($R_{\rm int}$ = 0.1094). This was due to the very poor quality of the crystal specimen which was a fragment cut from a very thin plate. This unfortunate experimental situation is reflected in the values of the wR and R indices which are rather higher than the standard values usually found for this kind of structure. Nevertheless, as sometimes happens, the molecular geometry (bond distances and angles) obtained in the present analysis is quite as expected and allows the interpretation given in the *Comment*.

The calculations were carried out on the ENCORE91 and GOULD-POWERNODE 6040 computers of the Centro di Studio per la Strutturistica Diffrattometrica del CNR (Parma), and on a COMPAQ-486c portable computer.

Data collection: local programs. Cell refinement: *LQPARM* (Nardelli & Mangia, 1984). Data reduction: local programs. Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1965) and *PLUTO* (Motherwell & Clegg, 1978). Software used to prepare material for publication: *PARST* (Nardelli, 1983) and *PARSTCIF* (Nardelli, 1991).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HA1141). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–S19.
Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
Belletti, D., Ugozzoli, F., Cantoni, A. & Pasquinelli, G. (1979). *Gestione on Line di Diffrattometro a Cristallo Singolo Siemens AED con Sistema General Automation Jumbo* 220. Internal Report 1-3/79. Centro di Studio per la Strutturistica Diffrattometrica del CNR, Parma, Italy.
Casagrande, C. & Santangelo, F. (1987). US Patent 4 673 671.
Casagrande, C. & Santangelo, F. (1990). *Peripheral Dopamine Pathophysiology*, edited by F. Amenta, pp. 307–343. Florida: CRC Press.
Casagrande, C., Merlo, L., Santangelo, F., Doggi, F., Gerli, F., Pocchiari, F., Pataccini, R. & Semeraro, C. (1988). *Xth International Symposium on Medicinal Chemistry*, Budapest, Hungary, p. 87.
Casagrande, C., Santangelo, F., Saini, C., Gerli, F. & Cerri, O. (1986). *Arzneim. Forsch.* **36**, 291–303.
Goldberg, J. (1972). *Pharmacol. Rev.* **24**, 1–29.
Ince, F. (1990). *Comprehensive Medicinal Chemistry: Membranes and Receptors*, Vol. 3, edited by C. Mousch, P. G. Sammes, J. B. Taylor & J. C. Emmett, pp. 291–322. Oxford: Pergamon Press.
Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
Lehmann, M. S. & Larsen, F. K. (1974). *Acta Cryst.* A**30**, 580–589.
Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO. Program for Plotting Molecular and Crystal Structures*. Univ. of Cambridge, England.
Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.
Nardelli, M. (1991). *PARSTCIF. Program for Creating a CIF from the Output of PARST*. Univ. of Parma, Italy.
Nardelli, M. & Mangia, A. (1984). *Ann. Chim. (Rome)*, **74**, 163–174.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. Univ. of Göttingen, Germany.

Acta Cryst. (1995). C**51**, 1341–1345

Conformation at the Amide N Atom of 1-Carboxamide Indole Derivatives

SANDRA IANELLI, MARIO NARDELLI* AND DANIELE BELLETTI

Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica, Università degli Studi di Parma, Centro di Studio per la Strutturistica Diffrattometrica del CNR, Viale delle Scienze 78, I-43100 Parma, Italy

BRIGITTE JAMART-GRÉGOIRE, CATHERINE CAUBÈRE AND PAUL CAUBÈRE

Laboratoire de Chimie Organique I, UA CNRS No. 457, Université de Nancy I, BP 239, 54506 Vandoeuvre-Les-Nancy CEDEX, France

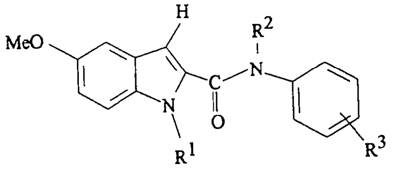
(*Received* 21 *November* 1994; *accepted* 17 *January* 1995)

Abstract

Knowledge of the conformation at the amide N atom of *N*-3-methoxyphenyl-2-(5-methoxyindole)carboxamide, $C_{17}H_{16}N_2O_3$, and *N*-methyl-*N*-phenyl-2-(5-methoxyindole)carboxamide, $C_{17}H_{16}N_2O_2$, allows an interpretation of the ^{1}H NMR behaviour of the two compounds. The structures and conformations of the two molecules are compared.

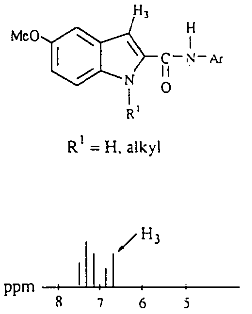
Comment

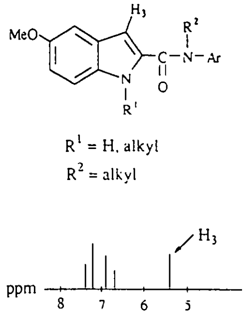
During a study of 1-carboxamide indole derivatives, an intriguing observation was made concerning the ^{1}H NMR spectra (Caubère, Caubère, Renard, Bizot-Espiart, Jamart-Grégoire, 1994). From an examination of the aromatic part of these spectra it appears that simply changing the H atom of the amide N atom into a methyl group leads to a dramatic shielding of an aromatic or pseudo-aromatic proton. This observation is very general and effective when R^2 is different from H.



(1*a*) R^1 = H, R^2 = H, R^3 = OMe
(1*b*) R^1 = H, R^2 = Me, R^3 = H

A possible interpretation of this finding is that the presence of the methyl group forces the molecule into a conformation so that the H atom at C3 (C8 in Fig. 1) is in the shielding cone of the aromatic ring. To support this hypothesis, the X-ray crystal structure analysis of *N*-3-methoxyphenyl-2-(5-methoxyindole)carboxamide (1*a*) and *N*-methyl-*N*-phenyl-2-(5-methoxyindole)carboxamide (1*b*), for which suitable single crystals were obtained, was carried out.





The *ORTEP* (Johnson, 1965) drawings of Fig. 1 show that the conformation at the amide N atom is quite different in the two molecules: the phenyl group is *cis* to the carbonyl O atom with respect to the carboxamide C—N bond [O2—C10—N2—C11 = 0.6 (3)°] in (1*a*) while it is *trans* [O2—C10—N2—C11 = −167.9 (2)°] in (1*b*). This difference of conformation is responsible not only for the observed ^1H NMR behaviour, but also causes remarkable variations in bond angles of the carboxamide group (Table 3): C10—N2—C11 and O2—C10—N2 are larger, while N2—C10—C9 and C8—C9—C10 are narrower in (1*a*) and the differences are highly significant (Δ/σ = 16.1–21.0).

Furthermore, the degree of π conjugation between the substituents and the amide group is significantly different in the two compounds; the phenyl group is almost coplanar with the amide system in compound (1*a*) [C10—N2—C11—C12 = 160.2 (2)°] and almost perpendicular in (1*b*) [C10—N2—C11—C12 = −117.2 (2)°]; consequently, the N2—C11 distance is shorter [1.420 (2) Å] in (1*a*) where conjugation is relevant, and longer [1.437 (2) Å] in (1*b*) where conjugation is practically absent. The conformation assumed by the phenyl substituent in (1*a*) is imposed by the conjugation between the two systems aided by the attractive interaction exerted by O2 on H16: C16—H161 = 1.01 (2), C16···O2 = 2.890 (2), H161···O2 = 2.30 (2) Å, C16—H161···O2 = 116.5 (1.5)°. On the other hand, coplanarity, necessary for π conjugation, is prevented in (1*b*) by the repulsive interactions exerted between H8 and the *ortho* H atoms of the phenyl ring when this rotates around the N2—C11 bond.

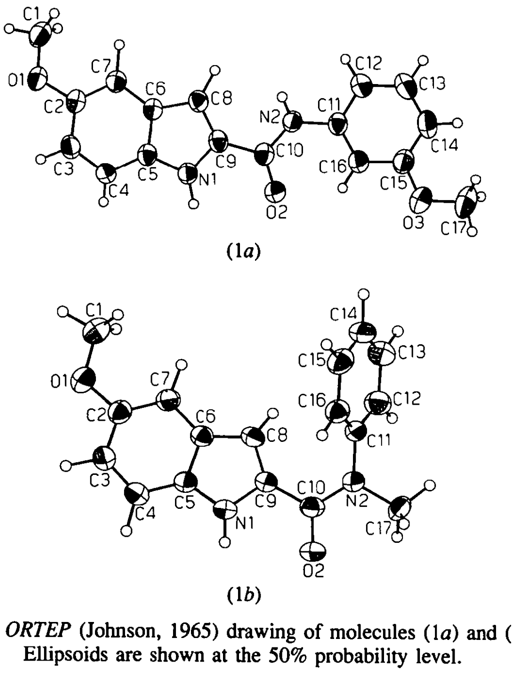


Fig. 1. *ORTEP* (Johnson, 1965) drawing of molecules (1*a*) and (1*b*). Ellipsoids are shown at the 50% probability level.

The conjugation of the amide group with the indole system is a little more favoured in compound (1*a*) [O2—C10—C9—N1 = 7.9 (2)°] than in (1*b*) [O2—C10—C9—N1 = 12.9 (3)°].

In both compounds the exocyclic angles N2—C11—C12 and N2—C11—C16 are asymmetric, the first being narrower (Table 3).

The methoxy group bound to indole is coplanar with the benzene ring [C1—O1—C2—C7 = −0.5 (3)°] in (1*b*), but significantly displaced [C1—O1—C2—C7 = 16.9 (3)°] in (1*a*), while the methoxy group bound to the phenyl substituent in (1*a*) is practically coplanar with the phenyl ring [C14—C15—O3—C17 = 1.8 (3)°].

All the other relevant structural parameters (bond distances and angles) are as expected and in acceptably good agreement in the two compounds.

The packing contacts of major relevance are hydrogen bonds of the type N—H···O involving the indole N atom and the amide O atom of an adjacent molecule in both compounds. In (1*a*) there is an additional weaker hydrogen bond between the amide N atom and the O atom of an indole methoxy group of an adjacent molecule. The geometry of these hydrogen bonds is illustrated in Table 4.

The analysis of the 'thermal' motion of the molecules in the crystals of the two compounds, carried out in terms of the Schomaker & Trueblood (1968) **TLS** rigid-body approximation using the *THMV* program (Trueblood, 1984), shows a satisfactory agreement between the observed and calculated atomic displacement parameters: R_{wU} is 0.105 and 0.130 for (1*a*) and (1*b*), respectively, and improves to 0.074 and 0.093 if internal motions are considered according to Dunitz & White (1973).

Experimental

The two compounds were prepared by condensing the crude 5-methoxyindole-2-carboxylic acid chloride, prepared *in situ* from the corresponding acid and PCl_5, with 3-methoxyaniline [compound (1*a*)] or *N*-methylaniline [compound (1*b*)] in a mixture of dioxane–ether. The solids formed were filtered, washed with petroleum ether and recrystallized from ethanol. Melting points (from a Tottoli apparatus): (1*a*), 456 K; (1*b*), 467 K.

Compound (1*a*)

Crystal data

$C_{17}H_{16}N_2O_3$
$M_r = 296.33$
Monoclinic
$P2_1/c$
$a = 6.926\,(1)$ Å
$b = 15.054\,(3)$ Å
$c = 14.471\,(2)$ Å
$\beta = 99.94\,(1)^\circ$
$V = 1486.2\,(4)$ Å^3
$Z = 4$
$D_x = 1.324$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 30 reflections
$\theta = 22\text{–}34^\circ$
$\mu = 0.714$ mm^{-1}
$T = 293\,(2)$ K
Small tabular prism
0.61 × 0.31 × 0.26 mm
Colourless, slightly brown

Data collection

Siemens AED diffractometer
$\theta/2\theta$ scans
Absorption correction: none
2950 measured reflections
2841 independent reflections
1913 observed reflections $[I > 2\sigma(I)]$
$R_{\text{int}} = 0.0170$

$\theta_{\max} = 70.14^\circ$
$h = -8 \rightarrow 1$
$k = -18 \rightarrow 18$
$l = -16 \rightarrow 17$
1 standard reflection monitored every 50 reflections
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0375$
$wR(F^2) = 0.0923$
$S = 0.968$
2841 reflections
264 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0630P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.010$

$\Delta\rho_{\max} = 0.239$ e Å^{-3}
$\Delta\rho_{\min} = -0.207$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.007 (1)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (1*a*)

$$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
O1	0.1603 (2)	0.68304 (9)	0.7990 (1)	0.0598 (5)
O2	−0.3915 (2)	1.01255 (9)	0.39329 (9)	0.0550 (5)
O3	−0.5671 (3)	1.1152 (1)	0.0822 (1)	0.0855 (7)
N1	−0.2856 (2)	0.9035 (1)	0.5465 (1)	0.0476 (5)
N2	−0.1417 (3)	0.9602 (1)	0.3246 (1)	0.0477 (5)
C1	0.3619 (4)	0.6729 (2)	0.7953 (2)	0.0834 (11)
C2	0.0522 (3)	0.7382 (1)	0.7332 (1)	0.0477 (6)
C3	−0.1292 (3)	0.7644 (1)	0.7558 (1)	0.0537 (7)
C4	−0.2529 (3)	0.8196 (1)	0.6978 (1)	0.0522 (7)
C5	−0.1928 (3)	0.8488 (1)	0.6159 (1)	0.0440 (6)
C6	−0.0142 (3)	0.8214 (1)	0.5914 (1)	0.0427 (5)
C7	0.1128 (3)	0.7652 (1)	0.6518 (1)	0.0479 (6)
C8	−0.0046 (3)	0.8605 (1)	0.5025 (1)	0.0464 (6)
C9	−0.1716 (3)	0.9104 (1)	0.4779 (1)	0.0440 (5)
C10	−0.2438 (3)	0.9658 (1)	0.3957 (1)	0.0439 (6)
C11	−0.1773 (3)	1.0049 (1)	0.2370 (1)	0.0465 (6)
C12	−0.0217 (4)	1.0106 (2)	0.1883 (2)	0.0604 (8)
C13	−0.0503 (4)	1.0527 (2)	0.1022 (2)	0.0731 (9)
C14	−0.2288 (4)	1.0889 (2)	0.0637 (2)	0.0693 (8)
C15	−0.3819 (3)	1.0824 (1)	0.1123 (1)	0.0588 (7)
C16	−0.3580 (3)	1.0395 (1)	0.1990 (1)	0.0531 (6)
C17	−0.6046 (6)	1.1573 (3)	−0.0072 (2)	0.0955 (14)

Compound (1*b*)

Crystal data

$C_{17}H_{16}N_2O_2$
$M_r = 280.33$
Triclinic
$P\overline{1}$
$a = 11.311\,(8)$ Å
$b = 10.220\,(7)$ Å
$c = 6.586\,(1)$ Å
$\alpha = 79.59\,(2)^\circ$
$\beta = 79.20\,(4)^\circ$
$\gamma = 78.86\,(3)^\circ$
$V = 725.5\,(7)$ Å^3
$Z = 2$
$D_x = 1.283$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 27 reflections
$\theta = 11\text{–}18^\circ$
$\mu = 0.0854$ mm^{-1}
$T = 293\,(2)$ K
Small prism
0.65 × 0.55 × 0.48 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
2566 measured reflections
2566 independent reflections
1329 observed reflections $[I > 2\sigma(I)]$

$\theta_{\max} = 25.05^\circ$
$h = -12 \rightarrow 13$
$k = -11 \rightarrow 12$
$l = 0 \rightarrow 7$
1 standard reflection frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0374$
$wR(F^2) = 0.0594$
$S = 0.994$
2566 reflections
255 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0204P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.004$

$\Delta\rho_{\max} = 0.132$ e Å^{-3}
$\Delta\rho_{\min} = -0.132$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.008 (1)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (1*b*)

$$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
O1	−0.0289 (1)	0.3419 (2)	−0.0159 (2)	0.0610 (7)
O2	0.6327 (1)	0.0242 (1)	0.3081 (2)	0.0577 (6)
N1	0.3954 (2)	0.1294 (2)	0.2935 (3)	0.0474 (7)
N2	0.7019 (1)	0.1422 (2)	0.0015 (2)	0.0462 (7)
C1	−0.0226 (3)	0.4040 (4)	−0.2285 (5)	0.0671 (13)
C2	0.0799 (2)	0.2869 (2)	0.0534 (3)	0.0479 (9)
C3	0.0670 (2)	0.2297 (2)	0.2652 (4)	0.0540 (10)
C4	0.1670 (2)	0.1737 (2)	0.3608 (3)	0.0535 (10)
C5	0.2813 (2)	0.1752 (2)	0.2404 (3)	0.0423 (9)
C6	0.2965 (2)	0.2298 (2)	0.0273 (3)	0.0424 (9)

C7	0.1925 (2)	0.2869 (2)	−0.0675 (3)	0.0471 (9)
C8	0.4235 (2)	0.2144 (2)	−0.0445 (3)	0.0466 (9)
C9	0.4822 (2)	0.1529 (2)	0.1207 (3)	0.0425 (9)
C10	0.6102 (2)	0.1033 (2)	0.1489 (3)	0.0449 (9)
C11	0.6870 (2)	0.2513 (2)	−0.1680 (3)	0.0416 (8)
C12	0.7155 (2)	0.2234 (3)	−0.3692 (4)	0.0577 (10)
C13	0.7048 (2)	0.3271 (3)	−0.5333 (4)	0.0733 (12)
C14	0.6640 (2)	0.4572 (3)	−0.4971 (4)	0.0713 (12)
C15	0.6363 (2)	0.4855 (3)	−0.2950 (5)	0.0633 (12)
C16	0.6487 (2)	0.3818 (2)	−0.1279 (4)	0.0502 (10)
C17	0.8277 (2)	0.0772 (3)	0.0243 (5)	0.0615 (11)

Table 3. *Comparison of bond distances* (Å), *bond angles* (°) *and selected torsion angles* (°) *in the two compounds*

	(1*a*)	(1*b*)
O1—C1	1.418 (3)	1.423 (3)
O1—C2	1.387 (2)	1.375 (3)
O2—C10	1.241 (2)	1.238 (2)
O3—C15	1.376 (3)	–
O3—C17	1.429 (4)	–
N1—C5	1.373 (2)	1.372 (3)
N1—C9	1.377 (2)	1.375 (2)
N2—C10	1.351 (2)	1.349 (3)
N2—C11	1.420 (2)	1.437 (2)
N2—C17	–	1.471 (3)
C2—C3	1.411 (3)	1.404 (3)
C2—C7	1.377 (3)	1.370 (3)
C3—C4	1.372 (3)	1.375 (3)
C4—C5	1.398 (3)	1.386 (3)
C5—C6	1.409 (3)	1.405 (3)
C6—C7	1.415 (2)	1.411 (3)
C6—C8	1.429 (2)	1.414 (3)
C8—C9	1.378 (2)	1.372 (3)
C9—C10	1.471 (2)	1.473 (3)
C11—C12	1.389 (3)	1.372 (3)
C11—C16	1.381 (3)	1.377 (3)
C12—C13	1.375 (3)	1.376 (4)
C13—C14	1.384 (3)	1.368 (5)
C14—C15	1.376 (3)	1.379 (4)
C15—C16	1.394 (3)	1.391 (4)
C1—O1—C2	117.3 (2)	116.9 (2)
C15—O3—C17	117.8 (2)	–
C5—N1—C9	108.5 (1)	109.4 (2)
C10—N2—C11	128.2 (1)	124.6 (2)
C10—N2—C17	–	118.3 (2)
C11—N2—C17	–	116.9 (2)
O1—C2—C3	114.1 (2)	113.9 (2)
O1—C2—C7	123.8 (2)	124.7 (2)
C3—C2—C7	122.1 (2)	121.4 (2)
C2—C3—C4	121.3 (2)	121.4 (2)
C3—C4—C5	117.4 (2)	117.6 (2)
C4—C5—C6	121.9 (2)	122.1 (2)
N1—C5—C4	129.8 (2)	130.4 (2)
N1—C5—C6	108.3 (1)	107.5 (2)
C5—C6—C7	120.1 (2)	119.3 (2)
C5—C6—C8	106.7 (2)	106.7 (2)
C7—C6—C8	133.2 (2)	134.0 (2)
C2—C7—C6	117.2 (2)	118.3 (2)
C6—C8—C9	106.7 (1)	108.0 (2)
C8—C9—C10	132.2 (2)	135.4 (2)
N1—C9—C8	109.8 (2)	108.2 (2)
N1—C9—C8	109.8 (2)	108.2 (2)
N1—C9—C10	118.0 (1)	116.3 (2)
N2—C10—C9	115.7 (1)	120.4 (2)
O2—C10—C9	120.7 (2)	119.3 (2)
O2—C10—N2	123.7 (2)	120.4 (2)
N2—C11—C12	116.9 (2)	118.8 (2)
N2—C11—C16	122.9 (2)	120.2 (2)
C12—C11—C16	120.1 (2)	120.9 (2)
C11—C12—C13	119.2 (2)	119.6 (2)
C12—C13—C14	121.6 (2)	120.5 (3)
C13—C14—C15	118.7 (2)	120.0 (3)
O3—C15—C14	125.0 (2)	–
O3—C15—C16	114.3 (2)	–
C14—C15—C16	120.7 (2)	120.0 (3)
C11—C16—C15	119.6 (2)	118.9 (2)
C1—O1—C2—C7	16.9 (3)	−0.5 (3)
C17—O3—C15—C14	1.8 (3)	–
C5—N1—C9—C10	179.6 (2)	−177.1 (2)
C11—N2—C10—O2	0.6 (3)	−167.9 (2)
C10—N2—C11—C12	160.2 (2)	−117.2 (2)
C11—N2—C10—C9	179.3 (2)	13.1 (3)
C17—N2—C10—O2	–	6.4 (3)
C17—N2—C11—C12	–	68.5 (3)
N1—C9—C10—N2	−170.8 (2)	−168.1 (2)
N1—C9—C10—O2	7.9 (2)	12.9 (3)
C8—C9—C10—N2	9.1 (3)	15.7 (4)

Table 4. *Hydrogen-bonding geometry* (Å, °)

D—H···*A*	*D*—H	*D*···*A*	H···*A*	*D*—H···*A*
(1*a*)				
N1—H1N···O2^{i}	0.92 (3)	2.834 (2)	1.97 (3)	156 (2)
N2—H2N···O1^{ii}	0.88 (2)	3.071 (2)	2.25 (2)	156 (2)

Symmetry codes: (i) $-1 - x, 2 - y, 1 - z$; (ii) $x, \frac{3}{2} - y, z - \frac{1}{2}$.

D—H···*A*	*D*—H	*D*···*A*	H···*A*	*D*—H···*A*
(1*b*)				
N1—H1N···O2^{i}	0.88 (2)	2.800 (2)	1.98 (2)	154 (2)

Symmetry code: (i) $1 - x, -y, 1 - z$.

The integrated intensities were obtained by a modified version (Belletti, Ugozzoli, Cantoni & Pasquinelli, 1979) of the Lehmann & Larsen (1974) peak-profile analysis procedure. All reflections were corrected for Lorentz and polarization effects, but not for absorption.

The structures were solved by direct methods and refined by anisotropic full-matrix least squares. For (1*a*), a number of H atoms were found from a $\Delta\rho$ map and some were put in calculated positions; in particular H1N was not found at the $R = 0.0415$ refinement level, but, put in a calculated position and refined, gave an improved R index of 0.0378. For (1*b*) all the H atoms were put in calculated positions except H1N and H8. For both compounds all the H atoms were refined isotropically as free atoms in the last stages of refinement.

The calculations were carried out on the ENCORE91 and GOULD-POWERNODE 6040 computers of the Centro di Studio per la Strutturistica Diffrattometrica del CNR (Parma), and on a COMPAQ-486*c* portable computer.

For both compounds, data collection: local programs; cell refinement: *LQPARM* (Nardelli & Mangia, 1984); data reduction: local programs. Program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1986) for (1*a*); *SIR*88 (Burla *et al.*, 1989) for (1*b*). For both compounds, program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ORTEP* (Johnson, 1965); software used to prepare material for publication: *PARST* (Nardelli, 1983), *PARSTCIF* (Nardelli, 1992).

Financial support from the European Community Commission under contract No. SC1000657 is gratefully acknowledged.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: LI1132). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Belletti, D., Ugozzoli, F., Cantoni, A. & Pasquinelli, G. (1979). *Gestione on Line di Diffrattometro a Cristallo Singolo Siemens AED con Sistema General Automation Jumbo* 220. Internal Reports 1-3/79. Centro di Studio per la Strutturistica Diffrattometrica del CNR, Parma, Italy.

Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Polidori, G., Spagna, R. & Viterbo, D. (1989). *J. Appl. Cryst.* **22**, 389–393.
Caubère, C., Caubère, P., Renard, P., Bizot-Espiart, J. G. & Jamart-Grégoire, B. (1994). *Synth. Commun.* **24**(13), 1809–1816.
Dunitz, J. D. & Withe, D. N. J. (1973). *Acta Cryst.* A**29**, 93–94.
Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794, Oak Ridge National Laboratory, Tennessee, USA.
Lehmann, M. S. & Larsen, F. K. (1974). *Acta Cryst.* A**30**, 580–589.
Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.
Nardelli, M. (1992). *PARSTCIF. Program for the Creation of a CIF from the Output of PARST*. Univ. of Parma, Italy.
Nardelli, M. & Mangia, A. (1984). *Ann. Chim. (Rome)*, **74**, 163–174.
Schomaker, V. & Trueblood, K. N. (1968). *Acta Cryst.* B**24**, 63–76.
Sheldrick, G. M. (1986). *SHELXS86. Program for the Solution of Crystal Structures*. Univ. of Göttingen, Germany.
Sheldrick, G. M. (1993). *SHELXL93. Program for Crystal Structure Refinement*. Univ. of Göttingen, Germany.
Trueblood, K. N. (1984). *THMV. Program for Thermal Motion Analysis*. Univ. of California, Los Angeles, USA.

Acta Cryst. (1995). C**51**, 1345–1347

A Naphthalene-Fused Tricyclic Orthoamide

M. Mehdi Baradarani,† Roy L. Beddoes,
Owen S. Mills and John A. Joule

*Department of Chemistry, University of Manchester,
Manchester M13 9PL, England*

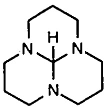
(*Received* 4 *October* 1994; *accepted* 19 *December* 1994)

Abstract

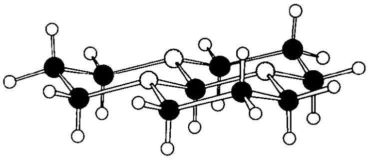
The crystal structure of 3a,6a,12b-triaza-1,2,3,3a,4,5,6,-6a,12b,12c-decahydroperylene, $C_{17}H_{19}N_3$, (6), shows that the naphthalene unit adopts an orientation orthogonal to the average plane of the triaza-*trans*-decalin moiety. This forces two aromatic N-atom lone pairs to orient equatorially and thus allows only partial overlap with the naphthalene π system.

Comment

We have been examining the effect of fusing aromatic rings onto hexahydro-3a,6a,9a-triazaphenalene, (1). The tricycle (1) displays the remarkable ability of extruding the central H atom as a hydride which then reacts with a proton to produce hydrogen gas at only 423 K (Erhardt & Wuest, 1980). This is attributed to its three-dimensional structure, (2) (Beddoes, Edwards, Joule, Mills & Street, 1987), which enables three N-atom lone pairs to assist the process by overlapping with the σ_{CH^*} orbital. [For the crystal structure of an analogue of (1) carrying a central methyl group instead of an H atom, see Seiler, Weisman, Glendening, Weinhold, Johnson & Dunitz (1987).]

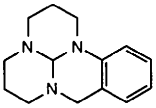


(1)

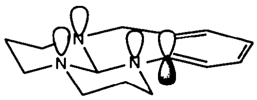


(2)

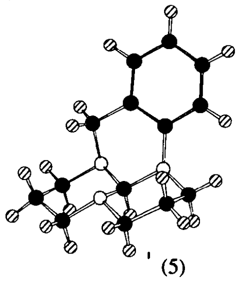
It was our aim to synthesize analogues of (1) and to test whether the energy necessary to drive hydride expulsion, and thus, hydrogen production could be made available by photochemical excitation. To this end we synthesized (3), incorporating a UV chromophore, in which we hoped that the π system of the aromatic ring would lie in the plane of the saturated part, in a conformation idealized as (4), thus allowing for electronic interactions between the π system and the N-atom lone pairs of the desired type. However, a crystal structure determination showed that in (3) the benzene ring actually adopts an orientation, shown in (5), orthogonal to the triaza-*trans*-decalin, which is inappropriate for our aims (Beddoes, Edwards, Joule, Mills & Street, 1987).



(3)

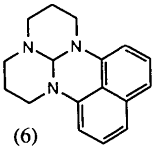


(4)

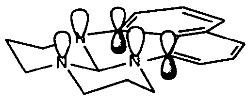


(5)

In order to increase, as we thought, the chances of achieving the desired orientation between the N atoms and the aromatic system, we synthesized the title compound 3a,6a,12b-triaza-1,2,3,3a,4,5,6,6a,12b,12c-decahydroperylene, (6), in which two of the N atoms are directly bonded to an aromatic system and so the additional overlap stabilization from the interaction of two N-atom lone pairs with two benzene rings would favour the desired conformation, idealized as (7).



(6)



(7)

---

† On leave from the Faculty of Science, University of Orumia, Orumia, Iran.