Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

1-(4-Chlorophenyl)-3-[3-(4-chlorophenyl)-pyrazol-1-yl]propan-1-one

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Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.003 Å
R factor = 0.055
wR factor = 0.124
Data-to-parameter ratio = 18.7

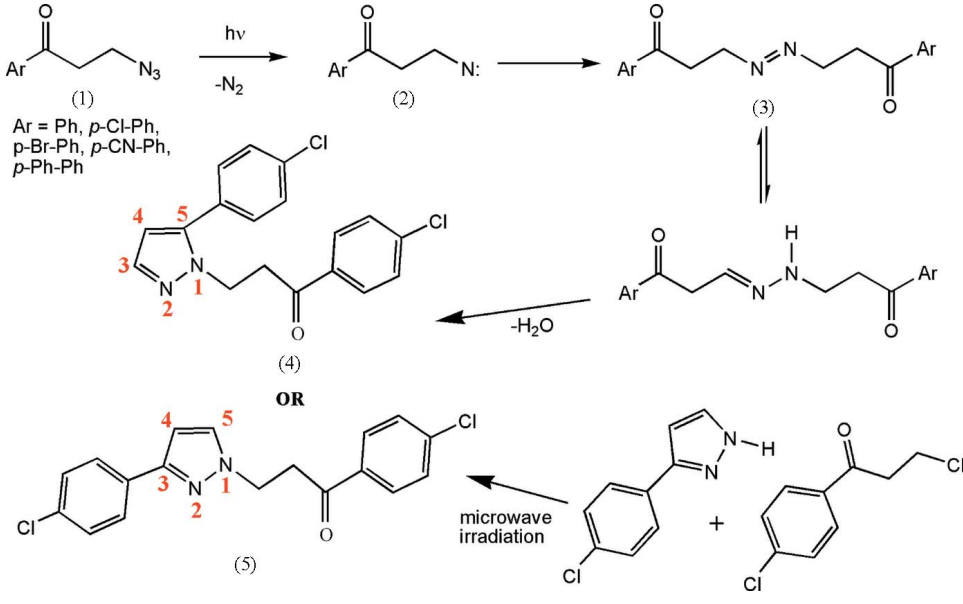
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 9 November 2006
Accepted 6 January 2007

The title compound, $C_{18}H_{14}Cl_2N_2O$, is an isomer of the triplet alkyl nitrene decay product formed upon photolysis of β-azido propiophenone complexes. The molecule exhibits an overall twist with dihedral angles of 10.32 (7) and 24.94 (4)° between the pyrazole plane and the planes of the chlorophenyl rings. The crystal packing of the title compound features stacks of molecules in alternating orientations running along the *b* axis; the approximate separation distance between the planes of neighboring molecules in the stack is 3.66 Å.

Comment

Photolysis of β-azido propiophenone derivatives (1), having a built-in sensitizer, leads to selective formation of triplet alkyl nitrenes (2). We detected the triplet alkyl nitrene intermediates directly with laser flash photolysis and further characterized them with matrix isolation, isotope labeling and molecular modeling studies (Singh *et al.*, 2007). Interestingly, the triplet alkyl nitrenes are unreactive, long-lived intermediates that decay by dimerizing with another triplet alkyl nitrene to form azo products (3), rather than reacting with an azide precursor (see the scheme). This dimerization reactivity has been observed previously with triplet aryl nitrenes (Platz, 2004). The azo dimer (3) can tautomerize and lose water to form the heterocyclic pyrazole derivative, which can represent either isomer (4) or (5).



As the precursor to isomer (5) is commercially available, we synthesized (5) by an independent route from 3-(4-chloro-

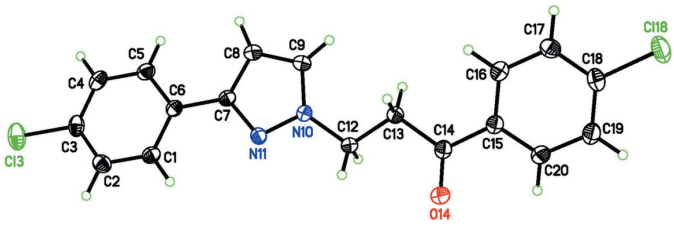


Figure 1
The molecular structure of (5), showing atomic numbering scheme and 50% probability ellipsoids; H atoms are drawn as small circles of arbitrary radius.

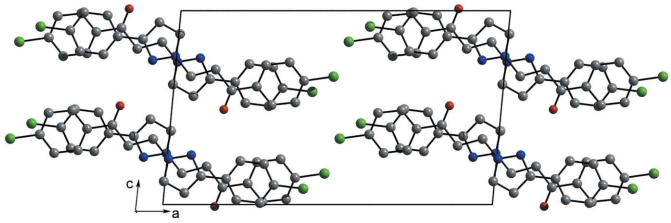


Figure 2
Packing diagram of (5), viewed down the *b* axis. H atoms have been omitted.

phenyl)pyrazole and 3-chloro-1-(4-chlorophenyl)propan-1-one (see the scheme) and fully characterized it by X-ray crystallography and spectroscopic methods. Comparing these results with the spectroscopic signature of the heterocyclic pyrazole derivative resulting from the tautomerization of (3), it was determined that the reaction, in fact, results in the exclusive formation of (4). Here we report the results of these studies.

The ^{1}H and ^{13}C NMR spectra for (4) and (5) are very similar. The major difference is the ^{13}C signal for the C-4 position of the pyrazole ring [refer to scheme for position labeling of the pyrazole ring for (4) and (5)], which appears at 106.5 p.p.m. for (4) and 102.6 p.p.m. for (5). Furthermore, the C-4 proton appears at 6.27 p.p.m. in (4) and 6.47 p.p.m. in (5). These findings are in agreement with the spectroscopic characterization of 1-methyl-3-phenylpyrazole and 1-methyl-5-phenylpyrazole (Pavlik & Kebede, 1997) having ^{13}C signals at 103 and 106 p.p.m., respectively. The corresponding proton signals occur at 6.52 p.p.m. in 1-methyl-3-phenylpyrazole and 6.33 p.p.m. in 1-methyl-5-phenylpyrazole.

The structure of (5) (Fig. 1) contains three planar rings with the molecule exhibiting an overall twist; the pyrazole plane forms dihedral angles of 10.32 (7) and 24.94 (4)° with the planes of the benzene rings defined by C1–C6 and C15–C20, respectively. The central N10—C12—C13—C14—C15 chain of the molecule is planar to within 0.022 Å and forms dihedral angles of 22.2 (1) and 7.5 (1)° with the pyrazole plane and the benzene C15–C20 plane, respectively. Bond distances and angles of the pyrazole ring in (5) are similar to values reported by Low *et al.* (2001) for 4-(4-chlorophenyl)-3,7,7-trimethyl-1-[2-(4-nitrobenzoyl)ethyl]-4,7,8,9-tetrahydro-1*H*-pyrazolo(3,4-*b*)quinolin-5(6*H*)-one and by Mitkidou *et al.* (1990) for 1-(3,4,5-trimethyl-1*H*-pyrazolyl)-2,2-dimethylvinylbenzoate and 3,4,5-trimethyl-1-(3-aryl-1,3-dioxo-2-phenoxypropyl)-1*H*-pyrazole.

The crystal packing of (5) shows stacks of molecules running along the *b* axis with alternating orientations and a separation distance of approximately 3.66 Å between the planes of the neighboring molecules in the stack (Fig. 2). Additional C—H···O interactions link the molecules into chains running along the *c* axis [C9···O14^{i} = 3.418 (3) Å, H9···O14^{i} = 2.47 Å, C9—H9···O14^{i} = 173°; symmetry code: (i) $x, -y+\frac{1}{2}, z+\frac{1}{2}$].

Experimental

1-Azido-1-(4-chlorophenyl)propan-1-one was synthesized according to the procedure described by Singh *et al.* (2003). A solution of 1-azido-1-(4-chlorophenyl)propan-1-one (100 mg, 0.51 mmol) in dry distilled toluene (200 ml) was irradiated with a mercury arc lamp. The solvent was removed under vacuum and the resulting oil was purified on a silica column with a mixture of ethyl acetate and hexanes as the eluent. (4) was isolated as the major photoproduct (10.6 mg, 0.032 mmol, 12% yield) along with recovered starting material. Spectroscopic details for (4): ^{1}H NMR (250 MHz, $CDCl_3$): δ 3.59 (*t*, 2H, 7 Hz, –CO—CH_2–), 4.51 (*t*, 2H, 7 Hz, –CH_2—N<), 6.27 (*d*, 1H, 2 Hz, *C*-4$_{pyrazole}$H), 7.38–7.43 (*m*, 6H, aromatic H), 7.53 (*d*, 1H, 2 Hz, *C*-3$_{pyrazole}$H), 7.86 (*d*, 2H, 7.5 Hz, aromatic H) p.p.m. ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.2 (C=O), 142.7 C-5$_{pyrazole}$C), 140.0 (aromatic C), 139.9 (C3-$_{pyrazole}$C), 134.9, 134.7 (aromatic C), 130.3, 129.5, 129.1, 129.0 (aromatic C), 106.5 (*C*-4$_{pyrazole}$C), 44.3, 38.3 (CH_2) p.p.m. MS (ESI, M^+) calculated for $C_{18}H_{14}Cl_2N_2O$: 344.0483; found 344.0477.

(5) was synthesized *via* the method of Bogdal *et al.* (1997) as modified by Law *et al.* (2002) for water-moderated reaction in a conventional microwave oven (2350 MHz, 1100 Watt). A test tube was charged with a mixture of 3-(4-chlorophenyl)pyrazole (356.7 mg, 1.00 mmol), 3-chloro-1-(4-chlorophenyl)propan-1-one (746.5 mg, 3.70 mmol), tetrabutylammonium bromide (89.3 mg, 0.342 mmol) and potassium bicarbonate (1.4018 g, 21.6 mmol). The test tube was placed in a beaker filled with water (400 ml) and irradiated. The reaction progress was monitored with thin-layer chromatography and after 4 min of microwave irradiation the starting material was depleted. The reaction mixture was dissolved in water (200 ml) and extracted twice with dichloromethane (20 ml); the organic layer was dried with magnesium sulfate and filtered, and the solvent was removed under vacuum. Purification of the resulting oil by silica column chromatography using ethyl acetate–hexane (20%) as the eluent yielded (5) (0.53 g, 1.5 mmol, 93% yield). Further purification of (5) was accomplished by recrystallization from ethyl acetate–hexane. Diffraction-quality crystals were grown by slow evaporation of an ethanol solution. Spectroscopic details for (5): ^{1}H NMR (250 MHz, $CDCl_3$): δ 3.61(*t*, 2H, 7 Hz, –CO—CH_2–), 4.61 (*t*, 2H, 7 Hz, –CH_2—N<), 6.47 (*d*, 1H, 2 Hz, *C*-4$_{pyrazole}$H), 7.33 (*d*, 2H, 8 Hz, aromatic H), 7.37 (*d*, 2H, 8 Hz, aromatic H), 7.51 (*d*, 1H, 3 Hz, *C*-5$_{pyrazole}$H), 7.68 (*d*, 2H, 8 Hz, aromatic H), 7.89 (*d*, 2H, 8 Hz, aromatic H) p.p.m. ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.3 (C=O), 150.8 (C-3$_{pyrazole}$C), 140.0, 134.7, 132.1 (aromatic C), 131.8 (C-5$_{pyrazole}$C), 129.5, 129.0, 128.8, 126.8 (aromatic C), 102.6 (C-4$_{pyrazole}$C), 46.9, 38.8 (CH_2) p.p.m. MS (ESI, M^+) calculated for $C_{18}H_{14}Cl_2N_2O$: 344.0483; found 344.0502.

Crystal data

$C_{18}H_{14}Cl_2N_2O$
M_r = 345.21
Monoclinic, $P2_1/c$
a = 19.1362 (5) Å
b = 7.2803 (2) Å
c = 11.2860 (3) Å
β = 95.3770 (10)°
V = 1565.42 (7) Å^3
Z = 4
D_x = 1.465 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.42 mm^{-1}
T = 150 (2) K
Block, colorless
0.22 × 0.18 × 0.11 mm

Data collection

Bruker SMART 6000 CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
T_{min} = 0.822, T_{max} = 0.955
13291 measured reflections
3889 independent reflections
3188 reflections with $I > 2\sigma(I)$
R_{int} = 0.042
θ_{max} = 28.3°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.124
S = 1.12
3889 reflections
208 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0325P)^2 + 1.3572P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.42 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}

H atoms were placed in geometrically calculated positions (C—H=0.99 and 0.95 Å for $-CH_2$ and aromatic, respectively) and treated using a riding-model approximation in subsequent refinements. H-atom displacement parameters were defined as $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*); program(s) used to solve structure: *SHELXTL* (Bruker, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL* and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *SHELXTL*.

NSF support of this work is gratefully acknowledged (CAREER Award 0093622). JAK thanks Dr Alan Pinkerton, Department of Chemistry, University of Toledo, OH 43606, for use of the SMART 6000 diffractometer.

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