

Dmitry V. Albov,\* Victor B. Rybakov, Eugene V. Babaev and Alexander A. Tsisevich

Department of Chemistry, Moscow State University, 119992 Moscow, Russian Federation

Correspondence e-mail: albov@struct.chem.msu.ru

#### Key indicators

Single-crystal X-ray study

$T = 293$  K

Mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å

$R$  factor = 0.048

$wR$  factor = 0.059

Data-to-parameter ratio = 15.9

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

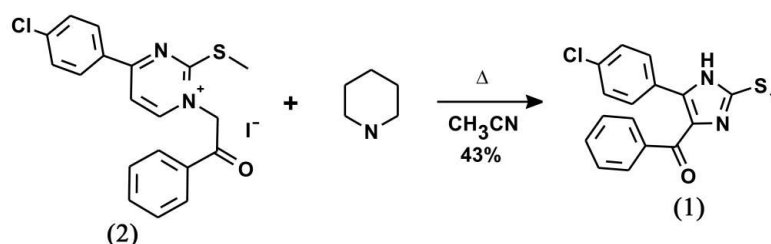
## 4-Benzoyl-5-(4-chlorophenyl)-2-(methylsulfanyl)-1*H*-imidazole

The title imidazole,  $\text{C}_{17}\text{H}_{13}\text{ClN}_2\text{OS}$ , was obtained by unusual rearrangement of the pyrimidinium salt. The structure was characterized by  $^1\text{H}$  NMR spectroscopy and X-ray diffraction. A mechanism of transformation (pyrimidinium salt  $\rightarrow$  title imidazole) is proposed.

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#### Comment

We observed the unusual formation of the title substituted imidazole, (1), in the reaction of the pyrimidinium salt (2) with a secondary amine.



Although the general class of *N*-phenacyl-2-(methylsulfanyl)pyrimidinium salts is known (Liebscher & Hassoun, 1988), few data are available on their reactivity. As was reported by Liebscher & Hassoun (1988), salts like (2) react with pyridine, leading to oxazolo[3,2-*a*]pyrimidinium salts.

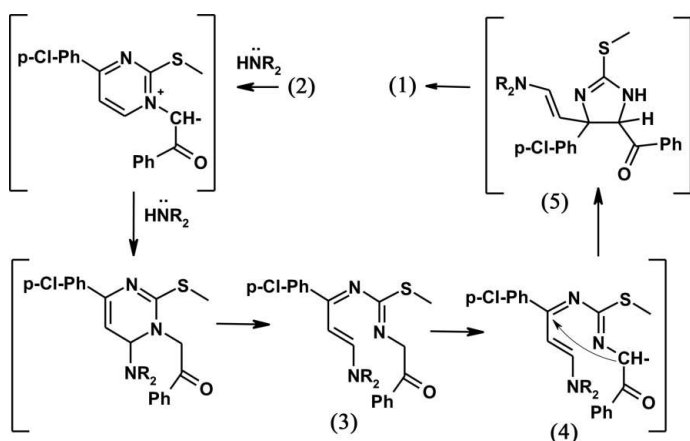
The suggested structure of imidazole (1) was proved by elemental analysis, X-ray diffraction, and NMR and mass spectroscopy. According to the  $^1\text{H}$  NMR data, there are two NH peaks as well as two SME singlets, and this clearly confirms that the imidazole exists as the expected mixture of two NH tautomers. However, only one tautomer, namely the 4-benzoyl-5-(4-chlorophenyl)-1*H* tautomer, is visible in the single-crystal structure according to the X-ray data.

The five-membered heterocycle (N1/C2/N3/C4/C5) (Fig. 1) is nearly planar and the attached chlorophenyl ring (C13–C18) makes a dihedral angle of  $36.0(1)^\circ$ . The second phenyl ring (C7–C12) of the benzoyl group forms a dihedral angle of  $50.6(1)^\circ$  with the five-membered heterocycle, indicating a low degree of conjugation between these rings. This phenomenon may be explained by steric effects of the packing of both phenyl rings.

An  $\text{N}-\text{H}\cdots\text{N}$  intermolecular hydrogen bond (Table 2) links the molecules in the crystal structure into extended chains (Fig. 2).

From the formal viewpoint, the structure of (1) has two C atoms fewer than (2). The mechanism of this unexpected transformation may be rationalized in terms of rearrangement of pyrimidine to imidazole. Indeed, if the secondary amine

caused ring cleavage leading to open form (3), the methylene group of the intermediate, (3), is acidic enough to lose a proton, giving the anion (4). In this case, the closure of the five-membered ring [intermediate (5)] may naturally follow from the polarity distribution along the chain. Final aromatization of the imidazole ring is associated with the elimination of the stable group – the enamine of the acetaldehyde from (5) to (1).



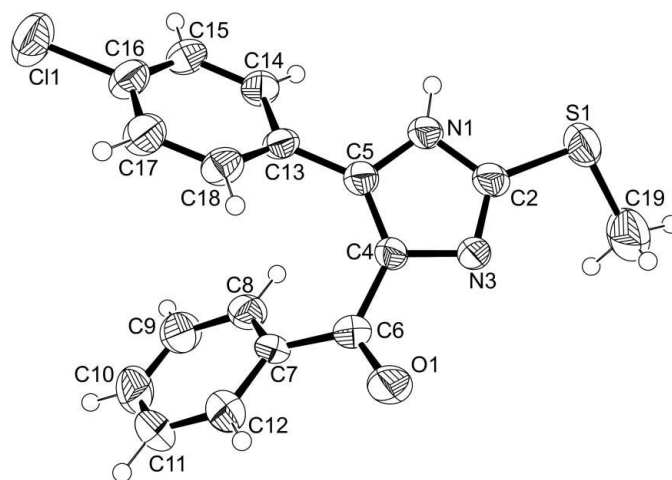
## Experimental

The pyrimidinium salt, (2), was obtained by the published method of Liebscher & Hassoun (1988). To synthesize compound (1), piperidine (2 ml, 0.02 mmol) was added to a suspension of salt (2) (0.965 g, 0.002 mmol) in acetonitrile (5 ml). The mixture immediately turned red, and the precipitate dissolved. The mixture was refluxed for 3 h. After cooling to room temperature, the mixture was poured into water (30 ml). The product was extracted with CHCl<sub>3</sub> (3 × 30 ml), and the extract was dried over CaCl<sub>2</sub>. The solvent was evaporated and the product was purified by column chromatography (SiO<sub>2</sub>, benzene–acetone, 15:1). Single crystals of (1) were formed from the mother solution after chromatography (yield 0.41 g, 43%; m.p. 466–469 K). Spectroscopic analysis: <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, δ, p.p.m.): 12.96 + 12.91 (*s* + *s*, 1H, NH), 8.12–8.10 (*m*, 1H, Ar), 7.73–7.71 (*m*, 1H, Ar), 7.55–7.32 (*m*, 5H, Ar), 7.26–7.22 (*m*, 1H, Ar), 7.09–7.07 (*m*, 1H, Ar), 2.69 + 2.63 (*s* + *s*, 3H, CH<sub>3</sub>); MS, *m/z* (%): 329 (15), 328/330 (57/22) [*M*+], 327 (12), 295/297 (31/10), 158 (12), 137 (14), 123 (27), 105 (88), 86 (11), 77 (100), 51 (21). Analysis, found: C 61.85, H 4.00, N 8.32%; calculated for C<sub>17</sub>H<sub>13</sub>ClN<sub>2</sub>OS: C 62.10, H 3.99, N 8.52%.

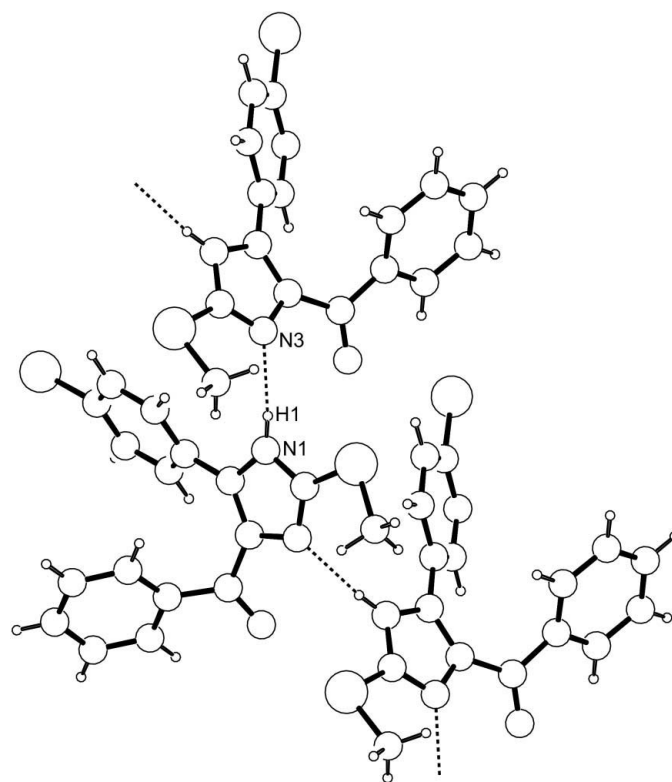
### Crystal data

C<sub>17</sub>H<sub>13</sub>ClN<sub>2</sub>OS  
*M<sub>r</sub>* = 328.81  
 Monoclinic, *P*2<sub>1</sub>/*c*  
*a* = 7.2814 (15) Å  
*b* = 23.650 (3) Å  
*c* = 9.752 (5) Å  
 β = 110.46 (3)°  
*V* = 1573.4 (9) Å<sup>3</sup>  
*Z* = 4

*D<sub>x</sub>* = 1.388 Mg m<sup>-3</sup>  
 Cu Kα radiation  
 Cell parameters from 25 reflections  
 θ = 32–35°  
 μ = 3.41 mm<sup>-1</sup>  
*T* = 293 (2) K  
 Prism, colourless  
 0.1 × 0.1 × 0.1 mm



**Figure 1**  
 The molecular structure of (1) and the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.



**Figure 2**  
 A plot showing the N–H...N hydrogen-bonded (dashed lines) chain.

### Data collection

Enraf–Nonius CAD4 diffractometer  
 Non-profiled ω scans  
 Absorption correction: none  
 3236 measured reflections  
 3236 independent reflections  
 1639 reflections with *I* > 2σ(*I*)

θ<sub>max</sub> = 74.9°  
*h* = -9 → 8  
*k* = 0 → 29  
*l* = 0 → 12  
 1 standard reflection  
 frequency: 120 min  
 intensity decay: 2%

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.048$   
 $wR(F^2) = 0.059$   
 $S = 0.86$   
 3236 reflections  
 204 parameters

H atoms treated by a mixture of independent and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.0051P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.23 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.21 \text{ e } \text{\AA}^{-3}$

Table 1

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

S1–C2	1.735 (3)	C7–C8	1.384 (3)
S1–C19	1.776 (3)	C7–C12	1.395 (3)
C11–C16	1.749 (3)	C8–C9	1.371 (3)
O1–C6	1.221 (3)	C9–C10	1.365 (4)
N1–C2	1.367 (3)	C10–C11	1.375 (4)
N1–C5	1.379 (3)	C11–C12	1.391 (4)
C2–N3	1.324 (3)	C13–C18	1.387 (3)
N3–C4	1.390 (3)	C13–C14	1.400 (3)
C4–C5	1.378 (3)	C14–C15	1.378 (3)
C4–C6	1.477 (3)	C15–C16	1.365 (3)
C5–C13	1.465 (3)	C16–C17	1.381 (3)
C6–C7	1.482 (3)	C17–C18	1.370 (3)
C2–S1–C19	99.66 (14)	C12–C7–C6	118.5 (3)
C2–N1–C5	107.2 (2)	C9–C8–C7	120.9 (3)
N3–C2–N1	111.9 (3)	C10–C9–C8	120.5 (3)
N3–C2–S1	126.7 (2)	C9–C10–C11	119.9 (3)
N1–C2–S1	121.4 (2)	C10–C11–C12	120.5 (3)
C2–N3–C4	105.0 (2)	C11–C12–C7	119.4 (3)
C5–C4–N3	110.2 (2)	C18–C13–C14	117.8 (3)
C5–C4–C6	132.4 (3)	C18–C13–C5	122.1 (2)
N3–C4–C6	117.4 (2)	C14–C13–C5	120.1 (3)
C4–C5–N1	105.6 (2)	C15–C14–C13	121.0 (3)
C4–C5–C13	133.5 (3)	C16–C15–C14	119.2 (3)
N1–C5–C13	120.9 (2)	C15–C16–C17	121.6 (3)
O1–C6–C4	118.8 (3)	C15–C16–C11	119.1 (2)
O1–C6–C7	120.3 (3)	C17–C16–C11	119.3 (2)
C4–C6–C7	120.8 (2)	C18–C17–C16	118.7 (3)
C8–C7–C12	118.8 (3)	C17–C18–C13	121.7 (3)
C8–C7–C6	122.4 (3)		

Table 2

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N1-H1 \cdots N3^i$	0.86 (3)	2.09 (3)	2.952 (3)	172 (3)

Symmetry code: (i)  $x, -y + \frac{3}{2}, z - \frac{1}{2}$ .

The H atom involved in the hydrogen bond was found in a difference Fourier map and refined independently. H atoms bonded to C atoms were included in calculated positions and refined as riding atoms, with calculated C–H bond lengths in the range 0.93–0.97  $\text{\AA}$ . For methyl H atoms,  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ , while for other H atoms,  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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