Stereochemistry of the C(sp^2)–N(sp^3) Fragment. II.* Structure of (*E*)-*N,N'*-Dicyclohexyl-4-morpholinecarboxamidine, C$_{17}$H$_{31}$N$_3$O

By F. Bellucci, V. Bertolasi, V. Ferretti and G. Gilli

Centro di Strutturistica Diffrattometrica, Università di Ferrara, 44100 Ferrara, Italy

Abstract. $M_r = 293\cdot46$, monoclinic, *Cc*, $a = 14\cdot043$ (2), $b = 9\cdot695$ (1), $c = 12\cdot727$ (3) Å, $\beta = 90\cdot32$ (1)°, $V = 1732\cdot8$ (4) Å^3, $Z = 4$, $D_x = 1\cdot12$ Mg m^{-3}, λ(Mo Kα) $= 0\cdot71069$ Å, $\mu = 0\cdot07$ mm^{-1}, $F(000) = 648$, $T = 293$ K, $R = 0\cdot031$ for 1515 unique observed reflections. The variations of the geometry of the amidine group caused by rotation around the single C–N bond are analysed in connection with the present and other related molecules. It is found that rotation around the C–N bond causes a decoupling of the π system with consequent lengthening of the d_{CN} bond distance and a rehybridization of the N atom from sp^2 to sp^3.

Introduction. Molecular structures containing the fragment (I) include amides, thioamides, amidines, enamines (*X*=O,S,N*R* and C*R$_2$*, respectively) and aromatic amines. By itself the group tends to be planar owing to the partial double-bond character (II) of the C–N bond. Situations of steric hindrance can cause distortions in the group which seem to be reducible to two different movements: (i) the out-of-plane bending of nitrogen (able to distort only slightly the overall geometry) and (ii) the rotation around the C–N bond associated with pyramidalization of the nitrogen, rehybridizing from sp^2 to sp^3 (Gilli & Bertolasi, 1979, 1981; Bertolasi, Bellucci, Ferretti & Gilli, 1984). The resistance to deformation is inversely related to the contribution of the polar canonical form (II). Accordingly amides or thioamides undergo very small distortions (Dunitz, 1979) while amidines (Gilli & Bertolasi, 1979) and enamines (Brown, Damm, Dunitz, Eschenmoser, Hobi & Kratky, 1978) can be more easily found rotated. The present paper reports the crystal structure of a new amidine displaying severe out-of-plane deformation.

(I)   (II)

---
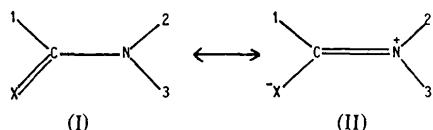
* Part I: Gilli & Bertolasi (1979).

Experimental. Crystal $0\cdot42 \times 0\cdot09 \times 0\cdot20$ mm, Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo Kα radiation, $\omega/2\theta$ scan ($2 \le \theta \le 27°$); cell parameters from 23 reflections in range $10 \le \theta \le 13°$; 1888 reflections collected ($0 \le h \le 17$, $0 \le k \le 12$, $-16 \le l \le 16$), 1515 with $I_o \ge 3\sigma(I_o)$ used in refinement; two standard reflections monitored every 2 h showed no significant variation during data collection; no absorption correction. Solution by direct methods (*MULTAN*81; Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1981); refinement by full-matrix least squares on *F*, anisotropic non-H and isotropic H atoms (located in ΔF map), final $R = 0\cdot031$, $wR = 0\cdot040$, $1/w^2 = \sigma^2(I_o) + 0\cdot05 |F_o|^2$, max. $\Delta/\sigma = 0\cdot22$, $S = 1\cdot6$; final difference-map peaks in range $-0\cdot14$–$0\cdot15$ e Å^{-3}. Scattering factors from *International Tables for X-ray Crystallography* (1974); all calculations performed with CAD-4-*SDP* system of programs (Frenz, 1978) and *PARST* (Nardelli, 1983).

Discussion. Atomic parameters are given in Table 1.† Bond distances, angles and a selection of torsion angles are reported in Tables 2, 3 and 4, respectively. An *ORTEP* (Johnson, 1971) view of the molecule is shown in Fig. 1.

The crystal consists of a van der Waals packing of monomeric units without significantly short intermolecular contacts.

The compound has a centre of *syn–anti* isomerism related to the presence of the C(5)–N(2) double bond. The observed configuration is *E*. The conformation around the C(5)–N(3) bond is synclinal. The conformations of the morpholine and cyclohexane rings are strictly chair. *Q* and *θ* puckering parameters (Cremer & Pople, 1975) are $0\cdot577$ (2) Å and $179\cdot1$ (2)° for morpholine, $0\cdot573$ (2) Å and $176\cdot5$ (3)° for the C(6)–C(11) ring and $0\cdot559$ (2) Å and $117\cdot1$ (2)° for the C(12)–C(17) one. It is of some interest that in this molecule the complete range of C–N bond distances is

---

Table 1. *Positional* ($\times 10^4$ *for non*-H *atoms*, $\times 10^3$ *for* H) *and isotropic thermal* ($\text{Å}^2 \times 10^3$) *parameters with e.s.d.'s in parentheses*

U_{eq} according to Hamilton (1959).

	x	y	z	U_{eq}/U
O	4985 (1)	−1757 (2)	8251 (1)	63 (1)
N(1)	3402 (1)	9 (2)	8553 (1)	44 (1)
N(2)	3011 (1)	2000 (2)	9471 (1)	45 (1)
N(3)	2139 (1)	1329 (2)	7936 (1)	48 (1)
C(1)	4350	−1451 (3)	7410	60 (1)
C(2)	3907 (1)	−53 (2)	7552 (2)	50 (1)
C(3)	4057 (2)	−322 (2)	9413 (2)	52 (1)
C(4)	4486 (2)	−1723 (3)	9211 (2)	62 (1)
C(5)	2833 (1)	1195 (2)	8702 (2)	42 (1)
C(6)	2379 (1)	3161 (2)	9660 (2)	41 (1)
C(7)	2392 (2)	3539 (3)	10826 (2)	53 (1)
C(8)	1731 (2)	4747 (3)	11041 (2)	72 (1)
C(9)	1994 (2)	5986 (3)	10391 (3)	80 (1)
C(10)	2026 (2)	5644 (3)	9227 (2)	65 (1)
C(11)	2672 (1)	4411 (2)	9019 (2)	52 (1)
C(12)	1561 (1)	146 (2)	7591 (1)	40 (1)
C(13)	1007 (1)	557 (2)	6608 (1)	46 (1)
C(14)	344 (1)	−588 (2)	6234 (2)	52 (1)
C(15)	−309 (2)	−1073 (3)	7098 (2)	63 (1)
C(16)	259 (2)	−1529 (3)	8050 (2)	63 (1)
C(17)	899 (2)	−368 (2)	8446 (2)	54 (1)
H(3)	178 (1)	201 (2)	800 (2)	52 (6)
H(11)	470 (2)	−151 (3)	676 (2)	65 (6)
H(12)	382 (2)	−218 (3)	738 (2)	72 (8)
H(21)	346 (1)	13 (3)	701 (2)	60 (6)
H(22)	442 (1)	63 (2)	752 (2)	51 (6)
H(31)	369 (2)	−30 (3)	1005 (2)	65 (6)
H(32)	456 (2)	35 (3)	947 (2)	72 (8)
H(41)	399 (2)	−241 (3)	921 (2)	72 (8)
H(42)	497 (2)	−190 (2)	978 (2)	67 (8)
H(61)	171 (1)	289 (2)	946 (1)	34 (5)
H(71)	306 (1)	381 (2)	1101 (2)	54 (6)
H(72)	220 (2)	268 (3)	1126 (2)	71 (8)
H(81)	180 (2)	500 (3)	1178 (3)	86 (9)
H(82)	105 (1)	444 (3)	1086 (2)	60 (6)
H(91)	159 (3)	678 (4)	1038 (3)	114 (11)
H(92)	265 (2)	641 (3)	1061 (2)	82 (9)
H(101)	223 (2)	642 (3)	882 (2)	68 (8)
H(102)	140 (2)	543 (2)	895 (2)	58 (6)
H(111)	267 (1)	417 (2)	826 (2)	58 (6)
H(112)	338 (1)	457 (2)	920 (2)	51 (6)
H(121)	199 (1)	−59 (2)	740 (2)	46 (5)
H(131)	142 (2)	85 (2)	605 (2)	51 (5)
H(132)	65 (1)	141 (2)	677 (2)	46 (5)
H(141)	72 (2)	−141 (3)	594 (2)	54 (6)
H(142)	−3 (1)	−20 (2)	570 (2)	57 (6)
H(151)	−80 (2)	−21 (3)	730 (2)	81 (8)
H(152)	−70 (2)	−184 (3)	681 (2)	96 (10)
H(161)	68 (1)	−226 (2)	789 (2)	49 (5)
H(162)	−16 (2)	−192 (3)	859 (2)	78 (9)
H(171)	128 (2)	−66 (3)	903 (2)	71 (8)
H(172)	51 (2)	40 (3)	864 (2)	77 (8)
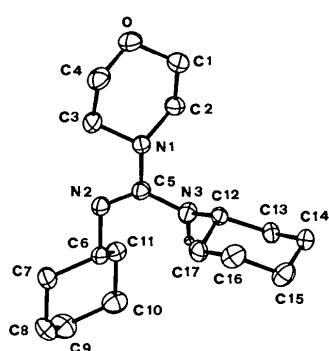
Table 2. *Bond distances* (Å) *with e.s.d.'s in parentheses*

O-C(1)	1·421 (2)	C(7)-C(8)	1·520 (4)
O-C(4)	1·412 (3)	C(8)-C(9)	1·506 (4)
N(1)-C(2)	1·463 (3)	C(9)-C(10)	1·519 (5)
N(1)-C(3)	1·461 (3)	C(10)-C(11)	1·525 (3)
N(1)-C(5)	1·414 (2)	C(12)-C(13)	1·523 (2)
N(2)-C(5)	1·276 (3)	C(12)-C(17)	1·519 (3)
N(2)-C(6)	1·454 (2)	C(13)-C(14)	1·523 (2)
N(3)-C(5)	1·381 (2)	C(14)-C(15)	1·511 (3)
N(3)-C(12)	1·471 (2)	C(15)-C(16)	1·513 (4)
C(1)-C(2)	1·503 (3)	C(16)-C(17)	1·524 (4)
C(3)-C(4)	1·509 (4)		
C(6)-C(7)	1·529 (4)	N(3)-H(3)	0·84 (2)
C(6)-C(11)	1·519 (3)	C-H (average)	0·98 |1|

Table 3. *Bond angles* (°) *with e.s.d.'s in parentheses*

C(1)-O-C(4)	109·6 (2)	C(7)-C(6)-C(11)	109·2 (2)
C(2)-N(1)-C(3)	109·7 (2)	C(6)-C(7)-C(8)	110·8 (2)
C(2)-N(1)-C(5)	115·3 (2)	C(7)-C(8)-C(9)	111·3 (2)
C(3)-N(1)-C(5)	115·6 (2)	C(8)-C(9)-C(10)	111·7 (2)
C(5)-N(2)-C(6)	118·9 (1)	C(9)-C(10)-C(11)	111·2 (2)
C(5)-N(3)-C(12)	121·6 (2)	C(6)-C(11)-C(10)	111·7 (2)
O-C(1)-C(2)	110·9 (1)	N(3)-C(12)-C(13)	108·6 (1)
N(1)-C(2)-C(1)	110·2 (1)	N(3)-C(12)-C(17)	112·4 (1)
N(1)-C(3)-C(4)	108·7 (2)	C(13)-C(12)-C(17)	111·2 (2)
O-C(4)-C(3)	111·6 (2)	C(12)-C(13)-C(14)	112·0 (1)
N(1)-C(5)-N(2)	119·5 (2)	C(13)-C(14)-C(15)	111·8 (2)
N(1)-C(5)-N(3)	112·3 (2)	C(14)-C(15)-C(16)	110·8 (2)
N(2)-C(5)-N(3)	128·2 (2)	C(15)-C(16)-C(17)	110·9 (2)
N(2)-C(6)-C(7)	110·0 (2)	C(12)-C(17)-C(16)	111·6 (2)
N(2)-C(6)-C(11)	111·2 (2)		

Table 4. *A selection of torsion angles* (°) *with e.s.d.'s in parentheses*

N(2)-C(5)-N(1)-C(2)	ω_4	−119·6 (2)	N(1)-C(5)-N(3)-C(12)	44·6 (2)
N(2)-C(5)-N(1)-C(3)	ω_1	10·1 (3)	C(5)-N(2)-C(6)-C(7)	152·2 (2)
N(3)-C(5)-N(1)-C(2)	ω_2	59·1 (2)	C(5)-N(2)-C(6)-C(11)	−86·8 (2)
N(3)-C(5)-N(1)-C(3)	ω_3	−171·1 (2)	C(5)-N(3)-C(12)-C(13)	−169·1 (2)
N(1)-C(5)-N(2)-C(6)		−175·6 (2)	C(5)-N(3)-C(12)-C(17)	67·3 (2)
N(3)-C(5)-N(2)-C(6)		5·8 (3)		

found. N(3)—C(12) of 1·471 (2) Å corresponds to the standard N(sp^3)—C(sp^3) distance and N(1)—C(2) and N(1)—C(3) of 1·463 (3) and 1·461 (3) Å are not far from it. N(2)—C(6) of 1·454 (2) Å can be considered a typical N(sp^2)—C(sp^3) bond length, while N(2)—C(5) of 1·276 (3) Å is almost a perfect double-bond distance (1·27 Å; Dunitz, 1979). C(5)—N(1) of 1·414 (2) Å and C(5)—N(3) of 1·381 (2) Å are intermediate between single- and double-bond lengths and correspond to different mixtures of the amidine resonance forms

$$\backslash N\!\!-\!\!C\!\!=\!\!N\diagup \quad \longleftrightarrow \quad \backslash \overset{+}{N}\!\!=\!\!C\!\!-\!\!N^-\diagup \ .$$
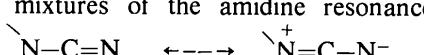
Another point concerns the C—C bond distances in the three saturated rings, which are on average 1·505 [3] Å in morpholine and 1·520 [3] Å in the cyclohexane rings. A glance at the crystallographic literature shows that the effect is not limited to the present molecule. It can be interpreted on the grounds of the Bent rule (Bent, 1960, 1961). The more electronegative N and O atoms in morpholine tend to increase the p character of the sp^3 C atoms in the C—O and C—N bonds, increasing the s character (and thus shortening the length) in the adjacent C—C bonds, *i.e.* C(1)—C(2) and C(3)—C(4) bonds.


Fig. 1. An *ORTEP* (Johnson, 1971) view of the molecule displaying the thermal ellipsoids at 40% probability. For the sake of clarity only the H atom linked to N(3) is shown.

Table 5. *Out-of-plane parameters for the* $C(sp^2)$—$N(sp^3)$ *fragment (with e.s.d.'s in parentheses) for a selection of amidines*

τ, χ_C *and* χ_N *are defined in the text.*

Compound	τ(°)	χ_N(°)	χ_C(°)	d_{CN}(Å)	Reference
(1) (Z)-2,6-cis-Dimethylpiperidyl-N-phenyl-2,2-dimethyl-propionamidine	$\begin{cases}-87.2\\-83.8\end{cases}$	$\begin{matrix}-47.6\\-45.5\end{matrix}$	$\begin{matrix}1.6\\3.2\end{matrix}$	$\begin{matrix}1.442(5)\\1.424(5)\end{matrix}$	(a)
(2) (E)-N,N'-Dicyclohexyl-4-morpholinecarboxamidine	34.6(4)	50.2(3)	1.2(4)	1.414(3)	(b)
(3) (E)-2,6-cis-Dimethylpiperidyl-N-phenylacetamidine	−9.8	−18.3	0.5	1.374(3)	(a)
(4) 1,5,N(4),N(4)-Tetramethylcytosine	−1.5	−3.6	−0.6	1.348(6)	(c)

References: (a) Gilli & Bertolasi (1979); (b) present work; (c) Dattagupta, Saenger, Bolewska & Kulakowska (1977).

The out-of-plane deformations of the $C(sp^2)$—$N(sp^3)$ group (I) can be more properly described by the internal coordinates τ, the mean twisting angle around the C—N bond, ranging from 0 (planar group) to 90° (when the two halves of the group are perpendicular), and χ_N and χ_C, respectively the out-of-plane bending angles of the N and C atoms, ranging from 0 (planar sp^2 atoms) to 60° (sp^3 atoms). These quantities are easily obtained as linear combinations of the torsion angles ω_1, ω_2, ω_3 and ω_4 (see Table 4) (Winkler & Dunitz, 1971; Dunitz, 1979).* Values of τ, χ_C, χ_N and d_{CN} for the present molecule and some related amidine molecules are given in Table 5. The data show that χ_C is always very small (0.5–3.2°) indicating that sp^2 carbon is resistant to out-of-plane bending. Conversely the observed range of χ_N (3.6–50.2°) is much wider. The data agree in indicating the following scheme for the rotation around the C—N bond. The equilibrium geometry of the $C(sp^2)$—$N(sp^3)$ group is planar (compound 4). Rotation of the amino group causes decoupling of the π system (II) and rehybridization of the nitrogen. For $\tau = 34.6$ (4)°

---

* $\tau = (\omega_1 + \omega_2)/2$, $\chi_C = \omega_1 - \omega_3 + \pi$ and $\chi_N = \omega_2 - \omega_3 + \pi$.

nitrogen is almost completely pyramidalized (compound 2). Further increment of τ does not change the situation (two independent molecules of compound 1). This point of view is supported by the trend of d_{CN} distances, which is found to increase both with τ and χ_N. The shortest length of 1.348 (6) Å is observed for the planar compound (4) while the largest ones [1.442 (5) and 1.424 (5) Å] are associated with the both pyramidalized and twisted compound (1).

References

BENT, H. A. (1960). *J. Chem. Educ.* **37**, 616–624.
BENT, H. A. (1961). *Chem. Rev.* **61**, 275–311.
BERTOLASI, V., BELLUCCI, F., FERRETTI, V. & GILLI, G. (1984). *Acta Cryst.* A40, C107.
BROWN, K. L., DAMM, L., DUNITZ, J. D., ESCHENMOSER, A., HOBI, R. & KRATKY, C. (1978). *Helv. Chim. Acta*, **61**, 3108–3135.
CREMER, D. & POPLE, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
DATTAGUPTA, J. K., SAENGER, W., BOLEWSKA, K. & KULAKOWSKA, I. (1977). *Acta Cryst.* B33, 85–89.
DUNITZ, J. D. (1979). In *X-ray Analysis and the Structure of Organic Molecules.* Ithaca: Cornell Univ. Press.
FRENZ, B. A. (1978). *Computing in Crystallography*, edited by H. SCHENK, R. OLTHOF-HAZEKAMP, H. VAN KONINGSVELD & G. C. BASSI, pp. 44–71. Delft Univ. Press.
GILLI, G. & BERTOLASI, V. (1979). *J. Am. Chem. Soc.* **101**, 7704–7711.
GILLI, G. & BERTOLASI, V. (1981). *Acta Cryst.* A37, C85.
HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
JOHNSON, C. K. (1971). *ORTEP.* Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee.
MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1981). *MULTAN81. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.
NARDELLI, M. (1983). *Comput. Chem.* **7**, 95–98.
WINKLER, F. K. & DUNITZ, J. D. (1971). *J. Mol. Biol.* **59**, 169–182.

Acta Cryst. (1985). C41, 546–548

4,4,4',4',6,6,6',6'-Octachloro-2,2'-dimethyl-2,2'-bi(cyclotriphosphazene), $C_2H_6Cl_8N_6P_6$

BY ROBERT R. WHITTLE, JAMES L. DESORCIE AND HARRY R. ALLCOCK*

Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802, USA

Abstract. $M_r = 583.58$, orthorhombic, *Pccn*, $a = 22.410$ (4), $b = 11.642$ (7), $c = 7.850$ (1) Å, $V = 2048$ (3) Å^3, $Z = 4$, $D_m = 1.882$, $D_x = 1.893$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0.71073$ Å, $\mu = 1.55$ mm^{-1}, $F(000) = 1144$, $T = 294$ K, $R = 0.041$ for 1432 unique reflections. The molecule lies on an inversion center with

---

* Author to whom correspondence should be addressed.