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Structure of 1-(4-Chlorophenacyl)-2-methyl-4-nitro-5-piperidinoimidazole

BY IRENA WOLSKA, TERESA BOROWIAK,* MARIAN GAWRON AND MAREK KRĘGLEWSKI

Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 *Poznań, Poland*

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Abstract. $C_{17}H_{19}ClN_4O_3$, $M_r = 362{\cdot}8$, triclinic, $P\bar{1}$, $a = 13{\cdot}960\ (1)$, $b = 17{\cdot}175\ (1)$, $c = 8{\cdot}194\ (1)$ Å, $\alpha = 108{\cdot}14\ (1)$, $\beta = 104{\cdot}82\ (1)$, $\gamma = 93{\cdot}42\ (1)°$, $V = 1784{\cdot}0\ (3)$ Å^3, $Z = 4$, $D_x = 1{\cdot}350$ g cm^{-3}, λ(Cu $K\alpha$) $= 1{\cdot}54178$ Å, $\mu = 19{\cdot}92$ cm^{-1}, $F(000) = 760$, room temperature, $R = 0{\cdot}050$ for 3012 observed reflections. The molecule possesses two basic centers, one at the imidazole N atom and the other at the piperidino N atom, yet the compound is inactive towards protonation. X-ray data and subsequent *CNDO*/2 calculations relate this chemical property to electronic effects of substituents and steric effects due to molecular overcrowding.

Introduction. In our previous paper on the structure of 1-(4-chlorophenacyl)-2-methyl-5-morpholino-4-nitroimidazole, hereafter (I) (Borowiak, Wolska, Baryła & Sobiak, 1989), we presented the reasons for synthesizing 4-nitro-5-aminoimidazoles. These compounds are expected to have radiosensitizing properties in cancer therapy, but unfortunately, they are poorly water soluble. Attempts to obtain a salt of (I) failed. In this work we present the X-ray structure of 1-(4-chlorophenacyl)-2-methyl-4-nitro-5-piperidinoimidazole, hereafter (II), which is another 4-nitro-5-aminoimidazole derivative, likewise inactive in a protonation reaction.

Experimental. Crystals grown from ethanol by slow evaporation. Crystal size $0{\cdot}1 \times 0{\cdot}1 \times 0{\cdot}4$ mm; Syntex $P2_1$ diffractometer, graphite-monochromated Cu $K\alpha$ radiation, θ–2θ scan mode, background and intensity of reflections calculated by peak-profile analysis (Lehmann & Larsen, 1974; Jaskólski, 1982); accurate cell parameters refined from setting angles of 15 reflections with $25{\cdot}7 \le 2\theta \le 33{\cdot}6°$. 4478 unique reflections measured up to $2\theta \le 115°$ ($0 \le h \le 16$, $-19 \le k \le 19$, $-10 \le l \le 10$); 3012 considered observed [$I \ge 2\sigma(I)$]; $R_{int} = 0{\cdot}0184$; two reference reflections monitored every 100 reflections showed no significant variation in intensity during data collection. Lp correction but no absorption correction. Structure solved by direct methods using *MULTAN*80 (Main *et al.*, 1980) and refined by full-matrix least-squares methods with *SHELX*76 (Sheldrick, 1976). Function minimized $\sum w(|F_o| - |F_c|)^2$, $w^{-1} = \sigma^2(F_o) + 0{\cdot}0002F_o^2$, $\sigma(F_o)$ based on counting statistics. Non-H atoms refined anisotropically; the H atoms of the methyl group located from difference synthesis and kept non-refined, the other H atoms placed at their theoretical positions. Empirical isotropic extinction parameter x used to correct F_c according to $F_c' = F_c(1 - xF_c^2/\sin\theta)$, x converged at $7{\cdot}7\ (9) \times 10^{-7}$. The final refinement of 452 parameters converged at $R = 0{\cdot}050$, $wR = 0{\cdot}060$, $S = 2{\cdot}4$, $(\Delta/\sigma)_{max} = 0{\cdot}06$ in final cycle; largest peak in final ΔF map 0·19, largest hole $-0{\cdot}34$ e Å^{-3}; atomic scattering factors were those incorporated in *SHELX*76. Other computer programs used: *ORTEP* (Johnson, 1976), *PLUTO*78 (Motherwell & Clegg, 1978) and *PARST* (Nardelli, 1983).

Discussion. Final positional parameters and U_{eq} values for non-H atoms are given in Table 1.† The molecule is shown in Fig. 1. Bond lengths and bond angles are listed in Table 2.

* To whom correspondence should be addressed.

† Lists of structure factors, anisotropic thermal parameters, torsion angles, H-atom parameters and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53994 (23 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Non-H fractional atomic coordinates* ($\times 10^4$), *and equivalent isotropic temperature factors* ($Å^2 \times 10^3$) *with e.s.d.'s in parentheses*

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

	x	y	z	U_{eq}
Molecule *A*				
N(1)	6365 (2)	4664 (2)	14083 (4)	57 (1)
C(2)	6032 (3)	4065 (3)	14695 (6)	63 (1)
N(3)	5943 (2)	4391 (2)	16310 (5)	67 (1)
C(4)	6229 (3)	5227 (3)	16753 (5)	60 (1)
C(5)	6524 (3)	5420 (3)	15424 (5)	56 (1)
N(6)	6101 (3)	5780 (3)	18340 (5)	76 (1)
O(7)	5786 (3)	5490 (2)	19349 (4)	103 (1)
O(8)	6285 (3)	6537 (2)	18657 (4)	103 (1)
C(9)	5827 (3)	3170 (3)	13647 (6)	80 (1)
C(10)	6739 (3)	4491 (2)	12520 (5)	58 (1)
C(11)	7862 (3)	4473 (2)	13054 (6)	62 (1)
O(12)	8315 (2)	4591 (2)	14601 (4)	96 (1)
C(13)	8368 (3)	4294 (2)	11606 (5)	57 (1)
C(14)	7889 (3)	4229 (2)	9849 (5)	63 (1)
C(15)	8390 (3)	4052 (3)	8549 (6)	73 (1)
C(16)	9371 (4)	3945 (2)	9014 (6)	72 (2)
C(17)	9872 (3)	4016 (3)	10748 (7)	78 (1)
C(18)	9368 (3)	4192 (3)	12060 (6)	75 (1)
Cl	10018 (1)	3700 (1)	7421 (2)	102 (0)
N(19)	6949 (2)	6118 (2)	15254 (4)	66 (1)
C(20)	7722 (4)	6705 (3)	16795 (6)	103 (2)
C(21)	8483 (4)	7061 (4)	16128 (7)	123 (2)
C(22)	8018 (4)	7465 (3)	14790 (7)	100 (2)
C(23)	7181 (4)	6854 (3)	13274 (6)	97 (2)
C(24)	6435 (3)	6477 (3)	13952 (5)	72 (1)
Molecule *B*				
N(1)	7150 (3)	1823 (2)	7678 (4)	67 (1)
C(2)	6534 (3)	2216 (3)	8636 (6)	68 (1)
N(3)	6912 (3)	2339 (2)	10365 (4)	65 (1)
C(4)	7780 (3)	2010 (2)	10480 (5)	61 (1)
C(5)	7960 (3)	1671 (2)	8856 (5)	65 (1)
N(6)	8395 (3)	2042 (2)	12212 (5)	72 (1)
O(7)	8095 (2)	2329 (2)	13514 (4)	92 (1)
O(8)	9197 (3)	1768 (2)	12292 (4)	100 (1)
C(9)	5595 (4)	2491 (3)	7842 (6)	91 (2)
C(10)	6949 (4)	1515 (2)	5745 (5)	74 (1)
C(11)	6530 (3)	597 (3)	4984 (6)	77 (1)
O(12)	6302 (3)	249 (2)	5924 (4)	113 (1)
C(13)	6444 (3)	145 (3)	3069 (5)	70 (1)
C(14)	6417 (3)	540 (2)	1830 (5)	64 (1)
C(15)	6303 (3)	90 (2)	45 (5)	68 (1)
C(16)	6242 (4)	−755 (3)	−463 (6)	79 (1)
C(17)	6281 (4)	−1163 (3)	746 (6)	107 (2)
C(18)	6383 (4)	−713 (3)	2514 (6)	101 (2)
Cl	6095 (1)	−1325 (1)	−2688 (2)	120 (1)
N(19)	8660 (3)	1238 (2)	8154 (4)	70 (1)
C(20)	8772 (4)	443 (3)	8456 (6)	82 (1)
C(21)	9357 (4)	−42 (3)	7275 (7)	96 (2)
C(22)	10357 (4)	450 (3)	7626 (7)	107 (2)
C(23)	10245 (4)	1282 (3)	7362 (8)	114 (2)
C(24)	9620 (4)	1754 (3)	8514 (7)	101 (2)

Table 2. *Bond lengths* (Å) *and bond angles* (°) *with e.s.d.'s in parentheses*

	Molecule *A*	Molecule *B*
N(1)—C(2)	1·382 (7)	1·377 (6)
N(1)—C(5)	1·377 (5)	1·383 (5)
N(1)—C(10)	1·458 (6)	1·449 (5)
C(2)—N(3)	1·308 (6)	1·322 (6)
C(2)—C(9)	1·477 (6)	1·481 (7)
N(3)—C(4)	1·373 (6)	1·361 (6)
C(4)—C(5)	1·380 (7)	1·371 (6)
C(4)—N(6)	1·412 (6)	1·441 (5)
C(5)—N(19)	1·367 (6)	1·395 (6)
N(6)—O(7)	1·241 (7)	1·217 (5)
N(6)—O(8)	1·241 (6)	1·234 (6)
C(10)—C(11)	1·521 (6)	1·519 (6)
C(11)—O(12)	1·209 (5)	1·200 (7)
C(11)—C(13)	1·493 (7)	1·488 (6)
C(13)—C(14)	1·389 (5)	1·380 (7)
C(13)—C(18)	1·386 (6)	1·390 (7)
C(14)—C(15)	1·386 (7)	1·387 (5)
C(15)—C(16)	1·364 (7)	1·370 (6)
C(16)—C(17)	1·377 (7)	1·373 (8)
C(16)—Cl	1·733 (6)	1·731 (5)
C(17)—C(18)	1·397 (8)	1·379 (6)
N(19)—C(20)	1·468 (5)	1·472 (7)
N(19)—C(24)	1·450 (6)	1·470 (7)
C(20)—C(21)	1·493 (9)	1·510 (8)
C(21)—C(22)	1·506 (9)	1·499 (8)
C(22)—C(23)	1·520 (6)	1·521 (8)
C(23)—C(24)	1·501 (8)	1·529 (8)
C(2)—N(1)—C(5)	108·0 (3)	108·5 (3)
C(2)—N(1)—C(10)	124·4 (4)	127·1 (4)
C(5)—N(1)—C(10)	125·6 (3)	123·9 (4)
N(1)—C(2)—N(3)	111·5 (4)	110·8 (4)
N(1)—C(2)—C(9)	123·4 (4)	124·4 (4)
N(3)—C(2)—C(9)	125·1 (4)	124·7 (4)
C(2)—N(3)—C(4)	104·6 (4)	104·4 (3)
N(3)—C(4)—C(5)	112·5 (4)	113·6 (3)
N(3)—C(4)—N(6)	119·4 (4)	119·1 (4)
C(5)—C(4)—N(6)	127·8 (5)	127·2 (4)
N(1)—C(5)—C(4)	103·3 (4)	102·7 (3)
N(1)—C(5)—N(19)	120·7 (3)	118·2 (3)
C(4)—C(5)—N(19)	135·8 (4)	139·1 (4)
C(4)—N(6)—O(7)	118·7 (4)	118·6 (4)
C(4)—N(6)—O(8)	119·0 (4)	118·0 (4)
O(7)—N(6)—O(8)	122·3 (4)	123·4 (4)
N(1)—C(10)—C(11)	110·6 (3)	110·7 (3)
C(10)—C(11)—O(12)	120·3 (4)	120·4 (4)
C(10)—C(11)—C(13)	117·7 (3)	117·9 (4)
O(12)—C(11)—C(13)	122·0 (4)	121·6 (5)
C(11)—C(13)—C(14)	123·4 (4)	122·8 (4)
C(11)—C(13)—C(18)	117·6 (4)	118·1 (4)
C(14)—C(13)—C(18)	119·0 (4)	119·0 (4)
C(13)—C(14)—C(15)	121·1 (4)	120·8 (4)
C(14)—C(15)—C(16)	119·1 (4)	118·8 (4)
C(15)—C(16)—C(17)	121·3 (5)	121·6 (4)
C(15)—C(16)—Cl	120·7 (4)	119·3 (4)
C(17)—C(16)—Cl	118·0 (4)	119·1 (4)
C(16)—C(17)—C(18)	119·7 (5)	119·3 (5)
C(13)—C(18)—C(17)	119·7 (4)	120·4 (5)
C(5)—N(19)—C(20)	119·2 (3)	115·6 (4)
C(5)—N(19)—C(24)	122·1 (3)	114·1 (4)
C(20)—N(19)—C(24)	114·3 (4)	113·6 (4)
N(19)—C(20)—C(21)	108·8 (4)	109·4 (4)
C(20)—C(21)—C(22)	112·1 (5)	110·7 (4)
C(21)—C(22)—C(23)	109·8 (5)	111·4 (5)
C(22)—C(23)—C(24)	112·2 (4)	110·0 (5)
N(19)—C(24)—C(23)	109·8 (4)	110·4 (4)

The two molecules of (II) in the asymmetric unit differ substantially in their conformations. The biggest differences concern the orientation of the piperidino and chlorophenacyl substituents, described by the following torsion angles: C(4)—C(5)—N(19)—C(20) 37·9 (8) and 59·1 (7)° in molecules *A* and *B*, respectively, N(1)—C(5)—N(19)—C(24) 68·1 (6) and 107·0 (5)°, and C(10)—C(11)—C(13)—C(14) 6·8 (6) and −21·0 (7)°.

These differences are probably caused by the combined effects of the molecular overcrowding diminution and packing forces.

Owing to the electron-withdrawing effect of the nitro group at C(4), the N(3)—C(4) bond is shortened in comparison with that in imidazole as required by the Walsh rule (Domenicano, Vaciago & Coulson, 1975). Also the C—N bonds of the nitro groups, 1·412 (6) and 1·441 (5) Å in molecules *A* and *B*, respectively, are shorter than the C—NO_2 bond in dinitrobenzene, 1·478 (2) Å (Di Rienzo, Domenicano & Riva di Sanseverino, 1980). The C(5)—N(19) bond lengths of 1·367 (6) and 1·395 (6) Å are very near to the C—N bond in aniline (Fukuyo, Hirotsu & Higuchi, 1982) and the sum of the bond angles around N(19) has an intermediate value between

those for sp^2- and sp^3-hybridized atoms, namely 355·6 and 343·3°, which was also the case for the morpholino derivative (I). The differences in N(piperidine)—C(5) and N(nitro)—C(4) bond distances in molecules *A* and *B* are larger than 3σ and cannot easily be rationalized. In order to explain why (II) is inactive towards protonation, semiempirical calculations were performed with the *CNDO*/2 procedure (Pople & Segal, 1966) on the basis of crystallographic results. Two effects could be responsible: (i) the electron charge distribution and/or (ii) the steric hindrances.

Molecule (II) was compared with its parent molecule, *i.e.* imidazole and some derivatives of imidazole. The calculation began with imidazole using its original geometry (Epstein, Ruble & Craven, 1982) and the geometry of the imidazole ring in the molecule of (II). No significant difference in net charge distribution was noted for these two slightly different structures. In further calculations the geometry of the respective molecular fragments of (II) was used for imidazole and its derivatives. The calculated absolute values of the net charges are not accurate but they can be used for comparison in a series of similar molecules. The net charges on N(3) of the imidazole ring and on the N(amine) atom of the substituent in position 5 are shown in Table 3.

They characterize the proton–acceptor properties of the nitrogen centers. The calculations were performed for molecules *A* and *B* and gave no significant differences. The 4-chlorophenacyl substitution on N(1) does not affect the net charges given in Table 3. The following conclusions result from Table 3:

(i) The NO_2 group decreases the net charge on the N(3) center but does not influence the net charge on the amino nitrogen.

(ii) In the piperidine ring, the net charge on the amino nitrogen is much lower than for the $—NH_2$ group.

It seems that the protonation occurs neither at the N(3) center (because of the combined effects of the substitution of the NO_2 and amino group) nor on the amino nitrogen (because of the electronic structure of the piperidine ring). Inactivity of the N(amino) center towards protonation may also be due to overcrowding. The hindered penetration of protons in molecule (II) is understandable if one takes into account short intramolecular contacts: N(19)···C(10)

Table 3. *Net charges on the* N(3) *and* N(*amine*) *centers of imidazole and its derivatives* (*in units of electronic charge*)

	N(3)	N(amine)
Imidazole	−0·202	–
5-Aminoimidazole	−0·177	−0·243
4-Nitro-5-aminoimidazole	−0·145	−0·246
5-Piperidinoimidazole	−0·176	−0·179
4-Nitro-5-piperidinoimidazole	−0·150	−0·175

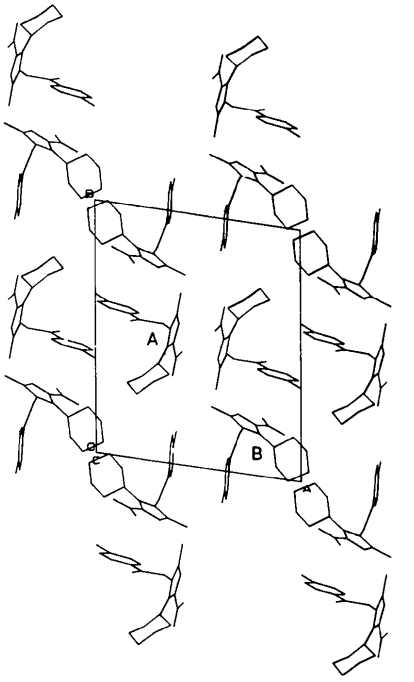

Fig. 2. The molecular packing as seen along the [001] axis. There are layers of *A*,*A*,*A*... and *B*,*B*,*B*... molecules.

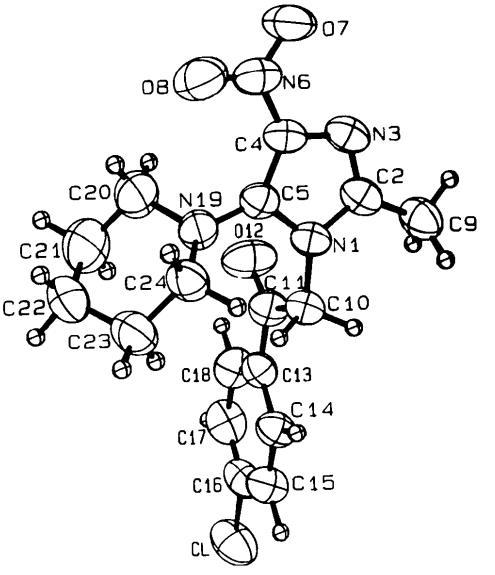

Fig. 1. *ORTEP* drawing of the molecule showing the conformation and the numbering scheme used. Only molecule *A* has been presented. The perspective view of molecule *B* is very similar.

2·929 (4) and 2·852 (6) Å, O(8)···C(20) 2·865 (7) and 3·137 (5) Å in molecules *A* and *B*, respectively. They are observed despite the non-coplanarity of N(19), N(6), C(9) and C(10) with the imidazole plane.

In the molecular packing, which is presented in Fig. 2, no significant short contacts are observed.

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Structure of a 4-Phenylcoumarin Derivative

BY KALYAN DAS AND U. C. SINHA*

Department of Physics, Indian Institute of Technology, Bombay 400 076, *India*

D. D. NARKHEDE AND P. R. IYER

Department of Chemistry, Indian Institute of Technology, Bombay 400 076, *India*

AND R. BOHRA

Department of Chemistry, University of Rajasthan, Jaipur 302016, *India*

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Abstract. 9-Hydroxy-6,7-*trans*-dimethyl-4-phenyl-6,7-dihydro-2*H*,8*H*-benzo[1,2-*b*:3,4-*b*′]dipyran-2,8-dione, $C_{20}H_{16}O_5$, m.p. = 512–513 K, M_r = 336·34, triclinic, $P\bar{1}$, a = 8·414 (3), b = 9·929 (4), c = 10·358 (2) Å, α = 96·77 (3), β = 105·08 (2), γ = 99·47 (3)°, V = 812·39 Å^3, Z = 2, D_x = 1·363 Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ(Mo $K\alpha$) = 0·059 mm^{-1}, F(000) = 352, T = 295 K, final R = 0·062, wR = 0·072, for 2133 observed reflections. The crystal contains two isomers in approximately 60:40 proportions. Atoms C(6), C(7) and their attached H atoms occupy alternative positions in the two isomers. H(6)/H(6′) and H(7)/H(7′) are *trans* to each other.

* To whom correspondence should be addressed.

Introduction. In the past 30 years or so, several naturally occurring coumarins have been isolated from higher plants like, *Umbelliferae*, *Rutaceae*, *Guttiferae*, *Rubiaceae*, *Leguminosae* and also from various micro-organisms (Murray, Mendez & Brown, 1982). Many coumarins bearing a phenyl group at the 4-position have an isoprenoid (C_5) unit in the form of a six-membered pyran structure such as the 2,3-dimethyl-2*H*-1-pyran-4-one unit (Dewick, 1982). In the process of synthesizing a naturally occurring 4-phenylcoumarin derivative, the title compound was obtained. In order to study the orientations of the methyl groups and the H atoms, attached to the asymmetric centres [C(6) and C(7)], and the conformation of the chromanone ring (see below), the crystal structure of the above compound

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