# Triethylaminium 4-(2-chlorobenzoyl)-3-methyl-1-(p-tolyl)-1H-pyrazol-5-olate

**Xue-Min Duan,**[a]***** **Mei-Lian Fan,**[b] **Peng-Wu Zheng**[a] **and Qi-Dong Tu**[a]

[a]School of Pharmacy, Jiangxi Science and Technology Normal University, Nanchang 330013, People's Republic of China, and [b]College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, People's Republic of China

Correspondence e-mail: dxmlhp@yahoo.com.cn

Two independent ion pairs comprise the asymmetric unit of the title compound, $C_6H_{16}N^+ \cdot C_{18}H_{14}ClN_2O_2^-$. The pyrazole ring, the methylbenzene ring and the chlorobenzene ring are each essentially planar. The dihedral angles between the two benzene rings are 97.6 (3) and 97.1 (3)° for the two anions. Weak N—H···O interactions are observed in the crystal structure.

## Comment

Acylpyrazolones, which are $\beta$-diketone reagents, have been widely used for the extraction of metal ions. Zolotov (1970) considered 4-benzoyl-3-methyl-1-phenyl-1H-pyrazol-5-one (PMBP) as one of the most excellent extractants, which can extract many kinds of metal ions (Xiong *et al.*, 2000; Yang *et al.*, 2003). In our search for new and better extractants, we expected to obtain the analogue to PMBP, that is, 1-p-tolyl-3-methyl-4-(2-chlorobenzoyl)-5-pyrazolone. However, its (1:1) triethylamine complex, (I), was obtained unexpectedly. We report here the crystal structure of the title compound, (I).



(I)
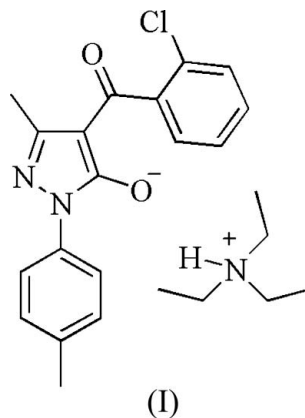
The asymmetric unit of (I) comprises two independent but similar ion pairs (Fig. 1). The pyrazole ring, methylbenzene ring and chlorobenzene ring in both anions are each essentially planar, with mean deviations of 0.0016 and 0.0062 Å, 0.0190 and 0.0255 Å, and 0.0028 and 0.0059 Å, respectively, for the two anions. The dihedral angle between the pyrazole and methylbenzene rings is 8.6 (3)°, that between the pyrazole and chlorobenzene rings is 93.1 (2)°, and that between the two benzene rings is 97.6 (3)° in the first anion; for the second anion, these dihedral angles are 14.2 (3), 91.3 (2) and 97.1 (3)°, respectively. The bond lengths and angles are in agreement with reported literature values (Allen *et al.*, 1987). Weak N—H···O interactions are observed in the crystal structure (Table 1).
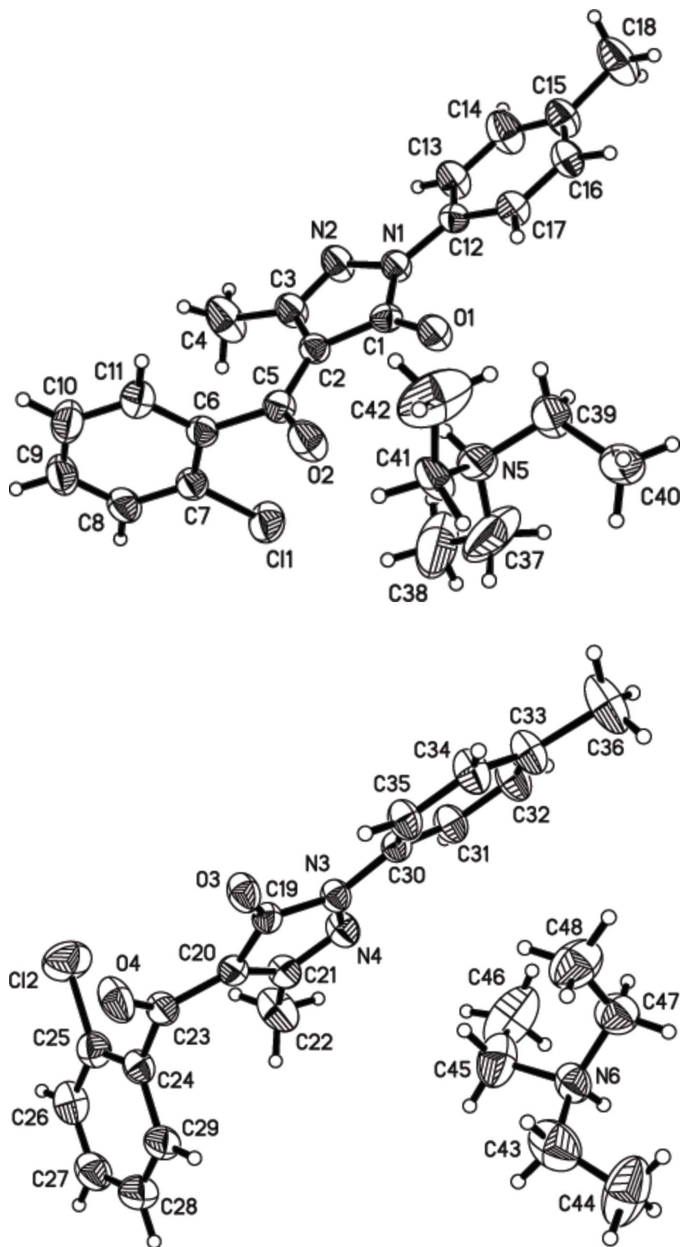
**Figure 1**
A view of the two independent cations and anions of (I). Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.



**Figure 2**
Part of the packing of (I), viewed down the *b* direction. Dashed lines indicate hydrogen bonds.

## Experimental

To an acetone solution (50 ml) of a mixture (2 g) of 1-*p*-tolyl-3-methyl-1*H*-pyrazol-5-yl-2-chlorobenzoate and 1-*p*-tolyl-3-methyl-4-(2-chlorobenzoyl)-5-pyrazolone, which was obtained by an acylation reaction, triethylamine (5 ml) was added. After stirring for 30 min at ambient temperature, the mixture was poured into distilled water (50 ml) and then filtered. Dilute hydrochloric acid (0.6 *M*) was added to the filtrate dropwise until a precipitate appeared. The precipitate was collected by filtration, dried *in vacuo* and recrystallized from ethanol to give a colourless solid (1.52 g). Single crystals of (I) suitable for X-ray analysis were obtained by slow evaporation of an ethanol solution.
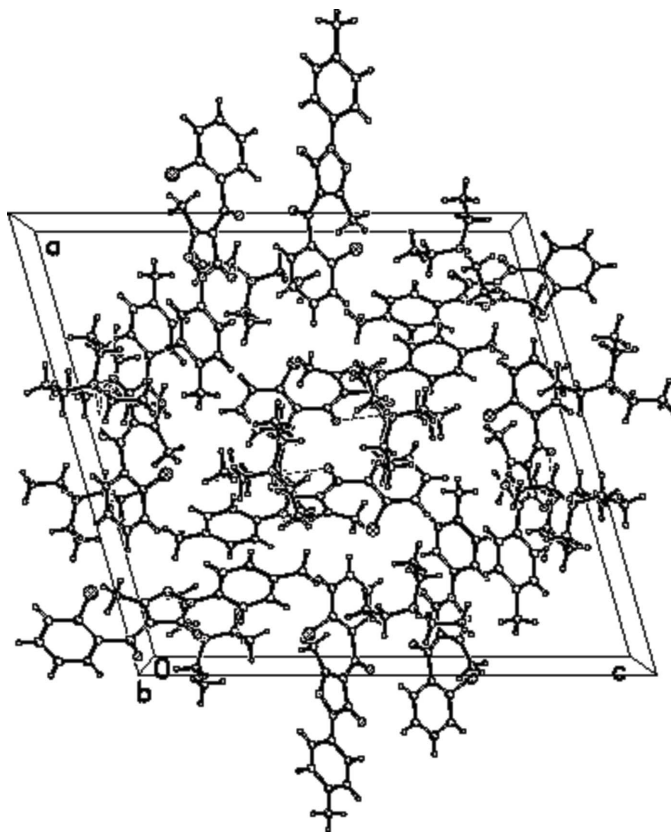
### Crystal data

| | |
|---|---|
| $C_6H_{16}N^+ \cdot C_{18}H_{14}ClN_2O_2^-$ | $D_x = 1.203$ Mg m$^{-3}$ |
| $M_r = 427.96$ | Mo $K\alpha$ radiation |
| Monoclinic, $P2_1/n$ | Cell parameters from 4315 |
| $a = 22.216$ (2) Å | reflections |
| $b = 9.2475$ (10) Å | $\theta = 2.7$–20.7° |
| $c = 23.913$ (2) Å | $\mu = 0.19$ mm$^{-1}$ |
| $\beta = 105.778$ (2)° | $T = 293$ (2) K |
| $V = 4727.6$ (9) Å$^3$ | Prism, colourless |
| $Z = 8$ | $0.22 \times 0.20 \times 0.10$ mm |

### Data collection

| | |
|---|---|
| Bruker SMART CCD area-detector diffractometer | 8307 independent reflections |
| | 5157 reflections with $I > 2\sigma(I)$ |
| $\varphi$ and $\omega$ scans | $R_{int} = 0.028$ |
| Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996) | $\theta_{max} = 25.0°$ |
| | $h = -26 \rightarrow 26$ |
| $T_{min} = 0.948$, $T_{max} = 0.982$ | $k = -10 \rightarrow 10$ |
| 24828 measured reflections | $l = -28 \rightarrow 25$ |

### Refinement

| | |
|---|---|
| Refinement on $F^2$ | $w = 1/[\sigma^2(F_o^2) + (0.0816P)^2$ |
| $R[F^2 > 2\sigma(F^2)] = 0.056$ | $+ 1.8822P]$ |
| $wR(F^2) = 0.180$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.04$ | $(\Delta/\sigma)_{max} = 0.001$ |
| 8307 reflections | $\Delta\rho_{max} = 0.38$ e Å$^{-3}$ |
| 614 parameters | $\Delta\rho_{min} = -0.30$ e Å$^{-3}$ |
| H-atom parameters constrained | |

**Table 1**
Hydrogen-bond geometry (Å, °).

| $D-\text{H}\cdots A$ | $D-\text{H}$ | $\text{H}\cdots A$ | $D\cdots A$ | $D-\text{H}\cdots A$ |
|---|---|---|---|---|
| N5—H5$B$⋯O1 | 0.90 | 1.90 | 2.703 (3) | 147 |
| N5—H5$A$⋯O2 | 0.90 | 2.39 | 3.029 (3) | 128 |
| N6—H6$A$⋯O3$^{\text{i}}$ | 0.93 (4) | 1.94 (4) | 2.744 (3) | 144 (3) |
| N6—H6$A$⋯O4$^{\text{i}}$ | 0.93 (4) | 2.27 (3) | 2.943 (4) | 129 (3) |

Symmetry code: (i) $x, y + 1, z$.

All H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H distances in the range 0.93–0.97 Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The quaternary ammonium group was found to be disordered and two distinct conformations were observed. The site occupancies refined to 0.541 (1):0.459 (1).

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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