)—C(12)	120·1 (3)	119·5 (2)
C(11)—C(12)—C(13)	120·2 (3)	120·4 (2)
C(12)—C(13)—C(8)	119·7 (2)	121·1 (2)
C(7)—C(14)—C(15)	122·0 (2)	121·6 (2)
C(7)—C(14)—C(19)	119·0 (2)	120·9 (2)
C(15)—C(14)—C(19)	119·0 (2)	117·5 (2)
C(14)—C(15)—C(16)	120·5 (2)	120·5 (2)
C(15)—C(16)—C(17)	119·8 (2)	119·6 (2)
C(16)—C(17)—C(18)	120·3 (2)	119·5 (2)
C(17)—C(18)—C(19)	120·6 (3)	120·9 (2)
C(18)—C)19)—C(14)	119·8 (2)	121·8 (2)

N(4*A*)···O(1*A*)	2·911 (2)	N(4*A*)···N(3*A*^{i})	2·983 (2)
N(4*B*)···O(1*B*)	2·972 (3)	N(5*A*)···N(3*A*^{ii})	3·288 (3)
N(5*A*)···O(1*B*)	2·946 (3)	N(5*B*)···N(3*B*^{iii})	3·022 (3)
N(5*A*)···O(1*A*)	2·894 (3)		

Symmetry code: (i) $x-\frac{1}{2}, -y+\frac{1}{2}, z$; (ii) $x+\frac{1}{2}, -y+\frac{1}{2}, z$; (iii) $-x, -y, -z+1$.

exocyclic angles at C(5) may be attributed to the participation of the amino group in intramolecular hydrogen bonding with the vicinal carboxamide moiety. Similar results have been found in the literature (Adamiak & Saenger, 1979; Afshar, Berman, Sawzik, Lessinger, Lim & Hosmane, 1987; Kálmán, Jozsef & Kálmán, 1980; Freeman & Hutchinson, 1979). The carboxamide group is positioned in such a way that the internitrogen distance [N(5)(carboxamide)—N(1)(imidazole)] of 4·55 (3) Å in molecule *A* and 4·51 (3) Å in molecule *B* is close to the internitrogen distance of 4·8 (2) Å in an active antihistaminic agent (Kier, 1968).

The conjugation of the N(4) amino group and the carboxamide moiety with the imidazole ring results in shortening of the N—C and C—C bonds of the imidazole rings. As in other imidazole derivatives (Zanoti & Delpra, 1978; Afshar *et al.*, 1987; Kiec-Kononowicz, Zejc, Mikolajczyk, Zatorski, Karolak-Wojciechowska & Wieczorek, 1981), the endocyclic angle at C(2) is larger than the other endocyclic angles of the imidazole ring.

The lengthening of the C(7)—N(1) bond distance [1·467 (2) in molecule *A* and 1·482 (3) Å in molecule *B*] compared to the C(sp^3)—N(planar) distance of 1·454 Å (Allen, Kennard, Watson, Brammer & Orpen, 1987) and deviation of the C(8)—C(7)—C(14) angle [113·9 (2)° in molecule *A* and 115·2 (2)° in molecule *B*] from the tetrahedral values relieve the steric hindrance due to bulky diphenyl substitution at C(7).

The conformation of the phenyl rings of the diphenylmethyl group bonded to C(7) is different in the two molecules. In molecule *A* the phenyl rings stand almost perpendicular to the plane of the imidazole ring, the dihedral angles between these two planes being 85·59 (8) and 86·74 (8)°. The phenyl rings are inclined to each other at an angle of 101·14 (7)°. This dihedral angle is similar to that between the two aromatic rings of active antihistaminic drugs like triprolidine, 106·5° (James & Williams, 1974*b*), DL-bromopheniramine, 103·6° (James & Williams, 1971) and (+)-chloropheniramine maleate, 113·6° (James & Williams, 1974*a*). In molecule *B* the phenyl rings are inclined to each other at an angle of 72·51 (8)° and make dihedral angles of 78·2 (1) and 70·68 (7)° with the plane of the imidazole ring.

An extensive hydrogen-bond network stabilizes the molecular packing shown in Fig. 2.

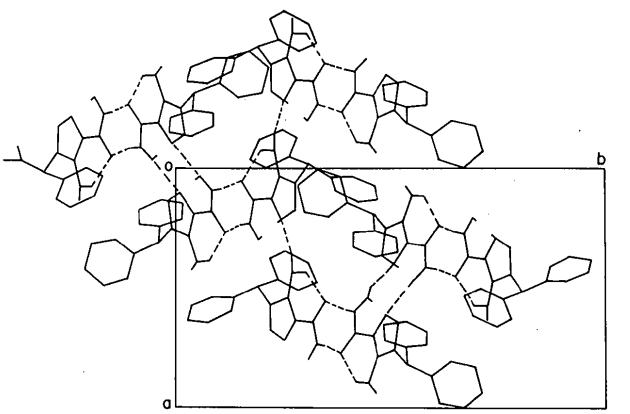

Fig. 2. A view of the molecular packing arrangement.

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Structure of 8-Dimethylamino-1-dimethylammonionaphthalene Hydrogen Squarate

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Abstract. (8-Dimethylamino-1-naphthyl)dimethylammonium 2-hydroxy-3,4-dioxocyclobut-1-en-1-olate, $C_{14}H_{19}N_2^+.C_4HO_4^-$, $M_r = 328{\cdot}37$, orthorhombic, *Pbca*, $a = 18{\cdot}319\ (3)$, $b = 14{\cdot}868\ (2)$, $c = 12{\cdot}219\ (1)$ Å, $V = 3328{\cdot}1\ (8)$ Å^3, $Z = 8$, $D_x = 1{\cdot}311$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 1{\cdot}0$ cm^{-1}, $F(000) = 1392$, $T = 150$ K, $R = 0{\cdot}036$ for 3003 observed reflections with $I \geq 2{\cdot}5\sigma(I)$. In the crystal structure of the title compound bis(dimethylamino)-naphthalene acts as a proton sponge by accepting a proton from squaric acid. In the 1-dimethylamino-8-dimethylammonionaphthalene cation a strong asymmetric intramolecular hydrogen bond is formed with N···N, N—H and N—H···N 2·583 (2), 1·08 (2) Å and 157 (2)° respectively. The N—H donor also is involved in a weak interaction with a squarate carbonyl group. The hydrogen squarate anions form planar strongly hydrogen-bonded cyclic dimers across centres of inversion with O···O, O—H and O—H···O 2·477 (2), 0·97 (2) Å and 170 (2)° respectively. In contrast to the free base which displays severe puckering of the aromatic system and opposite deviations of the N atoms of 0·40 Å from the best plane, the aromatic system including both N atoms of the cation is planar.

Introduction. The NHN hydrogen bonds in homoconjugated nitrogen bases play an important role in so-called proton sponges (Alder, Bowman, Steele & Wintermann, 1968; Hibbert, 1974; de Groot & Sikkema, 1976; Awwal & Hibbert, 1977; Alder, Goode, Miller, Hibbert, Hunte & Robbins, 1978; Glowiak, Malarski, Sobczyk & Grech, 1987). Among the NHN systems the bi-centre bases with 1,8-bis(dimethylamino)naphthalene (DMAN) as a representative proton sponge are of particular interest.

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