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Structural Studies of Radical Reaction Products. II.* 2,4-Bis(4-chlorophenyl)-5,5-dimethyl-3-pyrazolidinone

BY FABIO GANAZZOLI AND ATTILIO CITTERIO

Dipartimento di Chimica del Politecnico, Piazza Leonardo da Vinci 32, 20133 *Milano, Italy*

AND ALBERTO ALBINATI

Istituto di Chimica Farmaceutica dell'Università, Viale Abruzzi 42, 20131 *Milano, Italy*

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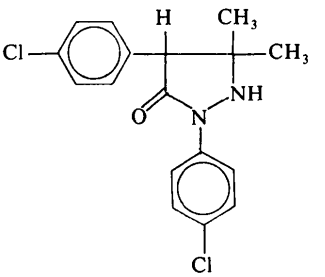
Abstract. $C_{17}H_{16}Cl_2N_2O$, $M_r = 335{\cdot}23$, triclinic, $P\bar{1}$, $a = 12{\cdot}280\ (3)$, $b = 10{\cdot}191\ (3)$, $c = 6{\cdot}633\ (2)$ Å, $\alpha = 83{\cdot}93\ (7)$, $\beta = 100{\cdot}05\ (8)$, $\gamma = 87{\cdot}70\ (8)°$, $U = 811{\cdot}3\ (5)$ Å^3, $Z = 2$, $D_x = 1{\cdot}37$ Mg m^{-3}, λ(Mo $K\bar{\alpha}$) = 0·71069 Å, μ(Mo $K\bar{\alpha}$) = 0·402 mm^{-1}, $F(000) = 348$, room temperature, $R = 0{\cdot}056$ for 2285 observed reflections, $S = 0{\cdot}85$. The title compound, which shows pharmacological activity *in vitro*, presents a puckered pyrazolidinone ring [puckering angle 36·0 (2)°] with an N—N bond [1·445 (4) Å] longer than those usually found in hydrazidic moieties. Geometric and electronic features of this part of the molecule have a close similarity with those of antipyrine, a 3*H*-pyrazol-3-one derivative used as an antiinflammatory drug.

Introduction. During our systematic studies of homolytic reactions of arenediazonium salts we have obtained new compounds resulting from the addition of carbon free radicals to the terminal N atom of the diazonium cation (Citterio, Minisci & Vismara, 1982; Albinati, Ganazzoli & Citterio, 1983; Citterio, Ramperti & Vismara, 1981). An X-ray structural determination of the title compound confirmed the structure of the product (1) obtained from decomposition of 4-chlorobenzenediazonium chloride by Ti^{III} ions in the presence of 3-methyl-2-butenoic acid. Compounds belonging to this class of 2,4-diaryl-3-pyrazolidinones have shown antiinflammatory activity *in vitro*.



(1)

Experimental. Prismatic colourless crystals obtained from ethyl acetate solution. Single crystal of approximate dimensions 0·35 × 0·25 × 0·20 mm. Philips PW 1100 diffractometer, graphite-monochromated radiation. Cell constants determined from least-squares fit of 20 high-order reflections ($22 \le 2\theta \le 43°$). $\omega/2\theta$ scan technique, scan speed 0·08° s^{-1}, scan width 1·20°, background measured for 6 s on each side of the peaks, $2\theta_{max} = 50°$ ($h \pm 14$, $k \pm 12$, l 0–7), two standard reflections (111 and $\bar{1}\bar{1}\bar{1}$) every 120 min, no significant

* Part I: Albinati, Ganazzoli & Citterio (1983).

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variation detected. 2848 independent reflections, observation criterion $I \geq 3\sigma(I)$ [$\sigma(I)$ based on counting statistics], no absorption or extinction correction. Structure solved by *MULTAN*80 (Main *et al.*, 1980), refined by block-diagonal least squares (all atoms with anisotropic thermal factors), H atoms refined from idealized positions with isotropic thermal factors. Function minimized $\sum w(k|F_o| - |F_c|)^2$, weighting scheme $w^{-1} = 9{\cdot}5 + |F_o| + 0{\cdot}0008|F_o|^2$ (Cruickshank, 1970), $wR = 0{\cdot}062$, $\Delta/\sigma = 0{\cdot}23$, final $\Delta\rho \leq 0{\cdot}3$ e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974) with correction for the real part of anomalous dispersion for Cl and O. Structure factors, Fourier transforms and least-squares calculations using local versions of programs written by Immirzi (1967, 1973), geometrical calculations with *PARST* (Nardelli, 1982*a*,*b*). Theoretical calculations with *CNDO*/2 program (Pople & Beveridge, 1970) using as input the experimental geometry.

Discussion. Final coordinates and equivalent isotropic thermal parameters are given in Table 1, selected bond lengths and angles in Table 2, and possible hydrogen bonds in Table 3.* An overall view of the molecule is shown in Fig. 1. The dihydropyrazolone ring is in a puckered conformation with atom C(9) being 0·563 (4) Å out of the mean plane defined by atoms N(1), N(2), C(7) and C(8). The puckering angle, defined as the dihedral angle between the latter plane and that of atoms C(8), C(9) and N(1), is 36·0 (2)°. The two phenyl rings are twisted by 15·0 (1)° [ring C(1) to C(6)] and 52·1 (1)° [ring C(12) to C(17)] with respect to the N(1) to C(8) plane.

The geometry around N(2) (see Table 2) suggests sp^2 hybridization, consistent with the expected amidic delocalization. In fact the N(2)—C(7) distance, 1·365 (3) Å, is half-way between the value of 1·325 (4) Å in diformylhydrazine (Tomiie, Koo & Nitta, 1958) and that of 1·400 (6) Å found in antipyrine [1,2-dihydro-1,5-dimethyl-2-phenyl-3(3*H*)-pyrazolone] (Singh & Vijayan, 1973), indicating different degrees of delocalization of the hydrazidic moiety in this series. On the other hand, the O—C(7) length [1·218 (4) Å] is nearly equal to the value of 1·214 (5) Å in diformylhydrazine (Tomiie *et al.*, 1958) and comparable to the value of 1·237 (5) Å in antipyrine (Singh & Vijayan, 1973), where a further conjugation is possible. The extent of these delocalizations may also be judged by the bond indices (Wiberg, 1968) and charge values calculated according to the *CNDO*/2 method and reported in Fig. 2.

The N(1)—N(2) distance, 1·445 (4) Å, is equal to that found in hydrazine in the gas phase, 1·442 (4) Å (Kohata, Fukuyama & Kuchitsu, 1982), but longer than 1·392 (7) Å reported for diformylhydrazine

Table 1. *Final positional and equivalent isotropic thermal parameters (Willis & Pryor, 1975) for non-*H *atoms*

$$B_{eq} = \tfrac{1}{3}\sum_i\sum_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2)
Cl(1)	0·23439 (7)	0·49815 (9)	−0·02772 (16)	5·31 (4)
Cl(2)	0·50822 (8)	0·39020 (10)	0·19831 (21)	6·66 (5)
N(1)	0·1301 (2)	0·2313 (2)	0·5211 (4)	3·2 (1)
N(2)	−0·0812 (2)	0·1777 (2)	0·3621 (3)	2·9 (1)
O	−0·0741 (2)	−0·0200 (2)	0·2244 (3)	3·9 (1)
C(1)	0·1398 (2)	0·4049 (3)	0·0856 (5)	3·4 (1)
C(2)	0·1005 (2)	0·2960 (3)	0·0028 (4)	4·0 (1)
C(3)	0·0269 (2)	0·2189 (3)	0·0873 (4)	3·5 (1)
C(4)	−0·0061 (2)	0·2540 (2)	0·2671 (4)	2·7 (1)
C(5)	0·0358 (2)	0·3633 (3)	0·3559 (5)	3·0 (1)
C(6)	0·1085 (2)	0·4400 (3)	0·2645 (5)	3·2 (1)
C(7)	−0·1095 (2)	0·0515 (3)	0·3373 (4)	2·8 (1)
C(8)	−0·1928 (2)	0·0179 (2)	0·4800 (4)	2·8 (1)
C(9)	−0·2321 (2)	0·1569 (3)	0·5237 (4)	3·1 (1)
C(10)	−0·2628 (3)	0·1555 (3)	0·7363 (5)	4·5 (2)
C(11)	0·3241 (3)	0·2240 (3)	0·3567 (5)	4·4 (1)
C(12)	0·2767 (2)	−0·0773 (3)	0·4056 (4)	3·1 (1)
C(13)	0·3078 (2)	−0·1730 (3)	0·5466 (5)	3·7 (1)
C(14)	0·3801 (3)	0·2675 (3)	0·4844 (6)	4·6 (1)
C(15)	−0·4221 (2)	0·2679 (3)	0·2808 (6)	5·3 (1)
C(16)	0·3950 (3)	−0·1729 (4)	0·1361 (6)	5·3 (1)
C(17)	0·3229 (3)	−0·0792 (4)	0·2006 (5)	4·6 (1)

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

Cl(1)–C(1)	1·749 (3)	C(8)–C(12)	1·500 (4)
Cl(2)–C(15)	1·738 (4)	C(9)–C(10)	1·521 (5)
N(1)–N(2)	1·445 (4)	C(9)–C(11)	1·521 (4)
N(1)–C(9)	1·492 (4)	N(1)–H(N1)	0·86 (5)
N(2)–C(4)	1·417 (4)	C(8)–H(C8)	1·01 (3)
N(2)–C(7)	1·365 (3)	⟨C–C⟩$_{ph}$*	1·384 + 0·010†
O–C(7)	1·218 (4)	⟨C–H⟩$_{ph}$*	0·98 + 0·03†
C(7)–C(8)	1·535 (4)	⟨C–H⟩$_{Me}$	1·01 + 0·05†
C(8)–C(9)	1·550 (4)		

Cl(1)–C(1)–C(2)	118·9 (3)	N(1)–C(9)–C(8)	101·9 (3)
Cl(1)–C(1)–C(6)	119·6 (3)	N(1)–C(9)–C(10)	108·4 (3)
Cl(2)–C(15)–C(14)	120·4 (3)	N(1)–C(9)–C(11)	108·7 (3)
Cl(2)–C(15)–C(16)	119·0 (3)	C(8)–C(9)–C(10)	112·4 (3)
N(2)–N(1)–C(9)	103·3 (2)	C(8)–C(9)–C(11)	113·3 (3)
N(1)–N(2)–C(7)	112·3 (3)	C(10)–C(9)–C(11)	111·5 (3)
N(1)–N(2)–C(4)	118·5 (3)	N(2)–N(1)–H(N1)	104 (4)
C(4)–N(2)–C(7)	128·9 (3)	C(9)–N(1)–H(N1)	111 (4)
N(2)–C(7)–O	126·0 (3)	C(7)–C(8)–H(C8)	101 (2)
O–C(7)–C(8)	127·2 (3)	C(9)–C(8)–H(C8)	106 (2)
N(2)–C(7)–C(8)	106·7 (3)	C(12)–C(8)–H(C8)	111 (2)
C(7)–C(8)–C(9)	102·0 (3)	⟨C–C–C⟩$_{ph}$*	120 + 1†
C(7)–C(8)–C(12)	115·1 (2)	⟨C–C–H⟩$_{ph}$*	120 + 3†
C(9)–C(8)–C(12)	119·7 (3)	⟨C–C–H⟩$_{Me}$	110 + 2†

* Average taken over the two phenyl rings.

† The ± sign refers to the root-mean-square deviation from the mean according to the formula $[\sum_i(x_i - \bar{x})^2/(n-1)]^{1/2}$, where $\bar{x}$ is the mean value and n is the number of observations.

Table 3. *Possible hydrogen bond distances* (Å) *and angles* (°)

C(3)–H(C3)	1·03 (3)	C(3)···O^i	3·151 (4)
H(C3)···O^i	2·38 (3)	C(3)–H(C3)···O^i	131 (2)
N(1)–H(N1)	0·86 (5)	N(1)···O^{ii}	3·331 (4)
H(N1)···O^{ii}	2·64 (5)	N(1)–H(N1)···O^{ii}	138 (5)

Symmetry operations: (i) $-x, -y, -z$; (ii) $-x, -y, 1-z$.

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, least-squares planes and torsion angles have been deposited with the British Library Lending Division as Supplementary Publiction No. SUP 42930 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

(Tomiie *et al.*, 1958), 1·412 (5) Å for antipyrine (Singh & Vijayan, 1973) and 1·365 (3) Å for 1,2-dihydro-5-methyl-3(3*H*)-pyrazolone (De Camp & Stewart, 1971). In these compounds the possibility of extensive π delocalization involving the N atoms, thus decreasing the electron density on both atoms, may lower the repulsion between lone pairs: this results in shorter N—N distances. It is also interesting to note that in all the compounds showing some conjugation the calculated bond indices between the two N atoms are the same, notwithstanding the difference in bond lengths (see Fig. 2).

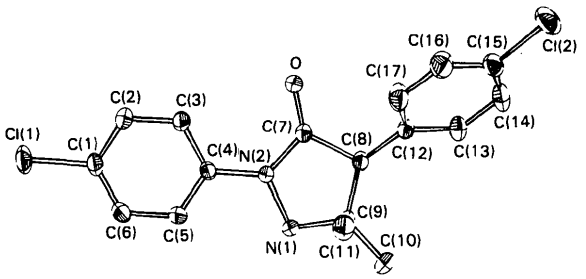

Fig. 1. An *ORTEP* view (Johnson, 1971) of the molecule. H atoms have been omitted for clarity.

Other bond lengths and angles have the expected values; deviations from the idealized geometry may be attributed to steric effects [see, for example, the intramolecular short contacts O···C(3) 2·908 (4) Å with O···H(C3) 2·33 (3) Å, and N(1)···C(5) 2·801 (4) Å with N(1)···H(C5) 2·47 (3) Å].

The O atom is involved in two hydrogen contacts (see Table 3): the first with the H atom bound to C(3) (Taylor & Kennard, 1982), the second with that bound to N(1). This weak interaction is consistent with the low acidity of the latter proton, unlike the corresponding proton in 3(3*H*)-pyrazolone rings (see, for example, De Camp & Stewart, 1971). As a final comment, we note that the similarities in geometry and in the electronic features present in the hydrazidic moiety of both the present compound and antipyrine (see the *CNDO*/2 values in Fig. 2) suggest that this part may be responsible for the pharmacological activity of these two molecules.

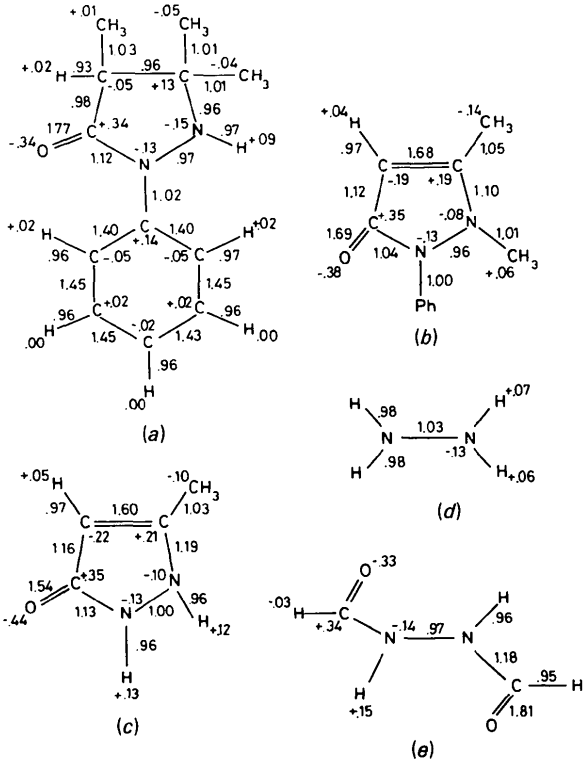

Fig. 2. *CNDO*/2 bond indices and charge residues. Input geometries were taken from (*a*) 2-phenyl-4,5,5-trimethyl-3-pyrazolidinone (present work); (*b*) antipyrine [1,2-dihydro-1,5-dimethyl-2-phenyl-3(3*H*)-pyrazolone] (Singh & Vijayan, 1973); (*c*) 1,2-dihydro-5-methyl-3(3*H*)-pyrazolone (De Camp & Stewart, 1971); (*d*) hydrazine (C_2 symmetry) (Kohata, Fukuyama & Kuchitsu, 1982); (*e*) diformylhydrazine (C_i symmetry) (Tomiie, Koo & Nitta, 1958). The phenyl ring values for (*b*) correspond to those given for (*a*).

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