10 s covered 0.3° in ω. The crystal to detector distance was 5.01 cm. Coverage of the unique set was over 91% complete to at least 25° in θ. Crystal decay was monitored by repeating the initial frames at the end of the data collection and analysing the duplicate reflections. H atoms were added at calculated positions and refined using a riding model. The hydroxyl H4 atom could not be located in a difference Fourier synthesis but it was added in the plane of the aromatic ring so as to maximize hydrogen bonding to the O5 atom. It is therefore not possible to comment on the significance of any O5···H4 interaction. Anisotropic displacement parameters were used for all non-H atoms; H atoms were given isotropic displacement parameters equal to 1.2 (or 1.5 for methyl H atoms) times the equivalent isotropic displacement parameter of the atom to which they are attached.

Data collection: *SMART* (Siemens, 1994*a*). Cell refinement: *SAINT* (Siemens, 1995). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL/PC* (Siemens, 1994*b*). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXTL/PC*.

We wish to acknowledge the use of the EPSRC's Chemical Database Service at Daresbury Laboratory (Fletcher, McMeeking & Parkin, 1996) for access to the Cambridge Structural Database (Allen & Kennard, 1993). AS and RK thank the Council for Scientific and Industrial Research (CSIR, New Delhi, India) for the award of research fellowships.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1185). Services for accessing these data are described at the back of the journal.

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N^1,N^2-Diphenylacetamidine

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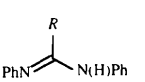
Abstract

The structure of the title compound, $C_{14}H_{14}N_2$, consists of amidine molecules hydrogen-bonded to form an alternating chain-like arrangement. Each molecule is bonded to two other molecules by N—H···N bonds. In each amidine N—C—N fragment, the C—N bond distances are different [1.281 (3) and 1.364 (3) Å], indicating some C=N imine character in one of the bonds.

Comment

The chemistry of amidines [R_2N—C(R)=NR] (R = H, alkyl, aryl) is becoming of increasing interest. This is because of the relevance of such species in the pharmaceutical and biological areas (Robert & Gagnon, 1994); for example, they are known to act as anti-pneumonia drugs in HIV therapy (Lowe, Sansom, Schwalbe & Stevens, 1989). In addition, amidines are versatile ligands and show a varied coordination chemistry towards both main group and transition metal elements (Barker & Kilner, 1994; Barker, Blacker *et al.*, 1996). As ligands they can bond either in the neutral form or, more usually, as the amidinate ion [RN—C(R)—NR]$^-$. Further structural information on amidine compounds is therefore desirable in order to understand better the relationship between their structure and reactivity. The N,N'-diphenyl-substituted amidines [H(Ph)NC(R)NPh] are of particular interest since they are often used as ligand species because of their availability and ease of handling, and their complexes involving the Group 13 elements have been shown to act as molecular precursors to useful electronic materials, such as gallium nitride, GaN (Barker, Blacker *et al.*, 1996). The structures of N,N'-diphenylformamidine (R = H), (I) (Anulewicz, Krygowski & Pniewska, 1987), and N,N'-diphenylbenzamidine (R = Ph), (II) (Alcock, Barker & Kilner, 1988), have already been



(I) R = H
(II) R = Ph
(III) R = Me

determined; we report here the structure of *N,N'*-diphenylacetamidine ($R = CH_3$), (III).

The asymmetric unit of (III) consists of discrete amidine molecules (Fig. 1). Each molecule hydrogen-bonds to two adjacent molecules (at $\frac{1}{2}-x, -\frac{1}{2}+y, z$ and $\frac{1}{2}-x, \frac{1}{2}+y, z$), thus forming alternating chain-like arrangements along the *b*-axis direction, as illustrated in Fig. 2 (the alternating molecular pattern is evident from the diagram and from the fact that the *x* coordinates are identical for every second molecule along the chain). The intermolecular hydrogen-bonded N···N distances are 3.091 (3) Å. This stacked arrangement is different from that in (I) and (II), where hydrogen-bonded dimers exist, due to the conformation of the two molecules limiting further interactions between the N—H bond and the N-atom lone pair.

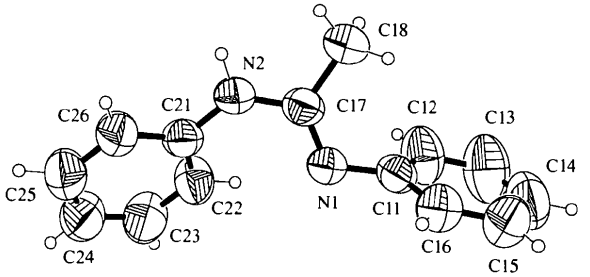


Fig. 1. View of the title molecule showing the atomic numbering. Displacement ellipsoids are drawn at the 50% probability level.

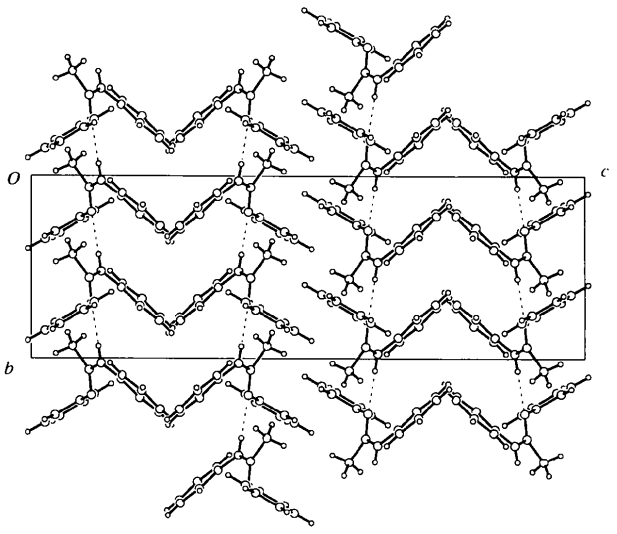


Fig. 2. View down the *a* axis showing the hydrogen bonding.

The skeletal C—N bond lengths are distinctly different, with values of 1.281 (3) (N1—C17) and 1.364 (3) Å (N2—C17) (Table 1), indicating a tendency towards double- and single-bond character, respectively. These values follow the trend observed in other amidines that carry a substituent, other than hydrogen, on the central C atom of the N—C—N fragment (Table 2). For example, the corresponding distances for the related species (II) are 1.302 (7) and 1.360 (8) Å, while N^2-(*m*-chlorophenyl)-N^1,N^1-pentamethylenebenzamidine has distances of 1.290 (6) and 1.365 (6) Å (Tykarska, Jaskolski & Kosturkiewicz, 1986*a*) and N^2-(*p*-methoxyphenyl)-N^1,N^1-pentamethylenebenzamidine has distances of 1.283 (5) and 1.372 (5) Å (Tykarska, Jaskolski & Kosturkiewicz, 1986*b*); the other compounds in Table 2 also show distinct differences in the C—N distances. However, it is significant that in formamidine derivatives, there is a much closer relationship between the two C—N bond distances. Thus, in (I), the values are 1.308 (3) and 1.319 (3) Å, while in N^2-(*p*-chlorophenyl)-N^1,N^1-hexamethyleneformamidine, they are 1.302 (6) and 1.334 (5) Å (Krajewski *et al.*, 1981). These values are consistent with a higher degree of delocalization over the N—C—N fragment within the structure. While the precise reasons for the observed variation in the N—C—N bond distances remain obscure, it has been noted that in (I) there is a relatively strong hydrogen bond with NH···N distances of 3.010 (11) and 2.984 (11) Å in the dimeric unit. The assumed lengthening of the N—H bond in (I), to 1.14 (5) and 1.17 (4) Å, would assist the delocalization over the N—C—N fragment (Anulewicz, Krygowski & Pniewska, 1987). It may be that the presence of a substituent on the central C atom, as found in acetamidine and benzamidine compounds, hinders the approach of the N—H proton towards the N-atom lone pair, thus limiting the hydrogen bonding in (III) and the extent to which delocalization can occur over the N—C—N unit. Further measurements on a wider range of compounds, especially those of the formamidine type, would help to clarify the structural variations which occur. It is of interest to note that in metal complexes containing the anion of (III), the bond distances within the N—C—N fragment become essentially the same (Gaylani *et al.*, 1991; Hursthouse *et al.*, 1993).

The central N—C—N angle does vary with variation of the attached substituents, but the changes are not systematic since in (I), (II) and (III), this angle is 122.6 (3), 121.5 (5) and 121.8 (3)°, respectively, while it rises to 124.4 (2) and 125. (1)° for benzamidine and acetamidine, respectively. The bond distances between the atoms of the N—C—N fragment and the C atoms of the substituent groups are in close agreement with those found in other amidines, and indicate the small effect which the substituents have upon such distances (Table 2). Angles of 81.4 (2) and 35.6 (3)° between the N—C—N skeleton and the two aryl ring systems indicate that very little interaction occurs between the two $p\pi$ orbitals located on the N atoms and the adjacent C atoms of the aryl rings. This is in contrast to the case of (II) where one of the dihedral angles is only 15.48 (8)°, but the change from a dimeric unit in (II) to the chain-like structure in (III) suggests that in the latter

it is the extended hydrogen-bonded system which is the dominant factor.

Experimental

N^1,N^2-Diphenylacetamidine was prepared by a modification of an earlier method (Oxley & Short, 1947). A mixture of triethyl orthoacetate (81 g, 0.5 mol), aniline (93 g, 1 mol) and glacial acetic acid (2.5 ml) was heated under reflux for 2 h by means of an oil bath maintained at 403–413 K. Ethanol and unchanged starting material were removed by distillation at 47 mmHg (1 mmHg = 133.322 Pa) from an oil bath held at 498 K. The residual liquid solidified upon cooling to room temperature. This solid was redissolved in hot benzene and on cooling the solution in an ice bath, an off-white solid deposited. Washing the solid repeatedly with petroleum ether (60–80°C) afforded colourless crystals. After drying under vacuum for several hours, the product was purified by sublimation at 353–373 K under vacuum.

Crystal data

$C_{14}H_{14}N_2$	Mo $K\alpha$ radiation
M_r = 210.27	λ = 0.71073 Å
Orthorhombic	Cell parameters from 250 reflections
Pbca	θ = 2.43–25.18°
a = 10.903 (2) Å	μ = 0.068 mm^{-1}
b = 8.603 (2) Å	T = 293 (2) K
c = 26.175 (5) Å	Block
V = 2455.2 (9) Å^3	0.28 × 0.28 × 0.20 mm
Z = 8	Colourless
D_x = 1.138 Mg m^{-3}	
D_m not measured	

Data collection

Delft Instruments FAST TV area-detector diffractometer	638 reflections with $I > 2\sigma(I)$
ω scans	R_{int} = 0.092
Absorption correction: none	θ_{max} = 25.18°
10 316 measured reflections	$h = -12 \rightarrow 11$
2007 independent reflections	$k = -9 \rightarrow 8$
	$l = -25 \rightarrow 30$

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max}$ = 0.001
$R[F^2 > 2\sigma(F^2)]$ = 0.045	$\Delta\rho_{max}$ = 0.117 e Å^{-3}
$wR(F^2)$ = 0.108	$\Delta\rho_{min}$ = −0.097 e Å^{-3}
S = 0.672	Extinction correction: none
2007 reflections	Scattering factors from *International Tables for Crystallography* (Vol. C)
147 parameters	
H atoms: see below	
$w = 1/[\sigma^2(F_o^2) + (0.0397P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. *Selected geometric parameters (Å, °)*

N1—C17	1.281 (3)	N2—C21	1.414 (3)
N1—C11	1.411 (3)	C17—C18	1.501 (3)
N2—C17	1.364 (3)		
C17—N1—C11	119.7 (2)	N1—C17—N2	121.8 (3)
C17—N2—C21	127.6 (2)	N1—C17—C18	124.5 (3)
C12—C11—C16	117.4 (3)	N2—C17—C18	113.6 (2)
C12—C11—N1	122.2 (3)	C26—C21—N2	118.5 (3)
C16—C11—N1	120.2 (3)	C22—C21—N2	122.7 (3)
C17—N1—C11—C16	103.6 (3)	C21—N2—C17—C18	170.0 (2)
N1—C11—C12—C13	−173.9 (3)	C17—N2—C21—C26	154.2 (3)
C11—N1—C17—N2	176.2 (3)	C17—N2—C21—C22	−27.3 (4)
C11—N1—C17—C18	−7.2 (4)	N2—C21—C22—C23	180.0 (3)
C21—N2—C17—N1	−13.0 (4)		

Table 2. *Variation in bond lengths (Å) and angles (°) for a series of amidines*

	C=N	C—N	N—C—N	C—X^a	N—Y^a	N—Z^a
(I)	1.308 (3)	1.319 (3)	122.6 (3)	–	1.411 (3)	1.410 (3)
(II)	1.295 (6)	1.351 (7)	122.7 (?)	1.488 (7)	1.412 (7)	1.412 (8)
(III)	1.281 (3)	1.364 (3)	121.8 (3)	1.501 (3)	1.414 (3)	1.411 (3)
(IV)^b	1.294 (3)	1.344 (3)	124.4 (2)	1.489 (3)	–	–
(V)^c	1.298 (1)	1.344 (1)	125.5 (1)	1.502 (1)	–	–

Notes: (*a*) *X*, *Y* and *Z* represent substituent groups (alkyl or aryl) on the atoms of the central N—C—N fragment; (*b*) [$H_2NC(Ph)NH$] (Barker, Phillips, Wallbridge & Powell, 1996); (*c*) [$H_2NC(Me)NH$] (Norrestam, Mertz & Crossland, 1983).

The temperature of the crystal was controlled using an Oxford Cryosystems Cryostream Cooler (Cosier & Glazer, 1986). Data were collected for 0.2° ω rotation exposures of 10 s each, with a crystal to detector distance of 5 cm. Coverage of the unique set was over 83% complete to at least 25° in θ. Crystal decay was found to be negligible by comparison of intensities of repeated reflections. H atoms were added at calculated positions and refined using a riding model. The H atom on N2 was added on the external bisector of the C—N—C bond angle, but the bond distance was allowed to refine. Anisotropic displacement parameters were used for all non-H atoms; each H atom was given an isotropic displacement parameter equal to 1.2 (or 1.5 for methyl H atoms) times the equivalent isotropic displacement parameter of the atom to which it is attached.

Data collection: *MADNES* (Pflugrath & Messerschmidt, 1992). Cell refinement: *MADNES*. Data reduction: *SHELXTL-Plus* (Sheldrick, 1990). Program(s) used to solve structure: *SHELXTL-Plus*. Program(s) used to refine structure: *SHELXL96* (Sheldrick, 1996). Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXTL-Plus*.

We wish to acknowledge the use of the EPSRC's Chemical Database Service at Daresbury Laboratory (Fletcher, McMeeking & Parkin, 1996) for access to the Cambridge Structural Database (Allen & Kennard, 1993). We also wish to thank Professor M. B. Hursthouse and the EPSRC X-ray service (University of Wales, Cardiff) for collecting the diffraction data, and Associated Octel for financial assistance (PRP).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AB1499). Services for accessing these data are described at the back of the journal.

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(3a*R*,7a*S*)-*N*-Triphenylmethyl-1,2,3,3a,5,6,7,7a-octahydropyrano[3,2-*b*]-pyrrol-2-one

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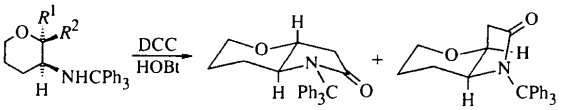
Abstract

The title compound, $C_{26}H_{25}NO_2$, is one of the two main products formed when an inseparable mixture of the diastereomeric (2*R*,3*S*)- and (2*S*,3*S*)-3-triphenylmethylaminooxinan-2-ylacetic acids is treated with *N*,*N*′-dicyclohexylcarbodiimide and 1-hydroxybenzotriazole. The crystal structure determination unambiguously shows that this compound has the tetrahydropyranyl and pyrrolidonyl rings fused in the *trans* configuration.

Comment

Reduction of γ-methyl (*S*)-*N*-triphenylmethylglutamate with $LiAlH_4$ (Barlos *et al.*, 1987), followed by *N*,*N*′-dicyclohexylcarbodiimide (DCC)-mediated lactonization, produced unexceptionally the (*S*)-*N*-tritylhydroxynorvaline lactone. When this lactone was subjected to an identical sequence of reactions to that used for the preparation of (2*RS*,3*S*)-3-triphenylmethylaminooxolan-2-ylacetic acid from (*S*)-*N*-tritylhomoserine lactone (Papaioannou *et al.*, 1991), an inseparable mixture of the diastereomeric acids (1*a*) and (1*b*) was obtained. Treatment of acid (1) with DCC in the presence of 1-hydroxybenzotriazole (HOBt), which is routinely used to prepare the corresponding 'active' hydroxybenzotriazolyl esters (Barlos, Papaioannou & Theodoropoulos, 1984), produced, *via* TLC, a mixture (approximately 1:1) of two main products, with R_f values of 0.21 and 0.10 using the solvent system toluene/ethyl acetate (8:2). This mixture could readily be separated by flash column chromatography (FCC). Spectroscopic and analytical data for the isolated products showed them to be the diastereomeric amides (2) and (3), respectively (Papaioannou, 1997). In particular, in the 400 MHz ^{1}H NMR spectra, the H3a proton appeared at δ 4.628 and 3.916 p.p.m. for amides (3) and (2), respectively, indicating an equatorial orientation of the C3a—H3a bond in (3) and an axial orientation in (2). This is taken to mean that amide (2) has the *trans* configuration and amide (3) has the *cis* configuration. In order to establish unambiguously the mode of fusion of the two heterocyclic rings in each of the two amides, we decided to determine the structure of the less polar (as determined by TLC) amide by X-ray analysis.



(1*a*) R^1 = H; R^2 = CH_2CO_2H (2) (3)
(1*b*) R^1 = CH_2CO_2H; R^2 = H

The crystal structure determination of the title amide (2) unambiguously shows that in the amide with R_f = 0.21, the tetrahydropyranyl and pyrrolidonyl rings are indeed *trans* fused. Moreover, the six-membered ring adopts a chair conformation [atoms C3a and C6 deviate by 0.707 (3) and −0.657 (4) Å, respectively, from the plane through atoms O4, C5, C7 and C7a], whereas the pyrrolidonyl ring is found in an envelope conformation [C3a deviates by 0.618 (3) Å from the plane formed by N1, C2, C3 and C7a]. The triphenylmethyl moiety