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The Synthesis of *N*-Benzoyl-1,2,4-triazole Oximes. Structures of Two Isomers, $C_{16}H_{14}N_4O$: 5-Methyl-3-phenyl-1,2,4-triazol-1-yl Phenyl Ketone Oxime (1) and 3-Methyl-5-phenyl-1,2,4-triazol-4-yl Phenyl Ketone Oxime (3)

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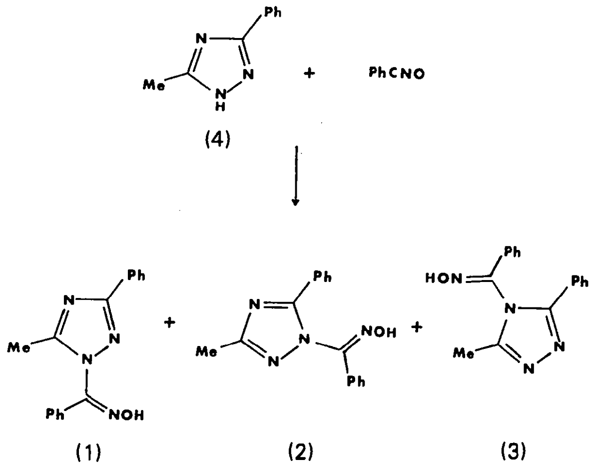
Abstract. (1): $C_{16}H_{14}N_4O$, $M_r = 278{\cdot}3$, orthorhombic, *Pbca*, $a = 23{\cdot}001\,(3)$, $b = 13{\cdot}155\,(2)$, $c = 9{\cdot}526\,(1)$ Å, $V = 2882{\cdot}4\,(6)$ Å^3, $Z = 8$, $D_x = 1{\cdot}28$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}78$ cm^{-1}, $F(000) = 1168$, $T = 293$ K, $R = 0{\cdot}054$ for 823 independent reflections. (3): $C_{16}H_{14}N_4O$, $M_r = 278{\cdot}3$, monoclinic, $P2_1/n$, $a = 9{\cdot}869\,(1)$, $b = 12{\cdot}656\,(2)$, $c = 12{\cdot}939\,(2)$ Å, $\beta = 108{\cdot}8\,(1)°$, $V = 1530\,(1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}21$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}74$ cm^{-1}, $F(000) = 584$, $T = 293$ K, $R = 0{\cdot}047$ for 1040 independent reflections. The reaction of benzonitrile oxide with N-unsubstituted 1,2,4-triazoles yields *N*-benzoyl oximes by nucleophilic addition at the dipole. In (1) and in (3) the heterocyclic ring is planar. The dihedral angles between the mean plane of the benzene ring and that of the triazole ring are 7·6 (2) and 35·9 (2)° for (1) and (3), respectively. The oxime fragment in both isomers is nearly perpendicular with respect to the triazole ring and has *Z* configuration.

Introduction. The reaction between N-unsubstituted 1,2,4-triazoles and benzonitrile oxide occurs by the 1,3-addition mechanism leading to the formation of *N*-benzoyl oximes (Foti, Grassi, Caruso, Risitano & Bruno, 1987). Depending on the symmetrical or unsymmetrical C-substitution, 1,2,4-triazoles would be expected to yield two or three isomeric oximes, respectively. In order to test this, 5-methyl-3-phenyl-1,2,4-triazole (4) was selected as a model substance and was reacted with benzonitrile oxide (scheme below).



Three products were isolated, the elemental compositions of which, $C_{16}H_{14}N_4O$, were identical. The chemical nature of these isomers (1), (2) and (3) was established from spectroscopic data (Table 1) and the X-ray analysis was carried out to confirm the structures of the 1- (1) and the 4-substituted (3) derivatives. In agreement with previous results (Uda, Hisazumi, Sato & Kubota, 1976), the nucleophilic addition

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Table 1. *Physical and spectral data*

Compound*	M.p.(K)	Yield%	ν(CN)†	$\delta_{\text{arom.}}$‡	δ_{OH}‡	δ_{Me}‡
(1)	524	60	1642	7·40(8H), 7·8–8·14(2H)	12·38	2·41
(2)	478	14	1631	7·40(8H), 7·57–7·8(2H)	11·97	2·44
(3)	469	4	1619	7·35(10H)	12·58	2·24

* All compounds gave satisfactory microanalyses (C ±0·25%; H ±0·10%; N ±0·15%).

† (cm^{-1}) Nujol mull.

‡ In DMSO-d_6 solutions with respect to tetramethylsilane ($\delta = 0$).

occurred preferentially at the N1 atom next to the electron-releasing group, with predominant formation of the isomer (1).

Experimental. IR spectra were recorded for Nujol mulls on a Perkin-Elmer 682 spectrophotometer and ^{1}H NMR spectra were obtained using a Perkin-Elmer R24A instrument (60 MHz) with DMSO-d_6 solution containing tetramethylsilane as reference. To a stirred solution of 5-methyl-3-phenyl-1,2,4-triazole (5 mmol) in benzene/tetrahydrofuran (2:1) (80 ml) was added dropwise benzonitrile oxide (10 mmol) in ice-cooled ether (40 mmol). After removal of ether, the reaction mixture was refluxed for 2 h. Then the solvent was evaporated under reduced pressure, and the residue chromatographed on silica gel (70–230 mesh). Elution with chloroform gave 3,4-diphenylfuroxan and the oximes described in Table 1.

Crystals suitable for X-ray analysis were obtained by recrystallization from methanol solutions. Crystals of dimensions 0·15 × 0·12 × 0·10 mm (1) and 0·10 × 0·11 × 0·16 mm (3) were used for intensity-data collection at 293 K with a Siemens–Stoe four-circle diffractometer using graphite-monochromated Mo $K\alpha$ ($\lambda = 0{\cdot}71069$ Å) radiation. Accurate unit-cell dimensions and crystal orientation matrices were obtained from least-squares refinement of 2θ, ω, χ and φ values of 20 strong reflections in the range $12 < 2\theta < 22°$. Crystals and electronic stability were confirmed by the constancy of three check reflections measured every 100 min of X-ray exposure. Of 1890 and 1650 independent reflections measured by the $\omega/2\theta$ scan technique, in the range $3 < 2\theta < 46°$ [(1) $h\,0\rightarrow24$, $k\,0\rightarrow14$, $l\,0\rightarrow10$; (3) $h\,-11\rightarrow10$, $k\,0\rightarrow13$, $l\,0\rightarrow13$] 823 and 1040 ($R_{\text{int}} = 0{\cdot}022$, 0·018) having net intensity $I > 3\sigma(I)$ were used in the solution and refinement of the structure. Corrections for Lorentz and polarization effects were made, but not for absorption ($\mu = 0{\cdot}78$ and 0·74 cm^{-1}).

The structures were solved by direct methods with the *MULTAN*80 system (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); subsequent calculations were mainly carried out by the *SHELX*76 (Sheldrick, 1976) and *PARST* (Nardelli, 1983) systems of programs on the IBM 4341 computer at the 'Centro di Calcolo dell'Università di Messina'. All the H atoms, found from the difference Fourier map, were added at calculated positions (C—H distance 0·98 Å) and included in the structure factor calculations with a common thermal parameter ($U = 0{\cdot}06$ Å^2). Structure (1) at the last stages was isotropically and anisotropically refined by the full-matrix least-squares method, while (3) was refined anisotropically. The final values were, for (1) $R = 0{\cdot}054$ and $wR = 0{\cdot}061$, for (3) 0·047 and 0·051. For (1), weighting scheme was $w = 1{\cdot}5569/[\sigma^2(F_o) + 0{\cdot}003188F_o^2]$, $S = 1{\cdot}29$; $w = 0{\cdot}238/[\sigma^2(F_o) + 0{\cdot}0177F_o^2]$, $S = 0{\cdot}50$ for (3). Final

Table 2. *Atomic coordinates* (× 10^4) *and equivalent isotropic thermal parameters* (Å^2 × 10^2) *for non*-H *atoms, with e.s.d.'s in parentheses, for* (1)

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

	x	y	z	$U_{\text{iso}}/U_{\text{eq}}$*
N1	3117 (2)	4623 (3)	8635 (5)	39 (2)*
N2	3594 (2)	4801 (4)	9465 (6)	44 (2)*
C3	3491 (3)	5714 (4)	9978 (7)	35 (2)*
N4	2979 (2)	6135 (4)	9529 (5)	41 (2)*
C5	2758 (3)	5427 (5)	8675 (7)	42 (2)*
C51	2217 (3)	5465 (5)	7850 (9)	62 (3)*
C21	3105 (3)	3749 (4)	7763 (7)	40 (2)*
N3	2776 (2)	2984 (4)	8014 (6)	50 (2)*
O1	2457 (2)	3106 (3)	9252 (5)	55 (2)*
C23	3662 (3)	2849 (5)	5885 (8)	51 (2)
C24	4045 (3)	2868 (5)	4763 (8)	62 (2)
C25	4272 (3)	3779 (6)	4305 (9)	71 (2)
C26	4118 (3)	4671 (5)	4933 (9)	71 (2)
C27	3725 (3)	4665 (6)	6057 (8)	61 (2)
C22	3500 (3)	3746 (5)	6543 (7)	43 (2)
C32	3752 (3)	7121 (5)	11606 (8)	58 (2)
C33	4148 (3)	7588 (6)	12516 (10)	71 (2)
C34	4671 (3)	7145 (5)	12763 (8)	69 (2)
C35	4818 (3)	6263 (6)	12128 (8)	70 (2)
C36	4427 (3)	5783 (5)	11215 (7)	57 (2)
C31	3893 (3)	6218 (5)	10958 (6)	40 (2)

* Starred atoms were refined anisotropically.

Table 3. *Atomic coordinates* (× 10^4) *and equivalent isotropic thermal parameters* (Å^2 × 10^2) *for non*-H *atoms, with e.s.d.'s in parentheses, for* (3)

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

	x	y	z	U_{eq}
O1	2159 (4)	1625 (2)	7783 (3)	56 (2)
N3	2055 (4)	1598 (3)	8825 (3)	47 (2)
N2	4876 (4)	4294 (3)	8641 (3)	43 (2)
C21	2629 (5)	2404 (3)	9390 (4)	39 (2)
N4	3290 (4)	3231 (2)	8942 (3)	38 (2)
N1	3521 (4)	4724 (3)	8174 (3)	46 (2)
C5	2583 (5)	4029 (3)	8357 (4)	46 (2)
C51	994 (6)	4200 (4)	7984 (5)	72 (2)
C3	4724 (5)	3405 (3)	9102 (4)	37 (2)
C31	5882 (5)	2682 (3)	9680 (4)	46 (2)
C32	5720 (6)	1591 (4)	9606 (5)	70 (3)
C33	6834 (9)	931 (5)	10119 (7)	93 (4)
C34	8139 (9)	1334 (6)	10721 (6)	93 (4)
C35	8314 (7)	2414 (7)	10805 (5)	88 (3)
C36	7201 (6)	3089 (5)	10289 (5)	66 (2)
C22	2678 (4)	2516 (3)	10538 (4)	41 (2)
C23	2138 (5)	1728 (4)	11057 (4)	52 (2)
C24	2217 (6)	1843 (4)	12145 (4)	64 (2)
C25	2813 (6)	2729 (5)	12717 (4)	68 (2)
C26	3349 (6)	3529 (5)	12214 (4)	71 (3)
C27	3285 (6)	3410 (3)	11142 (4)	54 (2)

Table 4. *Bond lengths* (Å), *bond angles* (°) *and some relevant torsion angles* (°) *for* (1)

N1–N2	1·373 (6)	N1–C5	1·342 (7)
N1–C21	1·419 (7)	N2–C3	1·317 (7)
C3–N4	1·370 (7)	C3–C31	1·472 (8)
C5–N4	1·337 (7)	C5–C51	1·472 (8)
C21–N3	1·282 (7)	C21–C22	1·476 (8)
N3–O1	1·398 (6)	C23–C22	1·387 (8)
C23–C24	1·385 (9)	C24–C25	1·378 (9)
C25–C26	1·364 (9)	C26–C27	1·401 (10)
C22–C27	1·394 (8)	C31–C32	1·376 (8)
C32–C33	1·400 (9)	C33–C34	1·356 (9)
C34–C35	1·351 (9)	C35–C36	1·401 (9)
C36–C31	1·378 (8)		

O1–N3–C21	112·2 (5)	N3–C21–C22	120·6 (6)
N3–C21–N1	122·6 (6)	N1–C21–C22	116·8 (5)
C21–N1–C5	130·0 (5)	C21–N1–N2	119·4 (5)
N2–N1–C5	109·9 (5)	N1–N2–C3	103·0 (5)
N2–C3–N4	114·0 (5)	N2–C3–C31	122·2 (5)
C31–C3–N4	123·8 (5)	C3–N4–C5	103·6 (5)
N4–C5–N1	109·4 (5)	N4–C5–C51	128·5 (5)
N1–C5–C51	122·1 (6)	C21–C22–C27	119·2 (6)
C23–C24–C25	120·1 (7)	C22–C23–C24	120·2 (6)
C21–C22–C23	121·5 (6)	C24–C25–C26	120·7 (7)
C25–C26–C27	119·8 (6)	C26–C27–C22	119·9 (6)

N2–C3–C31–C32	−172·8 (6)	N2–N1–C21–C22	−70·4 (7)
N1–C21–N3–O1	−2·2 (8)	N1–C21–C22–C23	159·6 (6)
N2–N1–C5–C51	178·2 (6)		

Table 5. *Bond lengths* (Å), *bond angles* (°) *and some relevant torsion angles* (°) *for* (3)

O1–N3	1·384 (6)	N3–C21	1·277 (5)
N2–N1	1·389 (5)	N2–C3	1·304 (6)
C21–N4	1·450 (6)	C21–C22	1·477 (8)
N1–C5	1·311 (6)	N4–C3	1·380 (6)
N4–C5	1·368 (5)	C5–C51	1·493 (7)
C3–C31	1·467 (6)	C31–C32	1·390 (6)
C31–C36	1·386 (7)	C32–C33	1·370 (9)
C33–C34	1·371 (11)	C34–C35	1·377 (12)
C35–C36	1·383 (9)	C22–C23	1·400 (7)
C22–C27	1·395 (6)	C23–C24	1·393 (8)
C24–C25	1·367 (8)	C25–C26	1·397 (9)
C26–C27	1·376 (8)		

O1–N3–C21	112·3 (3)	N3–C21–C22	121·2 (4)
N4–C21–C22	117·4 (3)	C21–N4–C3	128·8 (3)
C21–N4–C5	124·9 (4)	C5–N4–C3	105·9 (3)
N4–C5–N1	108·9 (4)	N4–C5–C51	123·7 (4)
N1–C5–C51	127·4 (4)	C5–N1–N2	108·3 (4)
N1–N2–C3	107·5 (4)	N2–C3–N4	109·3 (4)
N2–C3–C31	125·9 (4)	N4–C3–C31	124·8 (4)
C21–C22–C23	121·3 (4)	C21–C22–C27	120·7 (4)
C22–C23–C24	120·2 (5)	C25–C26–C27	119·2 (5)
C26–C27–C22	121·7 (4)		

N2–C3–C31–C36	35·5 (7)	C3–N4–C5–C51	178·7 (5)
C3–N4–C21–N3	−101·3 (6)	N4–C21–C22–C23	−176·4 (4)
N4–C21–N3–O1	0·3 (6)	C22–C21–N3–O1	−178·0 (4)

difference map peaks were in the range 0·24, $-0{\cdot}28\ \mathrm{e\ \AA^{-3}}$, $(\Delta/\sigma)_{\max} = 0{\cdot}11$ for (1) and 0·22, $-0{\cdot}20\ \mathrm{e\ \AA^{-3}}$, $(\Delta/\sigma)_{\max} = 0{\cdot}45$ for (3). Scattering factors for the non-H atoms were taken from Cromer & Mann (1968) and for H atoms from Stewart (1970).

Discussion. Fractional atomic coordinates and equivalent isotropic temperature factors for non-H atoms are given in Tables 2 and 3,* bond lengths, interbond angles and some relevant torsion angles in Tables 4 and 5. Figs. 1 and 2 show the molecules, including the labeling schemes.

Both molecules (1) and (3) may be divided into three parts: (i) 5-methyl-1,2,4-triazole ring, (ii) benzene ring (*A*) and (iii) benzoyl oxime group. This last is in the 1- or 4-position on the triazole ring of (1) and (3), respectively.

The atom-to-plane distances (Å) for the weighted least-squares plane were calculated through the triazole rings. The benzene ring (*A*) of (1) may be partially conjugated with the heterocyclic system, as suggested

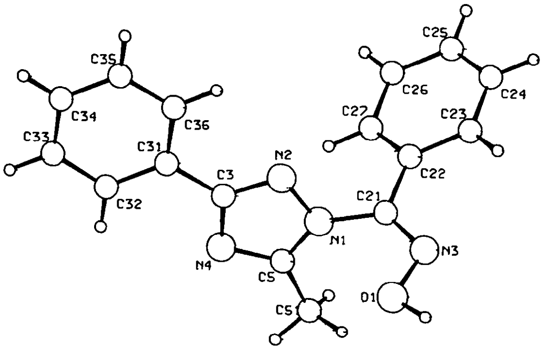

Fig. 1. Molecular structure of (1) with crystallographic numbering scheme.

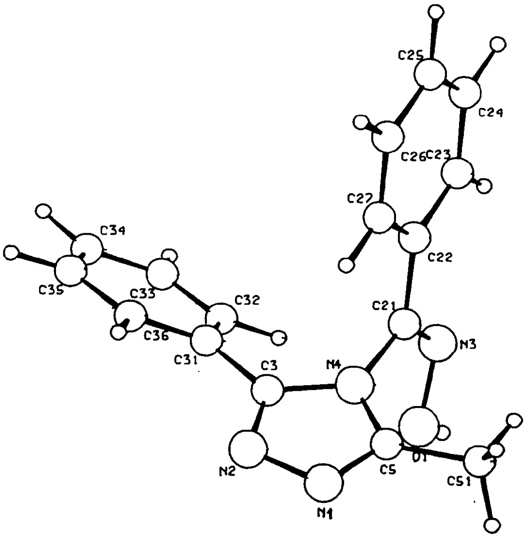

Fig. 2. Molecular structure of (3) with crystallographic numbering scheme.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and significant intra- and intermolecular contacts have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51445 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

by the dihedral angle of 7·6 (2)° between the two rings and the C3—C31 bond length [1·472 (8) Å]; corresponding values for (3) are 35·9 (2)° and 1·467 (6) Å, indicating less conjugation. All the C—N and the N—N bond distances in the heterocyclic rings are intermediate between the expected single- and double-bond lengths. The sums of the valency angles around N1 and N4 in (1) and (3) are 359·3 and 359·6° respectively, indicating no significant pyramidalization of these atoms. From the above results, it is suggested that the triazole rings have aromatic character and the hybridization of the exocyclic nitrogen atom is of the sp^2 type. As in previous reports (Branch & Nowell, 1985, 1986), the exocyclic angles around the N1 atom in compound (1) show considerable asymmetry: C21—N1—C5 [130·0 (5)°] being much larger than C21—N1—N2 [119·4 (5)°]; this asymmetry is also usual in 1,2,3-triazoles (Nagawa, Goto, Honda & Nakanishi, 1987). In molecules (1) and (3), bond angles around C3 are essentially symmetrical, but at C5 there is also a pronounced asymmetry: in (1), N4—C5—C51 and C51—C5—N1 are 128·5 (5) and 122·1 (6)° respectively, while in (3) they are 123·7 (4) and 127·4 (4)° respectively. The benzoyl oxime group is linked to N1 in (1) and to N4 in (3), of the triazole ring. Steric requirements lead the oxime group to be oriented nearly perpendicularly with respect to the heterocyclic ring, as can be seen from the torsion angles C5—N1—C21—N3 [−81·5 (7)°] for (1) and C5—N4—C21—N3 [86·6 (6)°] for (3). C21—N3 bond distances are 1·282 (7) and 1·277 (5) Å, while N3—O1 bond distances are 1·398 (6) and 1·384 (6) Å for (1) and (3) respectively. These values are in the range 1·22 to 1·33 Å for the C—N and 1·357 to 1·439 Å for the N—O bonds (Diànez, Vega, Lòpez-Castro & Màrquez, 1986, and references therein). The oxime configuration in both isomers is *Z*. The benzene ring linked to C21 at 1·476 (8) and 1·477 (8) Å makes angles of 159·3 (5)° and 3·6 (4)° with respect to the C=N—OH fragments of (1) and (3) respectively. This indicates that in (3) there is conjugation over the system.

There are several C···C, C···N, C···C and O···N inter- and intramolecular contacts less than the sums of the van der Waals radii. Some of these, involving the O atom of the oxime group, can be properly described as hydrogen bonds.

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The Structure of 10,11-Dihydro-10-hydroxy-5*H*-dibenz[*b*,*f*]azepine-5-carboxamide, an Anticonvulsant Drug Molecule

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Abstract. $C_{15}H_{14}N_2O_2$, $M_r = 253·40$, orthorhombic, *Pbca*, $a = 7·891$ (5), $b = 13·649$ (8), $c = 23·534$ (4) Å, $V = 2534·7$ (1) Å^3, $Z = 8$, $D_m = 1·33$, $D_x = 1·33$ g cm^{-3}, λ(Cu $K\alpha$) = 1·54184 Å, $\mu = 5·93$ cm^{-1}, $F(000) = 1064$, $T = 293$ K, $R = 0·038$ for 1058 observed reflections. The central azepine ring exists in a twist-boat conformation. Intermolecular hydrogen bonds are formed involving the amide N and hydroxyl O atoms [N···O = 2·916 (7) Å, N—H···O = 161 (5)°], and between the hydroxyl and carbonyl O atoms [O···O = 2·675 (7) Å, O—H···O = 166 (5)°].

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