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1-(4-Bromobenzoyl)-2,5-dimethyl-4-morpholino-5-phenyl-4,5-dihydroimidazole

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Abstract. $C_{22}H_{24}BrN_3O_2$, $M_r = 442 \cdot 4$, orthorhombic, *Pbca*, $a = 10 \cdot 356$ (1), $b = 14 \cdot 691$ (1), $c = 26 \cdot 724$ (1) Å, $Z = 8$, $\mu(Cu\ K\alpha) = 3 \cdot 22$ mm^{-1}, $D_x = 1 \cdot 445$, $D_m = 1 \cdot 438$ Mg m^{-3}. The structure of the monoadduct obtained by reaction of 1-morpholino-2-phenylpropene with N-benzoyl-N'-chloroacetamidine has been established to be that of the title compound. Bond-length extensions [up to $1 \cdot 578$ (3) Å for C(4)—C(5)] and bond-angle deformations are caused by strong steric hindrance between the substituent groups.

Introduction. The reaction (1) of 1-morpholino-2-phenylpropene with N-aroyl-N'-chloroacetamidine gives 1-aroyl-4,5-dihydroimidazole derivatives whose structure could not be determined unequivocally by chemical and spectroscopic methods (Stradi, 1978). In fact, two possible regioisomers can be obtained, 1-aroyl-2,5-dimethyl-4-morpholino-5-phenyl-4,5-dihydroimidazole (I), or 1-aroyl-2,4-dimethyl-5-morpholino-4-phenyl-4,5-dihydroimidazole (II). To establish the structure of the adduct, its X-ray analysis has been undertaken.

Cell dimensions (see *Abstract*) were obtained by a least-squares fit to the $\sin^2 \theta$ values of 60 *hkl* reflexions

measured on a diffractometer. The space group *Pbca* was indicated by the absences 0*kl* with *k* odd, *h*0*l* with *l* odd, and *hk*0 with *h* odd. The density was measured by flotation in a dilute K_2HgI_4 solution. For the data collection a crystal $0 \cdot 34 \times 0 \cdot 25 \times 0 \cdot 22$ mm was mounted on a computer-controlled four-circle diffractometer; graphite-monochromated Cu $K\alpha$ radiation ($\lambda = 1 \cdot 5418$ Å) and a variable θ–2θ scan technique were used. Background measurements were taken at both ends of the scan range, each for a time equal to one half of the scan time. The periodic measurement of two standard reflexions showed no appreciable trend. Out of 3857 measured reflexions ($2\theta \leq 140°$), 802 having $I < \sigma(I)_{c.s.}$ were assigned zero weight; all other reflexions were assigned variances $\sigma^2(I)$ based on counting statistics plus the additional term (0·03 scan count)^2. Diffraction data were corrected for absorption effects (Wehe, Busing & Levy, 1962), and then for Lorentz and polarization factors.

The structure was solved by interpretation of the Patterson map to derive the Br atom position. Subsequent application of direct methods led to an E map from which all non-hydrogen atoms could be clearly

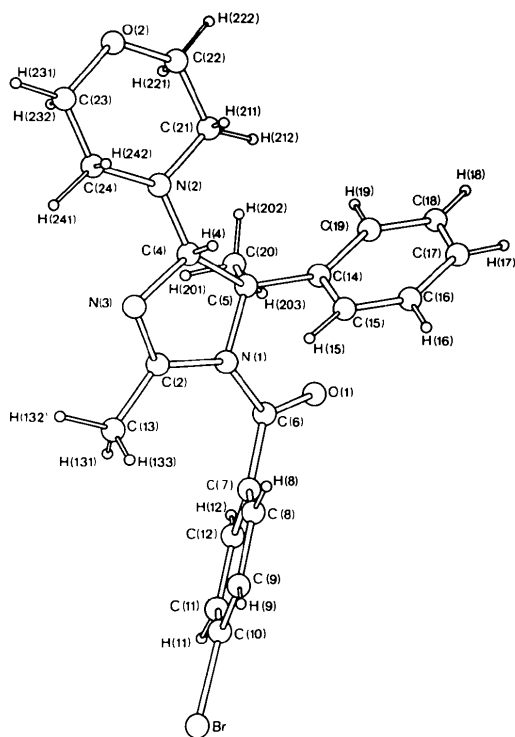(1)   (I)   (II)
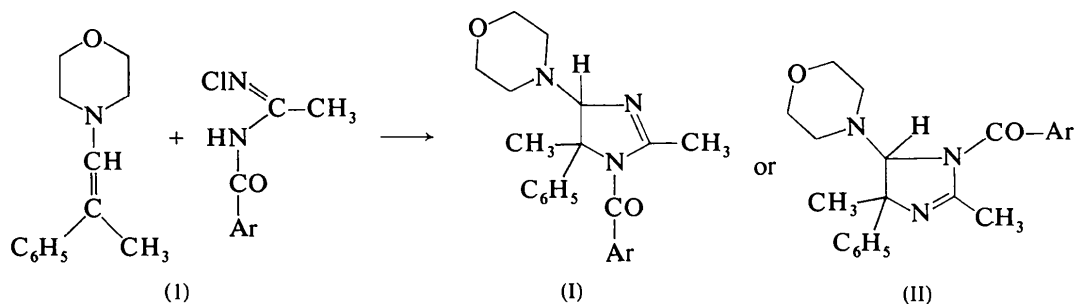
Fig. 1. The molecule viewed along a principal axis of inertia. The numbering scheme is shown.

Table 1. *Positional parameters* ($\times 10^5$) *for non-hydrogen atoms*

E.s.d.'s are in parentheses.

	x	y	z
Br	−368 (5)	65293 (3)	−21535 (1)
C(2)	14437 (26)	62461 (18)	3435 (9)
C(4)	16059 (26)	67114 (18)	11318 (9)
C(5)	1441 (26)	68529 (18)	9846 (9)
C(6)	−7921 (27)	68152 (18)	1181 (9)
C(7)	−5799 (25)	67774 (18)	−4332 (9)
C(8)	2709 (27)	73510 (18)	−6765 (10)
C(9)	4269 (29)	72882 (20)	−11907 (10)
C(10)	−2601 (31)	66482 (18)	−14521 (10)
C(11)	−11258 (32)	60785 (19)	−12184 (10)
C(12)	−12980 (28)	61523 (19)	−7086 (10)
C(13)	18153 (31)	57991 (21)	−1395 (10)
C(14)	−2807 (26)	78313 (20)	10742 (10)
C(15)	2239 (30)	85350 (20)	7847 (12)
C(16)	−1100 (39)	94325 (23)	8600 (15)
C(17)	−9834 (44)	96498 (27)	12359 (18)
C(18)	−14864 (37)	89747 (32)	15276 (15)
C(19)	−11403 (31)	80699 (24)	14525 (12)
C(20)	−7355 (29)	61302 (21)	12075 (10)
C(21)	15151 (34)	68117 (25)	20358 (10)
C(22)	17055 (44)	62764 (30)	25111 (12)
C(23)	32777 (34)	53972 (24)	21474 (11)
C(24)	31322 (29)	58973 (21)	16601 (10)
N(1)	2577 (19)	66906 (14)	4298 (7)
N(2)	18055 (22)	62282 (16)	16045 (7)
N(3)	21892 (21)	62006 (16)	7202 (8)
O(1)	−18626 (19)	69840 (16)	2835 (7)
O(2)	29814 (27)	59544 (18)	25655 (8)

Table 2. *Final coordinates* ($\times 10^4$) *for the hydrogen atoms*

|	x	y	z
H(4)	2017 (22)	7308 (15)	1141 (8)
H(8)	780 (30)	7817 (19)	−521 (10)
H(9)	1027 (27)	7665 (19)	−1364 (10)
H(11)	−1520 (28)	5642 (19)	−1396 (10)
H(12)	−1913 (28)	5745 (20)	−525 (10)
H(131)	1161 (30)	5389 (20)	−259 (11)
H(132)	2575 (32)	5379 (20)	−85 (11)
H(133)	2022 (30)	6242 (20)	−386 (11)
H(15)	855 (28)	8370 (18)	530 (10)
H(16)	236 (33)	9915 (24)	626 (13)
H(17)	−1198 (36)	10272 (23)	1288 (12)
H(18)	−2055 (34)	9079 (23)	1766 (12)
H(19)	−1535 (27)	7603 (18)	1654 (9)
H(201)	−420 (34)	5514 (23)	1115 (12)
H(202)	−727 (30)	6130 (20)	1570 (11)
H(203)	−1603 (31)	6135 (21)	1055 (11)
H(211)	2068 (31)	7357 (21)	2026 (11)
H(212)	564 (31)	7005 (20)	2012 (11)
H(221)	1109 (35)	5742 (24)	2491 (14)
H(222)	1442 (37)	6632 (25)	2802 (13)
H(231)	4214 (32)	5137 (21)	2198 (10)
H(232)	2710 (34)	4860 (22)	2150 (11)
H(241)	3441 (29)	5470 (19)	1374 (10)
H(242)	3705 (27)	6407 (18)	1636 (10)
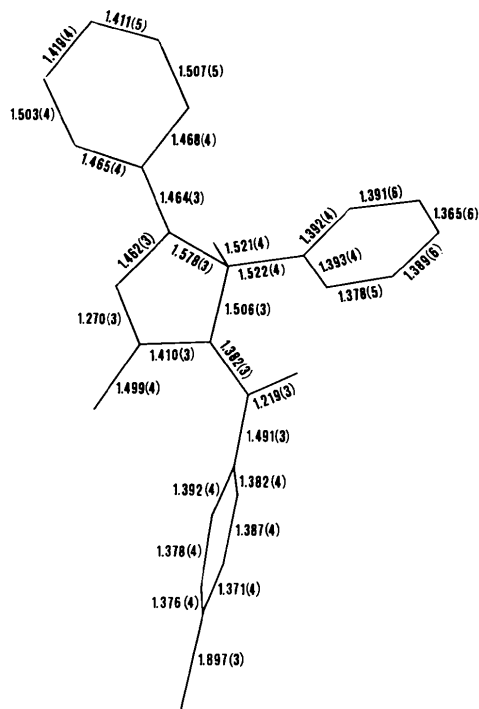
Fig. 2. Bond distances (Å).

located. The positions of the 24 H atoms were derived from difference syntheses during the course of the refinement, which was by least-squares minimization of the quantity $\sum w(|F_o| - |F_c|)^2$, with weights $w = 4F_o^2/\sigma(F_o^2)$. In the final stage (where four reflexions con-

Table 3. *Selected torsion angles* (°)

E.s.d.'s are in the range 0·2–0·4°.

C(4)—N(3)—C(2)—N(1)	−4·9	C(6)—N(1)—C(5)—C(20)	67·8	C(5)—N(1)—C(6)—C(7)	171·2
C(4)—N(3)—C(2)—C(13)	178·6	N(1)—C(5)—C(4)—N(3)	−19·6	C(5)—N(1)—C(6)—O(1)	−6·3
N(3)—C(2)—N(1)—C(5)	−9·1	N(1)—C(5)—C(4)—N(2)	−141·0	O(1)—C(6)—C(7)—C(8)	119·4
N(3)—C(2)—N(1)—C(6)	−175·9	C(14)—C(5)—C(4)—N(3)	−134·0	N(1)—C(5)—C(14)—C(15)	−40·1
C(13)—C(2)—N(1)—C(5)	167·3	C(14)—C(5)—C(4)—N(2)	104·5	C(5)—C(4)—N(2)—C(21)	−74·3
C(13)—C(2)—N(1)—C(6)	0·5	C(20)—C(5)—C(4)—N(3)	95·0	N(2)—C(21)—C(22)—O(2)	60·1
C(2)—N(1)—C(5)—C(4)	17·0	C(20)—C(5)—C(4)—N(2)	−26·5	C(21)—C(22)—O(2)—C(23)	−58·7
C(6)—N(1)—C(5)—C(4)	−174·6	C(5)—C(4)—N(3)—C(2)	16·1	C(22)—O(2)—C(23)—C(24)	57·9
C(2)—N(1)—C(5)—C(14)	133·1	N(2)—C(4)—N(3)—C(2)	140·4	O(2)—C(23)—C(24)—N(2)	−59·2
C(6)—N(1)—C(5)—C(14)	−58·5	C(2)—N(1)—C(6)—C(7)	−23·4	C(23)—C(24)—N(2)—C(21)	57·5
C(2)—N(1)—C(5)—C(20)	−100·6	C(2)—N(1)—C(6)—O(1)	159·2	C(24)—N(2)—C(21)—C(22)	−57·5
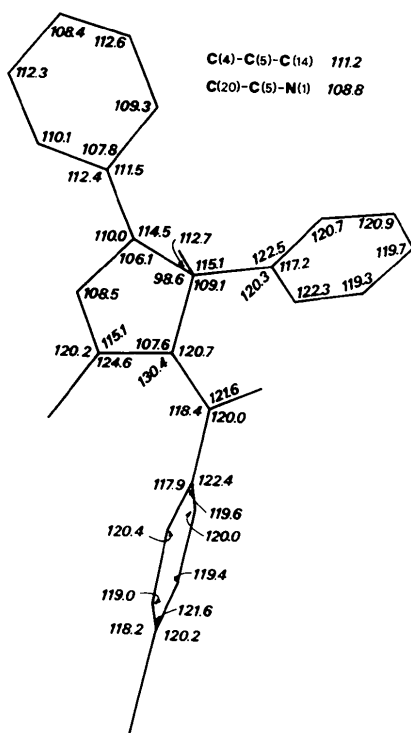
Fig. 3. Bond angles (°). E.s.d.'s are in the range 0·2–0·4°.

Table 4. *Deviations* (Å) *from least-squares planes*

The equations are referred to the orthorhombic axes and fractional coordinates; the distance is the origin-to-plane distance. Atoms marked with an asterisk were omitted from the least-squares calculations; the remaining atoms were given weights $w_i = \text{constant}/\sigma_i^2$, where σ_i is the average of σ_{xi}, σ_{yi} and σ_{zi} given by the least-squares refinement.

Plane A		Plane B		Plane C		Plane D	
N(1)	−0·009	C(2)	−0·193	C(14)	−0·004	C(6)	−0·005
C(2)	0·028	N(1)	0·062	C(15)	0·002	C(7)	−0·006
N(3)	−0·020	C(5)	0·130	C(16)	0·003	C(8)	0·004
C(4)	0·014	C(6)	0·000	C(17)	−0·005	C(9)	0·008
*C(5)	−0·325	C(7)	0·135	C(18)	−0·002	C(10)	−0·012
*C(6)	−0·050	O(1)	−0·116	C(19)	0·005	C(11)	−0·004
*C(13)	0·041	*N(3)	−0·123	*C(5)	0·029	C(12)	0·017
*N(2)	−0·900	*C(4)	0·328	*C(20)	−0·389	*Br	−0·048
				*N(1)	−0·859	*O(1)	0·910
						*N(1)	−1·032

Plane A	$4·3785x + 12·4785y − 8·4421z = 8·108$
Plane B	$2·9411x + 14·0299y − 2·2796z = 9·303$
Plane C	$7·8644x + 1·5044y + 17·1702z = 2·806$
Plane D	$−7·5454x + 9·8694y − 3·5650z = 7·287$

Dihedral angles (°)

A ∧ B	16·6 (1)	A ∧ C	78·2 (1)	A ∧ D	72·3 (1)
B ∧ C	75·0 (1)	B ∧ D	63·5 (1)	C ∧ D	124·8 (1)

The Br form factor was decreased by 0·96 to take into account the real component of anomalous dispersion (Cromer, 1965). The refined coordinates of the heavy atoms and their standard deviations are given in Table 1,* and the H atom parameters in Table 2. Fig. 1 is a perspective drawing showing the numbering scheme.

Discussion. The results of the analysis indicate that the product of reaction (1) has the structure (I). Bond distances between heavy atoms are reported in Fig. 2, and bond angles in Fig. 3. Some torsion angles of interest are listed in Table 3, and displacements of selected atoms from some least-squares planes are in

siderably in error were omitted), anisotropic non-hydrogen atoms and isotropic H atoms were separately refined in subsequent cycles. Convergence was assumed when no parameter shift was as much as 20% of its standard deviation. The final results for the 3048 reflexions included in the refinement were $R = 0·048$ and $R_w = 0·047$, with a secondary-extinction parameter (Larson, 1967), $g = 3·4\,(2) \times 10^{-6}$. A final difference map showed a maximum residue of 0·32 e Å^{-3} in the proximity of the Br atom. Form factors for Br, C, N and O were from Cromer & Waber (1965) and for H from Stewart, Davidson & Simpson (1965).

Table 4. The values of the geometrical parameters show that relief from overcrowding is achieved through a combination of factors: (i) extension of the C(4)–C(5) bond length, (ii) bond-angle deformations at C(4), C(5) and N(1), (iii) significant torsion around the C(2)–N(3) double bond, and (iv) slight (but possibly significant) deviation from planarity of the phenyl ring carrying the Br atom. All these distortions serve to reduce the intramolecular non-bonded interactions, among which of special note are C(7)$\cdots$C(13), 2·972 (4); C(8)$\cdots$C(13), 3·133 (4); C(8)$\cdots$H(133), 2·56 (3) Å; and perhaps C(6)$\cdots$C(15), 3·266 (4); N(1)$\cdots$H(15), 2·56 (3); O(1)$\cdots$H(203), 2·42 (3); and H(202)$\cdots$H(212), 2·20 (4) Å.

There are no intermolecular contacts shorter than the sum of van der Waals radii, with the exception of C(16)$\cdots$H(241) (at $\frac{1}{2} - x, \frac{1}{2} + y, z$), 2·68 (3) Å.

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The Photoproduct from Bis(*p*-bromophenyl) Tetraketone

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Abstract. $C_{31}H_{16}Br_4O_7$, $M_r = 820·15$, triclinic, $P\bar{1}$, $a = 13·682$ (7), $b = 15·078$ (8), $c = 7·796$ (4) Å, $\alpha = 96·26$ (2), $\beta = 95·78$ (2), $\gamma = 113·70$ (2)°, $Z = 2$, $D_x = 1·885$ Mg m^{-3}, $V = 1445·3$ Å^3. Four C atoms, out of the five present in the tricyclo moiety, are bonded to bromophenyl groups; three are bonded directly whilst the fourth is bonded through a diketone.

Introduction. Irradiation of bis(*p*-bromophenyl) tetraketone in benzene under nitrogen at $\lambda > 50·0$ Å proceeded with evolution of carbon monoxide (Rubin, Krochmal & Kaftory, 1979) and yielded yellow crystals. Attempts to obtain structural information by chemical and spectral methods led to an ambiguous result.

Intensities from a yellow crystal, 0·2 × 0·2 × 0·3 mm, were collected on a Philips PW 1100 four-circle computer-controlled diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0·71069$ Å) for θ between 3 and 23°. The ω–2θ scan mode was used; the scan width was 1·3°, each peak was scanned for 26 s and the background was counted for 13 s on each side of the peak. 4468 reflexions were measured of which 123 were of zero net intensity.

The four Br atoms were located by *MULTAN* 74 (Main, Woolfson, Lessinger, Germain & Declercq, 1974). The remaining heavy atoms were found by successive difference maps.

H atom positions were calculated from the heavy-atom positions, but not refined. The non-H atoms were refined by least-squares analysis in two separate blocks with *SHELX* (Sheldrick, 1976). Scattering factors for C, O were taken from Cromer & Mann (1968), for Br from Doyle & Turner (1968) with anomalous-dispersion corrections from Cromer & Liberman (1970) and for H from Stewart, Davidson & Simpson (1965). 123 reflexions with zero net intensity and 307 with $\theta > 23°$ were omitted.

For 4038 non-zero reflexions the final $R = 0·093$, $R_w = 0·105$. The weights were $w = k/[\sigma^2(F_o) + gF_o^2]$ where k and g refined to 0·4178 and 0·0135 respectively. Final positional parameters are listed in Table 1.* Bond distances and angles involving non-H atoms are given in Fig. 1 and Table 2 respectively.

Discussion. In the tricyclononane skeleton the six-membered ring [C(3), C(4), O(3), C(5), O(5), C(6)] adopts the boat configuration, the three five-membered rings having an envelope shape; two rings [C(3), O(4), C(5), O(5), C(6) and C(3), O(4), C(5), O(3), C(4)] are

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34293 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.