

Structure of Phenyl α -[(α -Phenylbenzyl)imino]benzyl Ketone

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Abstract. $C_{27}H_{21}NO$, $M_r = 375.5$, $P2_1/n$, $a = 15.347$ (2), $b = 9.0877$ (5), $c = 15.205$ (1) Å, $\beta = 100.850$ (6)°, $Z = 4$, $V = 2082.7$ (5) Å³, $F(000) = 792$, $D_x = 1.197$ g cm⁻³. The structure was solved by direct methods. Two sets of data were taken (Mo and Cu radiations) and the data obtained from Cu radiation were refined to $R = 0.051$ and $R_w = 0.052$ for 2789 observed reflexions. Comparison with other imines shows that the introduction of a new phenyl ring does not affect the bond distances and bond angles but causes a distortion in the central C–C=N–C skeleton.

Introduction. The structural characterization of some derivatives of benzyl imines involving various types of substituents has been reported (Fonseca, Martínez-Carrera & García-Blanco, 1979). In this paper the effect of the volume of the substituents on the molecular geometry has been studied. A colorless crystal of the title compound ($0.45 \times 0.27 \times 0.16$ mm) elongated along **b** was used for obtaining both Weissenberg and precession photographs and intensity data on a Philips PW 1100 four-circle diffractometer, with graphite-monochromatized Mo $K\alpha$ radiation. The space group was found to be $P2_1/n$ and the cell parameters were refined using 33 reflexions centered on the diffractometer. Intensity data were collected by the ω - 2θ scan technique out to a maximum θ value of 23°. Two reflexions monitored at regular intervals showed that the crystal was stable to X-rays. The reflexions used in the analysis were corrected for Lorentz and polarization factors but not for absorption. The experimental data are given in Table 1. The structure was solved by the multisolution procedure of *MULTAN 77* (Main, Lessinger, Woolfson, Germain &

Declercq, 1977). The solution was based on phases determined for 200 reflexions with $E_{Mo} > 1.95$. The E map with the best figure of merit revealed the positions of all the non-hydrogen atoms and several cycles of isotropic and anisotropic refinement were carried out; however, the low ratio of observations to variables made the anisotropic refinement difficult, so a new set of data with Cu $K\alpha$ radiation was collected. The same crystal was used and the data collection, carried out with the ω - 2θ scan technique up to $\theta = 65^\circ$, again proceeded as above. Lorentz and polarization factors were applied but no correction was made for absorption (Table 1). All full-matrix least-squares refinements in this analysis were performed with the XRAY

Table 2. Positional parameters ($\times 10^5$) and equivalent isotropic thermal parameters (Å² $\times 10^4$) for the non-hydrogen atoms, with *e.s.d.*'s in parentheses

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j \cos(a_i a_j).$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
C(1)	35270 (10)	37073 (17)	37893 (10)	532 (5)
C(2)	29441 (12)	41636 (20)	30216 (11)	602 (5)
C(3)	30351 (14)	36021 (24)	21991 (13)	744 (7)
C(4)	36767 (15)	25982 (27)	21289 (14)	851 (8)
C(5)	42519 (16)	21521 (29)	28771 (17)	933 (9)
C(6)	41869 (12)	27017 (24)	37052 (13)	744 (7)
C(7)	34468 (10)	42377 (17)	46853 (10)	546 (5)
C(8)	26983 (10)	52896 (17)	47868 (10)	528 (5)
C(9)	29476 (11)	68633 (18)	49315 (10)	582 (5)
C(10)	36888 (12)	74177 (21)	46399 (14)	737 (6)
C(11)	39020 (15)	88976 (24)	47441 (17)	880 (8)
C(12)	33978 (19)	98109 (23)	51651 (17)	951 (9)
C(13)	26746 (21)	92641 (24)	54647 (16)	958 (10)
C(14)	24335 (15)	77978 (21)	53403 (13)	762 (7)
C(15)	16601 (10)	33340 (17)	46661 (11)	559 (5)
C(16)	14554 (11)	27065 (19)	55364 (11)	606 (5)
C(17)	20409 (14)	29652 (23)	63313 (12)	742 (7)
C(18)	19178 (18)	23001 (31)	71193 (14)	935 (9)
C(19)	12147 (20)	13808 (34)	71254 (16)	1027 (11)
C(20)	6207 (19)	11444 (34)	63462 (18)	1048 (11)
C(21)	7396 (15)	18014 (27)	55537 (14)	834 (8)
C(22)	9003 (10)	32222 (17)	38720 (10)	556 (5)
C(23)	9300 (12)	21812 (22)	32186 (12)	703 (6)
C(24)	2443 (16)	20362 (27)	24944 (13)	847 (8)
C(25)	-4793 (16)	29377 (29)	24116 (14)	874 (8)
C(26)	-5186 (14)	39784 (28)	30530 (16)	887 (8)
C(27)	1686 (13)	41317 (22)	37812 (13)	720 (6)
O	39519 (9)	38571 (16)	53599 (8)	774 (5)
N	19083 (9)	48907 (14)	48010 (9)	580 (4)

Table 1. Experimental data

Radiation	Mo $K\alpha$	Cu $K\alpha$
λ (Å)	0.71069	1.5418
Technique	$\omega/2\theta$	$\omega/2\theta$
θ (max.) (°)	25	65
μ (cm ⁻¹)	0.78	5.71
Criterion for observed reflexions	$I > 3\sigma(I)$	$I > 2\sigma(I)$
No. of observed reflexions	1684	2789
Total No. of reflexions	3695	3799
No. of reflexions/No. of parameters	5	8

Table 3. *Positional parameters* ($\times 10^3$) and *isotropic thermal parameters* ($\text{\AA}^2 \times 10^3$) for the H atoms, with *e.s.d.'s in parentheses*

The thermal parameter is of the form $\exp(-8\pi^2 U \sin^2 \theta/\lambda^2)$.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
H(12)	355 (2)	1087 (3)	526 (2)	74 (7)
H(13)	228 (2)	984 (3)	574 (2)	81 (8)
H(2)	248 (1)	489 (2)	310 (1)	42 (5)
H(3)	263 (2)	389 (3)	168 (2)	71 (7)
H(4)	373 (2)	217 (3)	154 (2)	72 (7)
H(5)	473 (2)	147 (3)	281 (2)	85 (8)
H(6)	459 (1)	241 (3)	426 (1)	62 (6)
H(10)	408 (2)	674 (3)	435 (2)	72 (7)
H(11)	444 (2)	929 (3)	453 (2)	88 (8)
H(14)	190 (1)	740 (2)	553 (1)	53 (6)
H(15)	217 (1)	274 (2)	452 (1)	28 (4)
H(17)	256 (2)	361 (3)	633 (2)	64 (6)
H(18)	235 (2)	259 (3)	766 (2)	87 (8)
H(19)	113 (2)	92 (3)	766 (2)	88 (8)
H(20)	6 (2)	51 (4)	634 (2)	101 (10)
H(21)	28 (1)	169 (3)	498 (1)	58 (6)
H(23)	145 (2)	156 (3)	329 (2)	60 (6)
H(24)	24 (2)	128 (3)	201 (2)	76 (7)
H(25)	-97 (2)	280 (3)	189 (2)	73 (7)
H(26)	-100 (2)	464 (3)	301 (2)	79 (8)
H(27)	16 (1)	488 (2)	424 (1)	49 (5)

Table 4. *Bond distances* (\AA) for non-hydrogen atoms, with *e.s.d.'s in parentheses*

C(1)–C(2)	1.393 (2)	C(13)–C(14)	1.386 (3)
C(1)–C(6)	1.388 (3)	C(15)–C(16)	1.527 (3)
C(1)–C(7)	1.472 (2)	C(15)–C(22)	1.516 (2)
C(2)–C(3)	1.382 (2)	C(15)–N	1.469 (2)
C(3)–C(4)	1.361 (3)	C(16)–C(17)	1.384 (2)
C(4)–C(5)	1.364 (3)	C(16)–C(21)	1.377 (3)
C(5)–C(6)	1.375 (3)	C(17)–C(18)	1.386 (3)
C(7)–C(8)	1.524 (2)	C(18)–C(19)	1.366 (4)
C(7)–O	1.214 (2)	C(19)–C(20)	1.369 (4)
C(8)–C(9)	1.486 (2)	C(20)–C(21)	1.387 (4)
C(8)–N	1.270 (2)	C(22)–C(23)	1.379 (3)
C(9)–C(10)	1.391 (3)	C(22)–C(27)	1.380 (3)
C(9)–C(14)	1.384 (3)	C(23)–C(24)	1.379 (3)
C(10)–C(11)	1.386 (3)	C(24)–C(25)	1.367 (4)
C(11)–C(12)	1.373 (4)	C(25)–C(26)	1.368 (4)
C(12)–C(13)	1.370 (4)	C(26)–C(27)	1.385 (3)

system (Stewart, Kundell & Baldwin, 1970). The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). After several cycles of isotropic and anisotropic refinement the conventional *R* index reduced to 0.125. The H atoms were then located by a difference Fourier synthesis and included in further refinement with individual isotropic temperature factors. A suitable weighting scheme (Martinez-Ripoll & Cano, 1975) was applied in order to prevent bias in wF_o or $\sin \theta/\lambda$. The final derived values of *R* and R_w were 0.051 and 0.052 respectively. A difference Fourier map following the last cycle of least-squares refinement revealed no significant residual electron density; the highest peak

Table 5. *Bond angles* ($^\circ$) for non-hydrogen atoms, with *e.s.d.'s in parentheses*

C(6)–C(1)–C(7)	119.4 (2)	C(9)–C(14)–C(13)	119.4 (2)
C(2)–C(1)–C(7)	121.7 (2)	C(22)–C(15)–N	108.4 (1)
C(2)–C(1)–C(6)	118.9 (2)	C(16)–C(15)–N	109.2 (1)
C(1)–C(2)–C(3)	119.3 (2)	C(16)–C(15)–C(22)	114.4 (1)
C(2)–C(3)–C(4)	121.1 (2)	C(15)–C(16)–C(21)	122.3 (2)
C(3)–C(4)–C(5)	119.9 (2)	C(15)–C(16)–C(17)	119.2 (2)
C(4)–C(5)–C(6)	120.6 (2)	C(17)–C(16)–C(21)	118.3 (2)
C(1)–C(6)–C(5)	120.2 (2)	C(16)–C(17)–C(18)	120.6 (2)
C(1)–C(7)–O	122.5 (2)	C(17)–C(18)–C(19)	120.6 (3)
C(1)–C(7)–C(8)	119.7 (1)	C(18)–C(19)–C(20)	119.2 (3)
C(8)–C(7)–O	117.8 (2)	C(19)–C(20)–C(21)	120.6 (3)
C(10)–C(8)–N	124.3 (2)	C(16)–C(21)–C(20)	120.6 (2)
C(7)–C(8)–C(9)	116.1 (1)	C(15)–C(22)–C(27)	121.9 (2)
C(9)–C(8)–N	119.5 (2)	C(15)–C(22)–C(23)	119.7 (2)
C(8)–C(9)–C(14)	120.3 (2)	C(23)–C(22)–C(27)	118.4 (2)
C(8)–C(9)–C(10)	120.3 (2)	C(22)–C(23)–C(24)	121.2 (2)
C(10)–C(9)–C(14)	119.4 (2)	C(23)–C(24)–C(25)	120.1 (2)
C(9)–C(10)–C(11)	120.3 (2)	C(24)–C(25)–C(26)	119.5 (2)
C(10)–C(11)–C(12)	119.9 (2)	C(25)–C(26)–C(27)	120.7 (2)
C(11)–C(12)–C(13)	119.9 (2)	C(22)–C(27)–C(26)	120.2 (2)
C(12)–C(13)–C(14)	121.0 (2)	C(8)–N–C(15)	119.7 (2)

was 0.34 e \AA^{-3} . The final positional parameters for non-hydrogen atoms are given in Table 2, for H atoms in Table 3; bond-length and bond-angle data are listed in Tables 4 and 5.*

Discussion. An *ORTEP* view (Johnson, 1965) of the molecule is shown in Fig. 1 together with the atomic numbering scheme. The phenyl rings have been labeled *A*, *B*, *C* and *E*, and the central skeleton is labeled *D*. Bond distances and bond angles are not affected by the introduction of a new phenyl ring at C(15). Weighted average values (Sutton, 1958) of bond distances and bond angles in the phenyl rings are: (*A*) 1.380 (5) \AA , 120.1 (3) $^\circ$; (*B*) 1.383 (3) \AA , 120.0 (2) $^\circ$; (*C*) 1.380 (3) \AA , 119.3 (4) $^\circ$; (*E*) 1.378 (1) \AA , 120.0 (4) $^\circ$, with ranges 1.361 (3)–1.393 (2) \AA and 118.3 (2)–121.2 (2) $^\circ$. The distances C(7)–O and C(8)–N are not significantly different from those in previously studied compounds (Fonseca, Martinez-Carrera & Garcia-Blanco, 1979, 1982); the distance C(7)–C(8), significantly longer than those found in the literature (Drew, Vickery & Willey, 1981), and the displacement of the O atom out of the C(7)–C(8)–N–C(15) plane indicates the absence of conjugation effects in the O–C(7)–C(8)–N sequence. However, the bulky substituents at C(15) cause an appreciable distortion from planarity of the central skeleton as indicated by the sum of the squares of the ratios $\sum_i (d/\sigma)_i^2 = 190.6$ for the displacements of the atoms from the weighted least-squares plane (Nardelli, Musatti, Domiano & Andreotti, 1965). Some relevant torsion angles are reported in Table 6; they show how

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38023 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

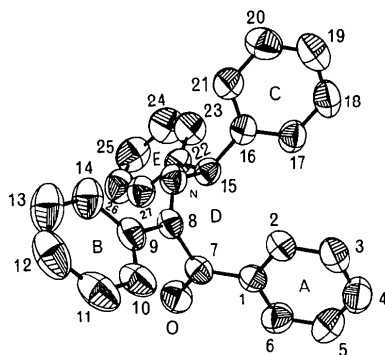


Fig. 1. An ORTEP view of the molecule with the atomic numbering.

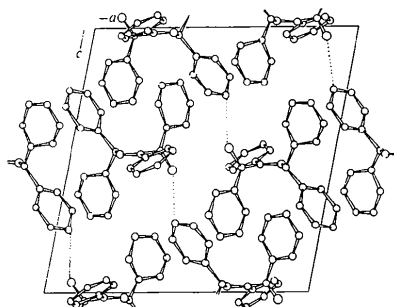


Fig. 2. The molecular packing viewed down *b*. Dotted lines indicate intermolecular distances less than 3.5 Å [3.483 (3) Å].

Table 6. Selected torsion angles (°)

C(2)–C(1)–C(7)–C(8)	1.3 (2)	C(7)–C(8)–C(9)–C(10)	24.6 (2)
C(6)–C(1)–C(7)–O	1.9 (3)	C(7)–C(8)–N–C(15)	–3.4 (2)
C(1)–C(7)–C(8)–N	81.2 (3)	C(16)–C(15)–N–C(8)	112.3 (2)
C(1)–C(7)–C(8)–C(9)	–102.7 (2)	C(22)–C(15)–N–C(8)	–122.5 (2)
O–C(7)–C(8)–N	–98.0 (2)	N–C(15)–C(16)–C(21)	137.0 (2)
O–C(7)–C(8)–C(9)	78.2 (2)	N–C(15)–C(22)–C(23)	133.0 (2)

Table 7. Dihedral angles (°)

A \wedge B	90.4 (1)	B \wedge E	68.6 (1)	B \wedge D	22.8 (1)
B \wedge C	100.2 (1)	C \wedge E	95.2 (1)	C \wedge D	86.5 (1)
A \wedge E	24.0 (1)	A \wedge D	78.8 (1)	E \wedge D	54.9 (1)
B \wedge C	103.8 (1)				

the molecule is distorted from planarity. The dihedral angles between the planes through the different parts of the molecule are listed in Table 7. Packing of the molecules in the unit cell is shown in Fig. 2; the intermolecular distance C(25)–O less than 3.5 Å (3.483 Å) is marked by the dotted line; the structure is stabilized by van der Waals interactions.

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1,4,5,8-Naphthalenetetrone

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Abstract. C₁₀H₄O₄, monoclinic, *P*2₁/*n*, *a* = 6.510 (4), *b* = 13.220 (5), *c* = 4.855 (4) Å, β = 110.0 (5)°, *D*_x = 1.592 g cm^{–3} for *Z* = 2. The compound crystallizes as yellow needles. The structure was refined to *R*_F = 0.07, using 1102 *I* measured on a four-circle diffractom-

eter (Mo *K*α). The molecules have (almost exactly) 2/*m* symmetry, with the twofold axis along C(9)–C(10); the carbonyl oxygens are displaced by ±0.265 Å from the plane through the central six C atoms. The molecular shape differs overall from that of