The structure of (I) was solved by direct methods (*SAPI*91; Fan, 1991) and expanded using Fourier techniques (Beurskens *et al.*, 1992). The weighting scheme was based on counting statistics and included a factor $P = 0.03$ to downweight the intense reflections. *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988) was used for data collection and cell refinement and *TEXSAN* (Molecular Structure Corporation, 1992) was used for data reduction, structure refinement and the preparation of material for publication.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1222). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Allen, F. H., Bellard, S., Brice, M. D., Cartwright, B. A., Doubleday, A., Higgs, H., Hummelink, T., Hummelink-Peters, B. G., Kennard, O., Motherwell, W. D., Rodgers, J. R. & Watson, D. G. (1979). *Acta Cryst.* B35, 2331–2339.

Berkovitch-Yellin, Z. & Leiserowitz, L. (1984). *Acta Cryst.* B40, 159–165.

Beurskens, P. T., Admiraal, G., Beurskens, G., Bosman, W. P., Garcia-Granda, S., Gould, R. O., Smits, J. M. M. & Smykalla, C. (1992). *The DIRDIF Program System*. Technical Report. Crystallography Laboratory, University of Nijmegen, The Netherlands.

Fan, H.-F. (1991). *SAPI*91. *Structure Analysis Programs with Intelligent Control*. Rigaku Corporation, Tokyo, Japan.

Krishnamohan Sharma, C. V. & Desiraju, G. R. (1994). *J. Chem. Soc. Perkin Trans.* 2, pp. 2345–2352.

Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1992). *TEXSAN. Single Crystal Structure Analysis Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Simonov, A. D. M., Pobedimskaya, E., Martin, A. & Masia, M. (1988). *Kristallografiya*, 33, 102–108.

Taylor, R. & Kennard, O. (1982). *J. Am. Chem. Soc.* 104, 5063–5070.

Bandrowski's Base

ALEXANDER J. BLAKE, PETER HUBBERSTEY AND DANIEL J. QUINLAN

Department of Chemistry, The University of Nottingham, University Park, Nottingham NG7 2RD, England. E-mail: a.j.blake@nott.ac.uk
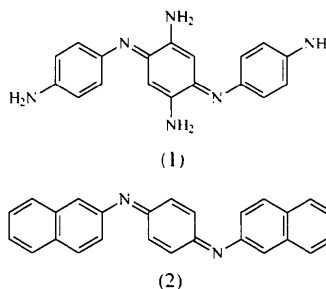
Abstract

Molecules of N,N''-(2,5-diamino-2,5-cyclohexadiene-1,4-diylidene)bis(1,4-benzenediamine), $C_{18}H_{18}N_6$, lie across crystallographic inversion centres. The angle between

the central ring and each of the terminal rings is $60.2\,(5)°$. Hydrogen bonding links molecules into chains along **b**.

Comment

Although first prepared over a century ago (Bandrowski, 1889) the title compound, (1), has been little studied. It is generally prepared by oxidation of 1,4-phenylenediamine with either $K_3[Fe(CN)_6]$ (Bandrowski, 1889; Bandrowski, 1894; Ritter & Schmitz, 1929) or H_2O_2 (*e.g.* Corbett, 1972; Rice, 1962), although nitrobenzene has also been used as the oxidizing agent (Crippa, Bellani & Marubini, 1930). It has also been observed as a product of cerruloplasmin oxidation of 1,4-phenylenediamine under *in vitro* enzymic conditions (Rice, 1962; Fan & Wang, 1984). We obtained a crystalline sample of (1) as a side product (see below) of an attempt to produce 1,4-bis(2-cyanoguanidinyl)benzene following the method described for the preparation of *N*-aryl-2-cyanoguanidines (Cunningham, Wan & Cox, 1994). The molecular structure of (1) was determined from early chemical studies (Green, 1913; Ritter & Schmitz, 1929; Lauer & Sunde, 1939; Sunde & Lauer, 1952) and from a determination of its formation mechanism (from 1,4-phenylenediamine *via* condensation of a quinonediimine intermediate; Corbett, 1972). Little is known of its chemistry; treatment with either acid or base results in decomposition to 1,4-phenylenediamine (Cox & Lewin, 1935; Feigl & Costa Neto, 1956).

(1)

(2)

Molecules of (1) lie across crystallographic inversion centres (Fig. 1) and the central ring is therefore ideally planar. The angle between central and terminal rings is $60.2\,(5)°$ and the two terminal rings are coplanar by symmetry. Comparison with the published structure of N,N'-(2,5-cyclohexadiene-1,4-diylidene)bis(2-naphthalenamine), (2) (Povet'eva, Chetkina & Kopilov, 1980) shows general similarities in the central N,N'-(2,5-cyclohexadiene-1,4-diylidene) moiety: the C==N double bonds are almost identical in length [1.298 (6) Å in (1) and 1.293 and 1.296 Å for the two independent half-molecules in (2)]. The C==C double bond length of 1.361 (7) Å in (1) is longer than in (2) where values of 1.322 and 1.326 Å are found; we attribute both this and the greater disparity between the C—C single bond lengths in (1) [1.432 (7) and 1.485 (6) Å] to the

presence of the amino substituents on the cyclohexa-dienyl ring. These groups show N—H distances in the range 0.87 (6)–1.12 (5) Å while the sum of the angles subtended at N4 and N13 are 352 (4) and 355 (4)°, respectively; the absence of significant deviations from planarity suggests sp^2 hybridization for the N atoms.
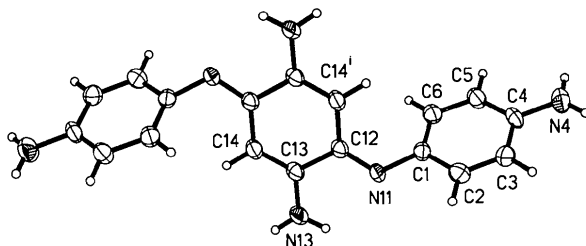

Fig. 1. A view of a molecule of (1) with atom-numbering scheme, lying across a crystallographic inversion centre. Displacement ellipsoids are drawn at 50% probability and H atoms are shown as spheres of arbitrary radius.

A packing diagram (Fig. 2) shows pairs of hydrogen bonds linking molecules into chains along the crystallographic *b* axis: hydrogen-bonding parameters are H13*B*· · ·N11^{ii} 2.23 (6) Å, N13—H13*B*· · ·N11^{ii} 151 (4)° [(ii) = −*x*, 1 − *y*, −*z*]. The amino groups on the benzene rings do not participate in any significant hydrogen bonding.
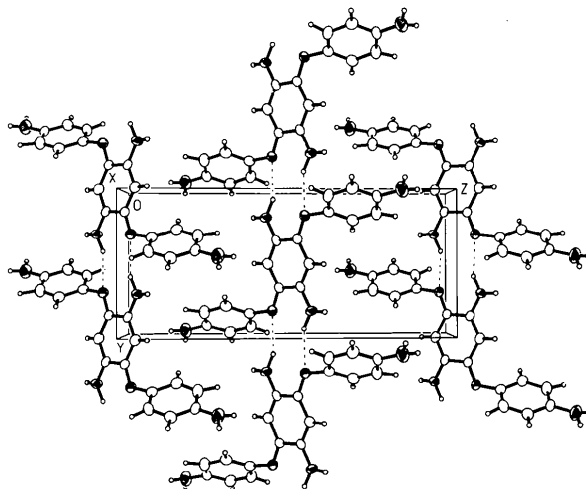

Fig. 2. A packing diagram showing the hydrogen bonds linking molecules into chains along the crystallographic *b* axis.

Experimental

Sodium dicyanamide (10.05 g, 0.113 mole) and 1,4-phenyl-enediamine (6.07 g, 0.056 mole) were refluxed in aqueous hydrochloric acid (250 cm³, 0.92 mol dm⁻³, 0.23 moles) for 120 min. After neutralization with aqueous sodium hydroxide (2 mol dm⁻³) and filtration, a brown precipitate was formed on reduction of solvent volume. Recrystallization from ethanol gave a small quantity of diamond-shaped brown

crystals (0.24 g, 0.75 mmol; 4% yield). Found (calculated for $C_{18}H_{18}N_6$): C 67.15 (67.90), H 5.70 (5.70) N 26.21 (26.40), m.p. 514–516 K [literature value 514–515 K (Sunde & Lauer, 1952)].

Crystal data

$C_{18}H_{18}N_6$	Mo $K\alpha$ radiation
$M_r = 318.38$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 22
$P2_1/n$	reflections
$a = 5.396 (2)$ Å	$\theta = 12.0$–$15.0°$
$b = 7.935 (3)$ Å	$\mu = 0.086$ mm⁻¹
$c = 18.311 (4)$ Å	$T = 298 (2)$ K
$\beta = 93.71 (3)°$	Lath
$V = 782.4 (4)$ Å³	$0.50 \times 0.25 \times 0.10$ mm
$Z = 2$	Dark red
$D_x = 1.351$ Mg m⁻³	
$D_m = 1.346$ Mg m⁻³	
D_m measured by flotation	

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{int} = 0.1349$
ω–2θ scans	$\theta_{max} = 24.94°$
Absorption correction: none	$h = -6 \rightarrow 6$
	$k = 0 \rightarrow 9$
	$l = -21 \rightarrow 15$
1809 measured reflections	3 standard reflections
1371 independent reflections	frequency: 60 min
541 observed reflections	intensity decay: <1%
$[I > 2\sigma(I)]$	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.108$
$R[F^2 > 2\sigma(F^2)] = 0.0771$	$\Delta\rho_{max} = 0.23$ e Å⁻³
$wR(F^2) = 0.2134$	$\Delta\rho_{min} = -0.24$ e Å⁻³
$S = 0.924$	Extinction correction:
1369 reflections	*SHELXL93* (Sheldrick,
137 parameters	1993)
H atoms introduced at	Extinction coefficient:
calculated positions,	0.027 (8)
thereafter allowed to	Atomic scattering factors
refine freely with $U_{iso}(H)$	from *International Tables*
$= 1.2U_{eq}$(parent atom)	*for Crystallography* (1992,
$w = 1/[\sigma^2(F_o^2) + (0.065P)^2]$	Vol. C, Tables 4.2.6.8 and
where $P = (F_o^2 + 2F_c^2)/3$	6.1.1.4)

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

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

	x	y	z	U_{eq}
C1	0.3398 (9)	0.3264 (7)	0.1121 (3)	0.0312 (13)
C2	0.5573 (11)	0.4190 (8)	0.1096 (3)	0.0383 (15)
C3	0.6936 (10)	0.4610 (7)	0.1731 (3)	0.036 (2)
C4	0.6228 (10)	0.4129 (7)	0.2410 (3)	0.0345 (14)
C5	0.4048 (10)	0.3187 (7)	0.2433 (3)	0.0386 (15)
C6	0.2654 (10)	0.2763 (7)	0.1797 (3)	0.0356 (14)
N11	0.1858 (8)	0.3057 (5)	0.0468 (2)	0.0346 (12)
C12	0.1065 (10)	0.1572 (7)	0.0268 (2)	0.0308 (13)
C13	−0.0869 (9)	0.1505 (7)	−0.0346 (2)	0.0308 (14)
C14	−0.1824 (10)	0.0005 (7)	−0.0590 (3)	0.0349 (14)
N13	−0.1600 (10)	0.3005 (6)	−0.0643 (2)	0.0430 (14)
N4	0.7669 (10)	0.4503 (7)	0.3056 (3)	0.052 (2)

Table 2. *Selected geometric parameters (Å, °)*

C1—N11	1.420 (6)	C12—C13	1.485 (6)
C4—N4	1.404 (6)	C13—N13	1.357 (6)
N11—C12	1.298 (6)	C13—C14	1.361 (7)
C12—C14^i	1.432 (7)		
C2—C1—N11	118.9 (5)	N11—C12—C13	116.7 (5)
C6—C1—N11	122.1 (5)	C14^i—C12—C13	116.6 (5)
C3—C4—N4	122.1 (5)	N13—C13—C14	122.8 (5)
C5—C4—N4	120.6 (5)	N13—C13—C12	116.3 (5)
C12—N11—C1	120.5 (4)	C14—C13—C12	120.9 (5)
N11—C12—C14^i	126.6 (5)	C13—C14—C12^i	122.5 (4)

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

The somewhat high R factor is attributed to the limited quality of the available crystals of (1).

Data collection: CAD-4 (Enraf–Nonius, 1980). Cell refinement: CAD-4. Data reduction: *HELENA* (Spek, 1993). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1992). Software used to prepare material for publication: *SHELXL*93.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1362). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Bandrowski, E. (1889). *Monatsh. Chem.* **10**, 123.
Bandrowski, E. (1894). *Chem. Ber.* **27**, 480–486.
Corbett, J. F. (1972). *J. Soc. Cosmet. Chem.* **23**, 683–693.
Cox, H. E. & Lewin, J. U. (1935). *Analyst*, **60**, 350–355.
Crippa, G. B., Bellani, G. & Marubini, A. (1930). *Gazz. Chim. Ital.* **60**, 644–647.
Cunningham, I. D., Wan, N. C. & Cox, B. G. (1994). *J. Chem. Soc. Perkin Trans.* 2, pp. 1849–1853.
Enraf–Nonius (1980). *CAD-4 Operation Software*. Enraf–Nonius, Delft, The Netherlands.
Fan, H. & Wang, Y. (1984). *Zhongguo Yike Daxue Xuebao*, **13**, 55–57.
Feigl, F. & Costa Neto, C. (1956). *J. Soc. Dyers Colour.* **72**, 239–240.
Green, A. G. (1913). *J. Chem. Soc.* pp. 925–933.
Lauer, W. M. & Sunde, C. J. (1939). *J. Org. Chem.* **3**, 261–264.
Povet'eva, Z. P., Chetkina, L. A. & Kopilov, V. V. (1980). *Zh. Strukt. Khim.* **21**, 118–122.
Rice, E. W. (1962). *Anal. Biochem.* **3**, 452–456.
Ritter, J. J. & Schmitz, G. H. (1929). *J. Am. Chem. Soc.* **51**, 1587–1589.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1992). *SHELXTL/PC Users Manual.* Version 4.3. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Spek, A. L. (1993). *HELENA. Program for Data Reduction.* Laboratorium voor Kristal- en Structuurchemie, University of Utrecht, The Netherlands.
Sunde, C. J. & Lauer, W. M. (1952). *J. Org. Chem.* **17**, 609–612.

5'-*O*-Benzoyl-2',3'-dideoxy-2'-oxo-α-uridine†

CHERAVAKKATTU G. SURESH,^{a}* KANDASAMY SAKTHIVEL^b AND TANMAYA PATHAK^b

^{a}*Division of Biochemical Sciences, National Chemical Laboratory, Pune 411 008, India, and ^{b}Organic Chemistry Division (Synthesis), National Chemical Laboratory, Pune 411 008, India. E-mail: suresh@ncl.ernet.in*
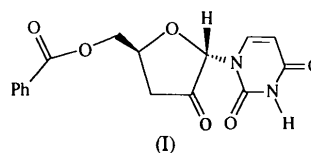
Abstract

The title compound, 1-(5-*O*-benzoyl-2,3-dideoxy-2-oxo-α-D-ribofuranosyl)-2,4(1*H*,3*H*)-pyrimidinedione, $C_{16}H_{14}N_2O_6$, is an α-nucleoside analogue. The glycosyl torsion angle [O4'—C1'—N1—C2 −76.9 (6)°] has a *syn* conformation. The sugar puckering is O4'-*endo*/C4'-*exo*, with pseudorotation parameters θ_m = 19.8 and *P* = 61.0. The exocyclic C3'—C4'—C5'—O5' torsion angle is *gauche–trans* [177.1 (6)°]. The pyrimidine N3 atom forms a hydrogen bond with the O4 atom of a symmetry-related molecule.

Comment

The pharmaceutical applications of nucleosides and nucleoside analogues have been widely recognized (Mitsuya, Yarchoan & Broder, 1990) and molecules like azidothymidine (AZT) are now marketed drugs. These drugs or potential drugs are all β-D-nucleosides and closely resemble the monomers of RNA and DNA. Their anomeric form, however, *i.e.* the α-nucleosides, which are resistant to nuclease digestion, have recently attracted attention as potential antisense drugs (Thuong & Helene, 1993). There are reports on the comparatively more efficient hybridization of modified α-nucleosides to natural DNA and on their high enzymatic stability (Abdel Aleem, Larsen & Pedersen, 1995). We are involved in the synthesis and analysis of α-nucleosides modified at the C2' and C3' positions and with various groups attached to the O5' atom in order to assess the effects of modifications on the overall geometry of the molecule (Sakthivel, Pathak & Suresh, 1994). As part of this study, we report herein the crystal structure of 5'-*O*-benzoyl-2',3'-dideoxy-2'-oxo-α-uridine, (I).

(I)