On products of reaction of imidazole with benzoyl chloride under conditions of the Regel—Buchel reaction

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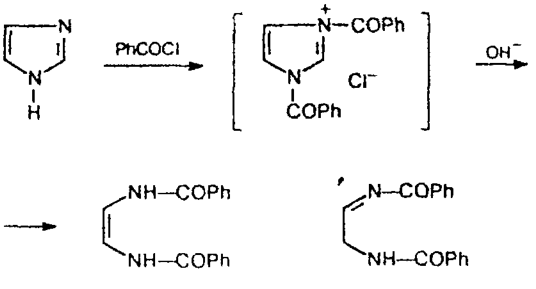
The reaction of imidazole with benzoyl chloride in pyridine afforded *cis*-1,2-bis(benzoylamino)ethylene (**1**) rather than 2-benzoylimidazole, as has been suggested previously. The structure of **1** was confirmed by ^{1}H NMR spectroscopy and X-ray diffraction study.

Key words: imidazole, benzoyl chloride, *cis*-1,2-bis(benzoylamino)ethylene, X-ray diffraction study.

It is known[1,2] that *N*-substituted imidazoles undergo rather smooth acylation with aroyl halides in MeCN in the presence of Et_3N at position 2 to form *N*-substituted aryl imidazol-2-yl ketones. The reaction is a nonclassical version of electrophilic substitution that involves formation of an acylimidazolium cation at the first stage. Subsequent stages involve, apparently, elimination of the H(2) proton to form highly reactive ylide and the attack by the acylating reagent at position 2 of this ylide.

Under analogous conditions, unsubstituted imidazole does not form 2-acyl derivatives[1,2] but, according to the results of more recent studies,[3] smoothly reacts with the PhCOCl—Et_3N system in pyridine to give 2-benzoylimidazole.

We attempted to reproduce the latter procedure. However, treatment of a solution of imidazole and triethylamine in pyridine with benzoyl chloride (according to the published procedure[3]) followed by alkaline hydrolysis of the reaction mixture afforded only one poorly soluble product, *cis*-1,2-bis(benzoylamino)ethylene (**1**), in 10% yield. This transformation is analogous to the decomposition of imidazole under the action of PhCOCl in aqueous alkali, which has long been known.[4—6] Apparently, the 1,3-dibenzoylimidazolium cation is the immediate precursor of compound **1**.



1 **2**

Compound **1** and some of its analogs prepared from substituted imidazoles[4—6] remain poorly studied. Compound **1** exists as enediamine rather than the prototropic tautomer (**2**), which was established by NMR spectroscopy and X-ray diffraction study.

Molecule **1** has a *cis* configuration (Fig. 1) and is virtually planar. The crystal structure of compound **1** is stabilized *via* the intermolecular hydrogen bonds between two NH groups of one molecule and the carbonyl oxygen atom of another molecule: N(1)—H(1N)...O(2) (x, $1.5-y$, $0.5+z$) (N...O, 2.890(2) Å; H...O, 2.01(2) Å; the N—H...O angle, 163(2)°) and N(2)—H(2N)...O(2) (x, $1.5-y$, $0.5+z$) (N...O, 2.881(2) Å; H...O, 2.03(2) Å; the N—H...O angle, 165(2)°) (Fig. 2).

Experimental

The ^{1}H NMR spectra of compound **1** were recorded on a Varian XL-300 spectrometer in DMSO-d_6.

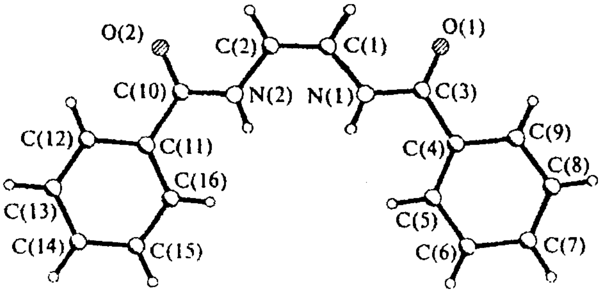


Fig. 1. Structure of molecule **1**.

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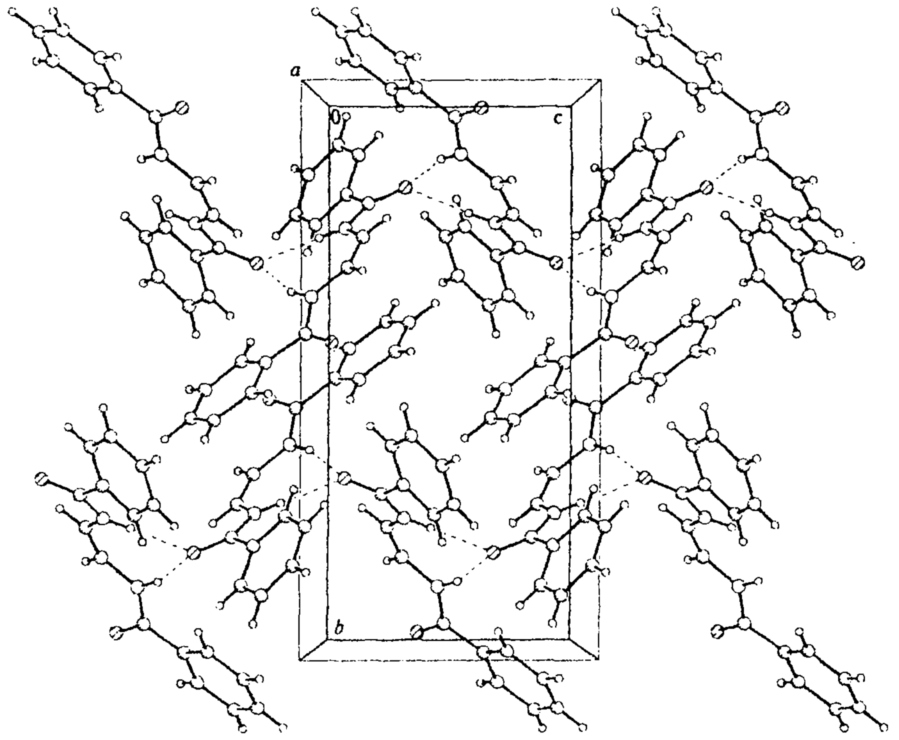

Fig. 2. Crystal packing of compound **1** (projection along the *x* axis); hydrogen bonds are indicated by dashed lines.

Table 1. Atomic coordinates (×10^4) and isotropic (equivalent for nonhydrogen atoms) thermal parameters (×10^3) for molecule **1**

Atom	*x*	*y*	*z*	*U*/Å^2
O(1)	−3398(1)	9514(1)	3965(1)	50(1)
O(2)	1170(1)	6856(1)	1483(1)	31(1)
N(1)	−1427(1)	8720(1)	4651(1)	29(1)
N(2)	633(1)	7542(1)	3501(1)	27(1)
C(1)	−1762(2)	8217(1)	3446(1)	32(1)
C(2)	−856(2)	7692(1)	2930(2)	31(1)
C(3)	−2308(2)	9363(1)	4841(2)	32(1)
C(4)	−1860(2)	9864(1)	6171(1)	31(1)
C(5)	−443(2)	9844(1)	6954(2)	33(1)
C(6)	−105(2)	10327(1)	8177(2)	40(1)
C(7)	−1189(2)	10826(1)	8633(2)	46(1)
C(8)	−2592(2)	10851(1)	7861(2)	47(1)
C(9)	−2934(2)	10379(1)	6624(2)	39(1)
C(10)	1577(2)	7124(1)	2742(1)	25(1)
C(11)	3113(2)	6974(1)	3470(1)	27(1)
C(12)	3844(2)	6295(1)	3074(2)	36(1)
C(13)	5265(2)	6127(1)	3733(2)	47(1)
C(14)	5988(2)	6635(1)	4768(2)	45(1)
C(15)	5275(2)	7312(1)	5155(2)	38(1)
C(16)	3839(2)	7483(1)	4517(1)	29(1)
H(1)	−2778(19)	8272(9)	2952(18)	36(4)
H(1N)	−610(19)	8637(10)	5307(19)	45(5)
H(2)	−1205(18)	7367(9)	2102(19)	40(4)
H(2N)	967(17)	7713(9)	4386(19)	35(4)
H(5)	346(18)	9509(9)	6663(17)	36(4)
H(6)	890(21)	10321(10)	8700(20)	48(5)
H(7)	−884(20)	11170(10)	9499(22)	54(5)
H(8)	−3359(21)	11178(11)	8162(20)	53(5)
H(9)	−3902(21)	10397(10)	6082(20)	50(5)
H(12)	3340(19)	5955(10)	2364(20)	45(4)
H(13)	5748(21)	5629(12)	3477(21)	58(5)
H(14)	7028(21)	6525(11)	5224(20)	55(5)
H(15)	5797(19)	7677(10)	5826(20)	43(4)
H(16)	3364(17)	7956(10)	4789(17)	36(4)

***cis*-1,2-Bis(benzoylamino)ethylene (1).** PhCOCl (28.2 g, 0.2 mol) was added with intense stirring to a solution of imidazole (6.8 g, 0.1 mol) and Et'_3N (20.2 g, 0.2 mol) in pyridine (30 mL) at 0—10 °C under argon. The reaction mixture was stirred at 20 °C for 3 h. Then a 7.5 *M* NaOH solution (20 mL) was added, the mixture was refluxed for 1 h, and water (100 mL) was added. The precipitate that formed was filtered off. The yield of product **1** was 2.4 g (10%), m.p. 207—209 °C (from EtOH) (*cf.* Ref. 4: m.p. 202—203 °C) ^{1}H NMR, δ: 6.35—6.44 (m, CH=CH); 7.50—7.95 (m, Ph); 10.12 (d, NH, $^3J_{HC,NH}$ = 7.8 Hz). After deuteration, the broadened doublet for protons of the NH groups disappeared, and the multiplet from the CH=CH fragment collapsed into a singlet.

X-ray diffraction study of compound 1. Crystals of **1** ($C_{16}H_{14}N_2O_2$, mol. weight 266.29) are monoclinic, space group $P2_1/c$, at 20 °C a = 8.971(2), b = 17.077(4), c = 9.043(2) Å, β = 95.84(2)°, V = 1378.1(5) Å^3, Z = 4, d_{calc} = 1.283 g cm^{-3}. The unit cell parameters and intensities of 2369 reflections were measured on an automated four-circle Siemens

Table 2. Bond lengths (*d*) in the structure of **I**

Bond	*d*/Å	Bond	*d*/Å
O(1)—C(3)	1.222(2)	C(6)—C(7)	1.387(2)
O(2)—C(10)	1.247(2)	C(7)—C(8)	1.377(3)
N(1)—C(3)	1.374(2)	C(8)—C(9)	1.387(2)
N(1)—C(1)	1.396(2)	C(10)—C(11)	1.488(2)
N(2)—C(10)	1.347(2)	C(11)—C(16)	1.397(2)
N(2)—C(2)	1.406(2)	C(11)—C(12)	1.397(2)
C(1)—C(2)	1.326(2)	C(12)—C(13)	1.382(2)
C(3)—C(4)	1.497(2)	C(13)—C(14)	1.388(2)
C(4)—C(5)	1.392(2)	C(14)—C(15)	1.382(2)
C(4)—C(9)	1.397(2)	C(15)—C(16)	1.388(2)
C(5)—C(6)	1.388(2)		

P3/PC diffractometer (20 °C, Mo-Kα radiation, graphite monochromator, $\theta/2\theta$ scanning technique, $\theta_{max} = 25°$). The structure was solved by the direct method and refined by the full-matrix least-squares method with anisotropic thermal parameters for nonhydrogen atoms. The hydrogen atoms were located from the difference Fourier synthesis and refined isotropically. The final values of the *R* factors were as follows: $R_1 = 0.037$ using 1940 independent reflections with $I > 2\sigma(I)$ and $wR_2 = 0.102$ using 2196 independent reflections. All calculations were carried out on an IBM PC/AT-486 computer using the SHELXTL PLUS and SHELXL-93 program packages. The coordinates and thermal parameters are given in Table 1. The bond lengths and bond angles are given in Tables 2 and 3, respectively.

Table 3. Bond angles (ω) in the structure of **I**

Angle	ω/deg	Angle	ω/deg
C(3)—N(1)—C(1)	120.5(1)	C(7)—C(8)—C(9)	120.4(2)
C(10)—N(2)—C(2)	122.2(1)	C(8)—C(9)—C(4)	120.0(2)
C(2)—C(1)—N(1)	126.8(1)	O(2)—C(10)—N(2)	121.3(1)
C(1)—C(2)—N(2)	126.0(1)	O(2)—C(10)—C(11)	120.9(1)
O(1)—C(3)—N(1)	121.4(1)	N(2)—C(10)—C(11)	117.9(1)
O(1)—C(3)—C(4)	122.1(1)	C(16)—C(11)—C(12)	119.4(1)
N(1)—C(3)—C(4)	116.5(1)	C(16)—C(11)—C(10)	122.7(1)
C(5)—C(4)—C(9)	119.2(1)	C(12)—C(11)—C(10)	117.9(1)
C(5)—C(4)—C(3)	123.5(1)	C(13)—C(12)—C(11)	119.9(1)
C(9)—C(4)—C(3)	117.4(1)	C(12)—C(13)—C(14)	120.6(2)
C(6)—C(5)—C(4)	120.4(1)	C(15)—C(14)—C(13)	119.8(1)
C(7)—C(6)—C(5)	120.0(2)	C(14)—C(15)—C(16)	120.3(1)
C(8)—C(7)—C(6)	120.1(2)	C(15)—C(16)—C(11)	120.0(1)

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