C(83) are in *cis* positions, whereas H(3a) and O(31) are in *trans* positions.

Packing. The crystal exhibits a hydrogen bond, O(31)—H(31)···N(2^i) [2·936 (2) Å, 174 (2)°] [(i) = 1 − *x*, −*y*, 1 − *z*].

When subjected to saponification, (5) was transformed into (6), another indeno[1,2-*c*]pyrrole derivative and a regioisomer of (3). Finally, the crystal structure determination of (5) enabled us to prove not only the formula of (6) but also that of (3).

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N-2-(2-Bromo-4,5-dimethoxyphenyl)-1-(2,3,4-trimethoxyphenyl)ethylformamide

By J. M. Arrieta,* E. Domínguez, E. Lete and M. J. Villa

Departamentos de Química Inorgánica y Orgánica, Facultad de Ciencias, Universidad del País Vasco,
Apdo 644, 48080-*Bilbao, Spain*

G. Germain and M. Vlassi

Unité de Chimie Physique Moléculaire et de la Cristallographie, Université de Louvain,
Place Louis Pasteur 1, 1348 *Louvain-la-Neuve, Belgium*

and R. Prewo and J. H. Bieri

Organisch-chemisches Institut, Universität Zürich, Winterthurerstrasse 190, *CH*-8057 *Zürich, Switzerland*

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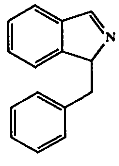
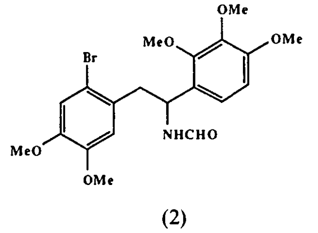
Abstract. $C_{20}H_{24}BrNO_6$, $M_r = 454{\cdot}3$, monoclinic, *Cc*, $a = 27{\cdot}479\ (4)$, $b = 5{\cdot}128\ (1)$, $c = 21{\cdot}811\ (3)$ Å, $\beta = 139{\cdot}35\ (1)°$, $V = 2002\ (1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}51$ Mg m^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, $\mu = 2{\cdot}07$ mm^{-1}, $F(000) = 936$, $T = 130$ K, $R = 0{\cdot}030$ for 4151 observed reflections. The X-ray study confirms that in the solid state the structure of the title compound is similar to that inferred from chemical and spectroscopic evidence. Steric hindrance from different chemical groups is minimized by the adoption of a staggered conformation at the central C(8)—C(9) bond, with aryl groups in an *anti* disposition. There is a delocalized orbital along the N—C—O fragment of the *N*-formylamino group.

Introduction. The title compound was prepared (Dominguez, Lete, Villa & Iriondo, 1984) as part of a program directed towards the synthesis of new heterocyclic compounds. We planned a new approach for the preparation of the 1-benzylisoindole (1) ring system, which consisted of adapting the Bischler–Napieralski reaction (Dominguez & Lete, 1983) to the synthesis of five-membered rings. However, it was found that the required substrates, 2′-bromo-1,2-diarylethylamides, always failed to undergo cyclization (Villa, Lete & Dominguez, 1986). In as much as the projected cyclization is formally a 5-*endo*-dig process and is favoured according to Baldwin's rules (Baldwin, 1976), we decided to determine the crystal structure of (2) to evaluate the structural factors inhibiting the desired cyclization.



(1)



(2)

Experimental. *NMR*. The ^{1}H and ^{13}C NMR spectra were run on a Bruker AC250 spectrometer at 298 K operating in the pulse-Fourier transform mode and provided with an ASPECT 3000 computer. 5 mm

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* Correspondence should be addressed to this author.

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Table 1. ^{1}H *and* ^{13}C NMR *data of the cis* (2*a*) *and trans* (2*b*) *rotamers of formamide* (2)

	^{1}H NMR (CDI_3/TMS)* δ, J (Hz)†	^{13}C NMR (CDI_3/TMS)§ δ
(2*a*)	2·98–3·25 (2H, *m*, —CH_2—), ‡ 3·78 (3H, *s*, MeO), 3·84 (3H, *s*, MeO), 3·87 (3H, *s*, MeO), 3·88 (3H, *s*, MeO), 3·98 (3H, *s*, MeO), 5·46–5·55 (1H, *m*, —CH—), 6·56–7·18 (4H, *m*, aromatic protons), ‡ 6·67 (1H, *bd*, NH), 8·09 (1H, *d*, $J = 0{\cdot}6$, CHO)	40·96 (CH_2), 48·93 (CH), 60·86 and 61·06 (MeO—), 111·25 (C—Br), 113·37, 114·83 and/or 115·15 (C-3′, C-6′ and/or C-5″), 125·40 (C-6″), 128·57 and/or 131·00 (C-1′ and/or C-1″), 148·21, 148·28, 150·88 and/or 150·90 (C-4′, C-5′, C-2″, C-3″ and/or C-4″), 180·19 (CHO)
(2*b*)	2·98–3·25 (2H, *m*, —CH_2—), ‡ 3·75 (3H, *s*, MeO) 3·85 (3H, *s*, MeO), 3·89 (3H, *s*, MeO), 3·90 (3H, *s*, MeO), 3·94 (3H, *s*, MeO), 4·82–4·93 (1H, *m*, —CH—), 6·56–7·18 (4H, *m*, aromatic protons), ‡ 6·79–6·87 (1H, *m*, NH), 7·82 (1H, *d*, $J = 11{\cdot}8$, CHO)	42·54 (CH_2), 53·37 (CH), 55·88 and 55·99 (MeO—), 111·17 (C—Br), 114·27, 114·52 and/or 115·45 (C-3′, C-6′ and/or C-5″), 125·14 (C-6″), 128·18 and/or 131·61 (C-1′ and/or C-1″), 147·25, 148·56 and/or 151·73 (C-4′, C-5′, C-2″, C-3″, and/or C-4″), 183·82 (CHO)

* *s*, singlet; *d*, doublet; *bd*, broad doublet; *m*, multiplet.

† The measurement of all the proton coupling constants was not possible due to overlap of the multiplets of both rotamers.

‡ The signals of both rotamers are overlapped.

§ Assignments made using DEPT experiments.

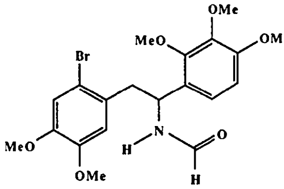
sample tubes containing solutions of the sample in $CDCl_3$ were used. The chemical shifts reference was tetramethylsilane (Me_4Si). The ^{1}H NMR spectrum was recorded at 250·13 MHz and the following experimental parameters were selected: pulse width 2·5 μs (flip angle $< 30°$), acquisition time 2·74 s for the determination of chemical shifts and ^{1}H–^{1}H coupling constants, scan sweep width 2994 Hz acquired in 16 K data points. The ^{13}C NMR spectrum was recorded at 62·83 MHz with Waltz proton decoupling (decoupler power of 0·5 W). Typical acquisition parameters were: pulse width 5·0 μs, acquisition time 1·15 s, number of scans 400, and sweep width 14285 Hz acquired in 32 K data points. Spectral editing was performed using the standard DEPT (distortionless enhancement by polarization transfer) sequence (Derome, 1988) of the Bruker micro program library.

Data collection, structure solution and refinement. Colourless plate-like crystals were grown from ethanol; the intensity data were collected from a crystal approximately 0·3 × 0·2 × 0·03 mm. The cell parameters were determined by least squares from 72 automatically centred reflections in the range $46 \leq 2\theta \leq 50°$. 4418 independent reflections were measured with ω scans up to $2\theta = 70°$ on a Nicolet *R*3 diffractometer with graphite-monochromated radiation. Three standards were measured every 100 reflections. They showed only random deviation from the mean intensity. Lorentz and polarization, but not absorption, corrections were applied. 4151 reflections [$I \geq 2{\cdot}5\sigma(I)$] were considered observed and included in the refinement; the index range was h 0→44, k 0→8, l −22→22. The structure was solved by Patterson and Fourier methods and refined by least squares with *SHELX*76 (Sheldrick, 1976). The function $\sum w(\Delta F)^2$ was minimized, with anisotropic thermal parameters for non-H atoms. The H atoms were included in the refinement in calculated positions with an overall isotropic temperature factor. Their coordinates were not refined and the amidic and formamidic H atoms were not taken into account. The final values of R and wR are 0·030 and 0·034 $\{w = K/[\sigma^2(F) + 0{\cdot}00241F^2]\}$. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The max. and min. electron densities in final difference map are 1·04 and −0·39 e Å^{-3}, Δ/σ (for non-H atoms) $\leq 0{\cdot}072$.

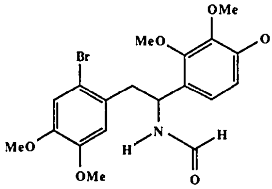
Table 2. *Fractional atomic coordinates* (× 10^4) *and equivalent isotropic temperature factors according to Willis & Pryor* (1975)

	x	y	z	B_{eq} (Å^2)
Br(1)	5000	5719 (1)	0	1·74
C(2)	3897 (1)	1815 (4)	−787 (1)	1·30
C(3)	4133 (1)	3695 (4)	−981 (1)	1·35
C(4)	3761 (1)	4140 (4)	−1894 (2)	1·55
C(5)	3136 (1)	2659 (4)	−2637 (1)	1·61
C(6)	2884 (1)	732 (4)	−2466 (2)	1·56
C(7)	3262 (1)	341 (4)	−1533 (1)	1·47
C(8)	4287 (1)	1263 (4)	184 (1)	1·38
C(9)	4043 (1)	3064 (4)	483 (1)	1·19
C(10)	4490 (1)	2445 (4)	1486 (1)	1·25
C(11)	5240 (1)	3262 (4)	2236 (1)	1·23
C(12)	5690 (1)	2615 (4)	3168 (1)	1·30
C(13)	5389 (1)	1164 (4)	3371 (1)	1·42
C(14)	4640 (1)	392 (4)	2631 (2)	1·69
C(15)	4203 (1)	1011 (4)	1701 (2)	1·54
O(16)	2726 (1)	2943 (4)	−3553 (1)	2·21
C(17)	2944 (2)	4953 (6)	−3757 (2)	2·30
O(18)	2271 (1)	−632 (4)	−3234 (1)	2·16
C(19)	1974 (1)	−2460 (5)	−3088 (2)	2·25
O(20)	5522 (1)	4513 (3)	1999 (1)	1·58
O(21)	5897 (2)	6932 (5)	2458 (2)	2·05
O(22)	6444 (1)	3124 (3)	3854 (1)	1·46
C(23)	6735 (1)	4940 (5)	4577 (2)	1·86
O(24)	5879 (1)	519 (3)	4291 (1)	1·77
C(25)	5632 (2)	−1348 (5)	4502 (2)	1·99
N(26)	3283 (1)	2805 (3)	−188 (1)	1·28
C(27)	2768 (1)	4837 (4)	−628 (2)	1·55
O(28)	2949 (1)	7140 (3)	−489 (2)	2·29

Discussion. *NMR.* The formamide (2) was analysed in solution by NMR spectroscopy. ^{1}H–^{1}H homodecoupling experiments were needed to interpret the ^{1}H NMR spectrum. In the following discussion, the molecular numbering defined in the X-ray structure analysis will be used. A mere examination of the ^{1}H and ^{13}C NMR spectra (Table 1) of this compound clearly reveals the presence of the two rotamers. In fact, almost all the signals are duplicated. Integration and coupling-constant measurements of the proton spectrum show that the major conformer at 298 K is the *cis* rotamer of *N*-2-(2-bromo-4,5-dimethoxyphenyl)-1-(2,3,4-trimethoxyphenyl)ethylformamide (2*a*). The most significant signals were those of the formamidic protons, which appeared as two distinct doublets at δ 8·09 (J 0·6 Hz) [major product (2*a*), 75%] and δ 7·82 (J 11·8 Hz) [minor product (2*b*), 25%]. The magnitude of the coupling constants permitted the conclusion that the *cis* rotamer is favoured, in agreement with the molecular structure in the solid state. Homodecoupling experiments enable the assignment of the aliphatic part of the proton spectrum. Protons belonging to the two rotamers were unambiguously located.



(2*a*)



(2*b*)

The ^{13}C NMR spectrum together with carbon multiplicities determination using the DEPT sequence are compatible with these conditions. In this spectrum, the most characteristic signals were those of the carbonyl atoms at δ 180·19 and 183·82 for (2*a*) and (2*b*) and the aliphatic methylene and methinic protons (40·96 and 42·54, and 48·93 and 53·37, respectively). The assignment of all carbons is rather straightforward (Table 1).

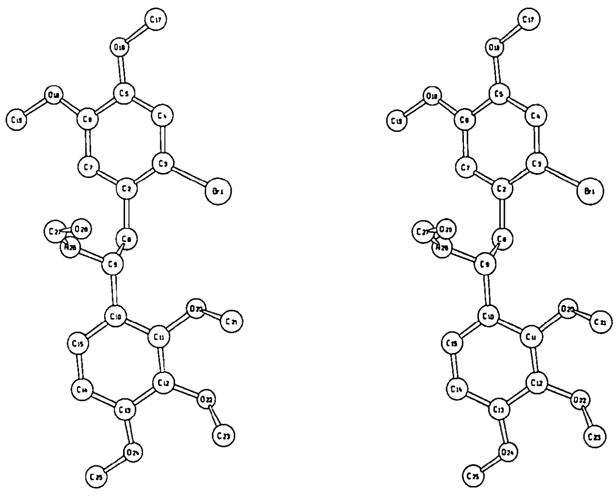


Fig. 1. Stereoview of the molecule with the atom numbering.

Table 3. *Bond lengths* (Å), *bond angles* (°) *and selected torsion angles* (°)

Br(1)—C(3)	1·896 (2)	C(11)—C(12)	1·399 (3)
C(2)—C(3)	1·395 (4)	C(11)—O(20)	1·374 (4)
C(2)—C(7)	1·398 (2)	C(12)—C(13)	1·411 (4)
C(2)—C(8)	1·507 (3)	C(12)—O(22)	1·377 (3)
C(3)—C(4)	1·405 (5)	C(13)—C(14)	1·399 (3)
C(4)—C(5)	1·389 (2)	C(13)—O(24)	1·360 (2)
C(5)—C(6)	1·410 (5)	C(14)—C(15)	1·400 (5)
C(5)—O(16)	1·366 (3)	O(16)—C(17)	1·423 (6)
C(6)—C(7)	1·433 (5)	O(18)—C(19)	1·429 (5)
C(6)—O(18)	1·361 (2)	O(20)—C(21)	1·427 (3)
C(8)—C(9)	1·546 (4)	O(22)—C(23)	1·442 (4)
C(9)—C(10)	1·523 (3)	O(24)—C(25)	1·436 (6)
C(9)—N(26)	1·372 (3)	N(26)—C(27)	1·396 (3)
C(10)—C(11)	1·408 (3)	C(27)—O(28)	1·227 (3)
C(10)—C(15)	1·394 (5)		

C(7)—C(2)—C(8)	117·6 (2)	C(11)—C(10)—C(15)	118·0 (2)
C(3)—C(2)—C(8)	123·9 (2)	C(10)—C(11)—O(20)	116·6 (2)
C(3)—C(2)—C(7)	118·5 (2)	C(10)—C(11)—C(12)	121·2 (2)
Br(1)—C(3)—C(2)	120·8 (1)	C(12)—C(11)—O(20)	121·9 (2)
C(2)—C(3)—C(4)	122·5 (2)	C(11)—C(12)—O(22)	118·5 (2)
Br(1)—C(3)—C(4)	116·8 (2)	C(11)—C(12)—C(13)	119·9 (2)
C(3)—C(4)—C(5)	119·4 (3)	C(13)—C(12)—O(22)	121·1 (2)
C(4)—C(5)—O(16)	124·5 (2)	C(12)—C(13)—O(24)	115·6 (2)
C(4)—C(5)—C(6)	119·7 (2)	C(12)—C(13)—C(14)	119·1 (2)
C(6)—C(5)—O(16)	115·9 (2)	C(14)—C(13)—O(24)	125·2 (3)
C(5)—C(6)—O(18)	115·6 (2)	C(13)—C(14)—C(15)	120·1 (3)
C(5)—C(6)—C(7)	120·1 (2)	C(10)—C(15)—C(14)	121·6 (3)
C(7)—C(6)—O(18)	124·3 (3)	C(5)—O(16)—C(17)	117·3 (2)
C(2)—C(7)—C(6)	119·8 (2)	C(6)—O(18)—C(19)	116·5 (2)
C(2)—C(8)—C(9)	114·0 (2)	C(11)—O(20)—C(21)	117·1 (3)
C(8)—C(9)—N(26)	106·8 (2)	C(12)—O(22)—C(23)	116·1 (3)
C(8)—C(9)—C(10)	110·3 (2)	C(13)—O(24)—C(25)	117·1 (2)
C(10)—C(9)—N(26)	115·4 (2)	C(9)—N(26)—C(27)	126·1 (2)
C(9)—C(10)—C(15)	123·2 (2)	N(26)—C(27)—O(28)	122·6 (3)
C(9)—C(10)—C(11)	118·8 (2)		

C(3)—C(2)—C(8)—C(9)	85·3 (3)	N(26)—C(9)—C(10)—C(15)	18·2 (4)
C(7)—C(2)—C(8)—C(9)	−94·8 (3)	C(8)—C(9)—N(26)—C(27)	−132·6 (3)
C(4)—C(5)—O(16)—C(17)	−2·1 (4)	C(10)—C(9)—N(26)—C(27)	104·5 (3)
C(6)—C(5)—O(16)—C(17)	177·1 (3)	C(10)—C(11)—O(20)—C(21)	129·9 (3)
C(5)—C(6)—O(18)—C(19)	−175·6 (3)	C(12)—C(11)—O(20)—C(21)	−55·8 (4)
C(7)—C(6)—O(18)—C(19)	3·5 (5)	C(11)—C(12)—O(22)—C(23)	118·1 (3)
C(2)—C(8)—C(9)—N(26)	56·5 (3)	C(13)—C(12)—O(22)—C(23)	−70·3 (3)
C(2)—C(8)—C(9)—C(10)	−177·5 (2)	C(12)—C(13)—C(14)—C(15)	1·4 (4)
C(8)—C(9)—C(10)—C(11)	74·5 (3)	C(14)—C(13)—O(24)—C(25)	7·8 (4)
C(8)—C(9)—C(10)—C(15)	−102·8 (3)	C(9)—N(26)—C(27)—O(28)	4·3 (5)
N(26)—C(9)—C(10)—C(11)	−164·5 (2)		

X-ray diffraction. Fractional atomic coordinates with their $B_{\rm eq}$ values (Willis & Pryor, 1975) are given in Table 2.* Fig. 1 shows a stereoscopic view of the molecule and atom numbering (Keller, 1988). Bond lengths, bond angles and torsion angles characterizing the molecular conformation are given in Table 3.

The aryl groups attached to C(8) and C(9) show significant deviations from planarity. The values of Ω^2 [$\Omega^2 = \sum(\Delta/\sigma)^2$, where Δ = atomic deviation from

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and selected torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54072 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the calculated mean plane and σ = standard deviation of Δ] are 27·7 (six atoms) and 38·5 (six atoms), respectively. A dihedral angle of 159·9 (1)° between these planes is observed. The *o*-dimethoxy groups are coplanar with the benzene ring as usual (Caillet, 1982; Karle, Flippen-Anderson, Chiang & Lowrey, 1984). The arrangement of the three adjacent methoxy groups is typical (Miravitlles, Solans, Bladé-Font, Germain & Declercq, 1982; Rius, Molins, Miravitlles & Bladé-Font, 1984; Vijayalakshmi, Rajan & Srinivasan, 1987). Thus, the C(13)—O(24)—C(25) group is nearly coplanar with the benzene ring, while the other groups, C(11)—O(20)—C(21) and C(12)—O(22)—C(23), point outside the main rings as can be deduced from Table 3. The C(27)—O(28) and C(27)—N(26) bond distances are 1·227 (3) and 1·396 (3) Å, respectively and these values compare well with those reported for other secondary amides. The observed lengthening of the C—O bond and the shortening of the C—N bond, together with the planarity of the C(9)—N(26)—C(27)—O(28) fragment (see Table 3) are characteristic of an amide function and demonstrate π delocalization. The torsion angles reported in Table 3 describe the conformation of the molecule and show that there is a favoured rotamer with the alkyl substituent at the N atom in a *cis* disposition relative to the carbonyl O atom. Steric hindrance from the different chemical groups is minimized by adoption of a staggered conformation at the central C(8)—C(9) bond, with aryl groups in an *anti* disposition.

The Bischler–Napieralski cyclization of the title compound (assuming that qualitative comparisons can be made concerning the conformation of the molecule in the liquid and solid states) requires that the trimethoxyphenyl ring approaches the carbon attack of the formyl group, which is turned out away from this ring. The disposition of the formyl group could explain the failure of the Bischler–Napieralski reaction to form isoindoles.

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Investigation of the Geometry of Substituted Dinitroanilines. III. Structural Study of *N*,*N*-Dicyclohexyl-2,4-dinitroaniline*

BY G. PUNTE†‡ AND B. E. RIVERO§

Departamento de Física, Facultad de Ciencias Exactas, UNLP, CC67, (1900) La Plata, Argentina

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Abstract. $C_{18}H_{25}N_3O_4$, triclinic, $P\bar{1}$, $M_r = 347·4$, $a = 9·881$ (1), $b = 12·687$ (2), $c = 15·438$ (5) Å, $\alpha = 109·65$ (1), $\beta = 90·94$ (2), $\gamma = 95·78$ (1)°, $V = 1811$ (1) Å^3, $Z = 4$, $F(000) = 744$, $D_x = 1·27$ g cm^{-3}, $T = 296$ (2) K, Mo $K\alpha$ radiation, $\lambda = 0·71073$ Å, μ(Mo $K\alpha$) = 0·89 cm^{-1}, final $R = 0·047$, $wR = 0·052$ for 2294 observed independent reflections. The two crystallographically non-equivalent molecules have similar valence geometry, but different conformation. Both are non-planar with their amino and *o*-nitro groups twisted out of the mean plane of aromatic rings. The four crystallographically non-equivalent cyclohexane rings have chair conforma-

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† Member of Carrera del Investigador Cientifico, CONICET, Argentina.

‡ Present address: The Henry A. Rowland Department of Physics and Astronomy, The Johns Hopkins University, Baltimore, MD 21218, USA.

§ Member of Carrera del Investigador Cientifico, CICPBA, Argentina.

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